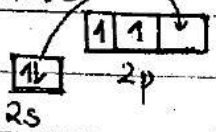
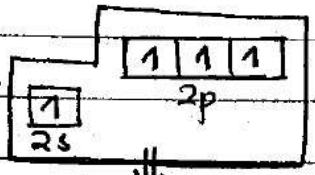
Organic Chemistry

$C_6 \rightarrow 1s^2 2s^2 2p^2$

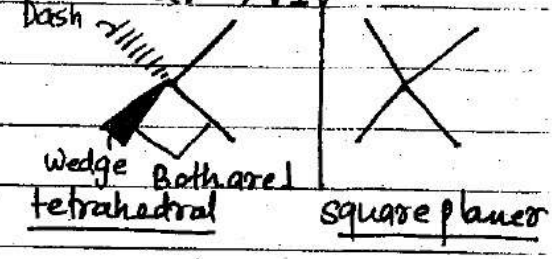
outer e⁻

Ground state - 

Excited State - 

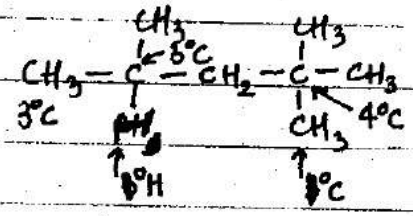
$sp^3 \Rightarrow$ Tetrahedral

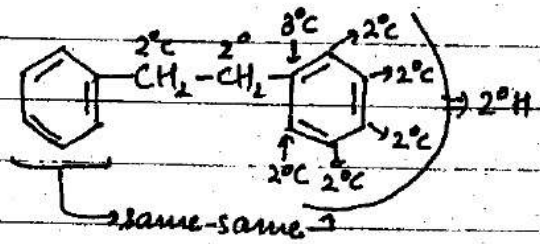
$2V \Rightarrow V \perp V$

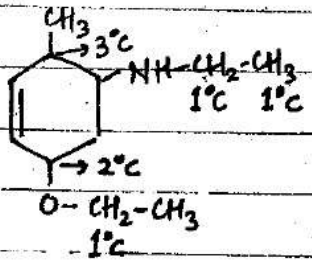


Catenation: Self linking of C atom is ya CATENATION. (Due to Bond Energy [Released energy])

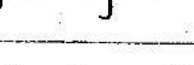
Type Of Carbon

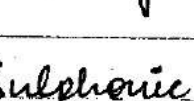
① 

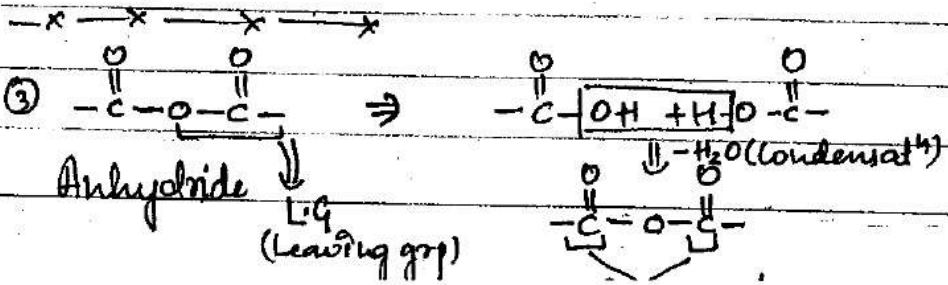
② 

③ 

Functional Groups

①  Carboxylic Acid

②  Sulphonic Acid



4. $-\overset{O}{\overset{\|}{C}}-\ddot{O}-R$ ⇒ $-\overset{O}{\overset{\|}{C}}-OH+H-O-R$ ($-H_2O$)

Ester (L.G)

$-\overset{O}{\overset{\|}{C}}-O-R$

From acid From alcohol

5. $-\overset{O}{\overset{\|}{C}}-X$ ⇒ $-\overset{O}{\overset{\|}{C}}-OH+H-X$ ($-H_2O$)

Acid Halide (L.G)

$-\overset{O}{\overset{\|}{C}}-X$

6. $-\overset{O}{\overset{\|}{C}}-NH_2$ ⇒ $-\overset{O}{\overset{\|}{C}}-OH+H-NH-R$ ($-H_2O$)

Amide L.G

$-\overset{O}{\overset{\|}{C}}-NH-R$ → Peptide bond Test of peptide bond

From acid From amine Biuret Test

7. $-C\equiv N$

Cyanide

8 $-N\overset{\rightarrow}{\equiv}C$

Isocyanide

⑨ (A) $-\overset{O}{\overset{\|}{C}}-H$ Aldehyde

⑩ $-\overset{O}{\overset{\|}{C}}-CH_3$ Ketone

⇒ Carbonyl compound [No L.G]

⑪ $-OH$

⑫ $-SH$

⑬ NH_2 — $\ddot{N}H_2$, $\ddot{N}H$, $N\dot{P}$

Degree Of Unsaturation [DU] Double Bond Equivalent [D.B.E]

① $CH_2-CH_2-CH_2-CH_2$ (H, H) MP C_4H_{10} GF C_nH_{2n+2}

$\downarrow -H_2, \Delta$

$CH_2-CH_2-CH_2-CH_2$

$\downarrow$

CH_2-CH_2 / CH_2-CH_2  M.F C_4H_8 G.F C_nH_{2n} $1H_2 \Rightarrow DU \Rightarrow 1$

② $CH_2-CH_2-CH_2-CH_2$ (H, H)

$\downarrow \Delta, -H_2$

$CH_2-CH_2-CH_2-CH_3$

$\downarrow$

$CH_2=CH_2-CH_2-CH_3$ M.F C_4H_8 $1H_2 \Rightarrow DU \Rightarrow 1$ GF C_nH_{2n}

$CH=CH-CH_2-CH_3$ (H, H)

$\downarrow$

$CH=C-CH_2-CH_3$

$\downarrow$

$CH_3 \equiv C-CH_2-CH_3$ M.F C_4H_6 $2H_2 \Rightarrow DU \Rightarrow 2$ GF C_nH_{2n-2}

KEY POINT

1 Double Bond $\Rightarrow 1H_2 \Rightarrow DU \Rightarrow 1$

1 Ring $\Rightarrow 1H_2 \Rightarrow DU \Rightarrow 1$

1 Triple Bond $\Rightarrow 2H_2$ $DU \Rightarrow 2$

Alkane

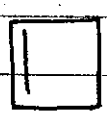
① C_2H_2 $C_2H_6 \Rightarrow 2H_2 \Rightarrow DU = 2$

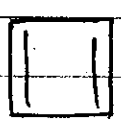
② C_3H_6 $C_3H_8 \Rightarrow 1H_2 \Rightarrow DU = 1$

③ C_4H_6 $C_4H_{10} \Rightarrow 2H_2 \Rightarrow DU = 2$

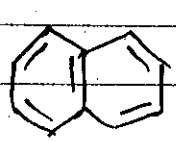
④ C_6H_6 $C_6H_{14} \Rightarrow 4H_2 \Rightarrow DU = 4$

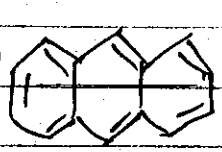
⑤ $C_{10}H_6$ $C_{10}H_{22} \Rightarrow 6H_2 \Rightarrow DU = 6$

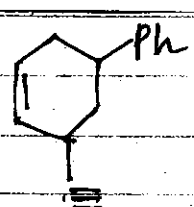
⑥  DU = 2 (1+1)

⑦  DU = 3 (1+2)

⑧  DU = 4 (1+3)

⑨  DU = 7 (1+3+1+2)

⑩  DU = 10 (1+3+1+2+1+2)

⑪  DU = 8 (1+1+2+4)

D.U in heteroatom containing compound

N-family	O-family	F family
$N \Rightarrow -H$	$O \Rightarrow X$	$F \Rightarrow +H$
eg. $N_2 \Rightarrow -2H$	$O_2 \Rightarrow X$	$F_2 \Rightarrow 2H$
$P_2 \Rightarrow -2H$	$S_2 \Rightarrow X$	$Cl_2 \Rightarrow +2H$

1. $C_4H_{10}\underset{X}{O} \Rightarrow C_4H_{10} \Rightarrow C_4H_{10} \Rightarrow DU = 0$

2. $C_4H_8\underset{X}{O} \Rightarrow C_4H_8 \Rightarrow C_4H_{10} \Rightarrow DU = 1$

3. $C_4H_8\underset{X}{O_2} \Rightarrow C_4H_8 \Rightarrow C_4H_{10} \Rightarrow 1H_2 \Rightarrow D.U = 1$

4. $C_5H_9\underset{-H}{N} \Rightarrow C_5H_{10} \Rightarrow C_5H_{12} \Rightarrow 2H_2 \Rightarrow DU = 2$

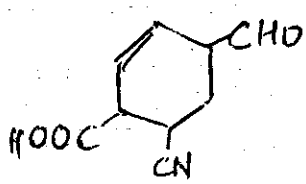
5. $C_5H_8\underset{X}{O_2}\underset{X}{S_2}\underset{-2H}{N_2}\underset{+2H}{F_2} \Rightarrow C_5H_8 \Rightarrow C_5H_{12} \Rightarrow 2H_2 \Rightarrow DU = 2$

6. $CH_3-C\equiv C-\underset{\underset{CH=CH_2}{|}}{CH}-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OH$ $\quad DU = 5$

D.U Deficiency of H_2 molecule with respect to acyclic alkane

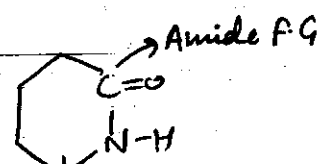
$$D.U = \text{No. of ring} + \text{No. of } \pi\text{-bond}$$

$$DU = \frac{\text{No. of H-atom in acyclic Alkane} - \text{No. of H-atom in given comp}}{2}$$

7. 

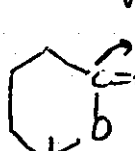
$DU = 6$

1. Lactum Ring



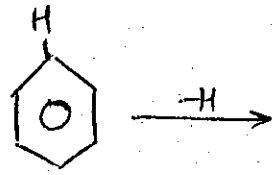
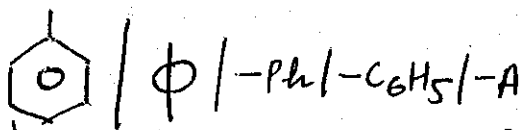
↳ cyclic amide ⇒ lactum → 1. Nylon-6
2. Penicillin → Cidal

2. Lactone Ring



↳ cyclic ester ⇒ lactone

Extra Point

1.  $\xrightarrow{-H}$ 

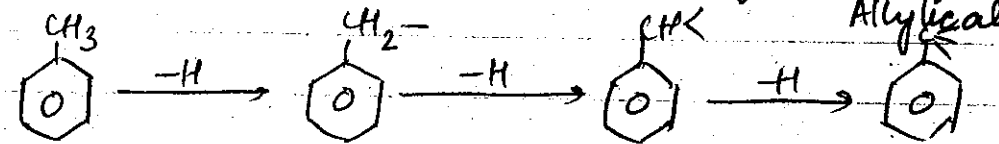
ϕ / -Ph / $-C_6H_5$ / -Ar

Same-Same

2. $CH_2=CH-H \xrightarrow{-H} CH_2=CH-$ eg. $CH_2=CH-Cl$ Vinyl chloride

$CH_2=CH-OH$ Vinyl alcohol

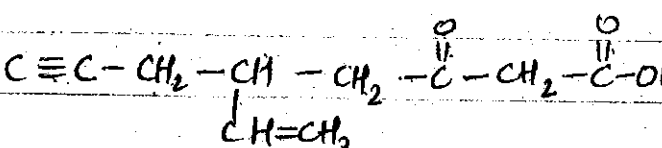
3. $CH_2=CH-CH_2-H \xrightarrow{-H} CH_2=CH-CH_2-$ eg. $CH_2=CH-CH_2-OH$ Allylic alcohol

4. 

Toluene → Benzyl → Benzal → Benzo

5. $CH_4 \xrightarrow{-H} CH_3- \xrightarrow{-H} -CH_2- \longrightarrow CH<$

Methane — Methyl — Methylene (Methylidene) — Methylidyne

Q 

a) D.U = 5

b) Total no. of π bond = 5

c) Total no. of Double bond = 5

d) Total no. of Triple bond = 3

e) No. of olefinic bond = 1 (C=C)

f) No. of Acetylinic bond = 1 (C≡C)

g) Total no. of σ bonds = 27

IUPAC System

Sec. Prefix + **Pri. Prefix** + **WORD ROOT** + **Pri. Suffix** + **Sec. Suffix**

Sec. Prefix
Give information about substituent in alphabetical order with their position

Pri. Prefix
used when compound is cyclic in this case 'CYCLO' prefix is used.

WORD ROOT
No. of C-atom in P.C.C
- 1C - Meth
- 2C - Eth
- 3C - Prop
- 4C - But
- 5C - Pent
- ⋮

Pri. Suffix
Give idea about Nature of H.C means, compound SATURATED/UNSATURATED with their position
- (C=C) → ene
- (C≡C) → yne
- $(C=C)_n$ ⇒ 'a' diene
- $(C\equiv C)_n$ ⇒ 'a' diyne

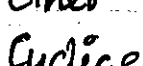
Sec Suffix
Give idea about Principle F.G with their position

eg.

Hexa-1,3-Diene

Selection Of Principle Functional Group (PFG)

A. If compound having only one fxnal group then it is considered as PFG of a compound. except Ether $-O-$.

Cyclic ether 

Halogen 

Nitro $-NO_2$

Nitroso $-N=O$

Nitrite $-O-N=O$ etc.

all are considered as a substituent.

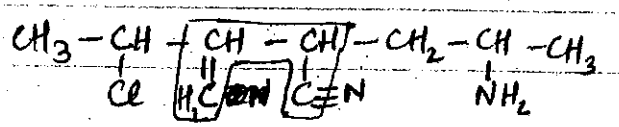
B. If compound have more than one fxnal group then select PFG according to given IUPAC series in this case rest of fxnal group considered as a substituent & their prefix are used.

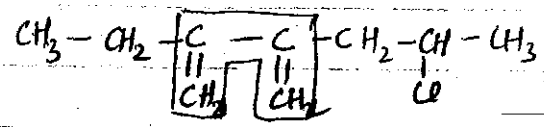
Selection of Principle Carbon Chain (PCC)

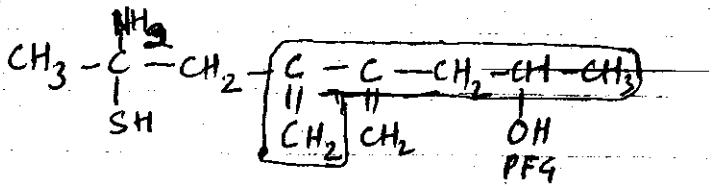
A If PFG having carbon then it considered first carbon of PCC (excluding KETONE)

B. In comp PFG not having C then considered that C which to PFG direcly attached in this case that C atom covered by both side of other C-atom (including Ketone)

C. **PFG > Multi-bond > No. of C-atom in PCC > No. of substituent**

① 

② 

③ 

④ $CH_2=CH-C(=CH_2)-CH_2-OH$

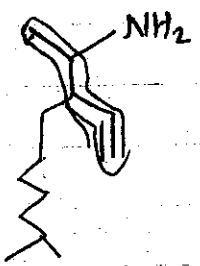
⑤ $CH_2=CH-C(=CH_2)-O-CH_2-CH_2-CH_2-CH_3$

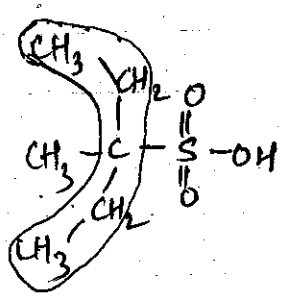
⑥ $CH\equiv C-CH_2-CH(CH=CH_2)-CH_2-CH_2-C(=O)-OH$

unsymm.

⑦ $CH\equiv C-CH(CH=CH_2)-CH_2-CH_2-C(=O)-OH$

symm.

⑧ 

⑨ 

⑩ $CH_3-CH(SH)-CH(NH_2)-CH_2-CH_2-C(=CH_2)-CH_2OH$

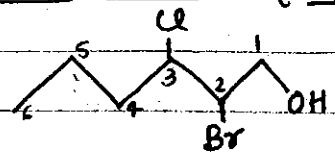
⑪ $CH_3-CH_2-CH(-CH_2-CH(-CH_2-CH_3)-CH_2-CH_3)-CH(CH_3)-CH(CH_3)-CH_3$

7C+2sub

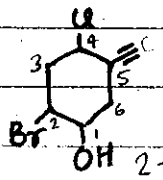
7C+3 sub

7C+4sub

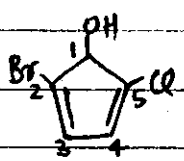
IUPAC NOMENCLATURE

① 

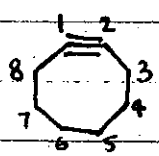
2-Bromo 3-chloro hexan-1-ol

② 

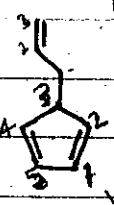
2-Bromo 4-chloro 5-methynyl cyclohexanol

③ 

2-Bromo 5-chloro cyclopenta-2,4-diene-1-ol

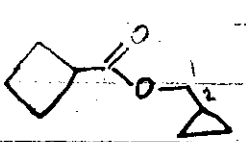
④ 

Cyclooctyne

⑤ 

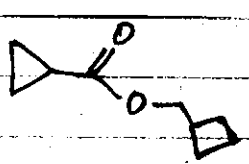
3-Propenyl cyclopenta-1-4-diene

~~5-Prop-2-ene 1 cyclopenta 1,3 diene~~

⑥ 

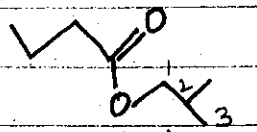
2-cyclopropylmethyl cyclobutyl methanoate

carboxylate

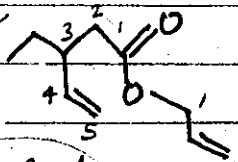
⑦ 

cyclobutyl methyl cyclopropyl methanoate

carboxylate

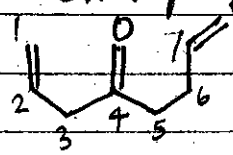
⑧ 

2-Methyl propyl butanoate

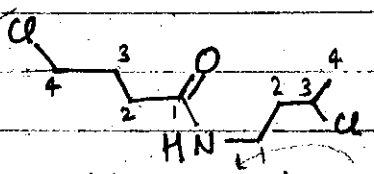
⑨ 

2-Propenyl 3-Ethyl Pent-4-en-oate

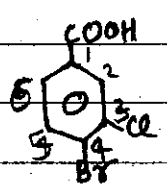
Prop-2-en-1-yl

⑩ 

Octa ~~Hepta~~-1,7-diene-~~4-one~~

⑪ 

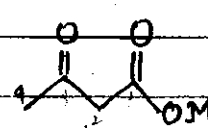
N-(3-chloro butyl) 4-chloro ~~butanamide~~

⑫ 

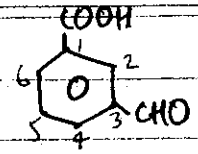
4 Bromo 3 Chloro ~~2-chloro 3-Bromo~~ benzanoic acid

⑬ $CH_2^1=CH^2CH_2^3NHCH_3$

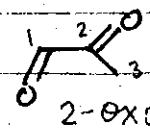
N-Methyl prop-2-en-1-amine

⑭ 

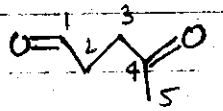
Methyl 3 oxo butanoate

(15) 

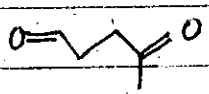
3 formyl benzanoic acid

(16) 

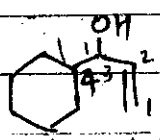
2-oxo propanal

(17) 

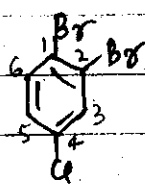
4-oxo pentan-1-al

(18) 

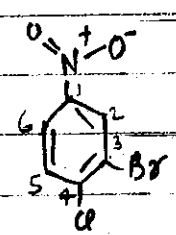
4-oxopentan-1-al

(19) 

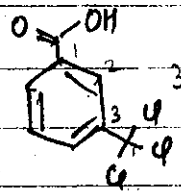
4-cyclohexyl pentan-2-en-1-ol

(20) 

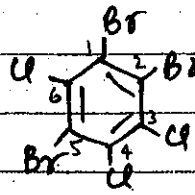
1,2 Dibromo 4-chloro benzene

(21) 

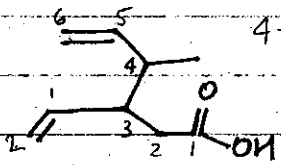
3-Bromo 4-chloro Nitrobenzene

(22) 

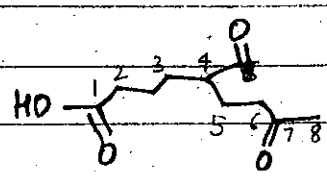
3-(1,1,1 Trichloromethyl) Benzanoic acid

(23) 

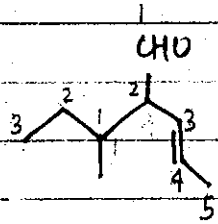
1,2,5 TriBromo-3,4,6 Trichloro benzene

(24) 

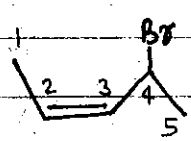
4-Methyl(3-ethynyl) Hex-5-en-oic acid

(25) 

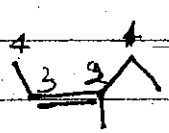
4-formyl 6-oxo octanoic acid

(26) 

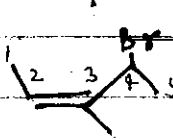
2(1-Methyl propyl) pent-3en-al

(27) 

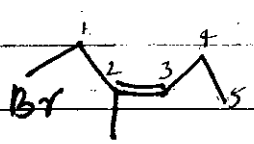
4-Bromo Pent-2-ene

(28) 

1-Bromo 2-Methyl but-2-ene

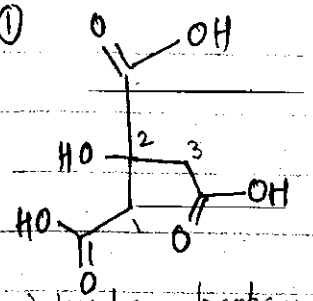
(29) 

4-Bromo 3Methyl Pent-2ene

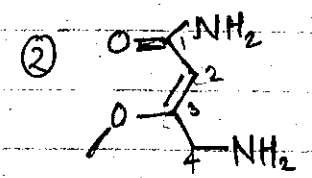
(30) 

1-Bromo, 2 Methyl Pent-2-ene

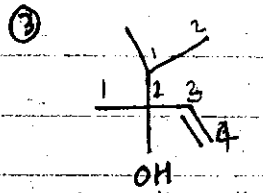
SKC

① 

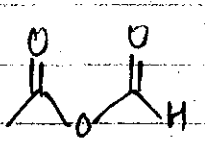
2-Hydroxy propane 1,2,3 Tricarboxylic Acid

② 

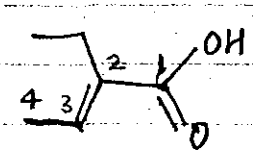
4-Amino 3-Methoxy But-2-en-amide

③ 

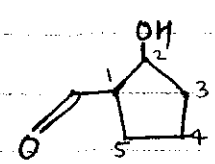
2(1-Methylethyl) but-3-ene-2-ol

④ 

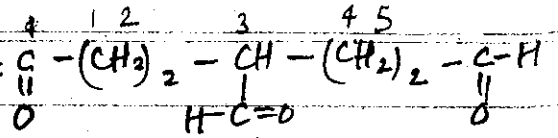
Methanoic Ethanoic Anhydride

⑤ 

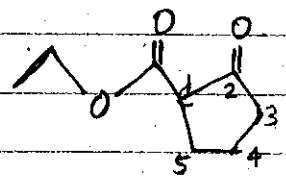
2-Ethyl But-2-en-oic Acid

⑥ 

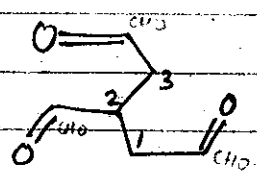
2-Hydroxy cyclopentyl methanal

⑦ 

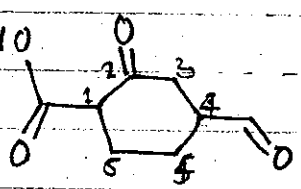
Pentan-1,3,5-Tricarbaldehyde

⑧ 

Ethyl 2-oxo cyclopentanoate

⑨ 

Propane-1,2,3-Tricarbaldehyde

⑩ 

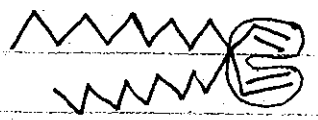
4-formyl,2-oxo cyclohexanoic acid

D.U, DoV, functional group

12 $CH_3-CH_2-\boxed{CH-CH_2-CH-CH_2-CH_2-CH_3} \Rightarrow 8C + 3sub.$

8C+2sub. $\quad CH_3-\boxed{CH}(CH_3)$; $CH-CH_3$; CH_3

13.



14. $CH_3-\boxed{CH(C_2H_5)-CH_2-CH_2-CH_2-CH(CH_3)-CH_2}$

Numbering In Selected P.C.C

Fxn group > multiple bond > = > ≡ > lowest set of locant > alphabetical ord. of substituent (locant's Rule)

15. $\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH_2}-O-CH_3$ (sub)

16. $\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH}(NO_2)(NO_2)$

17. $\overset{1}{CH}\equiv\overset{2}{CH}-\overset{3}{CH_2}-\overset{4}{CH_2}-\overset{5}{CH_2}-\overset{6}{CH_2}=\overset{7}{CH_2}-CH_3$

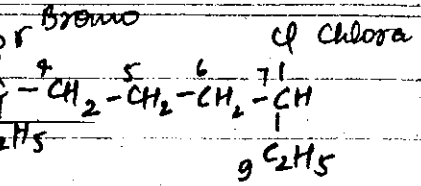
18. $\overset{8}{CH}\equiv\overset{7}{C}-\overset{6}{CH_2}-\overset{5}{CH_2}-\overset{4}{CH_2}-\overset{3}{CH_2}-\overset{2}{CH}=\overset{1}{CH_2}$

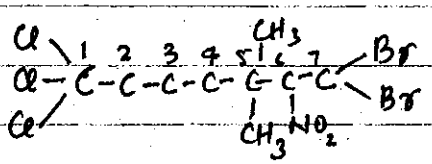
19. $\overset{1}{CH}\equiv\overset{2}{C}-\overset{3}{CH_2}-\overset{4}{CH}(OH)-\overset{5}{CH_2}-\overset{6}{CH_2}-\overset{7}{CH_2}-\overset{8}{CH}=\overset{9}{CH_2}$

20. $\overset{1}{CH}\equiv\overset{2}{C}-\overset{3}{CH}=\overset{4}{CH}-\overset{5}{CH_2}-\overset{6}{CH_2}-\overset{7}{CH}=\overset{8}{CH_2}$

21 $CH\equiv CH-CH(SO_3H)-CH(CH=CH_2)$ (5 4 3 ; 2 1)

22 $CH_3-\overset{1}{C}(Cl)(C_2H_5)-CH_2-CH_2-CH_2-C(Br)(C_2H_5)-H$

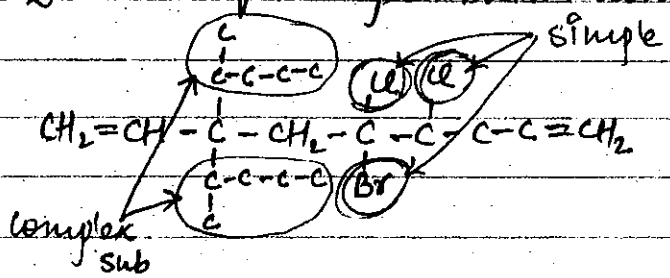
23. 

24. 

L→R	~~1~~	~~1~~	1	2	5	5	6	7	7
R→L	1	1	2	3	3	6	7	7	

Use Of Numerical Prefix

@ Di, tri, tetra.... used for simple substituent
Bis, tris, tetrakis... used for complex substituent



Complex Substituent

A substituted substituent is k/a COMPLEX SUBSTITUENT

** In case of complex substituent first C is that carbon having free valency.

① R• ⇒ Alkyl
↳ Total no. of C atom

eg. $-CH_2-CH_2-CH_2-CH_3$
Butyl (n-Butyl)

② $CH_2=CH-$ ⇒ Alkenyl ⇒ Ethenyl (vinyl) ex (a, e, i, o, u, y)

③ $HC\equiv C-$ ⇒ Alkynyl ⇒ Ethynyl

IUPAC Nomenclature Of Complex Substituent

25. $-\overset{1}{CH_2}-\overset{2}{CH_2}-\overset{3}{CH}(\overset{4}{CH_3})-CH_3$ (Isopentyl)

3-Methyl Butyl

26. $-\overset{1}{C}(CH_3)-\overset{2}{CH_2}-\overset{3}{CH_3}$ (Sec-Butyl)

1-Methyl Propyl

27. $-CH_2-C(CH_3)_2-CH_3$ (Neopentyl)

$\left[-CH(CH_3)_2\right]$ ISOPROPYL

2, 2 Dimethyl propyl

28. $-C(CH_3)_2-CH_3$ (tertiary butyl)

1, 1 Dimethyl ethyl.

29. $-CH_2-C(NH_2)=CH-CH_3$

NH_2 sub 2 Amino but-2-enyl

30. $-CH_2-CH(OH)-C\equiv CH$

OH sub 2 Hydroxy but-3-ynyl

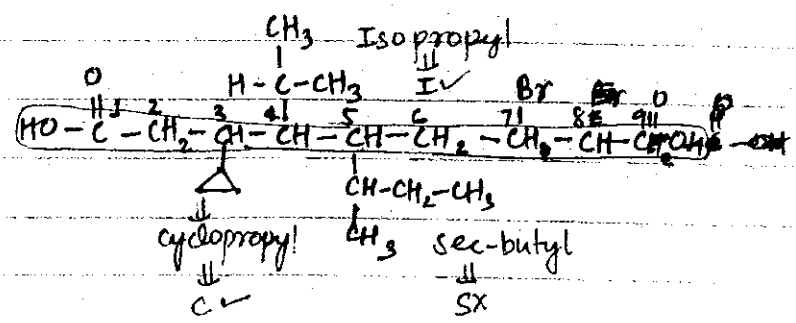
⑥ Alphabetical Order Of Substituent

FOR SIMPLE SUBS.

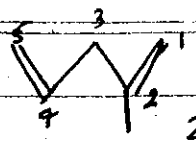
In case of simple substituent CYCLO, ISO, NEO (CIN) considered in alphabetical order rest like di, tri, Primary, Secondary avoided.

FOR COMLEX SUBS.

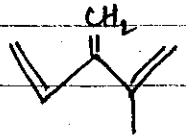
First alphabet of complex substituent decided alphabetical order always written in bracket.



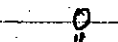
7 Bromo-5-sec-butyl-3 cyclopropyl-4-isopropyl nonan-1,9-dioic acid

32. 

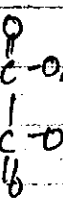
2 Methyl ~~-pentad~~ -1,4-diene

33. 

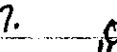
2-Methyl 3 Methylidene Penta 1,4 diene

34.  (formic acid) The only acid that can be oxidised

Methanoic acid

35.  (Oxalic Acid)

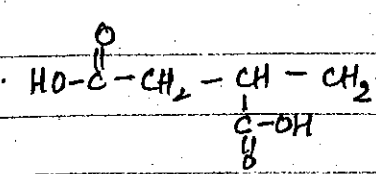
Ethan-1,2 dioic acid Fire extinguisher (Pyrene

36. CCl_4 ⟶  Phosgene (Poisonous)

1,1,1,1 tetrachloro Methane

Chloromethanoyl chloride

IUPAC 93

38.  Propane 1,2,3 Tricarboxylic acid

 Carboxylic acid

 Sulphonic acid

 Alkyl ... carboxylate

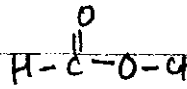
 Carbonyl chloride

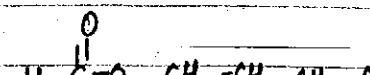
 Carboxamide

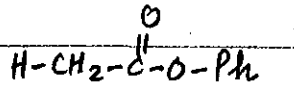
 carbonitrile

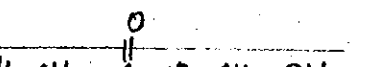
 Carbylamine

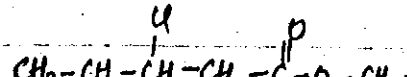
 Carbaldehyde

43.  Methyl methanoate.

44. 

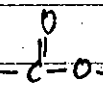
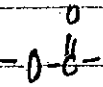
45.  Phenyl ethanoate

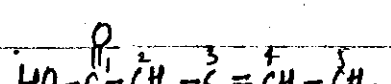
46.  Hydroxy methyl methanoate

47.  Butyl 3-Chloro, 4-Bromo Pentanoate

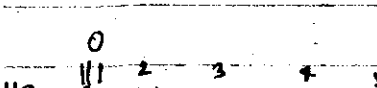
48.  Bromo methyl ethanoate.

Ester as a substituent

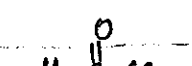
	sub	Prefix
1		Alkoxy carbonyl
C		Alkanoyl oxy

49.  3-Methoxy carbonyl hepta-3-ene 1,7-dioic.

ester ⇒ sub ⇒ prefix ⇒ Alkoxy carbonyl

50.  3-Ethanoyl oxy hept-3-en-1,7 dioic

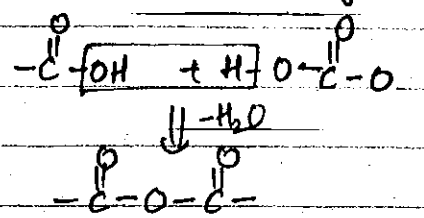
ester ⇒ sub ⇒ prefix ⇒ Alkanoyl oxy

51.  Methanoyl chloride

saturated

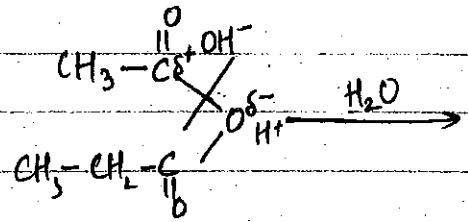
Anhydride
Mono prefix
kamuska suffix

IUPAC name of anhydride



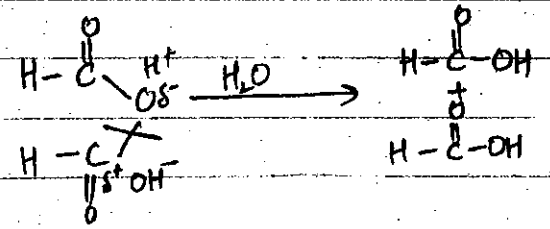
NOTE IUPAC name of anbride also give with their respective acid (follow alphabetical order)

40.



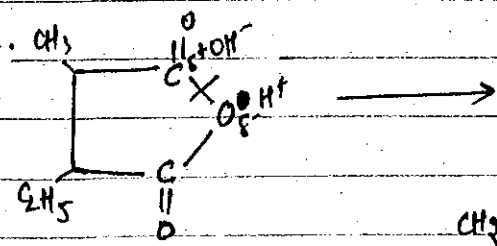
Ethanoic Propanoic anhydride

41

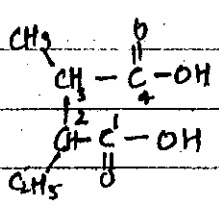


Methanoic Anhydride

42.

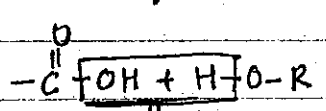


OR



2 Ethyl 3-Methyl Butan-1,4-dioic Anhydride

IUPAC Name Of Ester



suffix - Alkyl.....oate

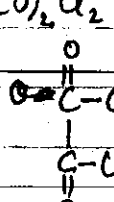
From acid → Main part (M.P)

From alcohol → Substituent

Alcohol

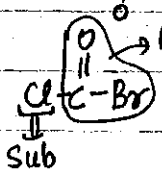
CHO CO group की chain में नहीं होगा ये chain से जोड़ा जाएगा।
⇓ ⇓
Oxo Oxo

S2. $(CO)_2Cl_2$



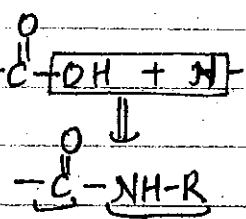
Ethane-1,2-di oyl chloride.

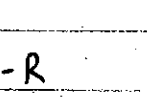
S3.



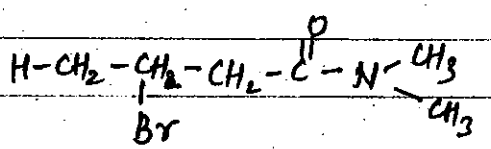
~~1-Bromo~~ 1-chloro Methanoyl chloride

S4. IUPAC name Of Amide

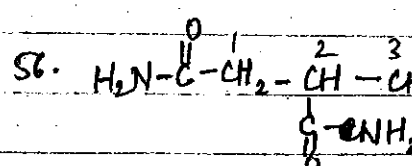


S4. 

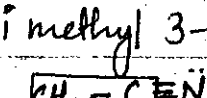
N-Ethyl N-Methyl Ethanamide

S5. 

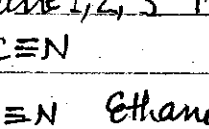
N,N Di methyl 3-Bromo butan-1-amide.

S6. 

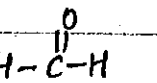
Propane 1,2,3 Tri carboxamide

S7. 

Ethane-1-nitrile

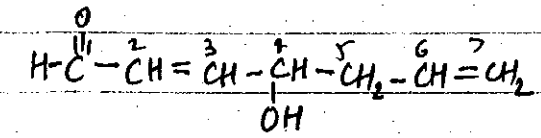
S8. 

Ethane-1,2-Dinitrile

S9. 

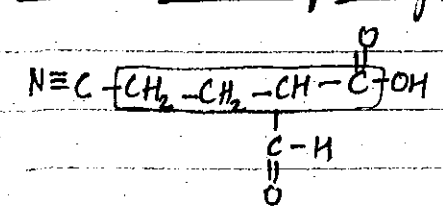
Methanal (Formaldehyde)

Single aldehyde which is used in making polymer is used by Melamine, Bakelite Polymer & Shee shor Polymer.

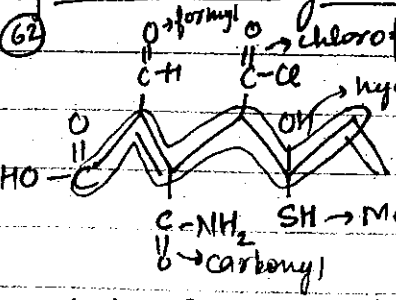
S10. 

4 hydroxy Hepta-2,6-diene-1-al.

S11. IUPAC Name Of Polyfunal Group Containing compound

(61) 

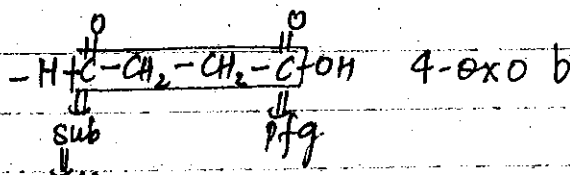
4-cyano 2 Formyl butan-1-oic Acid

(62) 

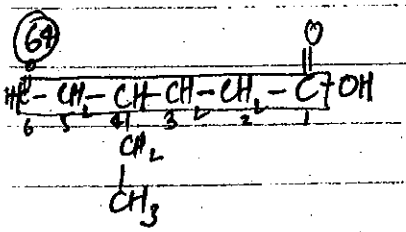
~~Octa~~ 3-carbonyl-4-chloroformyl-2 formyl-5-hydroxy-6-mercapto Hepta-2,6-diene-1-oic

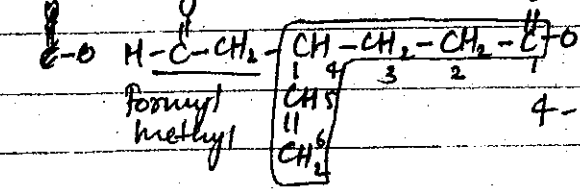
When C-containing fxnal group present as a substituent then its C- is not included in P.C.C & their prefix are used. But in case of aldehyde & ketone its C may be included in P.C.C & oxo prefix is used.

SPECIAL CASE FOR ALDEHYDE & KETONE (OXO CASE)

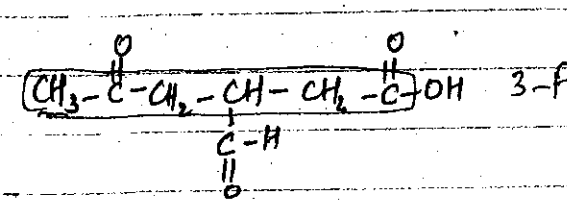
(63) 

4-oxo butanoicacid

(64) 
4-ethyl 6-oxohexan-1-oicacid

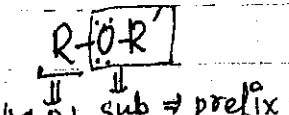
(65) 

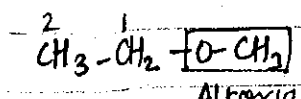
4-formyl methyl hex-5-en-1-oicacid

(66) 
3-formyl 5-oxo-hexan-1-oic acid (Keto)

IUPAC Name Of Ether

Ether can never be pfg. it always behave as a substituent
Incase of ether alkoxy prefix used



(67) 

Methoxy Ethane

(68) 
2-Methoxy-2-Methyl Propane

$\overset{1}{CH}=\overset{2}{CH}-O-C_2H_5$ 1-Chloro 2-ethoxy ethene
(2 (c)) (c)

IUPAC Name Of Cyclic Ether

In case of cyclic ether epoxy prefix used.
In case of cyclic ether compound treated as a open chain com

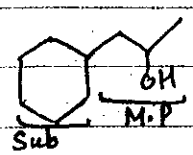
70. CH_2-CH_2 (O) → epoxy → oxirane
1,2 epoxy ethane

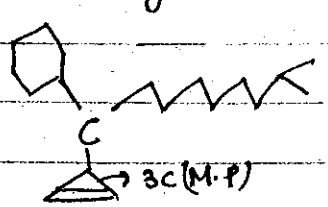
71. $CH_3-\overset{7}{CH_2}-\overset{6}{CH_2}-\overset{5}{CH}-\overset{4}{CH_2}-\overset{3}{CH_2}-\overset{2}{C}(=O)-\overset{1}{OH}$ (O between 6 & 4)
4, 6-epoxy heptan-1-oic acid

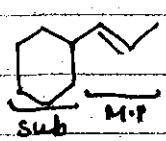
IUPAC Naming Of Cyclic Compound.

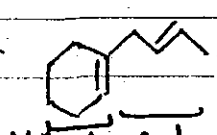
If given compound is combination of open chain & closed chain H.C part then select principle part acc. to given IUPAC series.

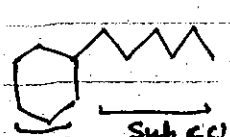
Pfg > M.B > No. of C-atom in P.C.C > Ring (if C-atom equal)

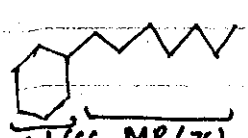
72. 

77. 

7.3 

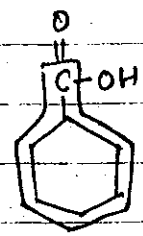
7.4 

75. 

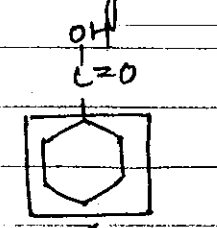
76. 

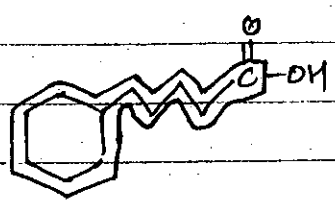
cyclic → behave as current carrying loop.

2. If ffg directly attached to C-atom of ring then it considered as a part of ring not a seperate part In case of ketone in may be present inside the ring



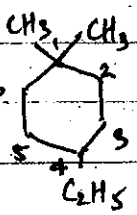
XXXX



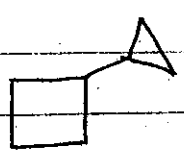


XXXY

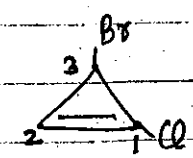
In case of cyclic compound to give IUPAC name cyclo prefix used

78. 

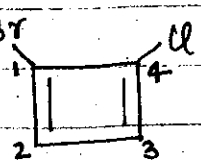
4-Ethyl 1,1 Dimethyl cyclohexane.

79. 

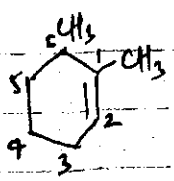
1-cyclopropyl cyclobutane.

80. 

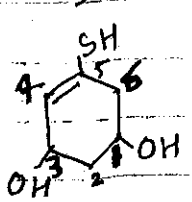
3-Bromo-1-chloro cylcoprop-1-ene

81 

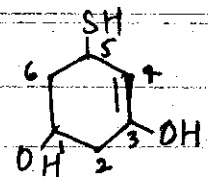
1-Bromo-4-chloro cyclobuta-1,3-diene.

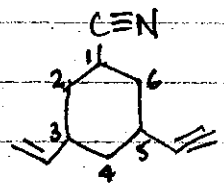
82. 

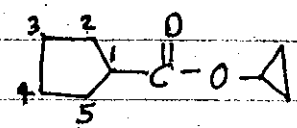
1,6-Dimethyl cyclohex-1-ene.

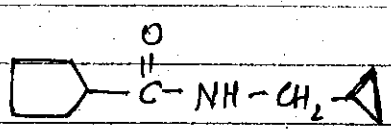
83. 

5-Mercapto cyclohex-4-en-1,3-diol

84.  5-Mercapto cyclohex-3-ene 1,3-diol

85.  3-ethenyl 5-ethynyl cyclohexan-1-carbonitrile

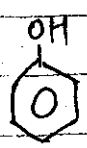
86.  cyclopropyl cyclopentane-1 carboxylate

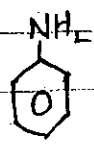
87.  N-cyclopropylmethyl cyclopentane-1-carboxamid

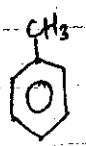
IUPAC Naming Of Aromatic Compounds

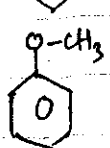
RULE 1 Common name of some compound has been retain in IUPAC system (

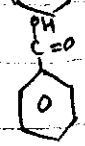
88.  Benzene

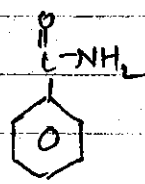
89  Phenol/Carbolic Acid

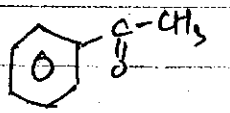
90.  Aniline

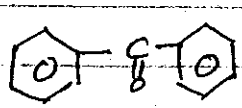
91.  Toluene

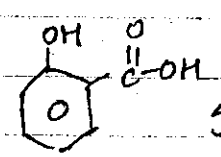
92  Anisole

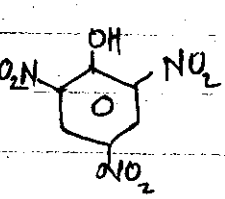
93.  Benzoic Acid/ Benzene Carboxylic Acid

94  Benzamide

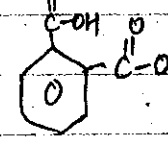
95.  Acetophenone

96.  Benzophenone

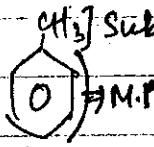
97.  Salicylic Acid

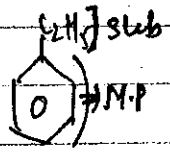
98.  Picric Acid

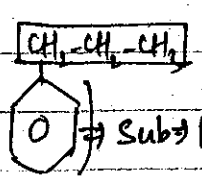
RULE-2 If more than one pfg present in a compound then their suffix are used according to IUPAC

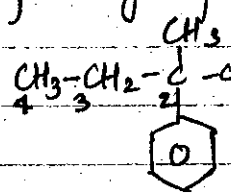
99. 
Benzene 1,2 Dicarboxylic Acid
[Pthalic Acid]

RULE-3 If given compound is combination of open chain & close chain hydrocarbon part then except ethyl & methyl benzene open chain part considered as a prenciple part In this case, benzene behave as a substituent & phenyl prefix used.

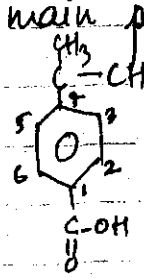
100. 
M.P Methyl benzene

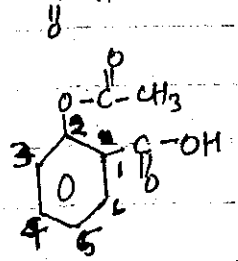
101 
M.P Ethyl benzene

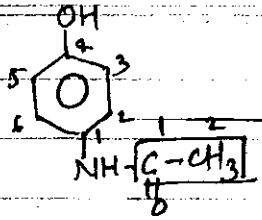
102. 
Sub → Prefix

103. 
2-Methyl 2-Phenyl Butane.

RULE-4 If any part having fxnal group then it considered as a main part.

104. 
4-(3-Hydroxy-1-Methyl Butyl) ~~Butyl~~ Benzene carboxylic acid.

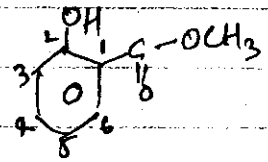
105. 
Aspirin
Acetyl salicylic Acid
Ethanoyl benzene carboxylic acid
2-Acetoxy benzene carbodylic acid
antiinflammetory, analgesic, antipyretic, anticoagulent

106. 

Paracetomol

1-[4-hydroxy phenyl] Ethanamide

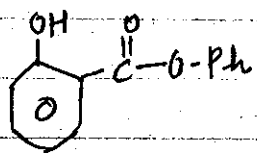
Antipyretic, Antiinflammetry, Analgesic

107. 

Methyl Salicylate

Oil of Wintergreen

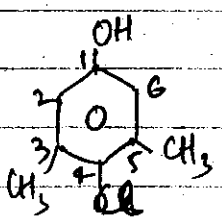
Methyl 2-hydroxy benzene carboxylate (IODGx)

108 

Phenyl Salicylate

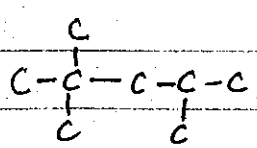
uses: Astringent (shrink blood vessel) (Aftershaver) [Fitkari bhi]

Antisceptic

109. 

Dettol (mix. of Chloroxylenol + Terepenol)

4 Chloro 3,5 - Dimethyl benzene-1-ol



→ Isooctane

Isomerism

ISOS (Equal) — MEROS (Part)

Same molecular formula.

⇒ Compound having same molecular formula, same molecular weight but different connectivity / different bonding pattern (Structural Isomerism) & different 3-D relative arrangement [stereoisomerism] is ga ISOMERS and this phenomenon is kla ISOMERISM.

① Isomers are different compound.
② Isomers have diff. physical, chemical / both properties
③ [Enantiomers have same physical properties]
④ Isomers have same D.B.V.
⑤ Isomerism is resultant due to thermodyanamic factor ENTROPY

① C_2H_6O, DU ⇒ 0

- $CH_3CH_2\overset{\delta-}{O}\overset{\delta+}{H}$ → Active H ⇒ due to hydrogen bonding ⇒ liquid
  - → Active H ⇒ give active metal test with Na ⇒ $H_2\uparrow$ (gud-gud)
- CH_3-O-CH_3 ⇒ No active H ⇒ No H-bonding ⇒ gas
  - → No active metal test ⇒ No H_2 ⇒ No gud-gud

F–H, O–H, N–H ⇒ ACTIVE-H Hydrogen attached that atom having EN 3 or more than 3 then it is Active H

Classification Of Isomerism

Sta. Iso. → connectivity change hoti hai.
Hijan ati Rapid accepting Tautomer

chain same
Position diff

Isomerism

due to different connectivity ** | due to same connectivity **

Structural Iso./Constitutional Iso.
- → Chain Isomerism (C.I)
- → Position Isomerism (P.I)
- → Fxnal Grp Isomerism (F.GI)
- → Ring chain Isomerism (RCI)
- → Metamerism
- → Tautomerism

Stereo Isomerism
- Configurational Iso.
  - → Geometrical
  - → Optical
- Conformational Iso. (Pseudoisomerism)

Structural Isomerism

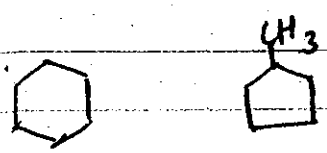
Due to different connectivity / diff bonding pattern.

CHAIN ISOMERISM.

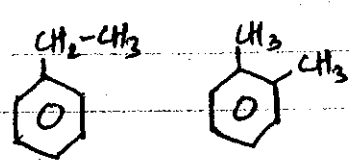
Same M.F, Same F.G, Same Position of fxnal grp & multible bond but diff P.C.C & side chain

① $CH_3CH_2CH_2CH_3$ (I, 4C) $\quad CH_3-\underset{CH_3}{CH}-CH_3$ (II, 3C) — Both are C.I

② $CH_3-\overset{*}{C}H_2-CH=CH_2$ (I) $\quad CH_3-\underset{CH_3}{C}=CH_2$ (II) — Both are C.I

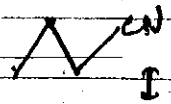
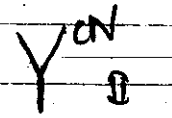
③  — Both are C.I

④ $C-C=C$ with C (Alkane) and □ (Alkane) — Not CI

⑤  — both are C.I

Catyon Resonance वाली उसे
Queen ध्यान रखो

⑤ $CH_3CH_2CH_2CH_2SO_3H$ (I) $CH_3-CH_2-CH(SO_3H)-CH_3$ (II) Not C.I

⑦  (I)  (II) Both are C.I

How many min C-atom required to give C.I for following compound.

① Alkane- 4 [C-C-C-C , C-C(C)-C]

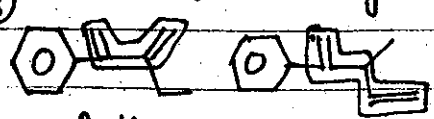
② Alkene 4 [C-C-C=C C-C(C)=C]

③ Alkyne 4 [C-C-C-C≡C C-C(C)-C≡C]

④ Alk-en-yne 5 [C-C=C-C≡C C=C(C)-C≡C]

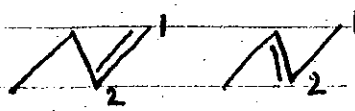
⑤ Alkadiene 5 [C-C=C-C=C C=C(C)-C=C]

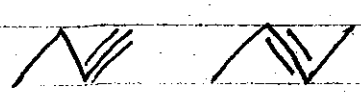
⑥ Alcohol 4 [C-C-C-C-OH C-C(C)-C-OH]

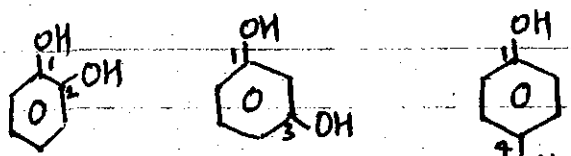
⑧ 
Both are C.I

POSITIONAL ISOMERISM

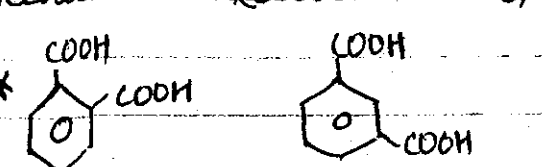
Compound having same M.F, same F.G, same P.C.C or side chain but diff position of FG, MB, Substituent

①  Both are P.I

②  Both are P.I

③  All are P.I

Catechol Resorcinol Quinol

④  All are P.I

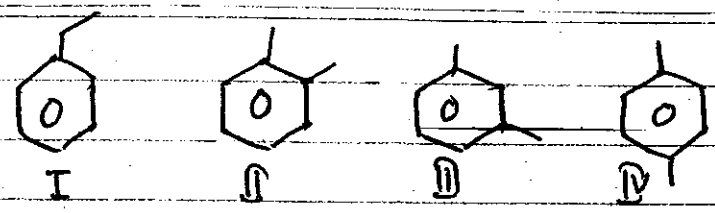
Phthalic Acid Isophthalic acid Terephthalic Acid

C.I PI can never be F.G.I ; or FGI only one min C is needed

↓

Chain isomerism

Q.5



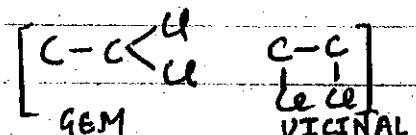
I II III IV

I, II → C.I II, III → P.I

I, III → C.I III, IV → P.I

I, IV → C.I II, IV → P.I

How many min. C atom required to give P.I for following Compounds.

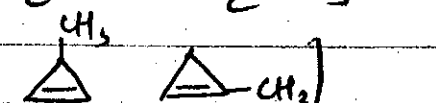
① Any comp. ⇒ 2 

GEM VICINAL

② Alkene ⇒ 4 [C-C-C=C C-C=C-C]

③ Alkyne ⇒ 4 [C-C-C≡C ~~C-C≡C-C~~

④ Alkane ⇒ ⑥ [C-C-C-C(C)-C C-C-C(C)-C-C]

⑤ ~~5~~ Cyclopropane ⇒ 4 

FUNCTIONAL GROUP ISOMERISM

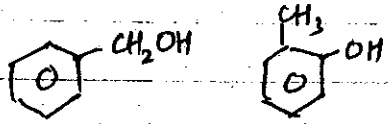
Following compounds give F.G.I

Compound having same M.F but diff F.G

1. Acid & Ester $CH_3CH_2-\overset{O}{\overset{\|}{C}}-OH$ $CH_3-\overset{O}{\overset{\|}{C}}-OCH_3$ FGI

2. Cyanide & Isocyanide $CH_3C\equiv N$ $CH_3-N\overset{+}{=}\overset{-}{C}$ FGI

3. Aldehyde & Ketone $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H$ $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ FGI

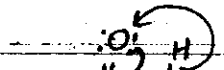
4. Alcoholic & Phenolic Comp. 

5. Alcohol & ether ⇒ CH_3CH_2OH CH_3OCH_3

6. Nitrate & Nitro ⇒ CH_3NO_2 CH_3ONO

Heat of hydrogenation — unhybridised p-orbital → π bond
heat of combustion — stability order

7. Keto & enol forms



Ketoform & enol form → FGI

8. 1°, 2° & 3° Amines ⇒ Diff. functional group

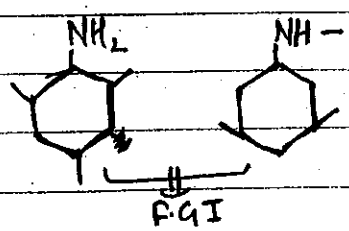
① $CH_3CH_2-CH_2-\ddot{N}H_2$
② $CH_3CH_2\ddot{N}H-CH_3$
③ $CH_3-\underset{CH_3}{\ddot{N}}-CH_3$

⇒ All are FGI

1. $CH_3CH_2CH_2CH_2CH_3$ DU = 0
$CH_3-CH_2-CH_2-CH=CH_2$ DU = 1
⇒ Not isomers.

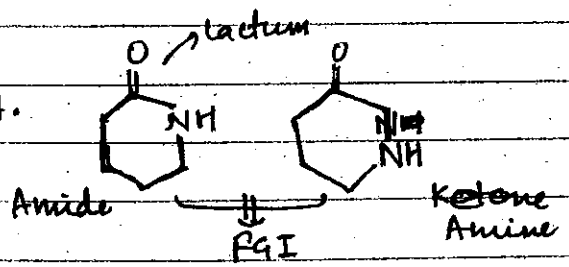
2. $CH_3-C\equiv C-CH_3$
$CH_2=CH-CH=CH_2$
⇒ F.G.I

3.



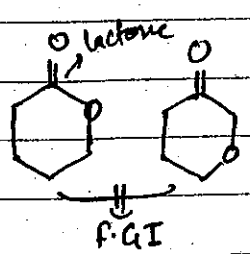
F.G.I

4.



Amide — FGI — Ketone Amine

5.



F.G.I

6. $CH_3-CH_2-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-OH$
$CH_2-CH_2-\underset{\underset{O}{\|}}{C}-CH_2-CH_3$
OH
⇒ F.G.I

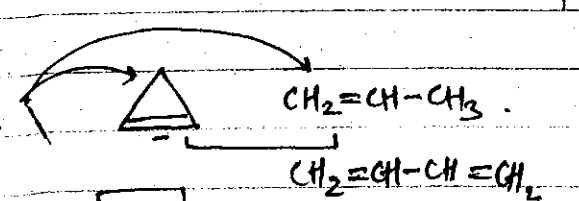
Q. How many min. C atom required to give F.G.I for any comp.
⇒ ① eg. CH_3-NO_2 CH_3ONO

RING CHAIN ISOMERISM

Comp. having same M.F but diff. mode of linking

Openchain — Closechain.

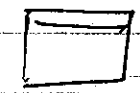
1. C_3H_6 DU = 1

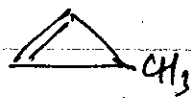


$CH_2=CH-CH_3$.
$CH_2=CH-CH=CH_2$

2. C_4H_6 ① $CH_3-C\equiv C-CH_3$ — 1,2 ⇒ FGI

② $CH_2=CH-CH=CH_2$ — 1,3 ⇒ RCI, FGI

③  — 1,4 ⇒ RCI, FGI

④  — 2,3 ⇒ RCI, FGI (Diff H·O·C & H·O·H)

2,4 ⇒ RCI, FGI (Diff H·O·C & H·O·H)

3,4 ⇒ CI

Note All RCI are FGI but vice versa not true

All RCI are FGI but priority give to RCI

METAMERISM

Compound having same M.F but diff alkyl group attached at polyvalent fxnal group

Polyvalent fxnal grp –

$-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-$	Anhydride
$-\overset{O}{\overset{\|}{C}}-O-$	Ester
$-\overset{O}{\overset{\|}{C}}-NH-$	Amide
$-\overset{O}{\overset{\|}{C}}-$	Ketone
$-O-$	Ether
$-S-$	Thioether
$-NH-$	Amine

1. $CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3$ $\quad$ $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-O-CH_3$

Meta.

2. 

Meta.

3. $CH_3-CH_2-CH_2-CH_2-O-CH_3$ $\quad$ $CH_3-CH_2-CH_2-O-CH_2-CH_3$

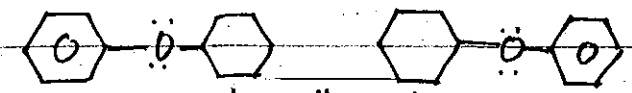
Meta.

Internal Unit Change (Two Unit Change) [4, 5 two]

Metamers में Unit में से change हो Inter unit change
और में change हो Intra unit change

4. $CH_3-CH_2-CH_2-CH_2-NH-CH_3$ $\quad$ $CH_3-CH_2-CH_2-NH-CH_2-CH_3$

⇓ Meta.

5. 

⇓ Same comp.

6. ✗ $CH_3CH_2-CH_2-CH_2-O-CH_3$ $\quad$ $CH_3-\underset{CH_3}{CH}-CH_2-O-CH_3$

⇓ Both are meta. & C.I

7. ✗ $\overset{3}{CH_3}-\overset{2}{CH_2}-\overset{1}{CH_2}-O-CH_3$ $\quad$ $CH_3-\underset{CH_3}{\overset{2}{CH}}-\overset{3}{O}-CH_3$

⇓ Both are meta. & P.I

Intra Unit change

Metamers

- Internal Unit change ⇓ Only Meta
- Intra Unit Change ⇓ Meta may be C.I. or P.I.

8. $C-C-C-C-C-NH_2$ (I) $\quad$ $C-C-C-C-NH-C$ (II) $\quad$ $C-C-C-NH-C-C$ (III)

I, II ⇒ Fg I

I, III ⇒ Fg I

II, III ⇒ Meta.

Isomers formation, Probability

Open Chain

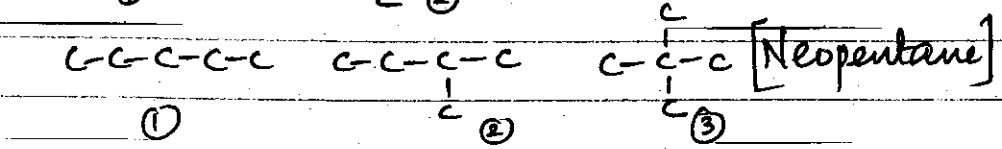
1C 1

2C 1 [C-C]

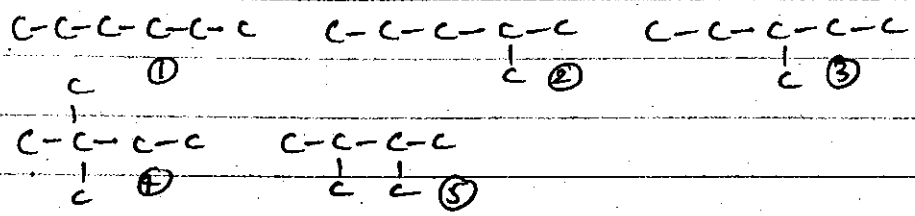
3C 1 [C-C-C]

4C ⇒ 2

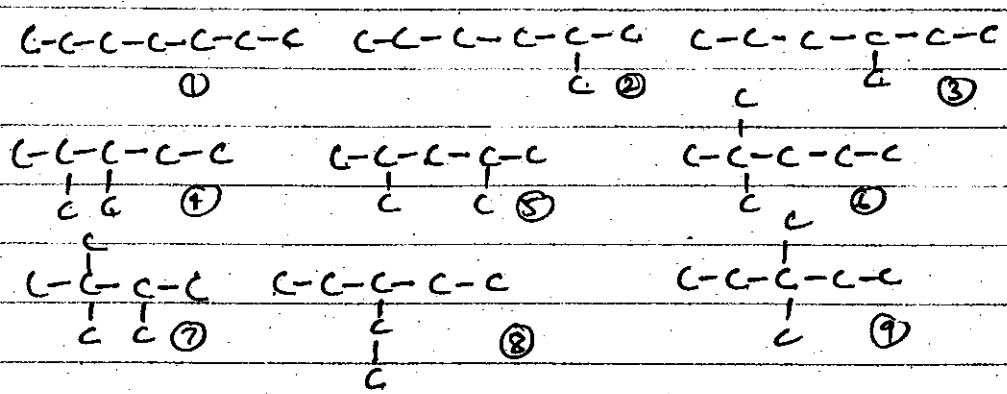
5C ⇒ 3



6C ⇒ 5



7C ⇒ 9

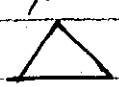


Closed Chain

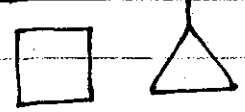
1C ⇒ X

2C ⇒ X

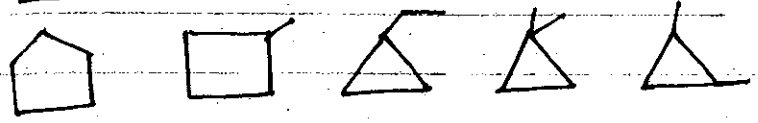
3C ⇒



4C ⇒

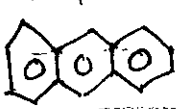
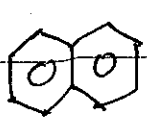


5C ⇒

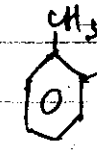


Diwali H.W

- How many structural isomers are possible with fo following M.F

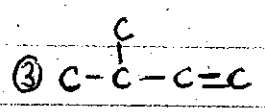
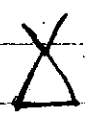
1. C_5H_{10} (Open + Close) ⇒ 10
2. C_6H_{10} (Terminal Alkyne) ⇒ 4
3.  (Monochloroproduct) ⇒ 3
4.  (Monochloroproduct) ⇒ 2

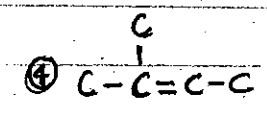
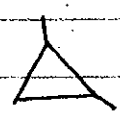
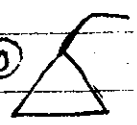
5. $C_2Br, F, Cl, I \Rightarrow$ (Structural Iso) $\Rightarrow 3$

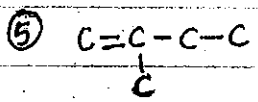
6.  (Total Benzoid Isomer) $\Rightarrow 5$

7. i) C_3H_8O
ii) $C_4H_{10}O$ $\Rightarrow$ No. of Alcohol
iii) $C_5H_{12}O$

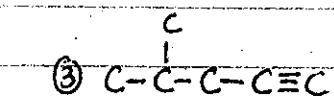
① C_5H_{10} DU $\Rightarrow 1$

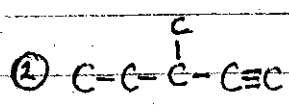
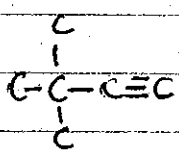
① C-C-C-C=C ③  ⑥  ⑧ 

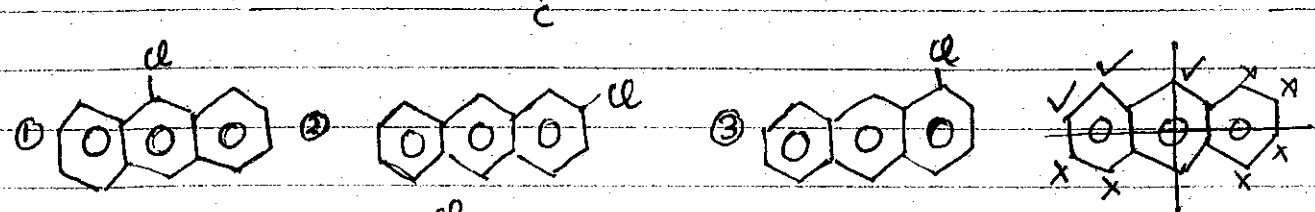
② C-C-C=C-C ④  ⑦  ⑨  ⑩ 

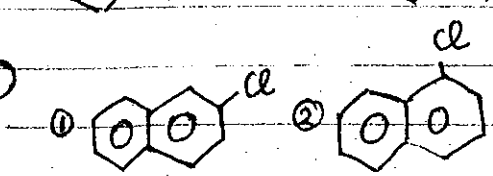
⑤ 

② C_6H_{10} DU $\Rightarrow 2$

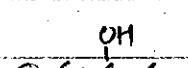
① C-C-C-C-C≡C ③ 

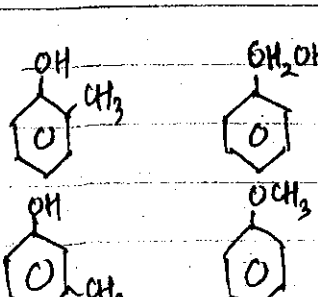
②  ④ 

③ 

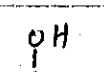
④ 

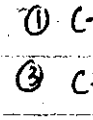
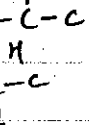
⑦ I C_3H_8O DU $\Rightarrow 0$

① C-C-C-OH ② 

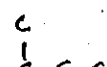
⑥ 

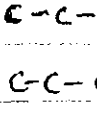
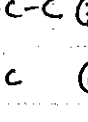
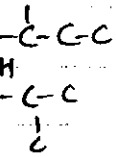
II $C_4H_{10}O$ DU $\Rightarrow 0$

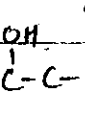
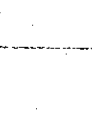
① C-C-C-C-OH ② 

③  ④ 

III $C_5H_{12}O$ DU $\Rightarrow 0$

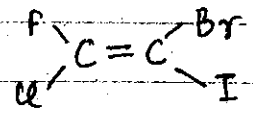
① C-C-C-C-C-OH ②  ③ 

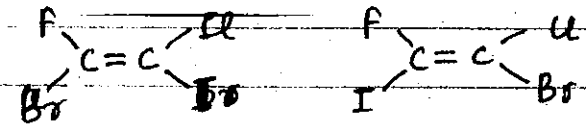
④  ⑤  ⑥ 

⑦  ⑧ 

⑤ $C_2FClBrI \Rightarrow C_2H_4$ (alkene) DU ⇒ 1

(+4H)

① 

② 

KEY POINT

CH_3-	C_2H_5-	C_3H_7-	C_4H_9-	$C_5H_{11}-$
1	1	2	4	8

for aldehyde (n-1) C is considered
4 Ke liye 3 wala
5 Ke liye 4 wala

Free valency

$-X$ (-F, -Cl, -Br, -I), $-OH$, $-\ddot{N}H_2$ $-N=O$ $-NO_2$ etc.

$C_5H_{11}I \Rightarrow 8$

$C_5H_{13}N \Rightarrow$ 1° amine $\Rightarrow 8$

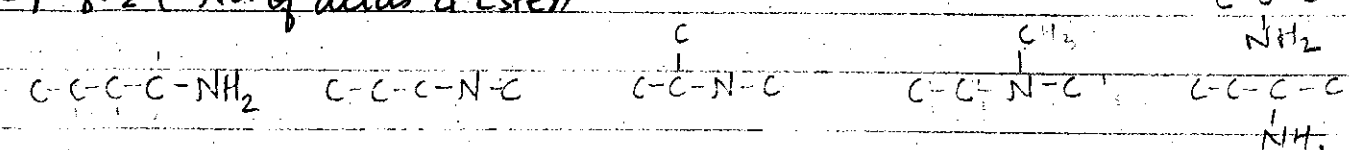
$C_4H_9Cl \Rightarrow$ 4

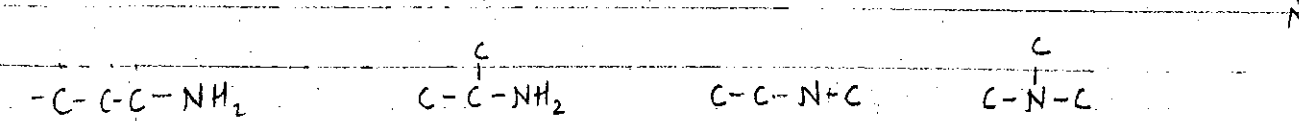
How many structural isomers are possible with following M.F

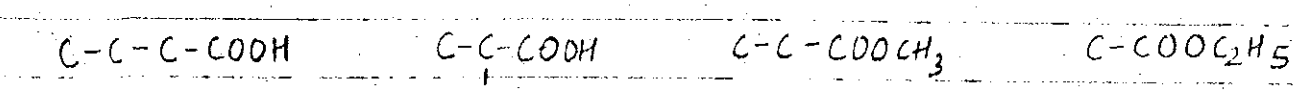
$C_4H_{11}N$ (No. of possible amine) 1° 2° 3°

C_3H_9N (No. of possible amine) C_3H_8NH

$C_4H_8O_2$ (No. of acids & ester)







Stereochemistry
(DUE TO SAME CONNECTIVITY)

CONFORMATIONAL ISOMERISM (Pseudo Isomers)

Infinite no of stereoisomers which are formed due to free rotation around a single bond is K/a CONFORMATION & this phenomenon is K/a CONFORMATIONAL ISOMERS.

conformation → ∞

conforms → stable conformations

Conformers also K/a ROTAMERS and this isomerism is also K/a ROTATIONAL ISOMER

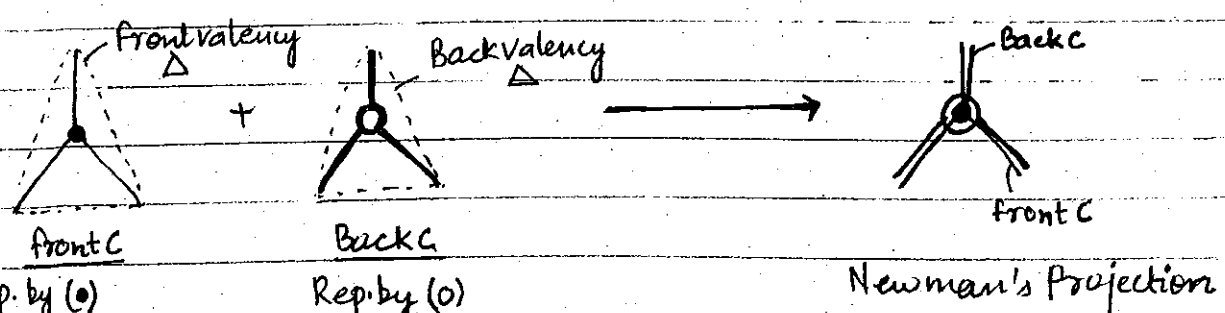
The energy needed for the rotation around a single bond is available at room temp. Thats why conformers interconverted to each other at room temp & it is K/a PSEUDO ISOMERS (not seperable)

Representation Of 3-D Molecule Into 2-D

1. NEWMANN'S PROJECTION → (Front view / Back View)

Front view projection of 3-D is K/a NEWMAN'S PROJECTION.

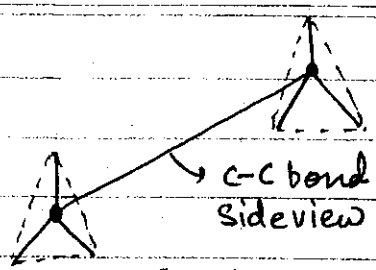
C–C bond does not represented in this formula



2. SAWHORSE PROJECTION FORMULA

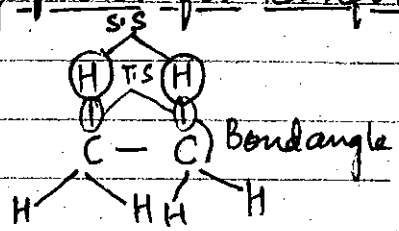
Side view projection of 3-D molecule is K/a SAWHORSE PROJECTION

C-C bond represented in this formula (Side view)



Sawhorse projection

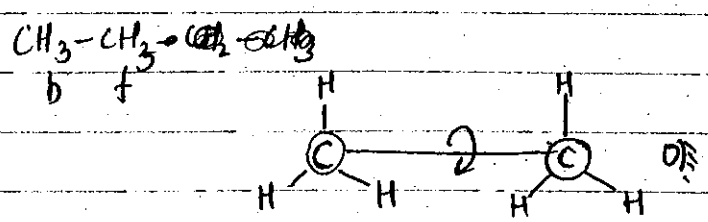
Stability factor for conformers

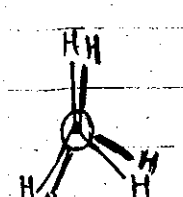


Steric Strain (SS) Due to repulsion b/w atom & group
Torsional strain (TS) Due to repulsion b/w bonding e⁻
Bond angle Angle b/w two bond of the same atom
Dihedral angle Angle b/w two bond of adjacent atom

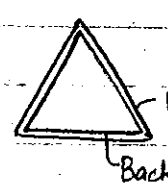
***
During conformational isomer Bond Angle remain SAME while dihedral angle changes

Conformer Of Ethane

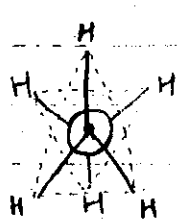




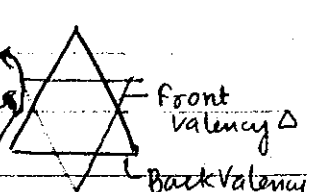
Eclipsed form
[θ = 0°, 120°, 240°, 360°]
↳ Max^m repulsion [SS, TS]
↳ Max^m inter e⁻ repulsion
↳ Max^m inter e⁻ energy
↳ Min. stability



Skew form (θ = All Rest)



Min. repulsion (SS, TS)
Min inter e⁻ repulsion
Min. inter e⁻ energy
Max^m stability



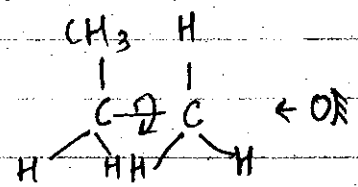
Staggered form

Energy Order Eclipsed > Skew > Staggered

Stability Order Stagerred > Skew > Eclipsed

Conformer Of Propane

$CH_3-\underset{2}{CH_2}-\underset{1}{CH_3}$

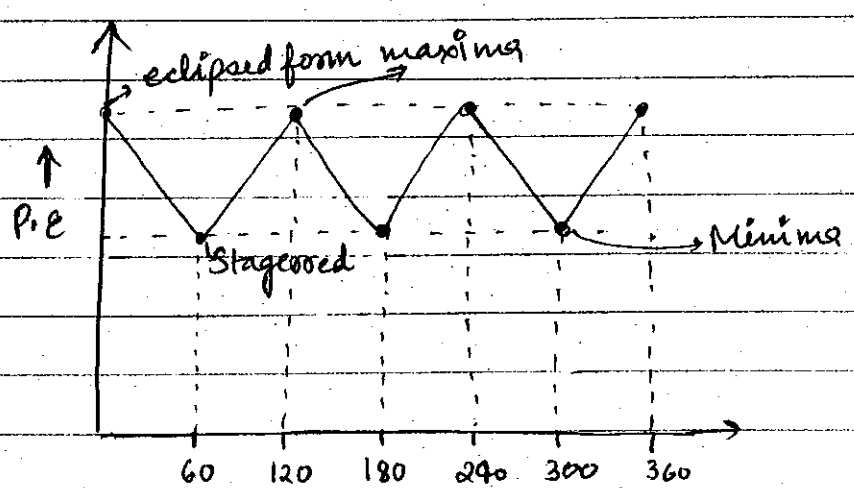


Conformers of ethane and propane are same

Conf Energy order Eclipsed > Skew > Staggered

Stability order Stagered > Skew > Eclipsed

Energy Profile Curve for Ethane & Propane



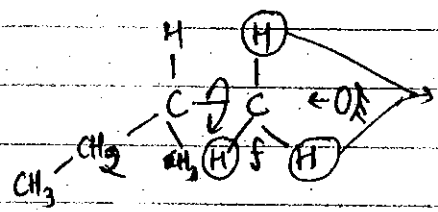
Skew Form

Infinite conformations in b/w eclipsed & staggered form is ka SKEW FORM

Conformer of butane

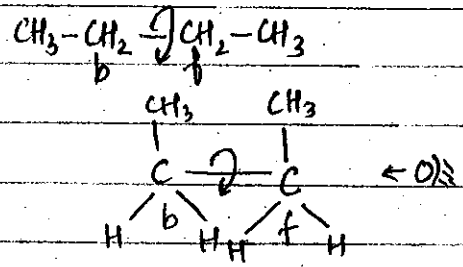
$\overset{4}{CH_3}-\overset{3}{CH_2}-\overset{2}{CH_2}-\overset{1}{CH_3}$

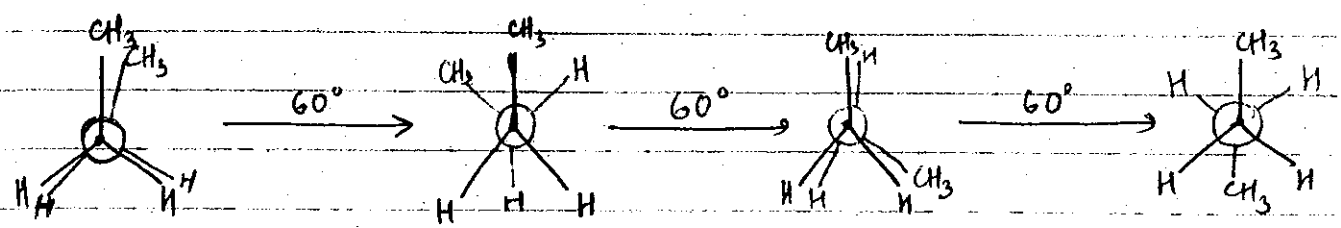
1. Rotation around C_1-C_2 carbon



Conformers of ethane, propane & n-butane (C_1-C_2 carbon) → same

2. Rotation around C_2-C_3 carbon



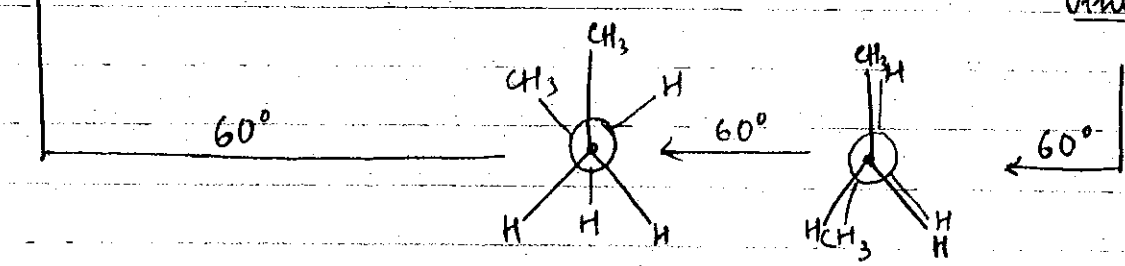


$\theta = 0°$ Eclipsed form I (fully eclipsed)

$\theta = 60°$ Gauche form II

$\theta = 120°$ Partially eclipsed III

$\theta = 180°$ Staggered form / Anti staggered / Anti form IV



$\theta = 300°$ Gauche form VI

$\theta = 240°$ Partially eclipsed V

1. Torsional Strain $I \simeq II$

$II \simeq IV$

$I > II > III > IV$

2. Steric strain $I \neq II$

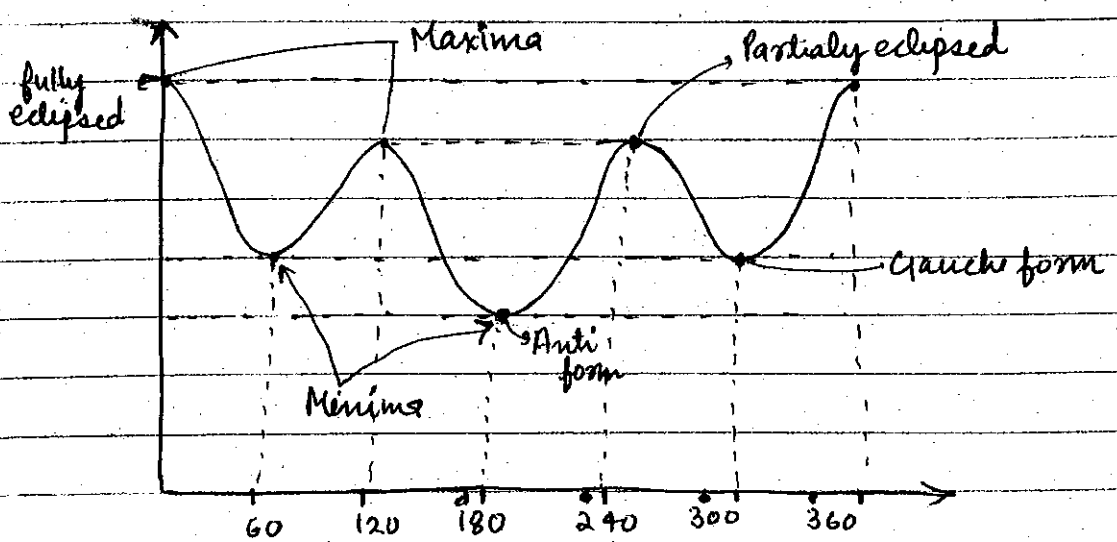
$II \neq IV$

$I > II > III > IV$

Energy Order Eclipsed > Partially Eclipsed > Gauche > Staggered

& ~~Eclipsed~~

Stability Order Staggered > Gauche > Partially Eclipsed > Eclipsed



Out of infinite conformer which are formed at minima position in energy profile curve is K/a CONFORMERS.

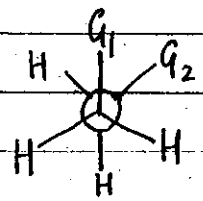
Judgement Of Stability

1. Wa'under Waal Repulsion (TS, SS)
2. Hydrogen Bonding
3. Strong electrostatic force of attraction

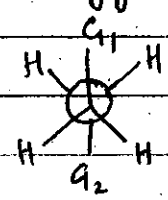
Gauche form more stable than staggered form
Gauche form may be stable than Staggered form if following factors are present in the molecule
① Hydrogen Bonding
② Electrostatic force of repulsion.

Q. CH_2-CH_2 (with G_1, G_2)

Gauche



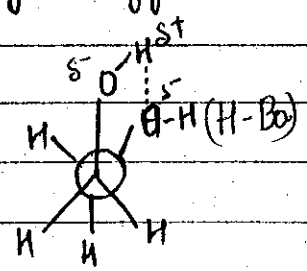
Staggered form

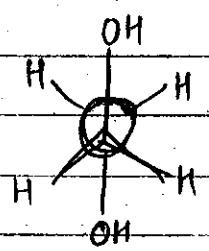


1. $G_1 = -CH_3$, $G_2 = -CH_3$ — Stability = Staggered > Gauche

2. $G_1 = -CH_3$, $G_2 = -H$ — Stability = Staggered > Eclipsed form

3. $G_1 = OH$, $G_2 = OH$
CH_2-CH_2 (Ethylene glycol)
OH OH





Stability = Gauche > Staggered

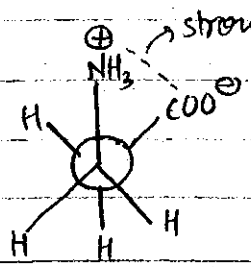
4. CH_2-CH_2
OH G_2

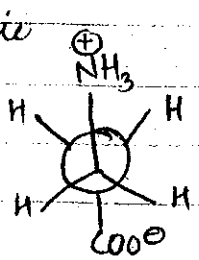
$G_2 = -OH\ -NH_2\ -F\ -\overset{O}{\overset{\|}{C}}-OH\ -\overset{O}{\overset{\|}{C}}-H$ ... etc.

Stability = Gauche > Staggered
Due to H bond.

5. CH_2-CH_2
$\overset{\oplus}{N}H_3$ $COO^{\ominus}$
Zwitter Ion.

Stability = Gauche > Staggered





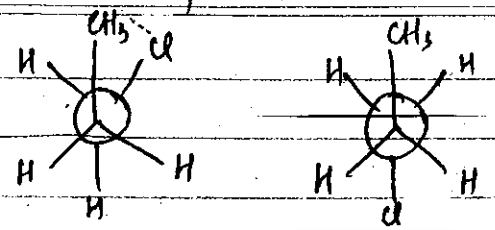
If 2 flourine attached then gauche more stable (due to reverse hyperconjugation)

cycloalkane give test of unsaturation

Dancing Resonance

Less % p character more

6. $CH_3 - CH_2$ (CH_3 and Cl)



Gauche > Staggered

7. $CH_2(COOH) - CH_2(COOH)$ —(pH > 7, Basic medium)→ $CH_2(COO^{\ominus}) - CH_2(COO^{\ominus})$

repulsion

Stability : Staggered > Gauche

8. $CH_2(COOH) - CH_2(COOH)$ —(pH < 7, Acidic medium)→ $CH_2(COOH) - CH_2(COOH)$

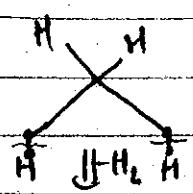
H bonding

Stability : Staggered < Gauche

Conformers In Cycloalkane

CYCLOPROPANE

Perfect planer



→ Bond angle in propane = 109°28'

→ Bond ∠ in cyclopropane = 60°

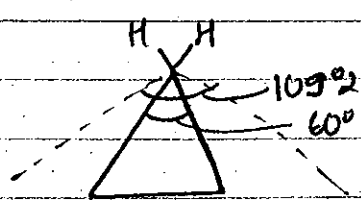
A.S = 49°28'

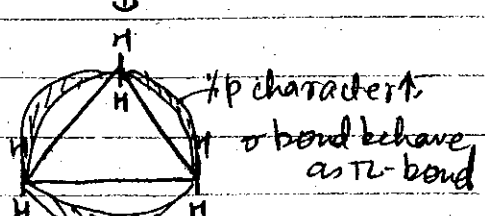
→ Ber bond deviation = 24.5°

→ No flexibility (Rigid)

→ Planer molecular

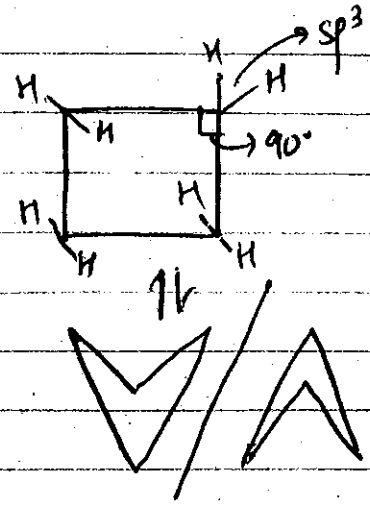
→ Highly angle strained





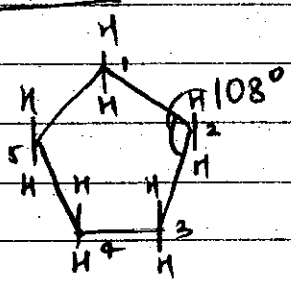
Cyclohexane only expand when react with alcohol ester

CYCLOBUTANE

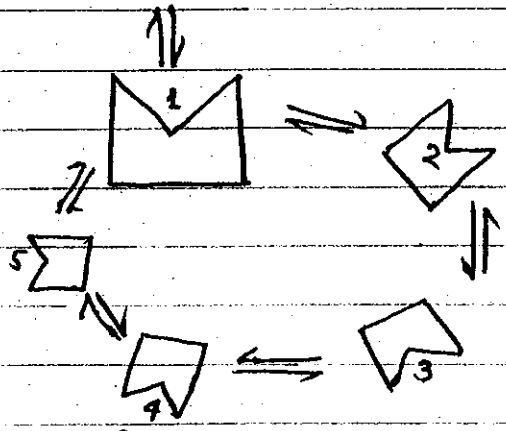


→ Real bond angle = 109°28'
→ bond ∠ in cyclobutane = 90°
A·S = 19°
→ More flexible than cyclopropane
→ Non-planer molecule
→ Form V Shape Structure

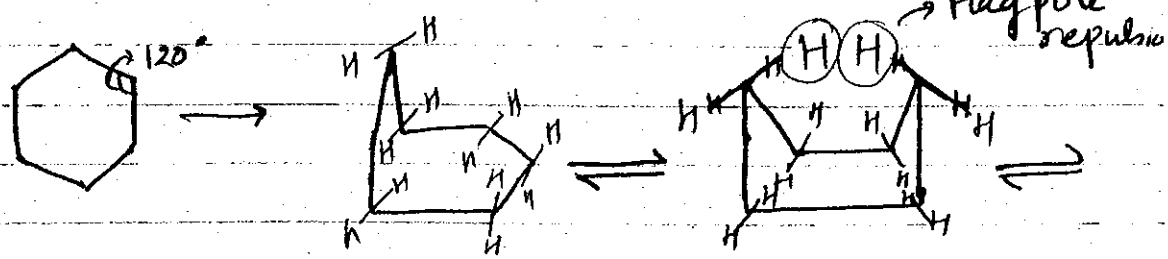
CYCLOPENTANE



Real bond angle = 109°28'
bond ∠ in cyclopentane = 108°
A·S = 1°
More flexible than cyclobutane
Non-planer molecule
Molecule form envelop like str...



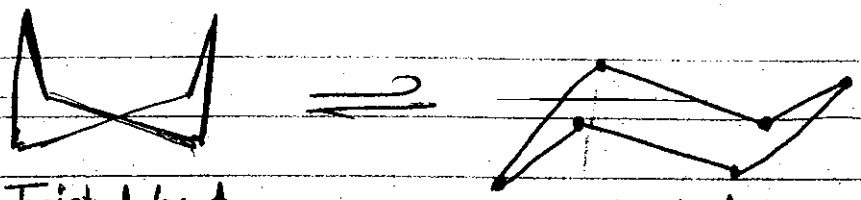
CYCLOHEXANE



Half chair
I

Boat form
II

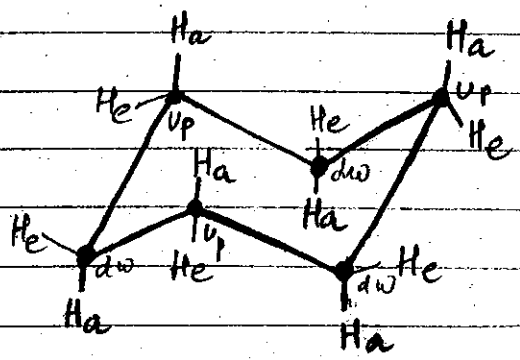
Methylcyclohexane is more soluble in water as non-polar molecule



⇒ Twisted boat
⇒ Optically active
⇒ No flag pole repulsion
II

Chair form
IV

Stability ⇒ IV > III > II > I



perfect tetrahedral
no angle strain
most symmetric molecule
Thermodynamically stable molecule

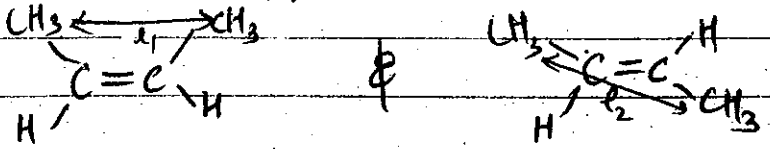
RRS
diff linked grp for a C
square planer envisaged

Configurational Isomerism

GEOMETRICAL ISOMERISM

Those stereoisomers which have diff 3D relative arrangement around a restricted rotatory system (R.R.S) is Ca G.Isomers & this phenomenon is K/a G.Isomerism.

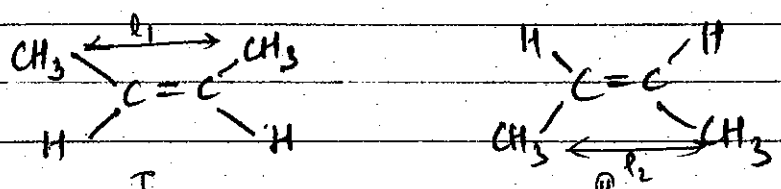
G.I occur due to diff areal distance b/w terminal groups

1. 

$l_1 \neq l_2$

Diff. areial distance

Both are G.I

2. 

$l_1 = l_2$

Same aerial distance

No G.I

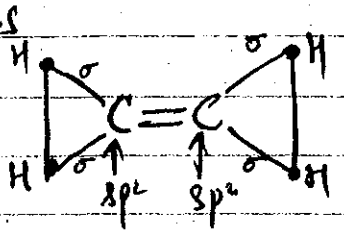
G.I do not interconvertible to each other at room temp.

Condition for G.I

Cond.I: Compound must have restricted rotatory system (R.R.S) / hindered rotation / frozen rotation / absence of free rotation

Type of R.R.S

① Double Bonded R.R.S



C–C bond alkane
C–N double bond Schiff base / imine $>C=\ddot{N}-H$

$C_6 \rightarrow 1s^2\ 2s^2\ 2p^2$ (2s², 2p² = outer)

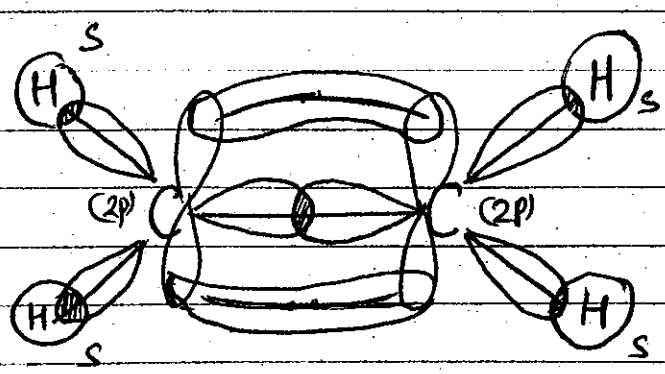
G.S → [↑↓]

E.S → 2s [↑] , 2p [↑ ↑ ↑]

[↑]* pure p-orbital (unhybridised orbital)

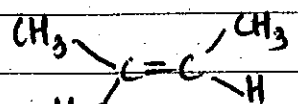
[↑]*

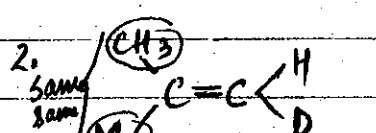
sp^2 [↑ ↑ ↑]



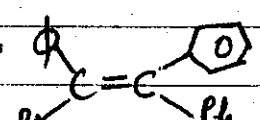
Following double bond containing R.R.S compound give G.I.

ALKENES SYSTEM

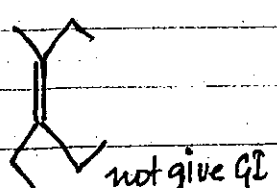
1. 
give GI

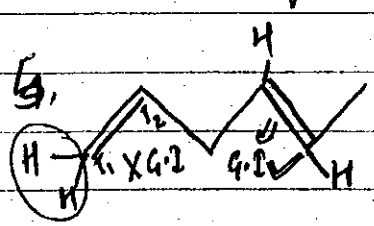
2. 

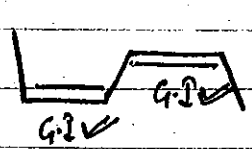
not give GI

3. 

not give G.I

4. 
not give GI

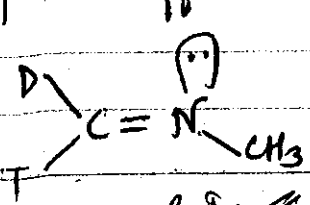
5. 

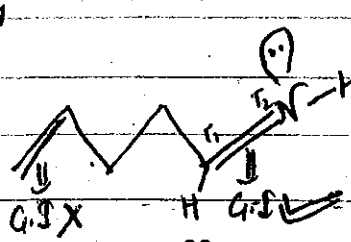
6. 

IMINE SYSTEM

$[>C=\ddot{N}-H]$ → pseudo Atom

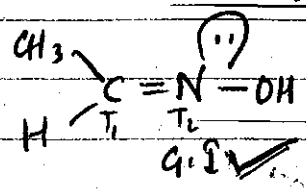
Isotopes are different atoms

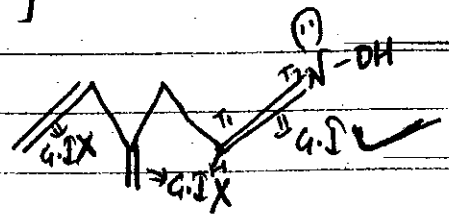
7. 

8. 

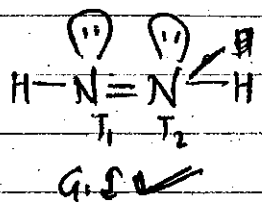
Azo always give G.I

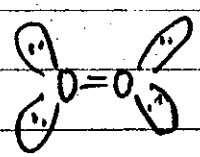
OXIME SYSTEM $\left[\rangle C=\ddot{N}-OH\right]$

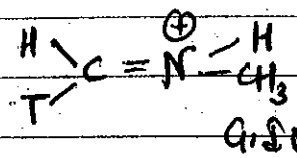
9. 

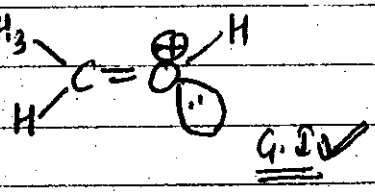
10. 

AZO COMPOUNDS $(\ddot{N}=\ddot{N})$

11. N_2H_2 

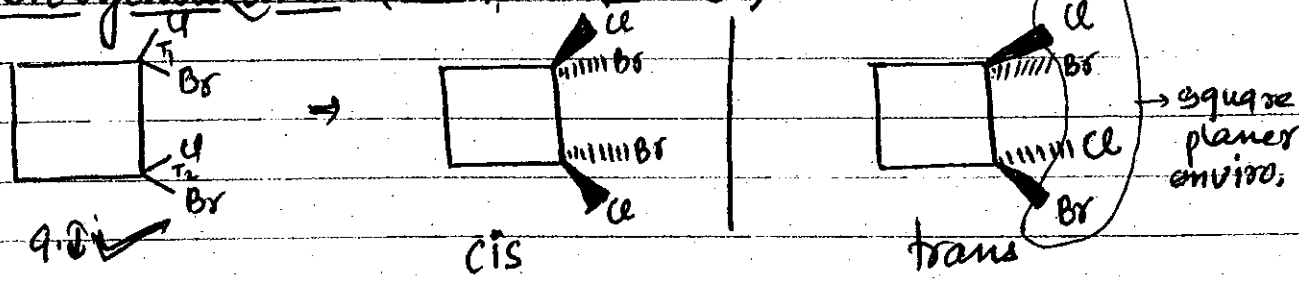
12. O_2  NO G.I ✗

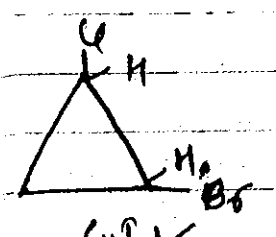
13.  (Acidic medium)

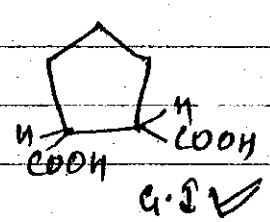
14. 

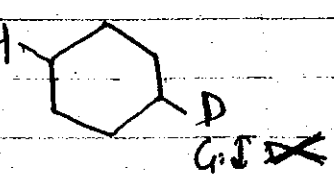
15.

G.I In Cycloalkane $(\triangle\ \square\ \pentagon\ \hexagon)$

15. 

16. 

17. 

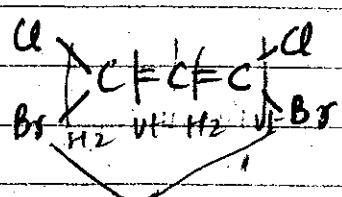
18. 

2, 4, 6, 8 - - - wale G.I Nahi hoga.
bondchake ring (phenyl/ya cyclo)

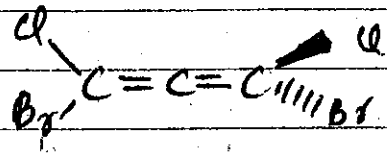
(III) G.I in Allene

When more than one double bond continue present then system is ya allene system

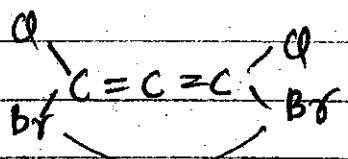
19



Tetrahedral environment
(Aerial distance same-same)
∥
No G.I ✗

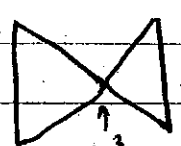


20.



square planer environment
∥
~~No~~ G.I ✓

(IV) G.I in Spiro Compound

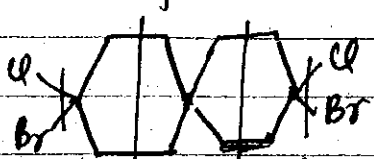


sp^3
∥
Tetrahedral

both rings are ✗

When two rings fused at same C atom then compound is ya SPIRO Comp.

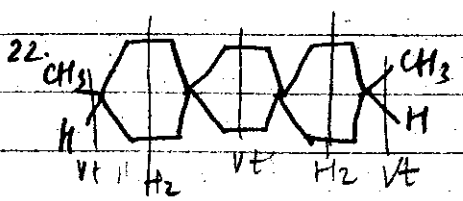
21.



Tetrahedral environment

No G.I ✗

22.

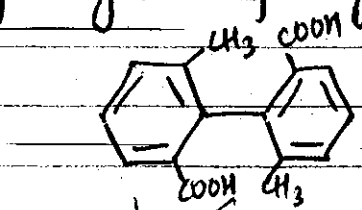


square planer environment
G.I ✓

O-pe Bulky group + repulsion resp ghum jaye gi, tetrahedral FROZEN ROTATION

No G.I

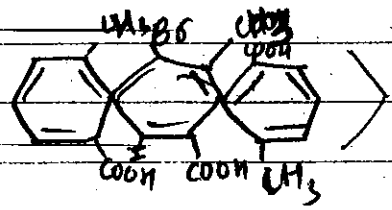
⑤ Biphenyl & Triphenyl System

28. 

G.I X

Tetrahedral environment

(Both ring are I°)

29. 

Square planer environment ⇓ give G.I

G.I ✓

Cond.I At R.R.S both terminal group must be different.

Cond.II At R.R.S both terminal valency should be in same plane (SQUARE PLANAR)

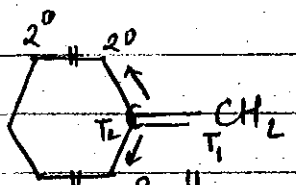
NOTE-I Alkyne will never give G.I due to its linear str. & 2 3-D arrangement not possible.

$R_1 - C \equiv C - R_1$

sp sp

⇓

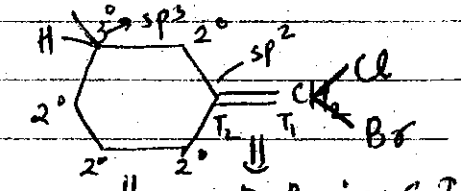
NO G.I

25. 

2° ⇓ ring system

D.Bond sys. ⇓

NO. G.I

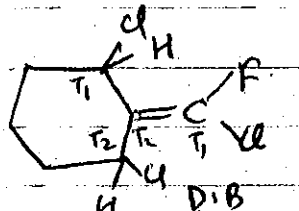
26. 

⇓ D.B give G.I

NO G.I

⇓

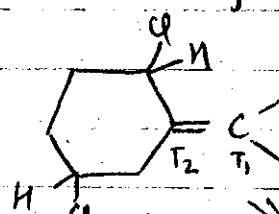
Comp. give G.I

27. 

D.B ⇓

G.I xx

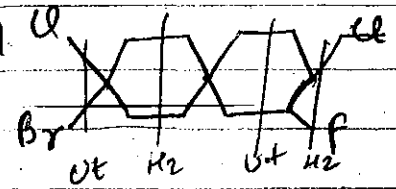
Ring give G.I

28. 

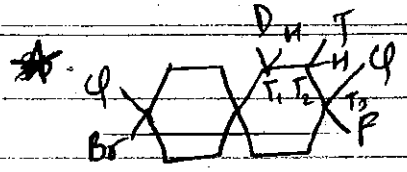
⇓ D.B G.I ✓

⇓

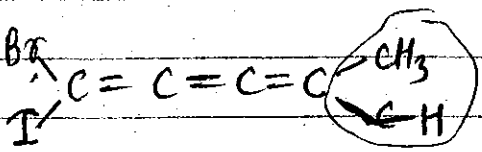
Ring G.I ✓

29 

Not give G.I

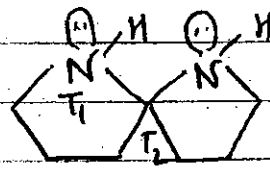


Give G.I

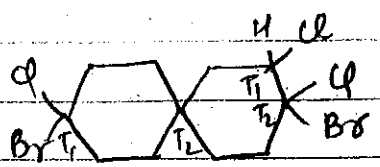
30 

same-same

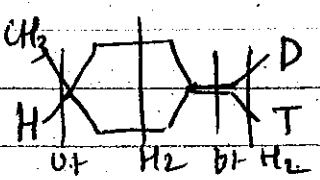
No G.I

31. 

Give G.I

32. 

Give G.I

33. 

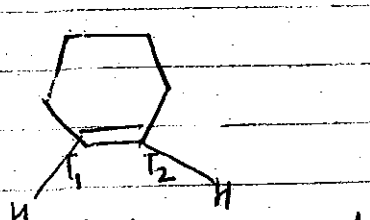
Tetrahedral

No G.I

If terminal group diff. then odd no double bond containing allene ~~spiro~~ system & odd no ring containing spiro system give G.I due to SQUARE PLANAR Environment

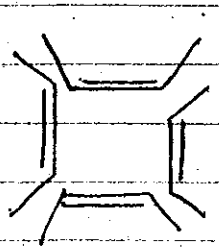
Even no. double bond & ring containing allene & spiro system do not give G.I due to TETRAHEDRAL Environment (inter aerial distance same.

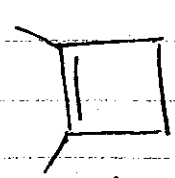
G.I in Encyclic π-bond



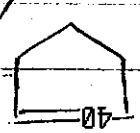
Endocyclic π-bond

cis in O.C



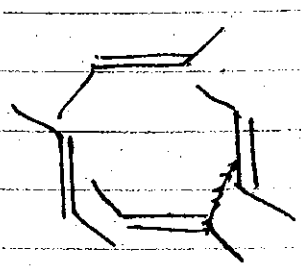
1. 

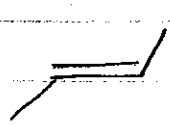
cis form

2. 

cis form

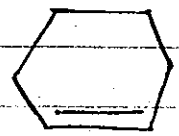
trans in O.C



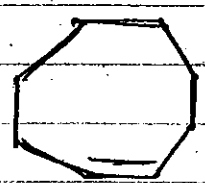
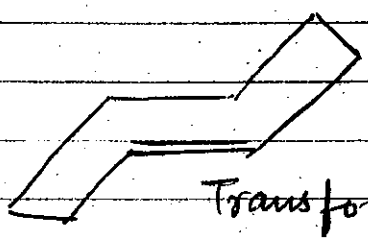
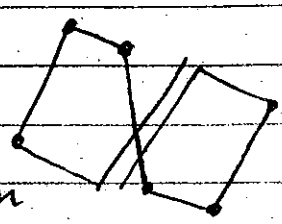


No trans form

No trans form

3.  cis form — no trans form

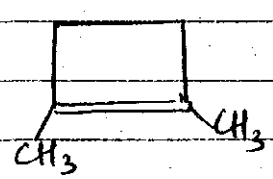
4.  cis form — no trans form

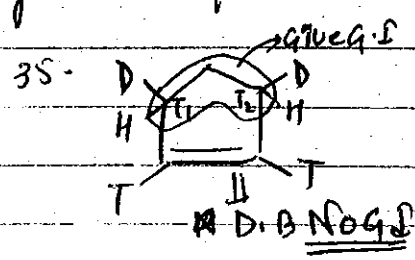
5.  cis form —  Trans form 

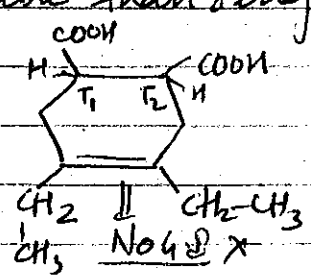
KEY POINT

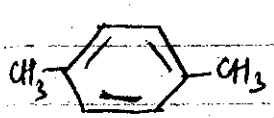
① In case of endocyclic π-bond trans orientation does not exist before 8-membered ring therefore after 7 membered ring give G.I across endocyclic π-bond.

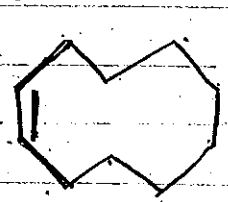
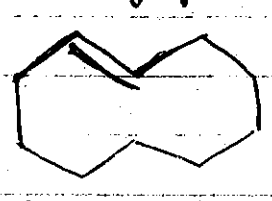
② In 8 to 11 membered ring cis form is more stable than trans. After 12 membered ring trans-form is more stable than ring.

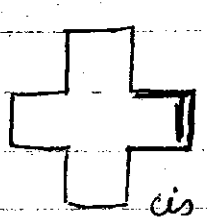
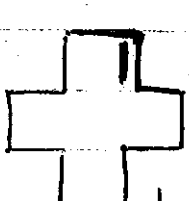
34.  No G.I

35.  give G.I — D.B No G.I — Ring ⇒ G.I ✓

36.  No G.I ✗ — Ring give G.I ✓

37.  No G.I

38.  I  II — Both are G.I

39.  cis I  trans II — Both are G.I — trans more stable (ring 12 K.)

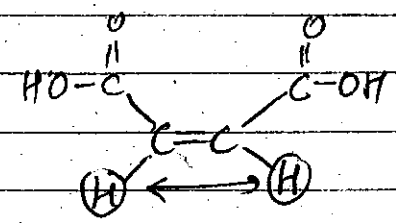
Nomenclature for G.I

Steps ① cis-trans system
② syn-anti system
③ E-Z system

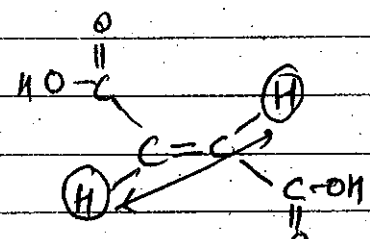
① **cis trans System** valid only when at least 2 groups are same.

If two identical group at R.R.S same side → cis
If two identical group at R.R.S oppsite side → trans

①

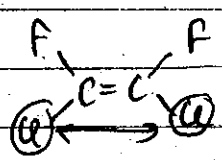


→ cis- Maleic Acid

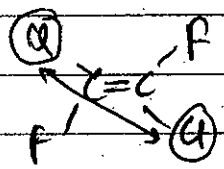


trans- fumaric Acid

②

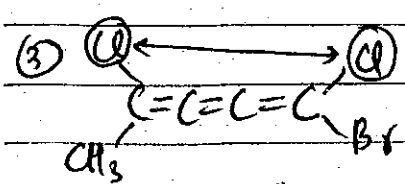


cis-

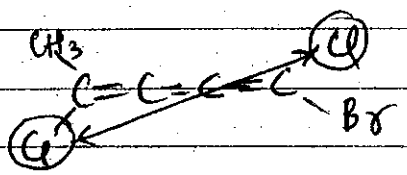


trans-

③

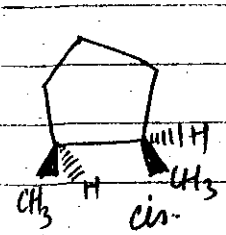


cis-

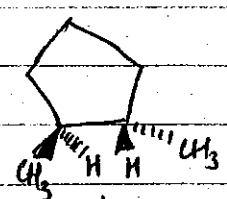


trans-

④



cis-



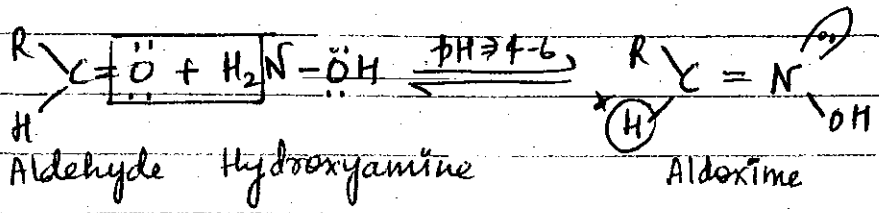
trans-

② **Syn Anti System** valid only when at least any one terminal have lone pair.

when one terminal or both terminal have lone pair then the new system SYN ANTI applied.

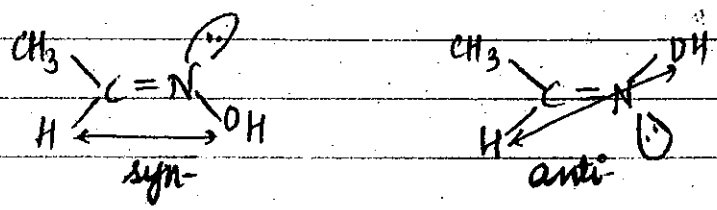
① Oxime

① Aldoxime

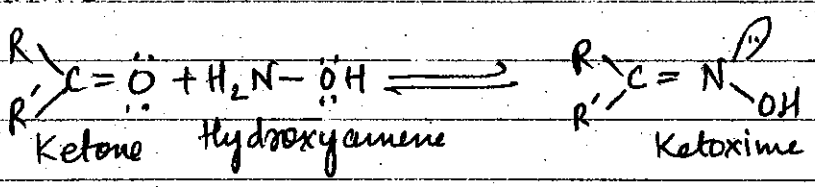


Aldehyde Hydroxyamine Aldoxime

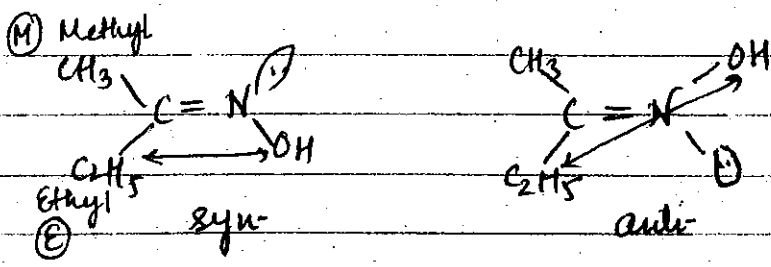
aldehyde से aldoxime बनाने के लिए pH 4-6 चाहिए



② Ketoxime



Ketone Hydroxyamine Ketoxime

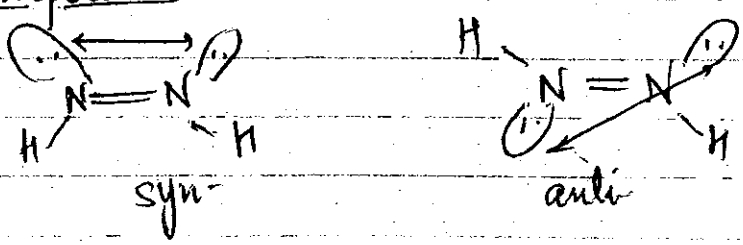


follow alphabetical order

opposite & opposite, same side to anti

In case of ketoxime unsymmetrical ketoxime give G.I.
Alphabetically preffered alkyl group & OH group both are same side ↳ SYN
& if on opposite side ↳ ANTI

② Azo Compounds



If both l.p are same side → SYN
opposite side → ANTI

E-Z System (CIP rule) when all four terminals are diff.
latest system
[Cann, Ingold, Prelong Rule]

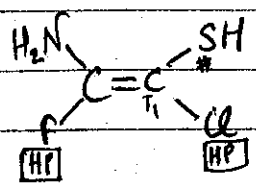
* When all four group are different at R.R.'s then the new system E-Z applied.

E ⇒ ENTGEGAN opposite side
Z ⇒ ZUSSEMAN same side

High priority [HP] group same side ⇒ Z
High priority [HP] group different group ⇒ E

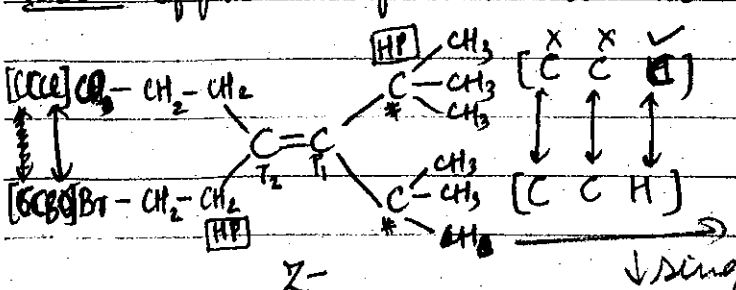
RULE-1 priority of atoms directly proportional to atomic no. of atom which is directly attached to terminal C of R.R.'s.

1.

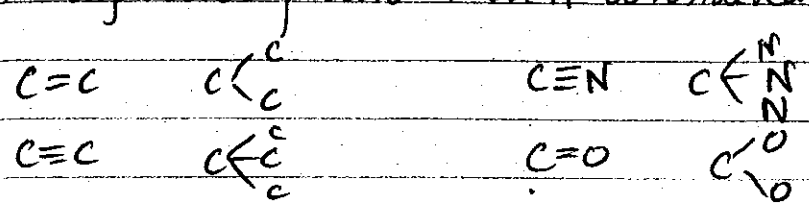


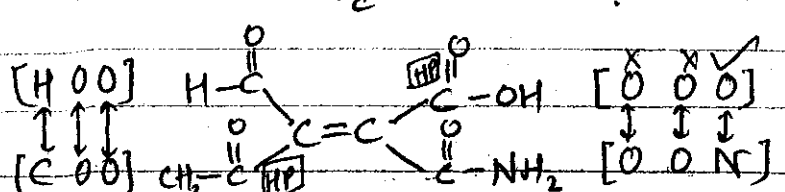
Z-

RULE-2 If first rule fail then atomic no. of first atom considered.



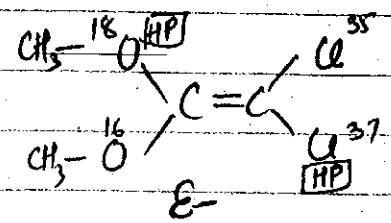
RULE-3 If multiple bonds present then it considered as a





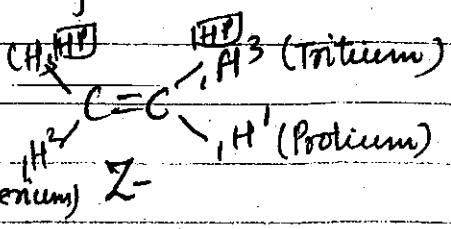
RULE 4 If isotopes are present then,
priority of ~~isotopes~~ ~~isotope~~ ∝ atomic mass of isotope

④



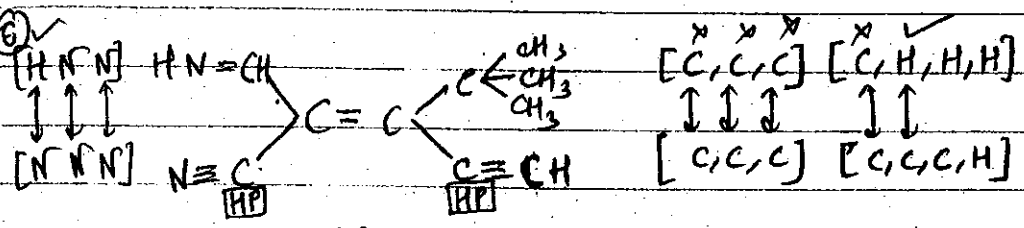
E-

⑤



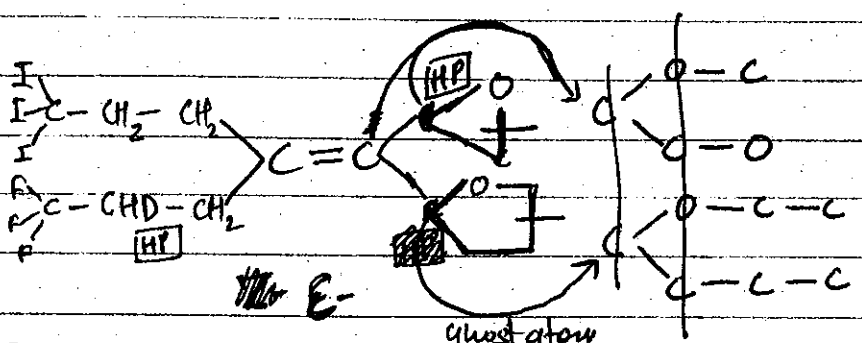
Z-

⑥



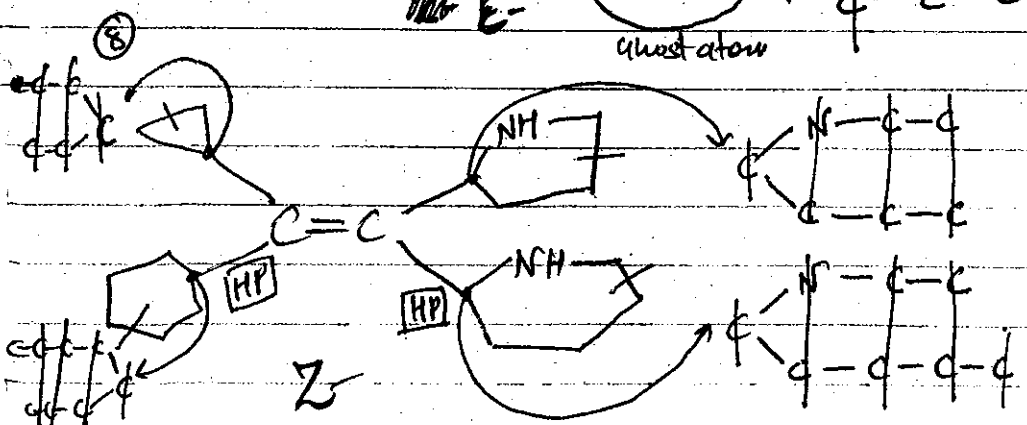
Z-

⑦



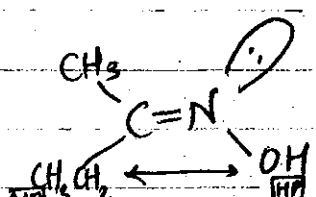
E-

⑧



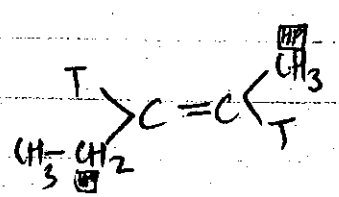
Z-

⑨



i) syn
ii) Z-

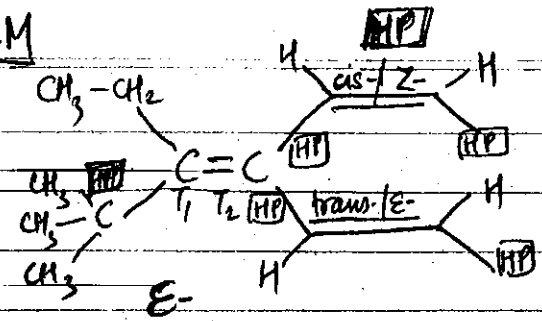
⑩



i) Trans
ii) E-

PSEUDOSYSTEM

(1)



For pseudosystem priority rule.

cis-> trans-

Z-> E-

R-> S-

No. Of G.I

(1)

No. of G.I

Unsymmetrical System

No. of G.I = 2^n

n = no. of site where G.I possible

Symmetrical System

→ n = even

No. of GI = $2^{n-1} + 2^{\frac{n}{2}-1}$

→ n = odd

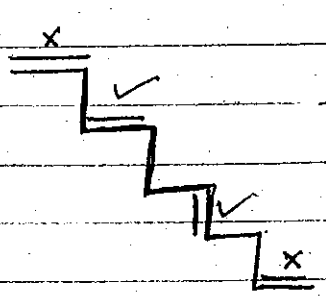
No. of G.I = $2^{n-1} + 2^{\frac{n-1}{2}}$

(1) $CH_2^{\times}=CH-CH_2-C^{\times}\equiv C-CH_2-CH^{\checkmark}=CH-CH_3$

(G.I) (G.I) (G.I)

n = 11

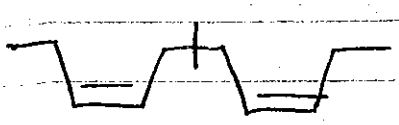
Unsymmetrical No. of G.I = $2^n = 2^2 = 4$

(2) 

n = 2

Unsymmetrical

No. of G.I = $2^n = 2^2 = 4$

(3) 

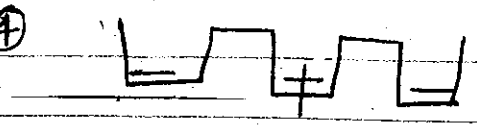
n = 2

Symmetrical

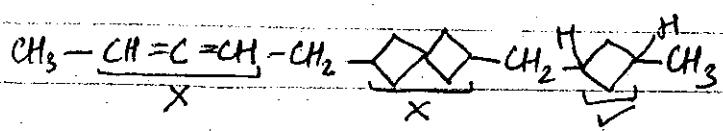
No. of G.I = $2^{n-1} + 2^{\frac{n}{2}-1}$

$= 2^{2-1} + 2^0 = 3$

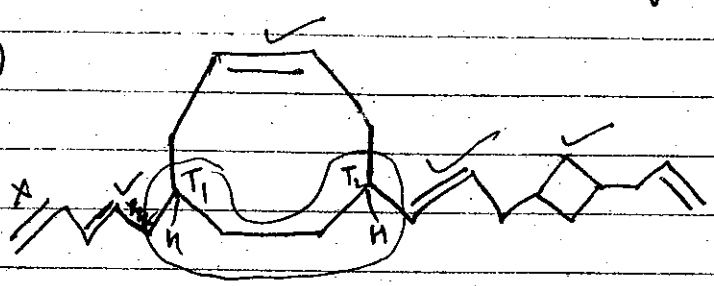
CSI → 2.5 EN

④ 

$n = 3$
Symmetrical
No. of G.I $= \frac{2^{n-1} + 2^{\frac{n-1}{2}}}{}$
$= 2^{3-1} + 2^{\frac{3-1}{2}}$
$= 2^2 + 2^1 = 4 + 2 = 6$

⑤ 

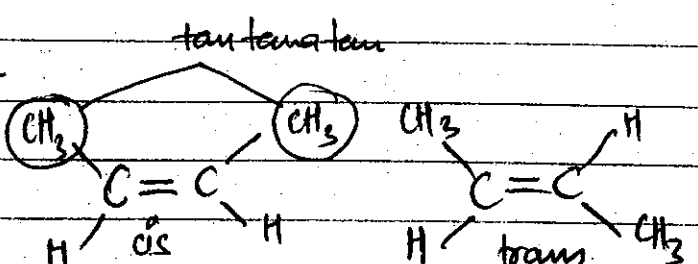
$n = 1$
Unsymmetrical No. of G.I $= 2^n = 2^1 = 2$.

⑥ 

$n = 5$
Unsymmetrical
No. of G.I $= 2^n = 2^5 = 32$.

PROPERTIES OF G.I

Stability :-



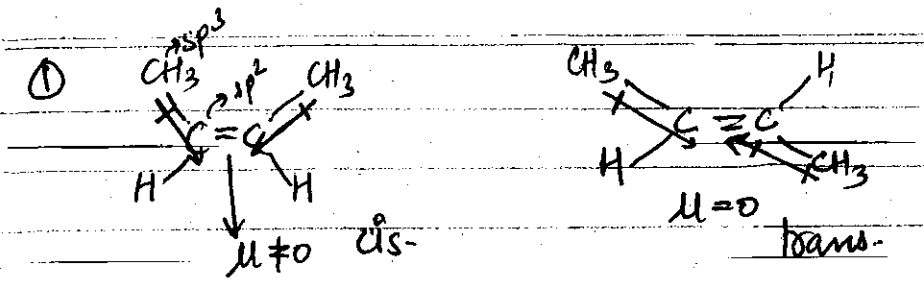
Stability ⇒ cis > trans

Dipole Moment :-

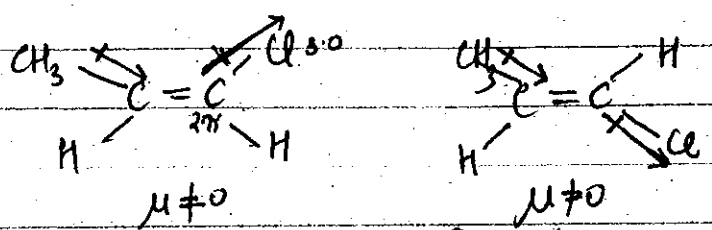
Degree of polarity will be measured by dipole moment
Vector quantity
less EN → more EN (direct^n)

$CH_3 - CH_3$	$CH_2 = CH_2$	$HC \equiv CH$
↳ sp3	↓ sp2	↳ sp
% S = 25	% S ⇒ 33	% S ⇒ 50%
EN = 2.5	EN = 2.75	EN ⇒ 3.25

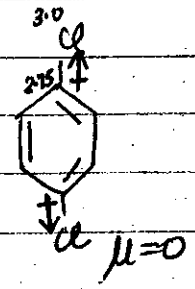
o/p conformation benzene is not necessary to cancel karke zero karna. Hence Nagraj ring discard

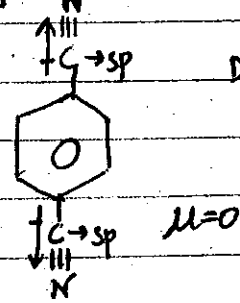
① 

μ cis- > trans-

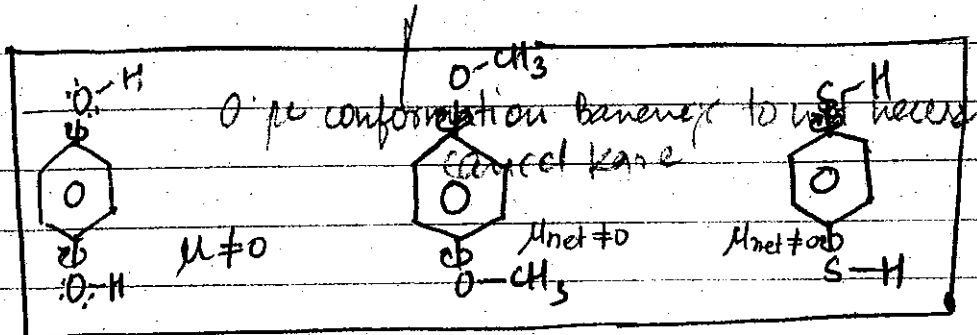
② 

μ cis- < trans-

③ 

④ 

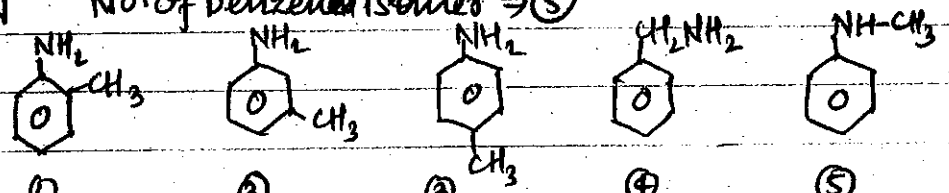
Diatomic linear

⑤ 

o/p conformation benzene is not necessary to cancel karke

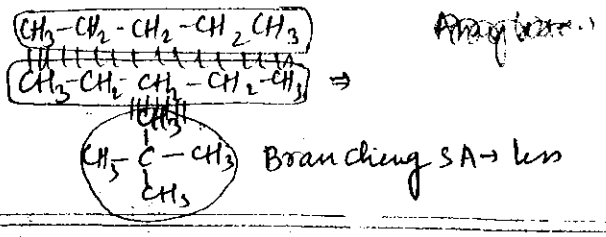
Diatomic angular group.

\# C_7H_9N No. of benzene isomer ⇒ ⑤



** 3 Nagraj of chemistry ⇒ -O-H, -O-CH₃, -S-H

In case of diatomic angular grp due to rotation around a single bond it forms ∞ conformation & the average μnet will be non-zero



① Boiling Point

Factors

① BP ∝ Molecular wt

BP ∝ 1/Branching ⇒ S.A ↓ Vander Waal force ↓

② BP ∝ Intermolecular Force of Attraction (IMF)

① → H-hydrogen ⇒ -O-H, -N̈H₂, -NH-, -C(=O)-OH, -C(=O)-NH₂

② → Dipole-Dipole Attraction ⇒ -C(=O)-H, -C(=O)-CH₃, R-X, R-O-R [Polar π-bond]

③ → VanderWaal Force → Unbranched Hydrocarbon ⇒ Alkane

Order of strength 1 > 2 > 3

① ① C-C-C-C-C
② C-C-C(-C)-C
③ C-C(-C)(-C)-C

B.P ① > ② > ③ due to branching

② C-Cl, C-Br, C(Br)(Br)(Br), C(-Br)(-Br)-Br

BP ④ > ③ > ② > ① (molecular wt.)

③ ① C-C-C-C-C-C

⑪ C-C-C-C-C-OH (strong H-bonding)
⑫ C-C-C-C-C-NH₂
⑬ C-C-C-C-NH-C

B.P ⑪ > ⑫ > ⑬ > ①

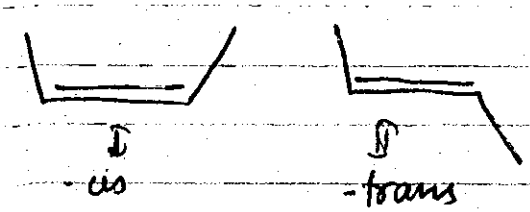
③ ① C-C-C-C-C

⑪ C-C-C(=O)-C

⑫ C-C-C-NH-C (H-bonding)

BP ⑫ > ⑪ > ①

④



M.P → cis > trans

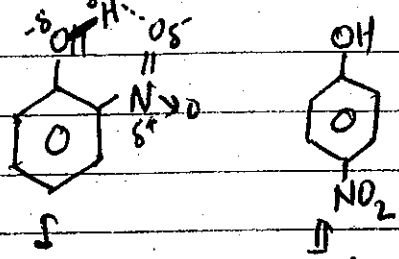
BP → cis > Trans

KEY POINT

Generally $\mu \propto B.P$

$\mu \propto$ Solubility $\propto$ Viscosity $\propto$

⑥



B.P (II) > (I)

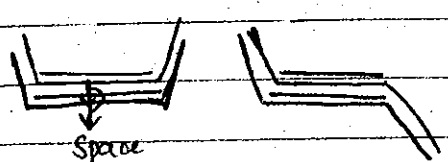
o-nitrophenol	p-nitrophenol
Here intramolecular H-bond hence no associatn with other molecules	Here intermolecular H-bond hence more asscociatn Hence ↑ B.P

o-nitrophenol is steam volatile that's why we can seperate it from mixture of p-nitrophenol by steam distillation

④ Melting Point

MP $\propto$ Molecular wt $\propto$ Packing Efficiency $\propto$ Symmetry

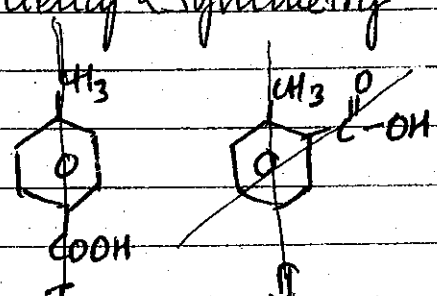
Q.1



P.E = trans > cis

M.P = trans > cis

Q.2



more symmetric

M.P I > II

⑤ Solubility

$\mu \Rightarrow$ cis- > Trans-

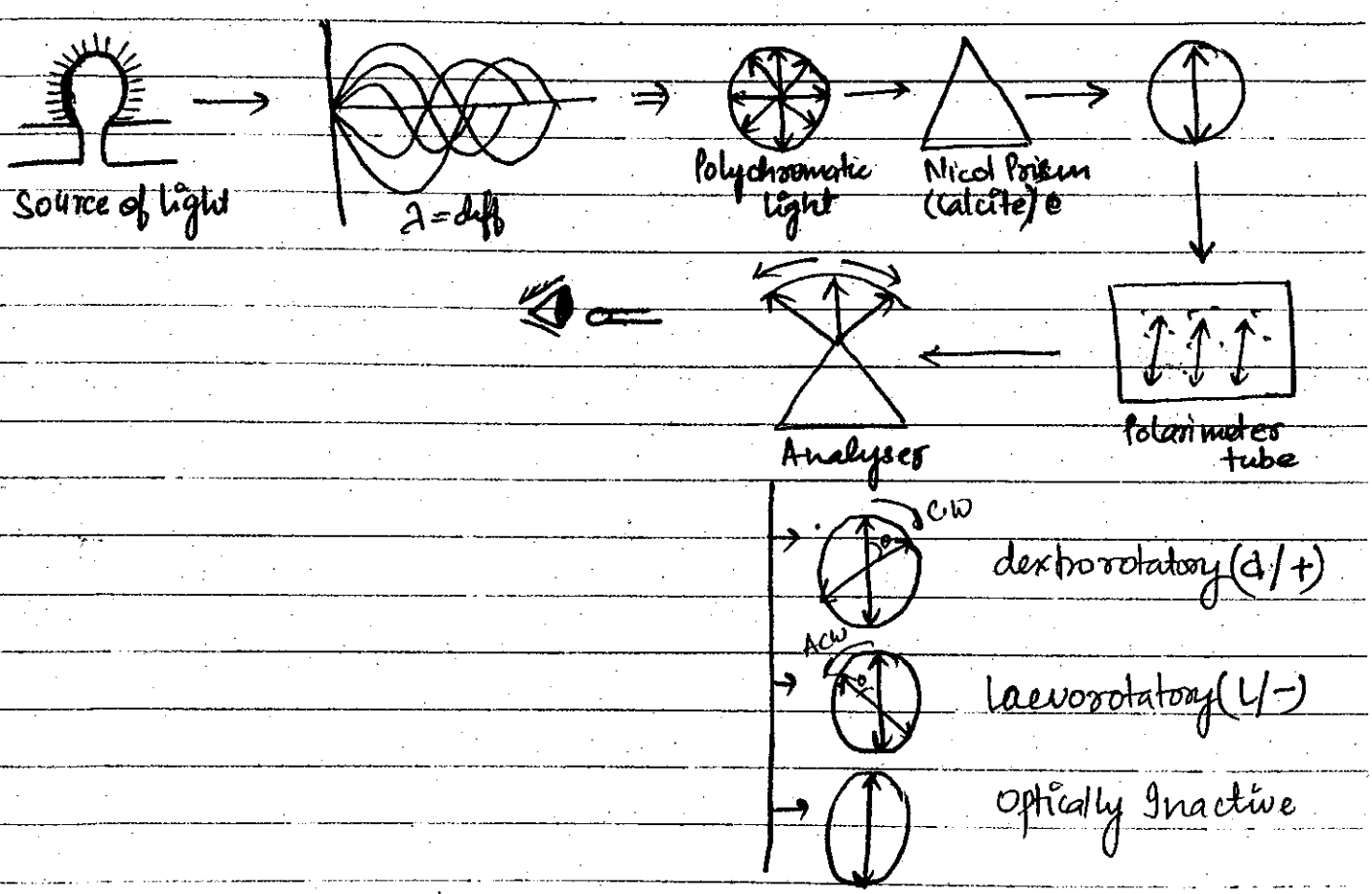
Solubility $\rightarrow$ cis- > Trans-

G.I having high dipole moment will be more soluble in Polar solvent &
G.I having less dipole moment will be more soluble in non-Polar solvent

Optical Isomerism

Compound having ~~same~~ M.F same structural formula, but diff behaviour towards Plane Polarised light is k/a Optical Isomers & this phenomenon is k/a Optical Isomerism.

POLARIMETER



Compound optically inactive due to three reasons.

① The given compound do not show optical isomerism (Achiral molecule)

② Compound give optical isomers but optically inactive (Meso compound)

③ The given compound may be mixture of 'd' & 'l' isomers. (Racemic Mixture)

1 C.C. ✓
>1 Check it

Some terms

1. **Optical Activity**: Tendency to rotate PPL in particular direct^n
2. **Optically Active Compound**: Compounds which are capable to rotate PPL
3. **Optically InActive Compound**: Compounds which are incapable to rotate PPL
4. **Chiral Molecule**: 'Unsymmetrical molecule' is k/a Chiral mol. All chiral molecules are optically active molecules (Always)
5. **Achiral Molecule**: 'Symmetrical molecule' is k/a Achiral molecule. All achiral molecules are optically inactive molecule.

Chiral molecule ⇒ Unsymmetrical molecule ⇒ O.A

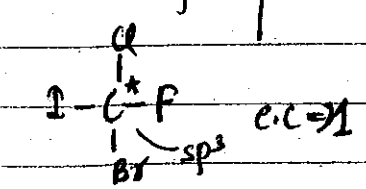
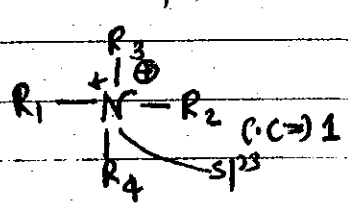
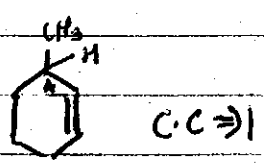
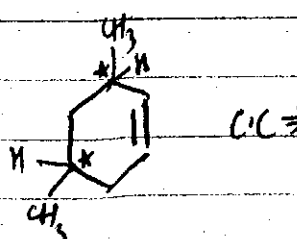
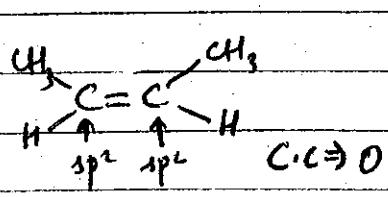
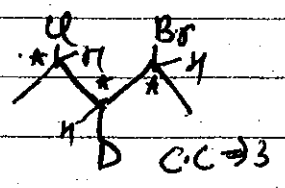
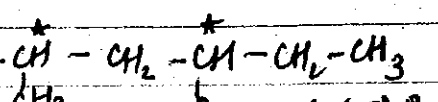
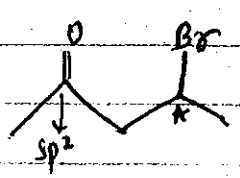
Achiral molecule ⇒ Symmetrical molecule ⇒ O.I

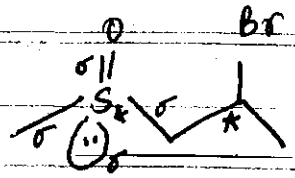
CHIRAL CENTRE (C.C)

Any sp^3 hybridised atom [C, N, O, S) which has all four diff group is k/a C.C

Chiral centre is not a necessary cond^n for optical activity

If compound having only 1 chiral centre then it is always optically active (except 'AMINE FLIPPING')

1.  C.C ⇒ 1
2.  C.C ⇒ 1
3.  C.C ⇒ 1
4.  C.C ⇒ 2
5.  C.C ⇒ 0
6.  C.C ⇒ 3
7.  C.C ⇒ 2
8.  C.C ⇒ 1

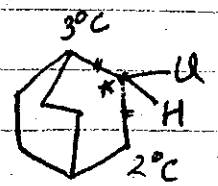
9. 

C.C ⇒ 2

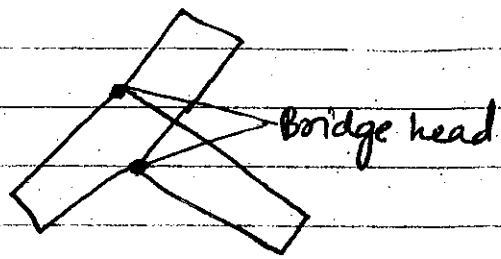
(10) 

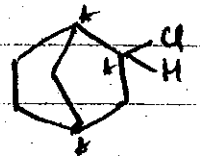
C.C ⇒ 2

$C_8H_{14} \rightarrow C_8H_{18} \Rightarrow 2H_2$ DU = 2

(11) 

C.C ⇒ 1



(12) 

C.C ⇒ 3

Condition for Optical Activity

⇓

For a molecule to be optically active

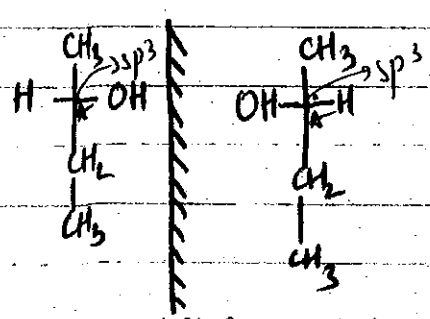
⇓

Compound must be chiral or unsymmetrical (compound & its mirror image both are non-superimposable)

⇓

COND^n-1

If compound having only 1 chiral centre then its sufficient cond^n for optical activity



Compound & its image both are non-superimposable

Optically active compound

COND^n-2

If compound having more than 1 chiral centre then chiral centre is not sufficient cond^n for optical activity

★ For this cond^n the whole molecule must be chiral or assymmetrical

★ For this cond^n in a compound symmetry element must be absent

SYMMETRY ELEMENT

COS (Centre of Symmetry)
POS (Plane of Symmetry)
AOS (Axis of Symmetry)

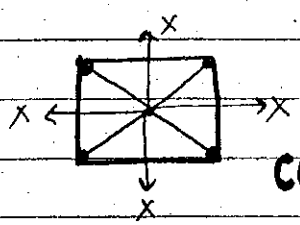
★ For a molecule to be optically active COS & POS must be absent

odd wale → COSX
even wale → COS✓

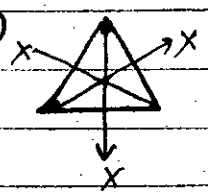
Symmetry Element

1) Centre Of Symmetry (COS)

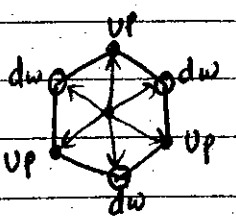
It is a Imaginary point situated at the centre of molecule from the centre if we draw straight line then they will meet at same atom same distance but in opposite direct" then molecule have COS

① 

COS✓

② 

COS XX

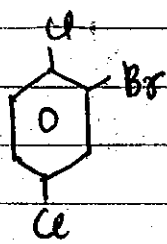
③ 

COS✓

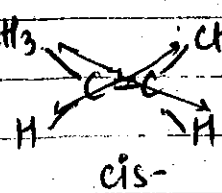
④ 
COS✓

⑤ 

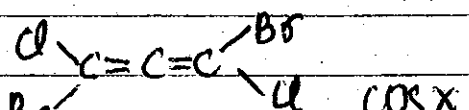
COS✓

⑥ 

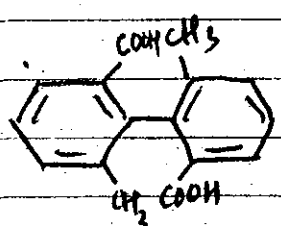
COSX

⑦ 

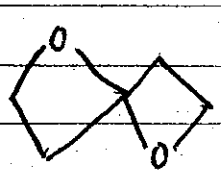
cis-
COSX

⑧ 

COSX
⇒ Tetrahedral
⇒ No cos.

⑨ 

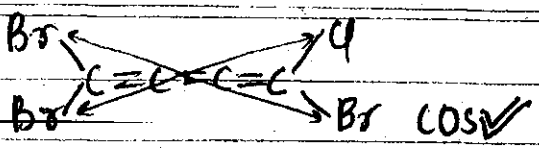
COSX
⇒ Tetrahedral
⇒ No COS

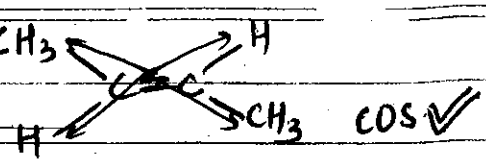
⑩ 

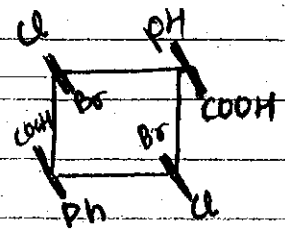
COSX
⇒ Tetrahedral
⇒ No COS

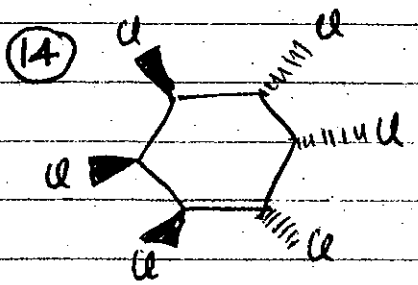
COS → होता है
POS → होता भी है
और नहीं भी है

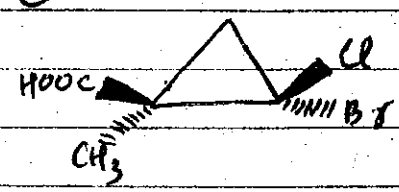
cis Platinum give SP² as square planer envir.
↳ anticancerous होता है
• परन्तु ये कभी SP³ नहीं देता Tetrahedral environment

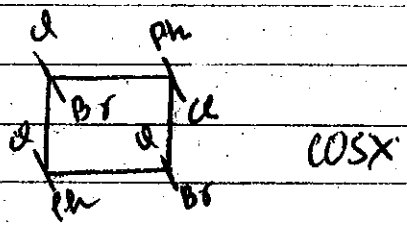
(11)  COS ✓

(12)  COS ✓

(13)  COS ✓

(14)  COS ✓

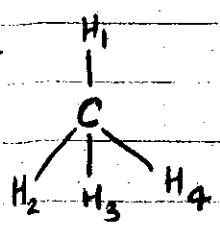
(15)  COS XX

(16)  COS X

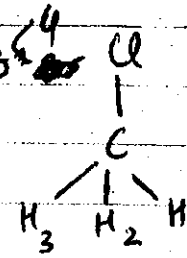
KEY POINT COS is absent in odd no. atom containing ring.
COS is absent in cis isomers
COS is absent in all molecule which can form tetra hedral environment.

(2) Plane Of Symmetry (POS)

It is a imaginary plane passing through a molecule which can bisect the molecule into two equal halves & both halves are mirror image of each other such plane is ½a POS.

(1) CH_4 

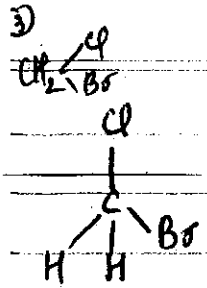
1,2 ⇒ 1POS
1,3 ⇒ 1POS
1,4 ⇒ 1POS
2,3 ⇒ 1POS
2,4 ⇒ 1POS
3,4 ⇒ 1POS
6POS

(2) CH_3Cl 

ClH_1 ⇒ 1POS
ClH_2 ⇒ 1POS
ClH_3 ⇒ 1POS
3POS

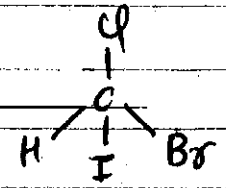
vertical - दबा Plane में
Horizontal - दबा से ऊपर Plane के लिए
Fisher Formula
Eclipse form में बनी है

③



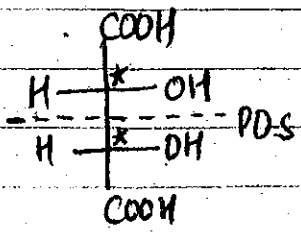
ClBr - 1 POS
1 POS

④



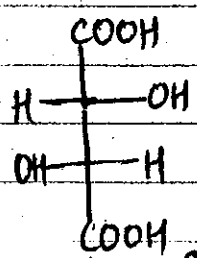
⇒ NO COS
⇒ No POS
⇒ C.C (Optically Active)
⇒ Unsymmetrical or Chiral molecule

⑤



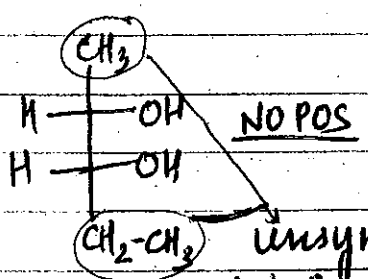
Tartaric Acid (Optically Inactive)

⑥



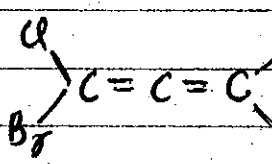
Tartaric Acid (Optically Active)

⑦



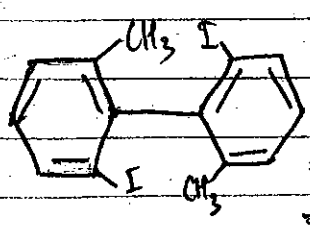
NO POS
Unsymmetrical
⇒ No POS
⇒ Optically Active

⑧



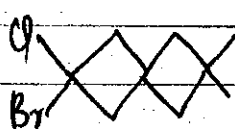
⇒ No COS
⇒ No POS
⇒ No. C.C
But Optically Active
Unsymmetrical

⑨



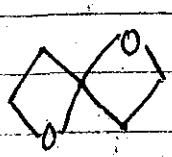
⇒ No COS
⇒ No POS
⇒ No C.C
But Optically Active

⑩



⇒ No POS
⇒ No COS
⇒ No CC
But Optically Active

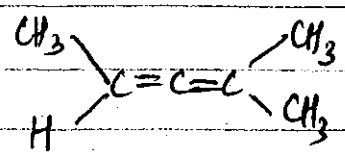
⑪



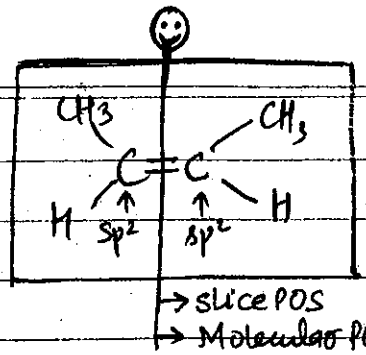
⇒ No COS
⇒ No POS
⇒ No CC
But Optically Active

KEY POINT Chiral centre is not necessary condition for optical activity for a molecule to be optically active COS & POS must be absent

Every Planar Mole. 360° ⊄ Plane ∴ not take it.

(12) 

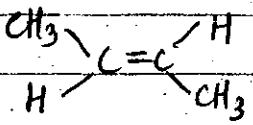
POS ✓

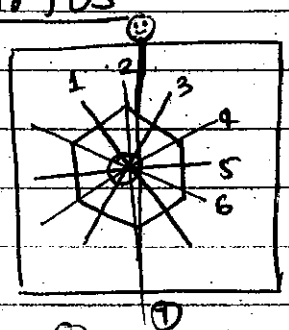
(13) 

POS ✓

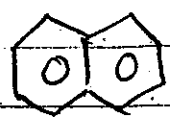
→ Slice POS
→ ~~Molecular POS~~

Example Of Slice / Molecular POS

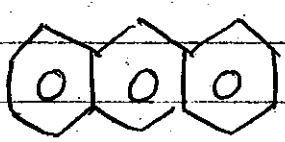
(14) 

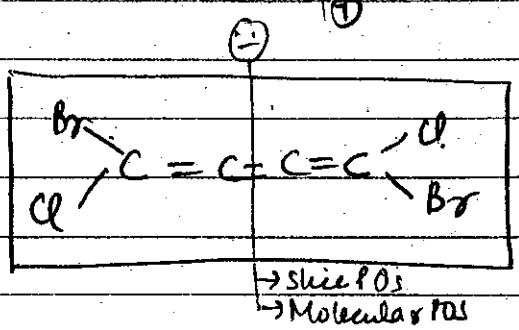
(15) 

7 POS

(16) 

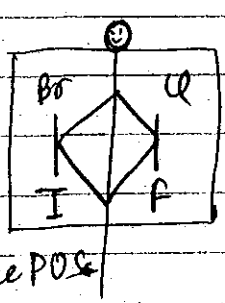
Slice POS

(17) 

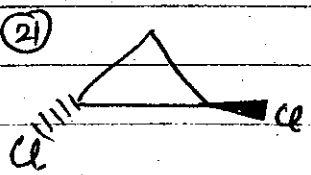
(18) 

→ Slice POS
→ Molecular POS

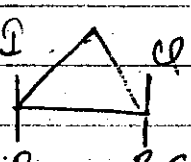
KEY PT: Every Planer molecule will have plane of symmetry along the plane in which they exist

(19) 

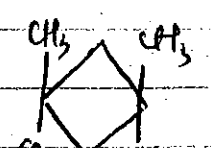
Slice POS

(21) 

POS XX
No COS
Optically Active

(20) 

POS XX
No COS
Optically Active.



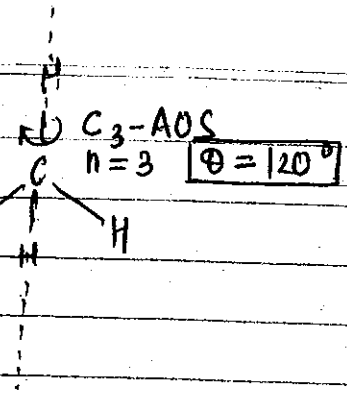
Slice POS also

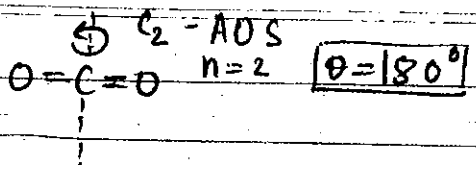
(3) Axis Of Symmetry (AOS)

If new image are obtain by rotation of a molecule by an angle θ about an axis passing through a molecule then it get similar orientation then molecule has AOS.

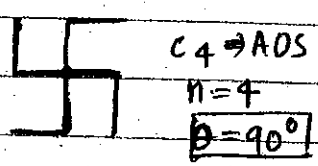
$$n = \frac{360}{\theta}$$

n = fold of axis





Axis of symmetry cannot not decide optical activity for a molecule to be optically active COS & POS should be absent



Polarimeter

Optical activity of a molecule can be predicted at plane of paper by absence of COS & POS but direct" of rotat" & angle of rotat" is experimental value & measured by polarimeter (Dextro & laevo)

Specific Rotation

$$\alpha_{sp} = \frac{\alpha_{obs}}{l \times c}$$

l ⇒ length of polarimeter tube (Taken in dm)

l = 1 dm

c ⇒ conc. of sol"

c = gm/ml (Taken in gm/ml)

It is a characteristic property of molecule & give information about OPTICAL STRENGTH

The angle of rotat" when length of polarimeter tube is 1 dm & conc. of sol" 1 gm/ml then the observed rotat" is called SPECIFIC ROTATION

Factor Affecting Angle Of Rotation (α Observed Rotat")

$\alpha_{\text{Observed Rotat"}} \Rightarrow \alpha_{sp} \times l \cdot c$

① Length of polarimeter tube ⇒ $\alpha_{obs} \propto l$ $\quad l \uparrow \rightarrow \alpha_{obs} \uparrow$

② conc. of sol" ⇒ $\alpha_{obs} \propto c$ $\quad$ conc ↑ ⇒ $\alpha_{obs} \uparrow$

③ Temp. ⇒ Polarimeter expt. carried out at room temp.

Chiral centre with symmetry : Meso

Solvent :- Solvent must be chemically & optically inert

Source of light :- Generally SODIUM LAMP used due to monochromatic light

[$\lambda = 589\,A^\circ$]

MESO COMPOUND

① Optical isomers having more than one chiral centre with symmetry element (COS, POS) is known as MESO COMP.

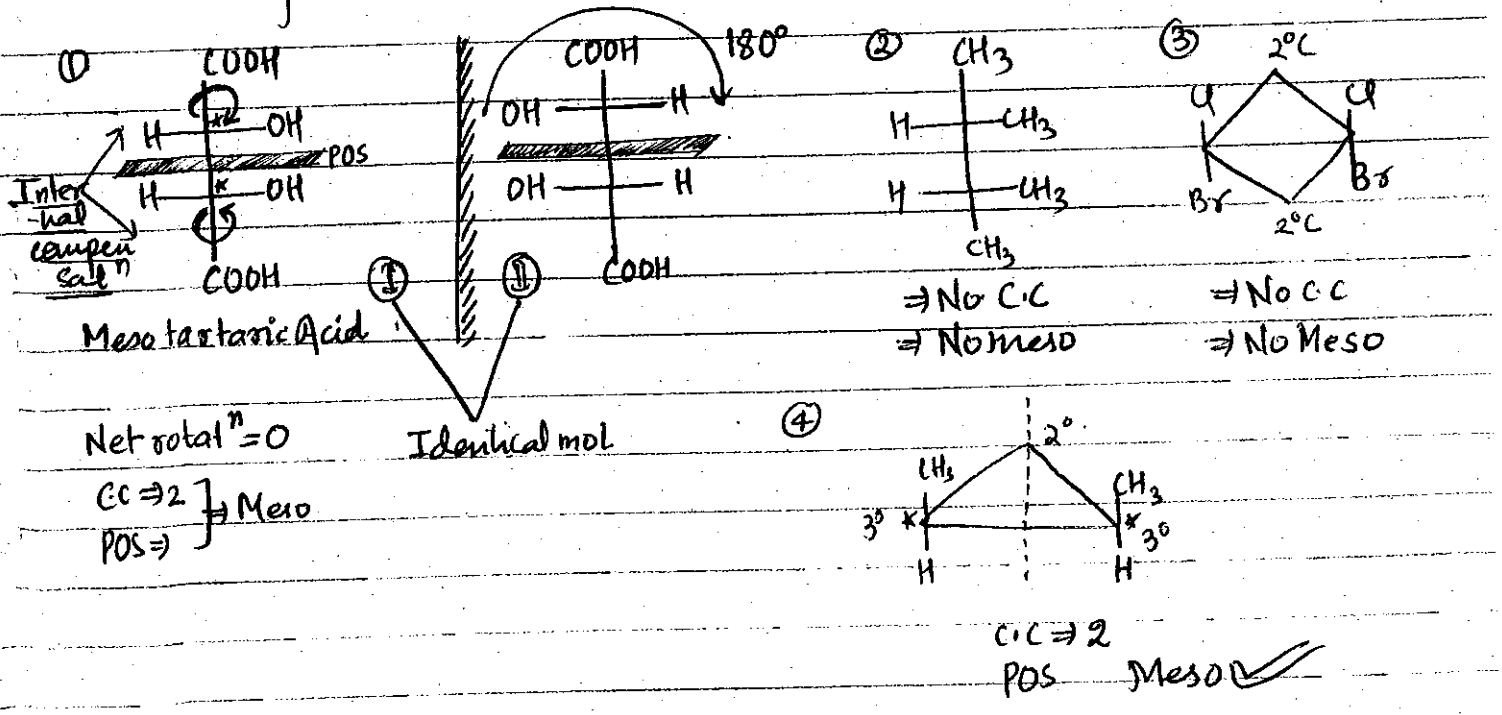
② Meso compound give optical isomerism but optically inactive.

③ Mirror image of meso compound represent its identical molecule

④ Meso compound is optically inactive due to INTERNAL COMPENSATION, INTRAMOLECULAR NEUTRALISATION or Molecular Symmetry

⑤ Meso compound are achiral compound

⑥ Meso compound cannot have enantiomers.



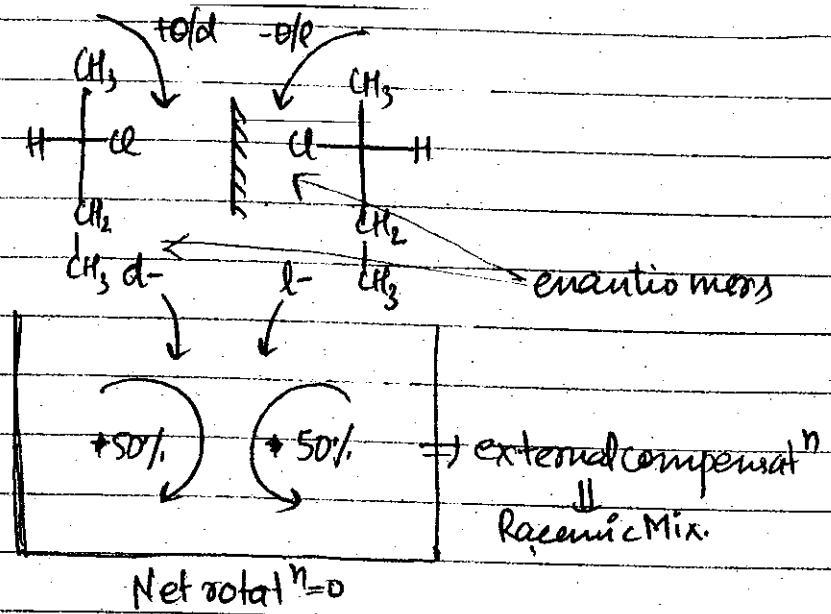
RACEMIC MIXTURE (R.M)

① Equimolar mixture of 'd' & 'l' isomer is known as RACEMIC MIXTURE

② R.M is optically inactive, due to EXTERNAL COMPENSATION or INTERMOLECULAR NEUTRALISATION.

R.M is a resolvable mixture & seperation of 'd' & 'l' isomer from

racemic mixture is k/a OPTICAL RESOLUTION



① d ⇒ 50 %. l ⇒ 50 %. RM ⇒ 100 %. Optical purity = 0 % (O.P)

② d = 100 %. l = 0 %. R.M = 0 %. OP = 100 %. → dextro

③ enantiomeric mix. d = 80 %. l = 20 %. RM = 40 %. OP = 60 % (enantiomeric excess) → dextro

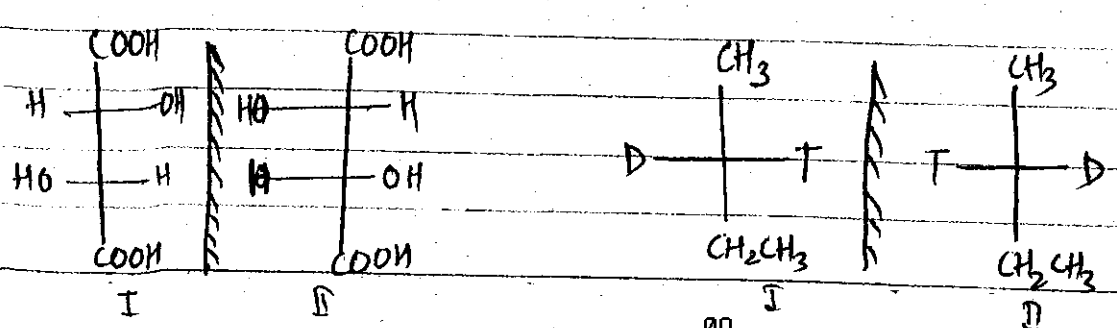
④ 20 gm. d = 12 gm. l = 8 gm. RM = 16 gm. OP = 4 gm. → dextro

Enantiomers

① Optically active compounds having non-superimposable mirror image of each other is k/a ENANTIOMERS.

② Enantiomers have same phy. properties

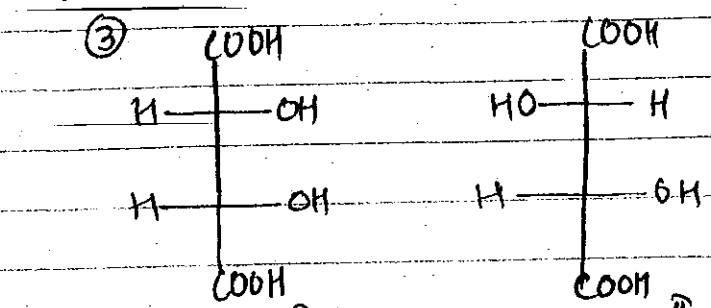
③ Enantiomers have diff behaviour towards P.P.L



All (+) ⇒ Diastereomers

DIASTEREOMERS

③

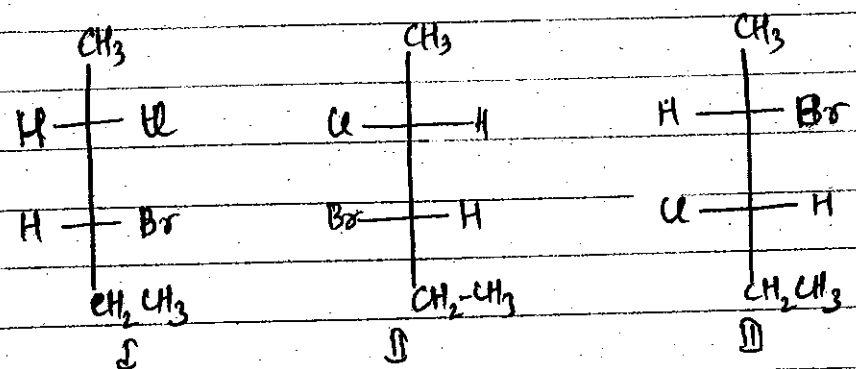


Mesotartaric Acid Ⅰ

Ⅱ (d/l-tartaricacid)

Ⅰ, Ⅱ ⇒ diastereomers.

④



Ⅰ, Ⅱ

Ⅰ

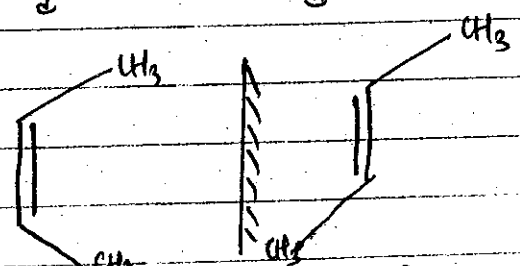
Ⅱ

Ⅰ, Ⅲ Enantiomer

Ⅰ, Ⅲ Diastereomer

Ⅱ, Ⅲ Diastereomer

⑤

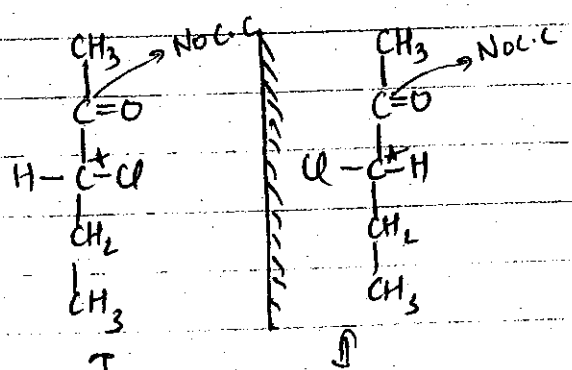


Cis Ⅰ

Trans Ⅱ

Ⅰ, Ⅱ ⇒ Diastereomer

⑥

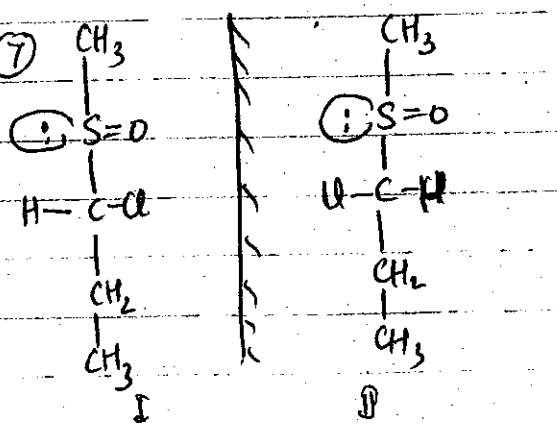


Ⅰ

Ⅱ

Ⅰ, Ⅱ Enantiomers

⑦

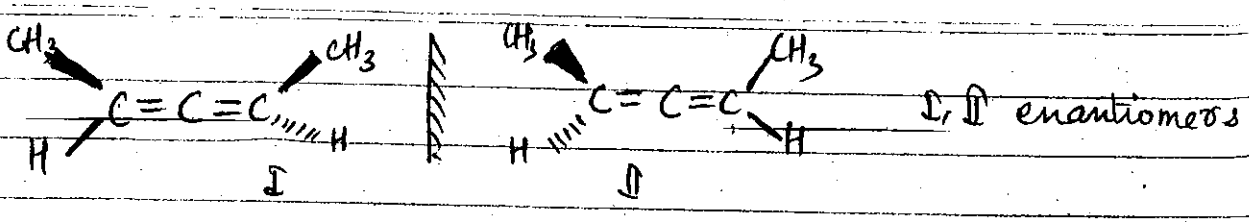


Ⅰ

Ⅱ

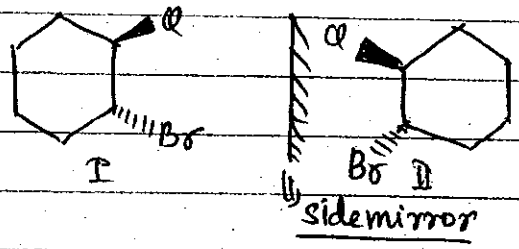
Ⅰ, Ⅱ Diastereomers.

(8)



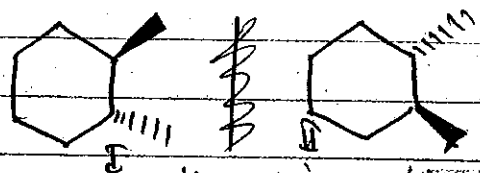
I, II enantiomers

(9)



I, II Enantiomers

(10)

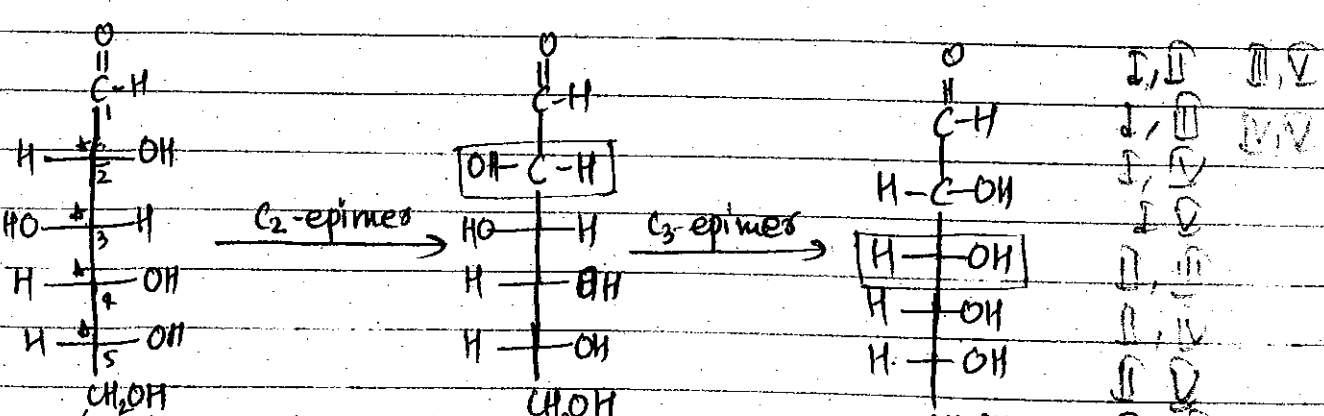


I, II Enantiomers

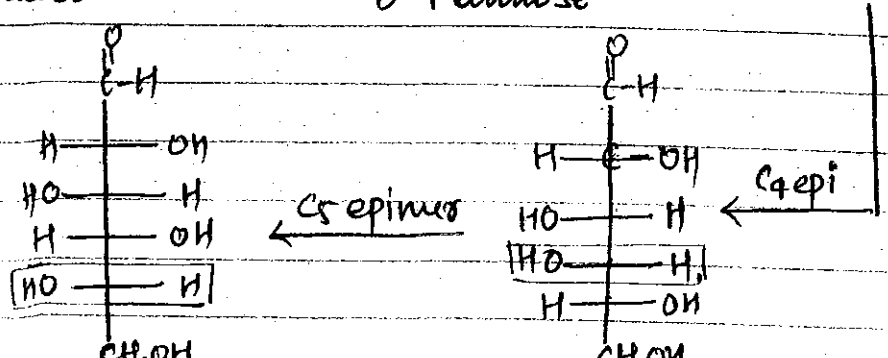
Upper mirror (ऊपर वाली लाईन, नीचे दर्पण है)

EPIMERS

When two monosaccharide differ from each other in their configuration around a single specific carbon then compound is called EPIMER of each other



D-Glucose D-Mannose D-Allose



D-Gulose D-Galactose

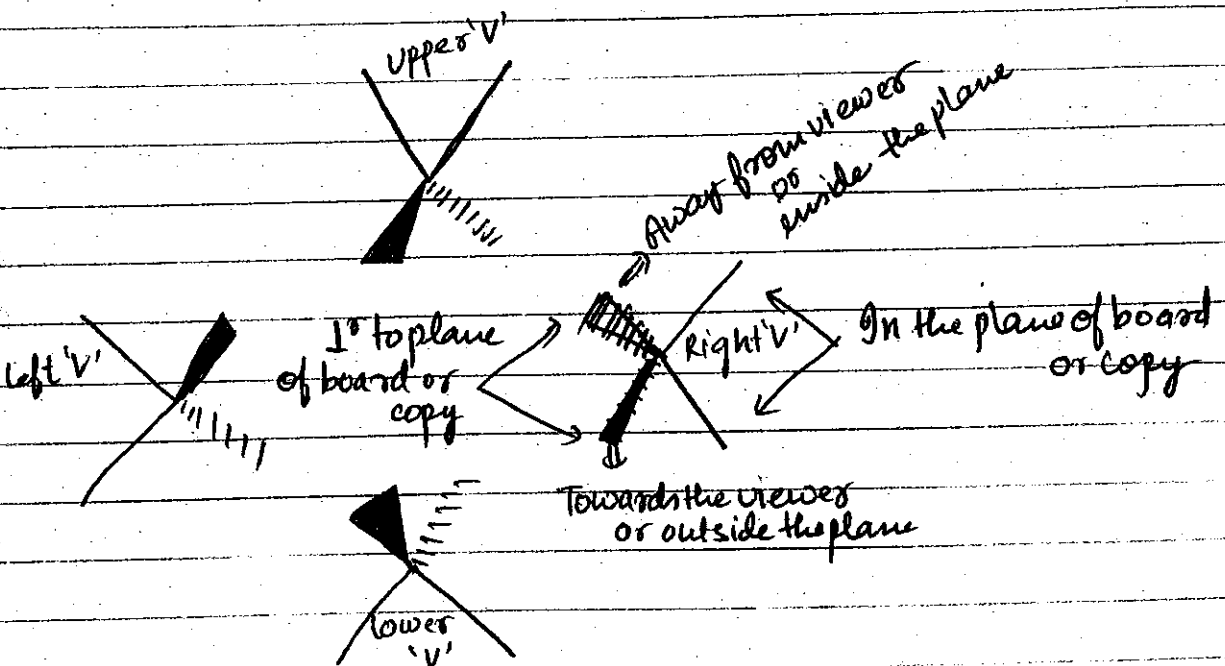
Glucose & Epimers अतिरिक्त अन्य Diastereomer

I, II - Diastereomers, I, III Diastereomer, II, IV Diastereomer,
I, III - Diastereomers " I, IV Diastereomer " II, IV Diastereomer "
I, IV Diastereomers " II IV Diastereomer " III, IV Diastereomer "
I, IV Diastereomers "

NOTE: All Epimers are diastereomer but vice-versa not true

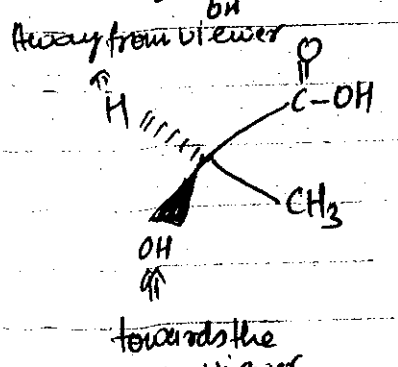
Representation Of Optical Isomers

① WEDGE DASH formula (3-D) ② FISCHER PROJECTION formula (2-D)



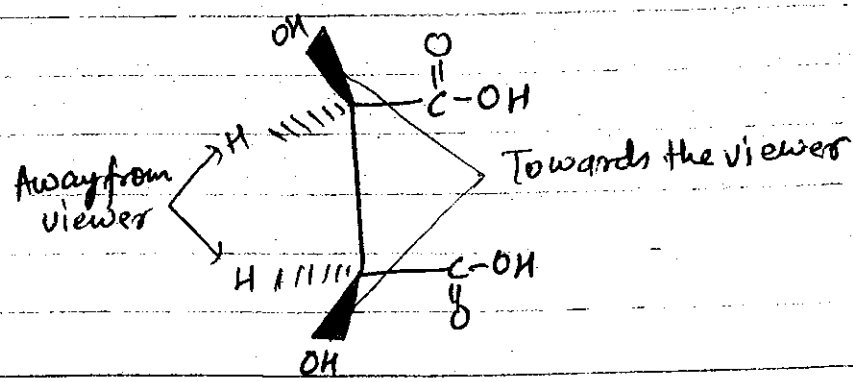
Lactic Acid

① $CH_3-\overset{*}{C}H(OH)-C(=O)-OH$



Tartaric Acid

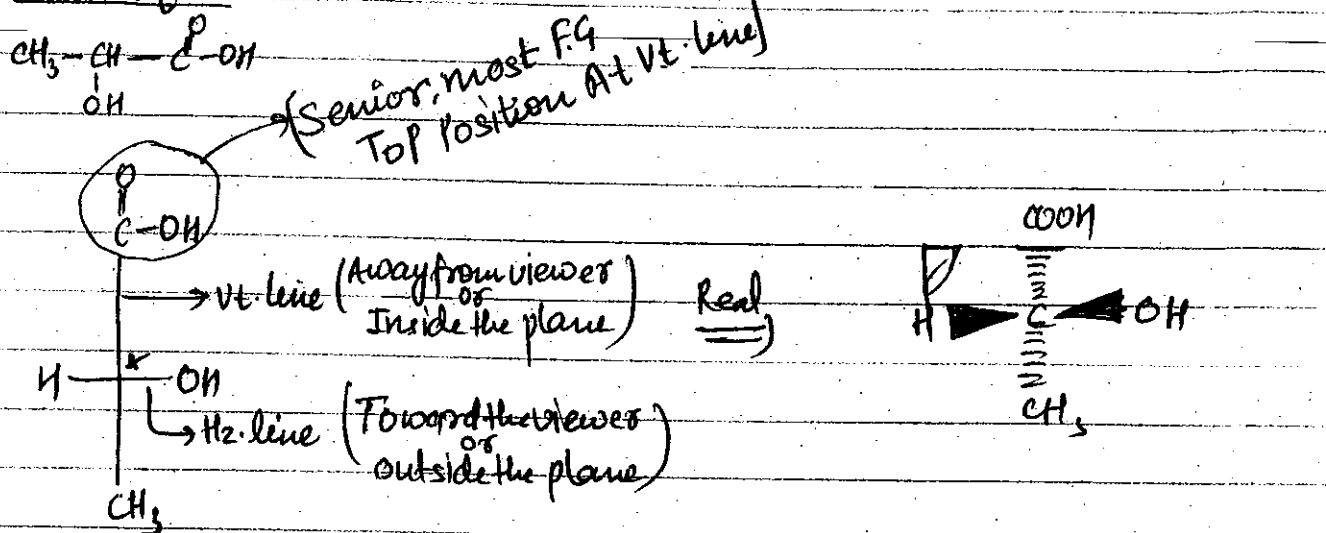
$OH-\overset{*}{C}H(OH)-\overset{*}{C}H(OH)-C(=O)-OH$



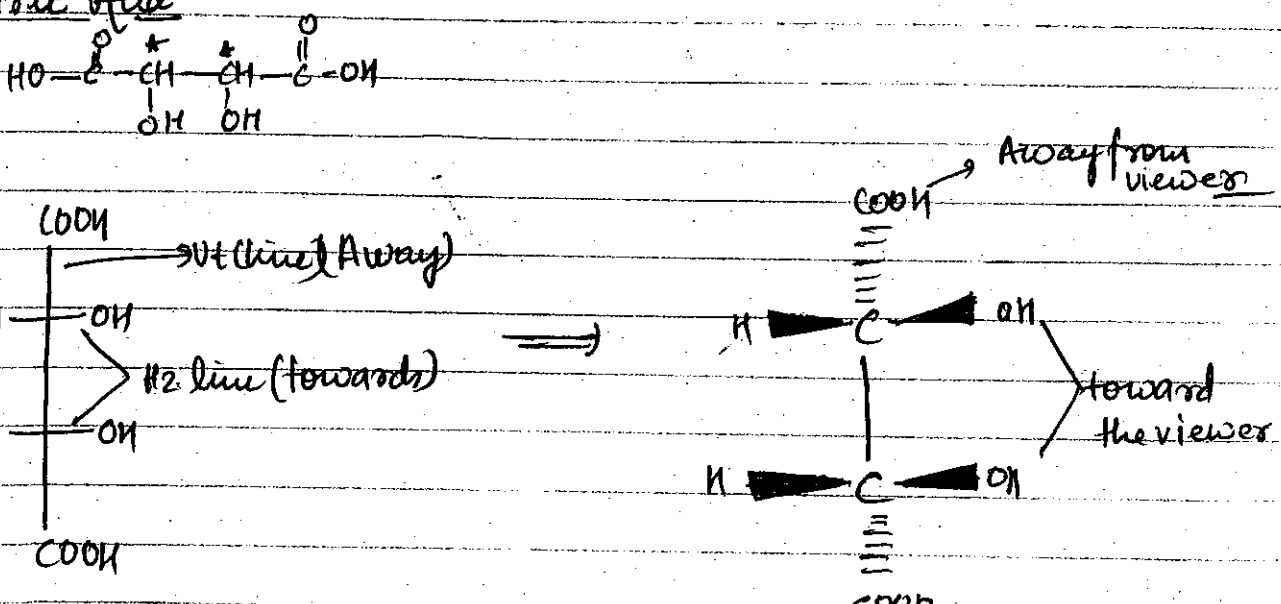
V.l → down
H2 → Toward

② FISCHER-PROJECTION formula

① Lactic Acid



② Tartaric Acid

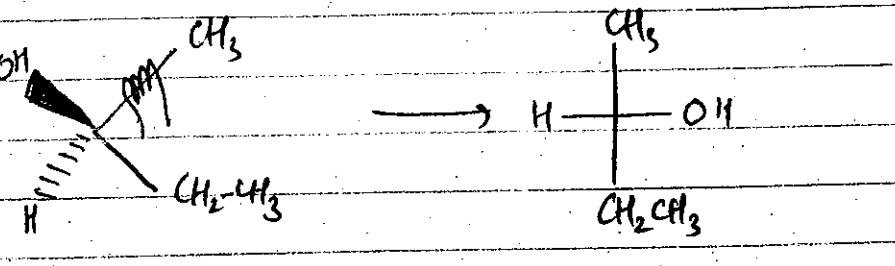


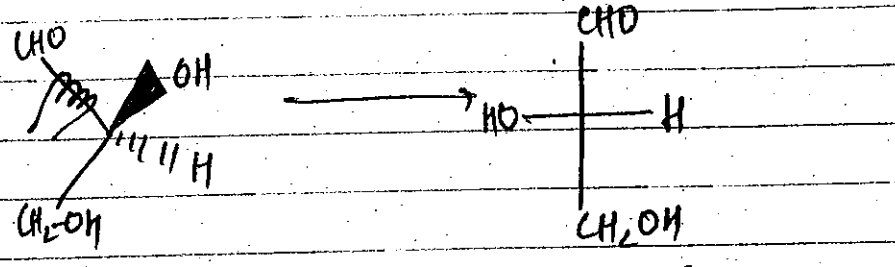
① Fischer projection is 2 plane projection formula
② In 2 plane projection formula one plane Vt (only 1) & other one is horizontal (one or more than one)
③ In fischer projection formula carbon chain always in vt line & senior top most fxnal group at top position of vt line
④ In fischer projection formula vertical line groups represent away from viewer & horizontal line group represent towards the viewer

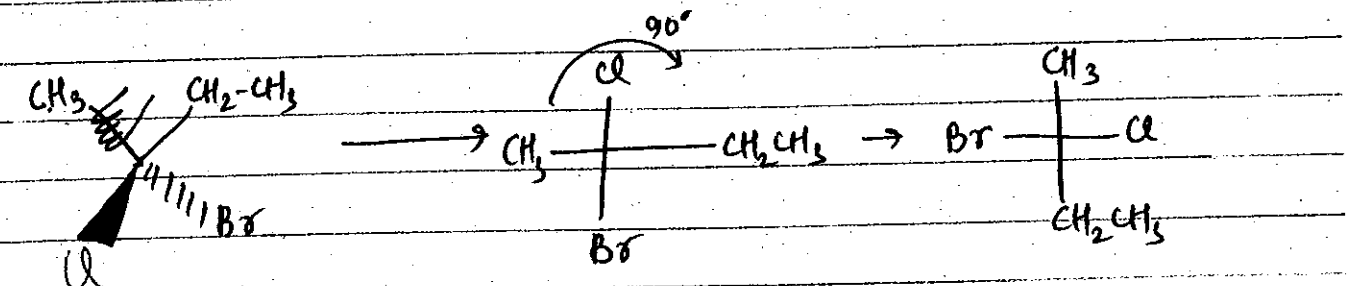
On writing wedge [illegible]
Fischer eclipse [illegible]

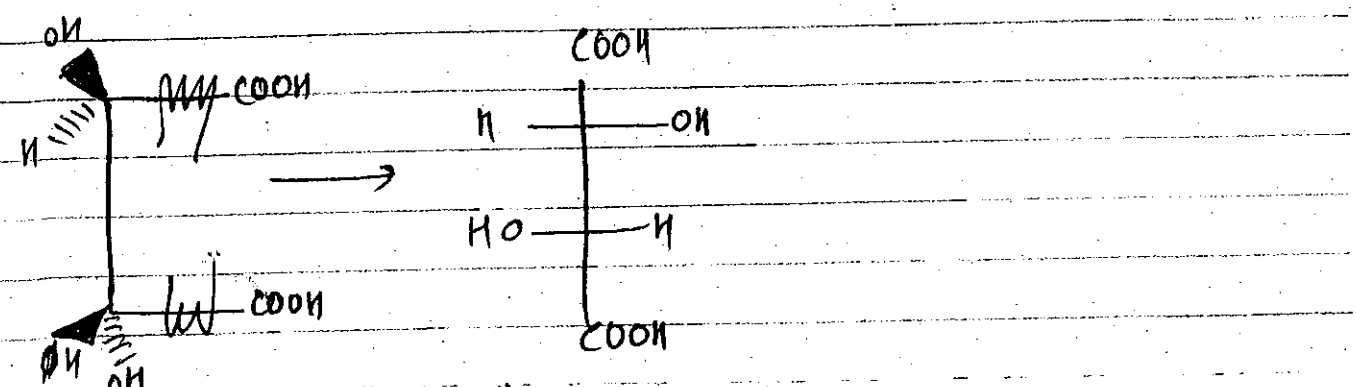
Various Conversion Of Different Projection Formula

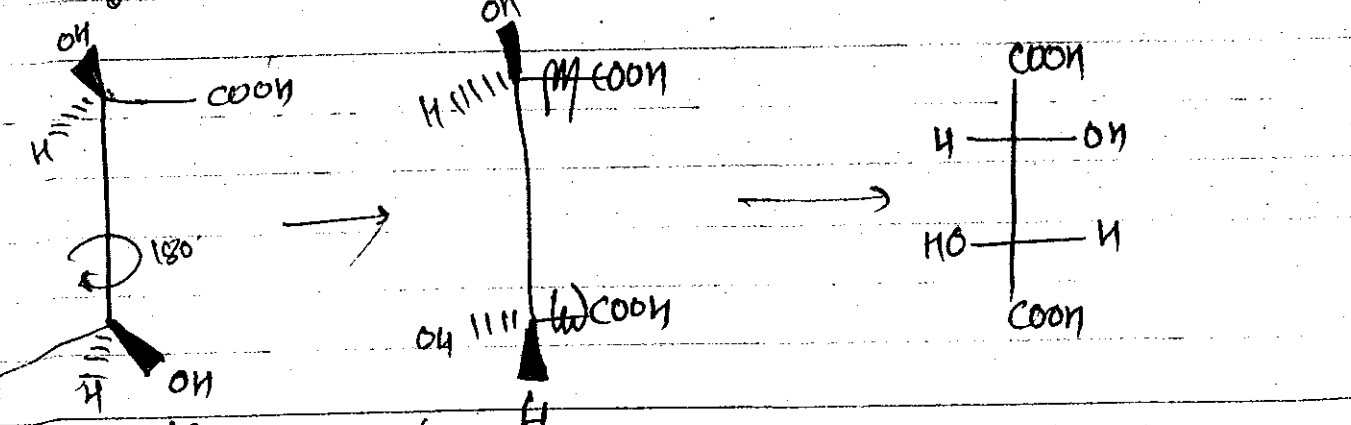
Wedge Dash Into Fischer

① 

② 

③ 

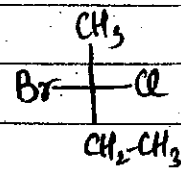
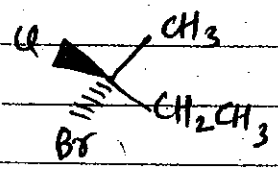
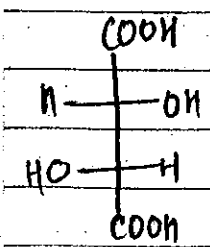
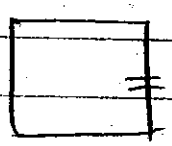
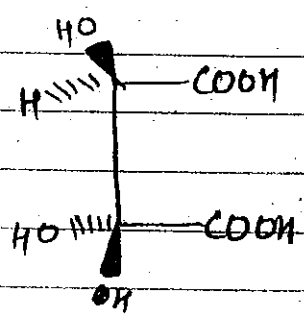
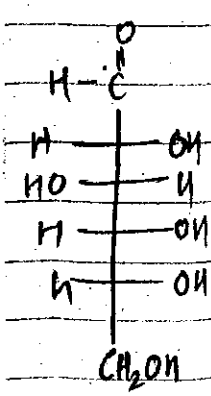
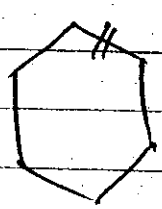
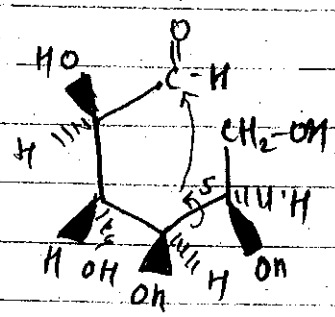
④ 

⑤ 

MUKKA TECHNIQUE

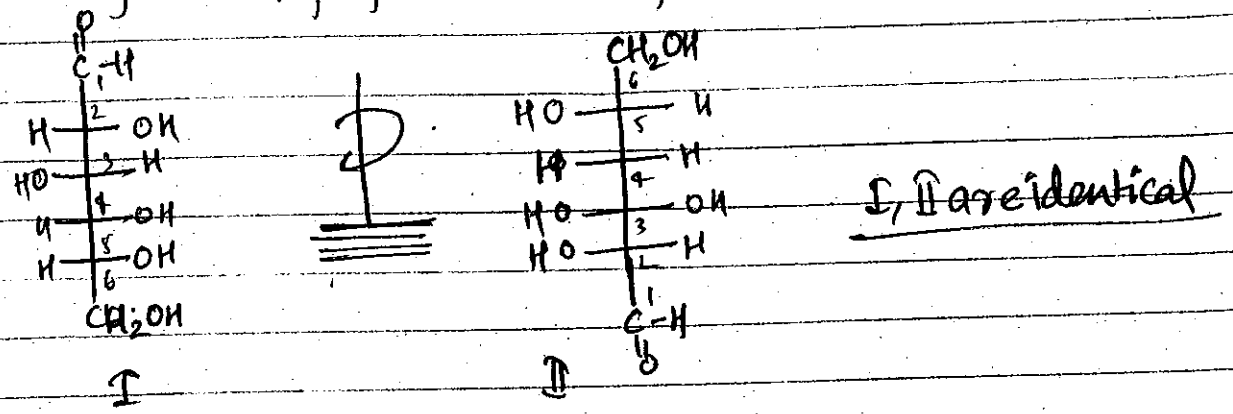
Jo V board ke plane me hoti hai usko jaha se punch kiya jata hai waha par WEDGE wala group aa jata hai

Fischer Into Wedge Dash

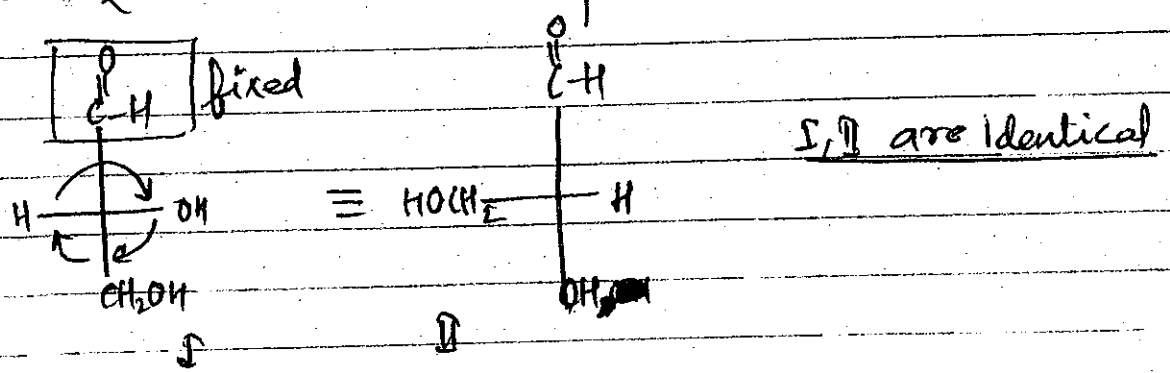
Fisher	No. of C.C	Polygon (Eclipsed)	Wedge-Dash
	1		
	2		
	4		

Fischer Into Fischer

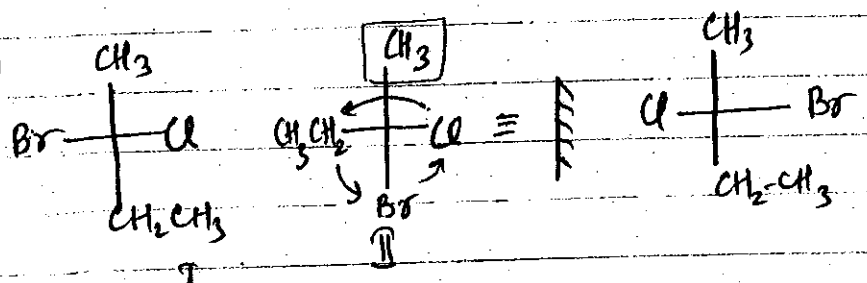
STATEMENT-1 If given fischer project" formula rotated by 180° angle in the plane of paper then it represent its identical molecule



STATEMENT-2 In given fischer projection formula out of 4 unit any one unit kept fixed & other three unit rotated in clockwise & anticlockwise direct" then it represent its identical molecule

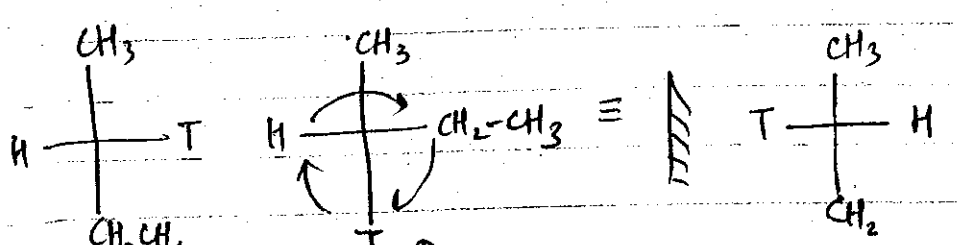


(1)



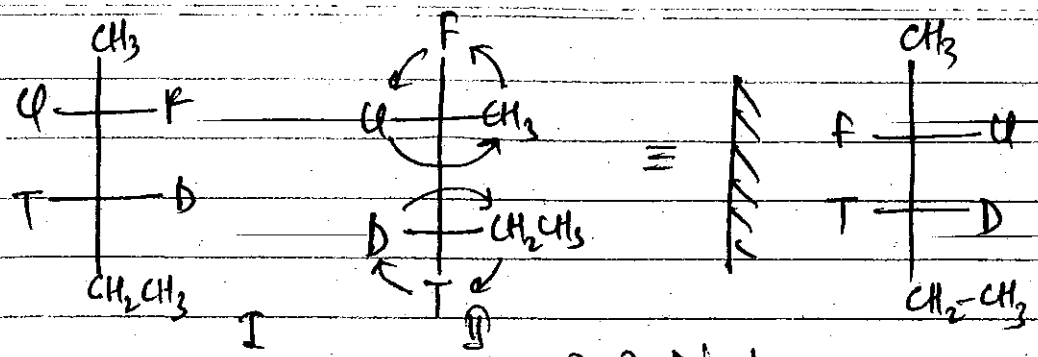
I, II enantiomers

(2)



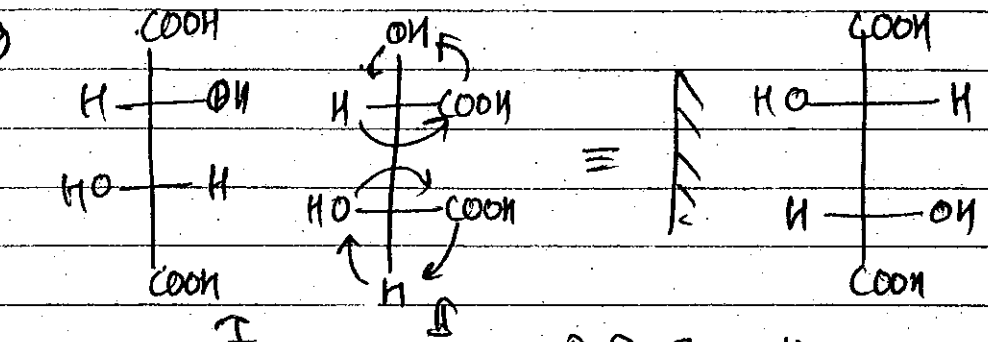
I, II enantiomer

③



I, II Diastereomer

④



I, II Enantiomer

Configuration Of Optical Isomers

Fischer

⇓

Perfect Fischer (if required)

⇓

Super imposable or non-superimposable

⇓

Superimposable ⇒ Identical

Non-superimposable ⇒ Mirror image ⇒ Enantiomers

Non-superimposable ⇒ Not mirror image ⇒ Diastereomers

Carbohydrate: no. of min. one chiral centre

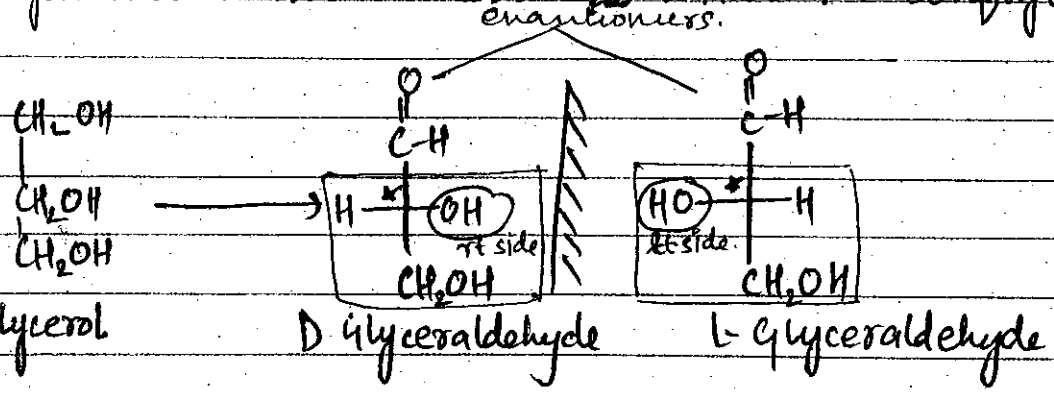
Configuration Of Optical Isomers.

D-L Configuration (Relative Configuration)
R-S Configuration (Absolute Configuration)

D-L Configuration

Carbohydrate: Compound having polyhydroxy aldehyde or ketonic group with min. one chiral centre

NOTE: D & L configuration is standard relative configuration of glyceraldehyde there is no relation with 'd' & 'l' configuration.



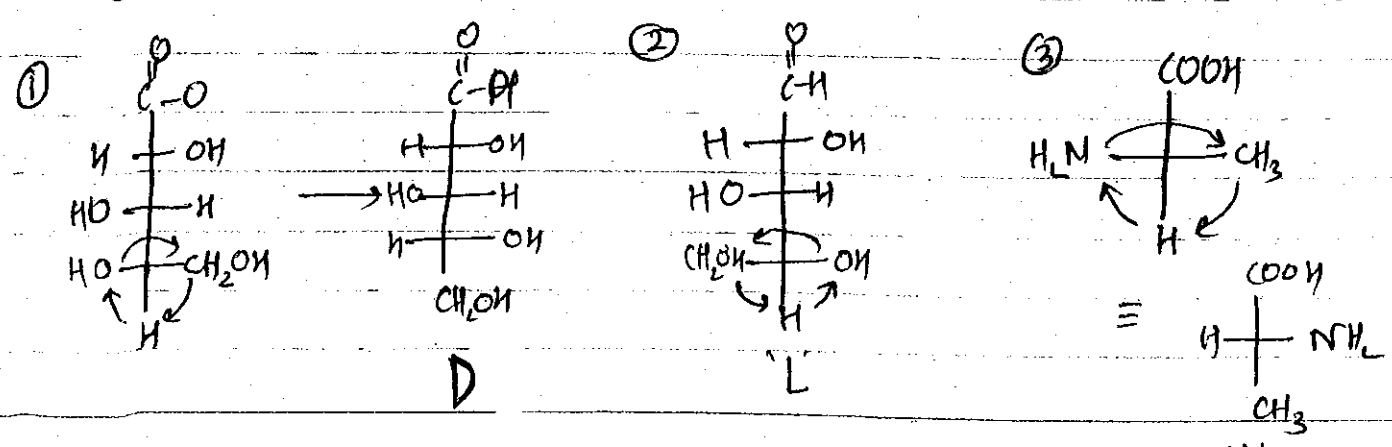
NOTE D & L have enantiomeric relation

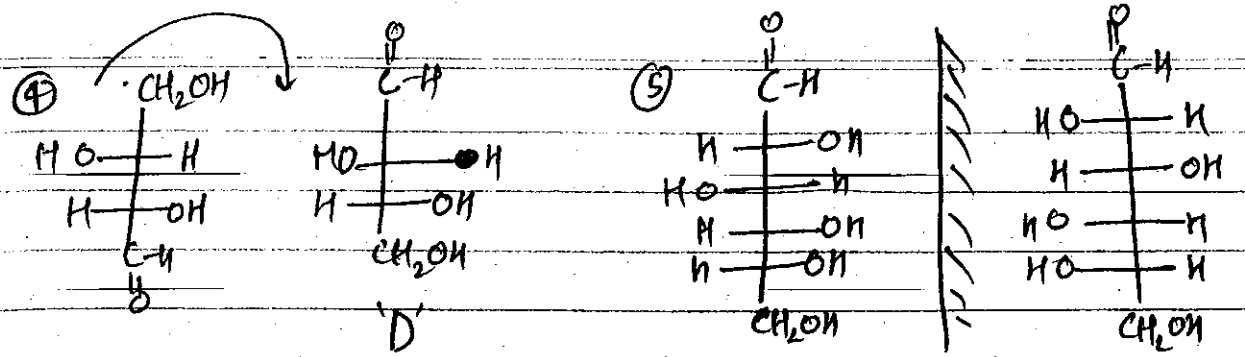
D & L configuration not valid for symmetrical system

If at last chiral centre OH group rt side → D

OH group left side → L

NOTE D & L configuration valid for carbohydrate & aminoacid & like molecule





R-S configuration

R → Rectus → Right / Clockwise
S → Sinister → Left / Anticlockwise

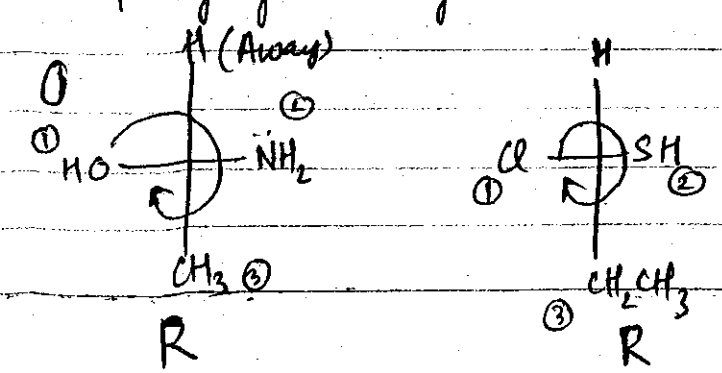
→ Arrangement of units at CC
Not rotation of P.P.L.

R-S configuration in Fischer Projection Formula

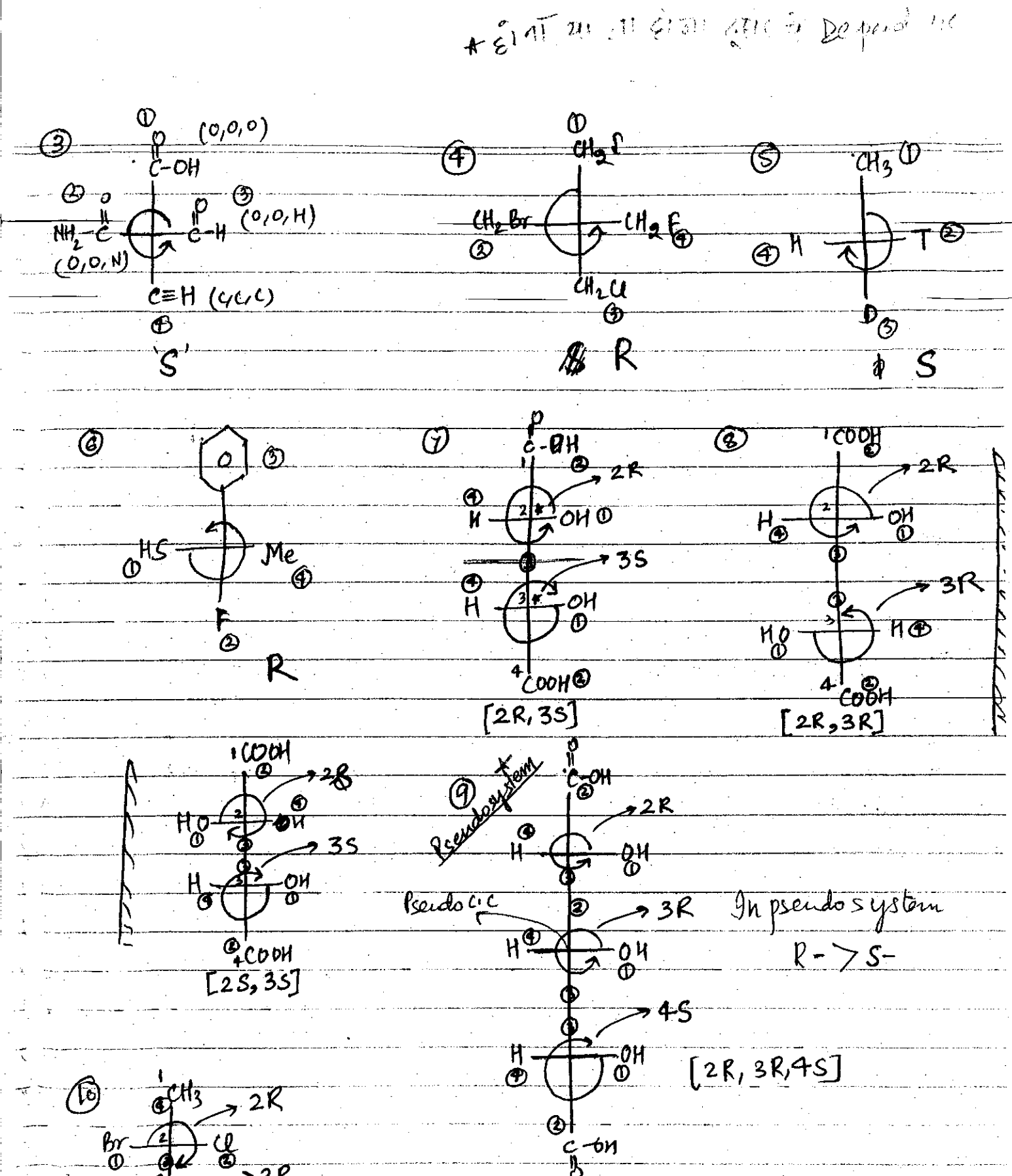
Assign the priority according to CIP rule
Priority of atoms directly proportional to atomic no.
If 4 priority group (no. 4) away from the viewer (Vt. line) then
clockwise → R
Anticlockwise → S

NOTE If 4th priority grp present towards viewer (Hz. line) then the real orientation just opposite to the observed orientation
(Jo aata hai uska ulta kar dete hai)

Always go through 1 → 2 → 3 if ④ present in b/w ignore it.



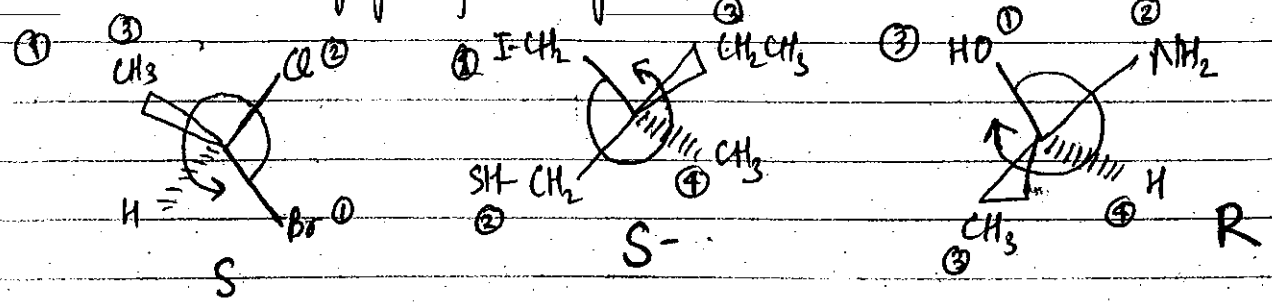
01

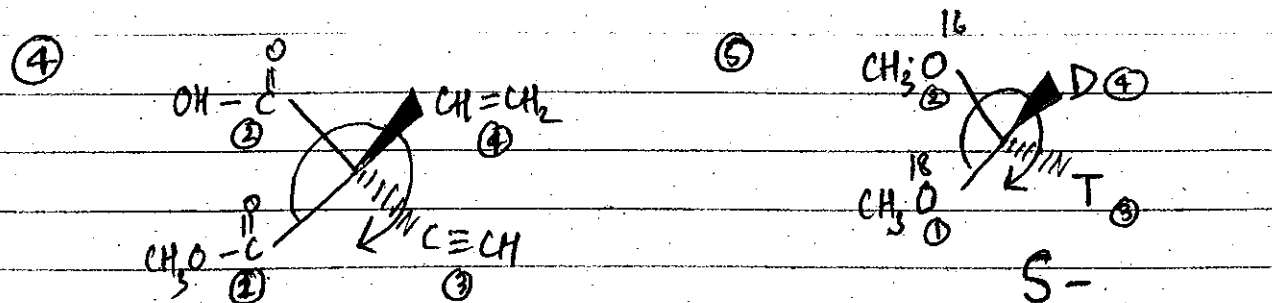

③
(0,0,0)
(0,0,N)
(0,0,H)
(C,C,C)
S
④
R
⑤
S
⑥
R
⑦
2R
3S
[2R, 3S]
⑧
2R
3R
[2R, 3R]
2S
3S
[2S, 3S]
⑨
Pseudo system
Pseudo C
2R
3R
4S
[2R, 3R, 4S]
In pseudo system
R -> S-
⑩
2R
3R
[2R, 3R]

R-S Configuration in Wedge-Dash Formula

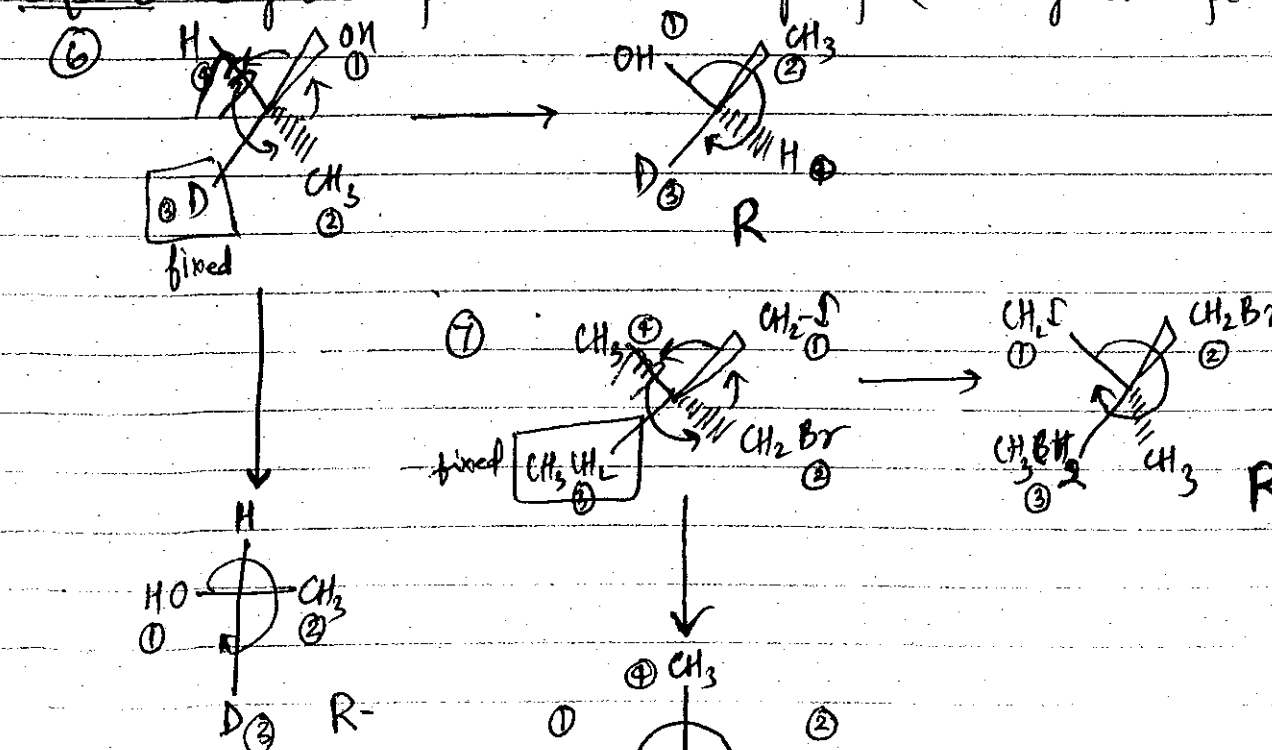
All rules of R-S configuration in Fischer & Wedge Dash are SAME

CASE-I 4 Priority group wedge या Dash पर होनी चाहिए। ना हो तो लेकर आए।

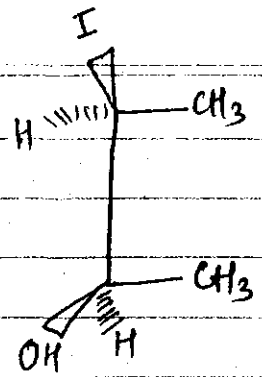


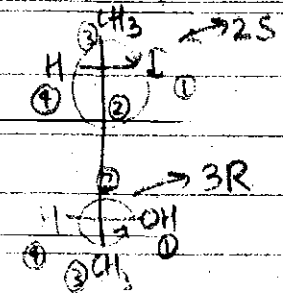


CASE-II Wedge dash pe na ho to 4th group ko wedge dash pe leke aaye

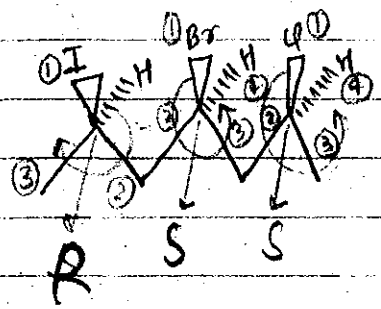


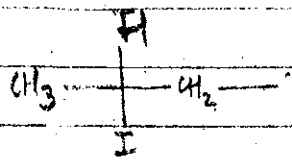
⑧





⑨





Comp. I	Comp. II	Relation
R	R	Identical
S	S	Identical
R	S	Enantiomer
RR	SS	Enantiomer
RS	SR	Enantiomer (if comp. symmetrical) Meso (if comp. unsymmetrical)
RR	RS/SR	Diastereomers

No. of Optical Isomers

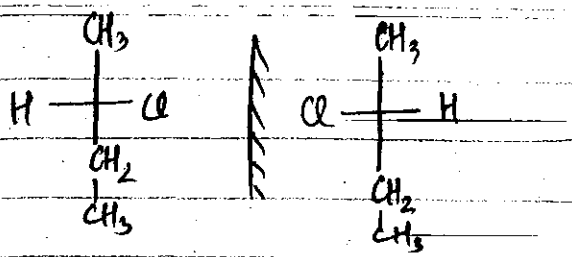
	Optically active comp. (d+l)	Optically Inactive comp. (Meso)
Unsymmetrical comp.	2^n	Zero
Symmetrical comp. ⇒ n = even	2^{n-1}	$2^{\frac{n}{2}-1}$
n = odd	$2^{\frac{n-1}{2}} - 2^{\frac{n-1}{2}}$	$2^{\frac{n-1}{2}}$

n → no. of stereogenic centd (C.I + O.I)

① $CH_3-\underset{\underset{Cl}{|}}{CH}-CH_2CH_3$ ⇒ unsymmetrical

⇒ n = 1

→ No. of O.I = $2^n = 2^1 = 2$

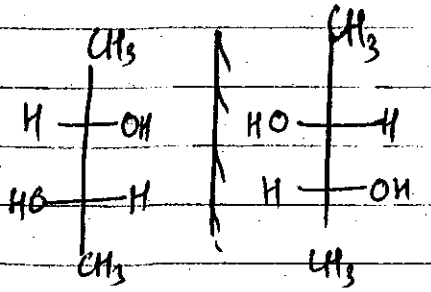


② $CH_3-\overset{*}{CH}(Br)-CH_2-CH_3$ ⇒ unsymmetrical ⇒ $n=1$

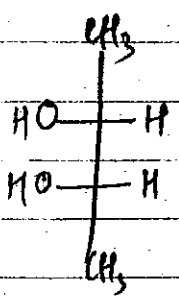
No. of optical isomers ⇒ 2
No. of optically active isomer ⇒ 2
No. of meso compound ⇒ 0
No. of racemic mix ⇒ 1
No. of enantiomeric pair ⇒ 1

③ $CH_3-\overset{*}{CH}(Br)-\overset{*}{CH}(Br)-CH_3$

symmetrical
$n=2$
No. of O.I $= 2^{n-1} \Rightarrow 2^{2-1} = 2^1 \Rightarrow 2$
No. of O.I (active) $= 2$
No. of optically inactive $= 2^{n/2-1} = 2^{2/2-1} = 2^0 = 1$



I II



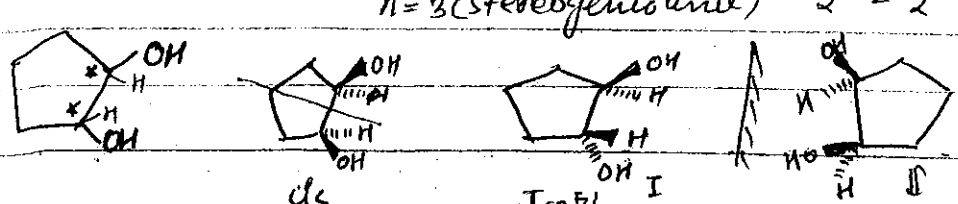
III (Meso)

No. of O.I = 3
No. of optically active = 2
No. of meso = 1
Enantiomeric pair = 1
Racemic mixture = 1 pair

④ $CH_3-CH=CH-\overset{*}{CH}(Br)-\overset{*}{CH}(Br)-CH_3$

unsymmetrical
$n=3$ (stereogenic unit) $2^n = 2^3 = 8$

⑤

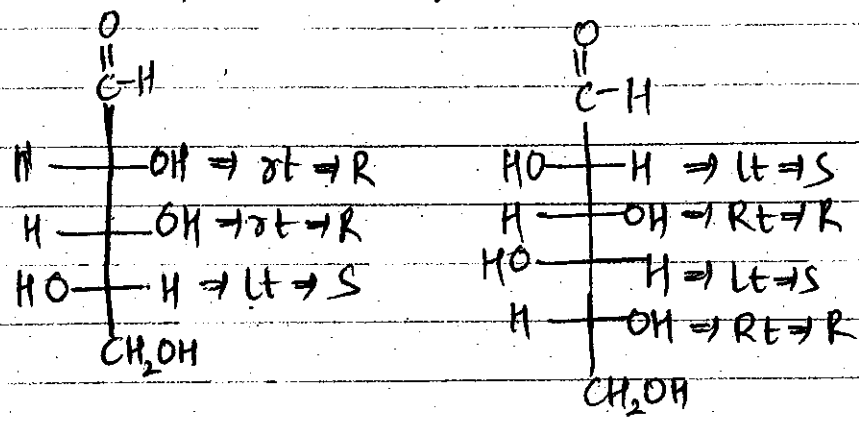


cis Trans- I II

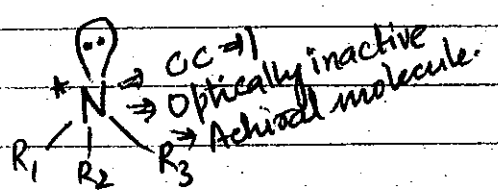
Dragohypotheses Npe lone pair basic strength
Ppe X

KEY POINT 1 If compound having chiral centre (1 or more than 1) then compound always give optical isomerism

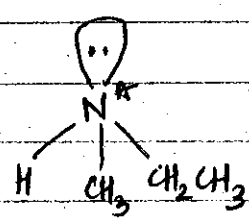
KEY POINT 2 (Only for carbohydrates)



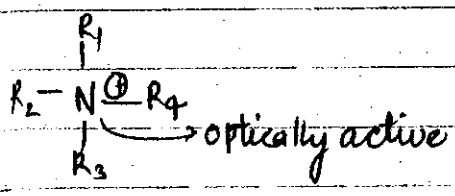
KEY POINT 3 In case of amine compound having C.C but due to AMINE FLIPPING/ UMBRELLA INVERSION compound is optically inactive & molecule is achiral

① 

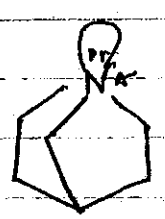
⇒ CC ⇒ Optically inactive ⇒ Achiral molecule.

② 

⇒ C.C ⇒ Optically active ⇒ Achiral

③ 

⇒ optically active

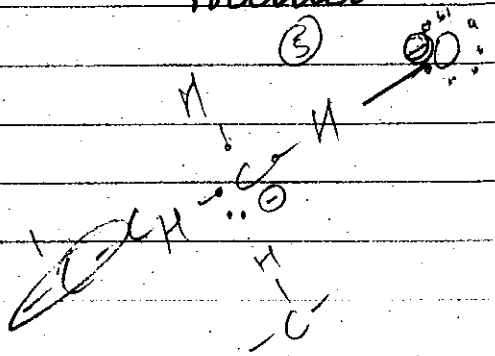
③ 

Optically Active

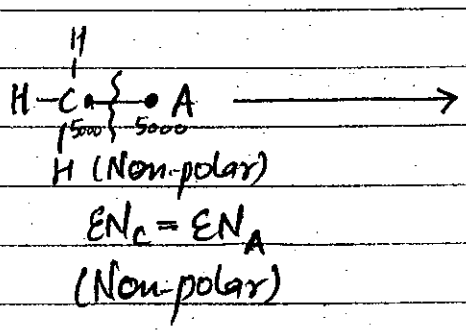
Stability Of Intermediate (GOC)

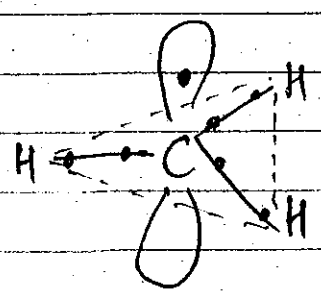
Reactant (Bond Breaking step) → Intermediate → Product

① C• (Free radical)
② C⁺ (Carbocation)
③ C⁻ (Carbanion)
④ Nitrene
⑤ Carbene



Bond Breaking

① 



formed by homolytic clevage
Incomplete octate
Stabilised by EDG
(+I / +H / +M)
hybridisat^{n} ⇒ sp^2 (planar)
Bond pair ⇒ 3 (6e⁻)
U.P ⇒ 1e⁻
L.P ⇒ 0
highly unstable
More reactive
Behave as a $E^{\oplus}$ (Electrophile)

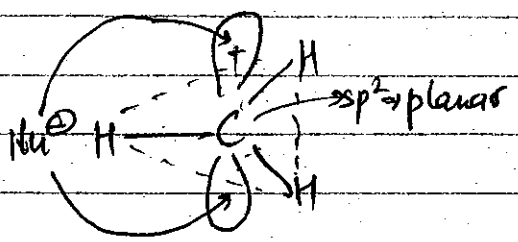
σ Bond ⇒ Polarisation ⇒ Inductive Effect
⇓
bond ⇒ due to EN Diff.

② $H-\overset{H}{\underset{H}{C}}\overset{\delta+}{\rightarrow}\overset{-\delta}{B}$ (slow) $\longrightarrow \oplus\ H-\overset{H}{\underset{H}{C}}\oplus + B^{\ominus}$

(Carbocation)

$EN_B > EN_C$
(Polar bond)

form by heterolytic fission
Incomplete octate
Stablised by EDG
(+I / +H / +M)



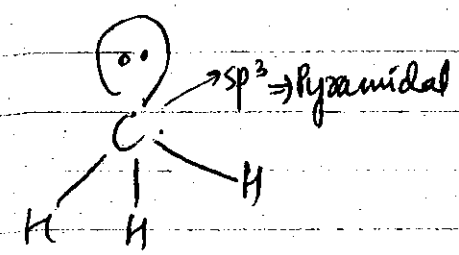
Hybridisation ⇒ sp^2 (planar)
B.P = 13 (6e⁻)
L.P ⇒ 0
V.P = 10
Highly unstable
More reactive
Behave as a Electrophile [E⊕]

Racemic mix. form if Nu⊖ attack & chiral centre gen

③ $H-\overset{H}{\underset{H}{C}}\overset{\delta+}{\rightarrow}D$ (slow) $\longrightarrow H-\overset{H}{\underset{:}{C}}\ominus + D^{\oplus}$

$EN_C > EN_D$
(Polar bond)

Formed by heterolytic cleavage
octate complete
Stablised by EWG
(−I / −H / −M)



hybridisat^n ⇒ sp^3 (pyramidal)
highly unstable
More reactive
Behave as Nu⊖

EN

C, S, I = 2.5

INDUCTIVE EFFECT

$CH_3-CH_2-\overset{\delta+}{CH_2}\bullet\!\!-\!\!\bullet\overset{\delta-}{Cl}$

Induct^n of dipole

⇓

Inductive Effect

Reason

Due to E·N difference

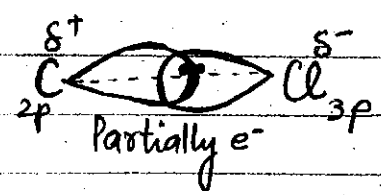
$CH_3-CH_2-CH_2-CH_3$

✗✗ not observed.

permanant effect

partially polarisat^n in σ bond e$^-$ due to EN diff b/w two atoms or group

NOTE: In inductive effect e$^-$ remain in same ~~effect~~ orbital



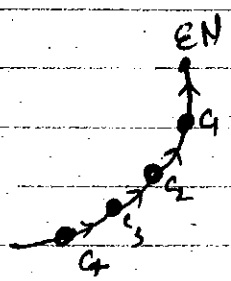
NOTE: Inductive effect is a distance dependent effect. After 3 or 4 C Inductive effect will be zero.

$\overset{+\delta_3}{CH_3}\rightarrow\overset{+\delta_2}{CH_2}\rightarrow\overset{+\delta_1}{CH_2}\rightarrow\overset{-\delta}{\ddot{Cl}}$

$+\delta_1 > +\delta_2 > +\delta_3$

Distance ↑

I-effect ↓



Diff. hybridised C-atom

$CH\equiv CH$	$CH_2=CH_2$	CH_3-CH_3
⇓	⇓	⇓
sp	sp^2	sp^3
%S ⇒ 50%	%S = 33%	%S ⇒ 25
⇓		
Near to Nucleus	EN = 2.75	EN ⇒ 2.5
⇓		
Attraction force ↑		
⇓		
EN ⇒ 3.25		

Standard

Inductive effect of C-H bond = 0

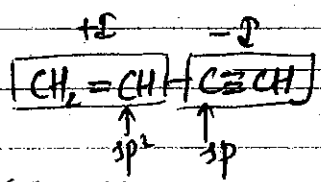
On the basis of hydrogen atom

Inductive effect are of two type :-

(+I) EDG EWG (-I)

① $CH_3-CH_2=CH_2$ (sp^3, sp^2)

②



③ $\overset{\delta-}{CH_3}-\overset{\delta+}{Mg}-X$ (Grignard Reagent)

-I

I- Effect

- +I-Effect {EDG}
- -I Effect {EWG}

Order Of +I Effect

$-CH_2^{\ominus} > -NH^{\ominus} > -O^{\ominus} > -C(=O)-O^{\ominus} > -C(CH_3)_3 > -CH(CH_3)_2 > -CH_2-CH_3$

Acc to EN | Distance | 3° Alkyl grp | 2° Alkyl grp

$-CT_3 > -CD_3 > -CH_3$

Acc. to [Kinetic Isotopic Effect K.I.E]

NOTE All Anion + All Alkyl Group ⇒ -I Effect

except $-C\equiv CH$,  , $-CH=CH_2$ } -I effect

Kinetic Isotopic Effect (K.I.E)

Also C-H bond polar & N diff. & Polar C-H bond

C——H ($_1H^1$ n=0) — C⌇⌇⌇⌇⌇⌇⌇H (weak bond) — More SHM, More vibrat^n } less e$^-$ density ⇒ less donate

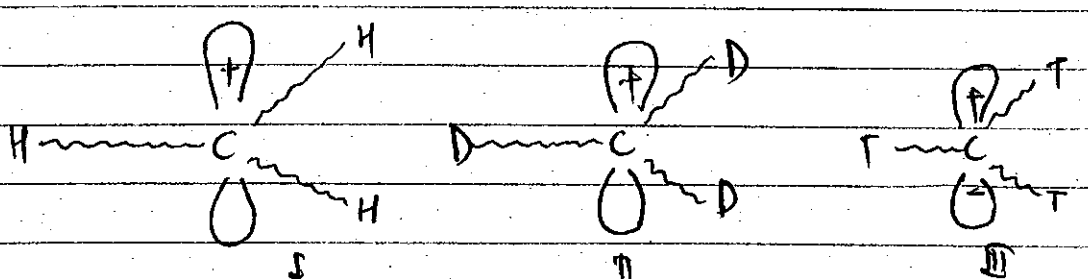
C——D ($_1H^2$ n=1) — C⌇⌇⌇⌇D — less SHM, less vibrat^n } More e$^-$ density than C-H bond ⇒ more donate

C—T ($_1H^3$ n=2) — C⌇⌇⌇T (Strong bond) — No SHM (least), Vibrat^n } Max^m e$^-$ density ⇒ max^m donate

Order Of Strength

C-T > C—D > C——H

Q-1



I II III

Stability III > II > I

Order Of -I Effect

$-\overset{\oplus}{N}H_3 > -\overset{\oplus}{N}R_3 > -\overset{\oplus}{N}H_3 > -\overset{+\delta}{N}(=\overset{-\delta}{O})(\rightarrow O) > -C\equiv\overset{-\delta}{N} > -\overset{+\delta}{C}(=\overset{\delta-}{O})-OH > -\overset{+\delta}{C}(=\overset{\delta-}{O})-H$

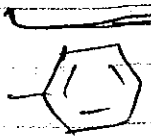
Solvat^n effect

$-\overset{\oplus}{N}H_3 > -\overset{\oplus}{N}R_3 > -\overset{\oplus}{N}H_3$: complete ⊕ charge

$-N(=O)(\rightarrow O) > -C\equiv N > -C(=O)-OH > -C(=O)-H$: Partially +δ charge

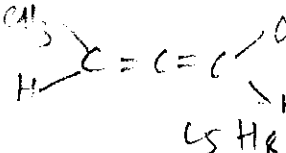
> Halogen (-F > -Cl > -Br > -I) > -O-R > -O-H > $-C\equiv CH$ > $-\dot{N}H_2$ >

Solvat^n effect

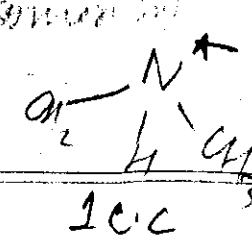
 > $-CH=CH_2$

2.75 × 6 (Phenyl) (Alkene) (Alkene)

Acc. to EN

(25)  (Smallest 11 C show optical isomerism)

$C_5H_8 \rightarrow 68$

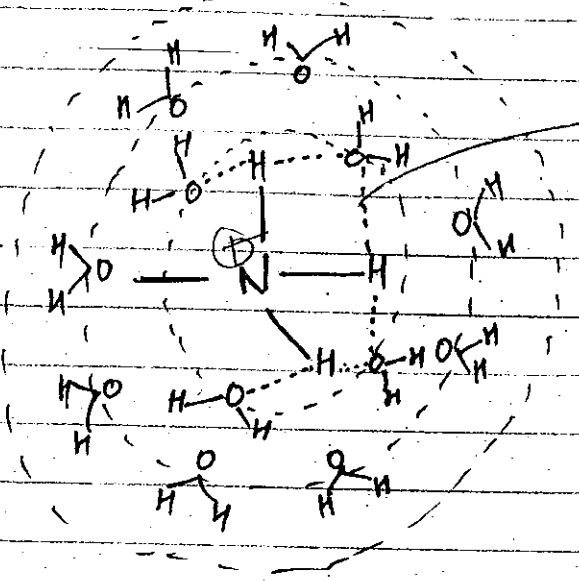


1 C.C but Optically inactive

1st layer → ion dipole (H-bonding) 2nd layer → dipole-dipole

Keypt: Complete ⊕ charge > Partially ⊕ charge > E.N

Explain I effect of $-\overset{\oplus}{N}R_3 > -\overset{\oplus}{N}H_3$



H bonding

Lattice energy > hydration energy

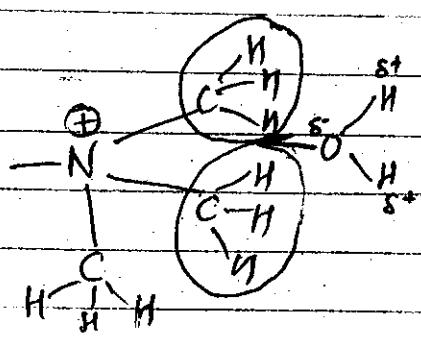
~~Soluble~~ Insoluble

Max^m solvat^n (H_2O → hydrat^n)

Max^m charge seperat^n

No accumulated charge

-I effect ↓



No active H

No solvat^n (least)

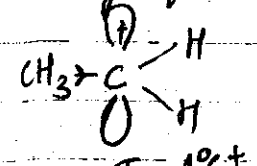
No charge seperat^n

accumulated charge present

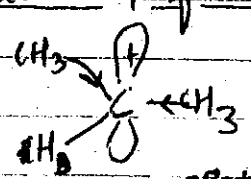
-I effect ↑

Application Of I Effect

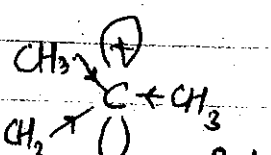
① Stability of carbocation & free radical

i) 

I 1°C+



II 2°C+

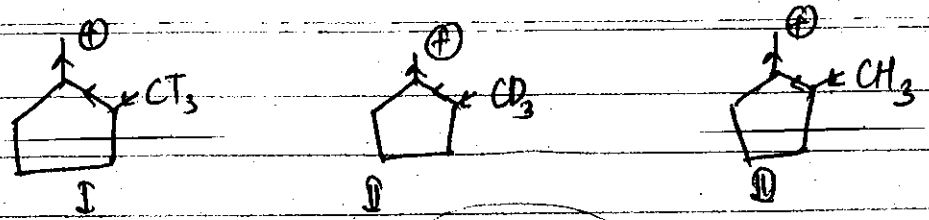


III 3°C+

Stability → III > II > I

(3°C+ > 2°C+ > 1°C+)

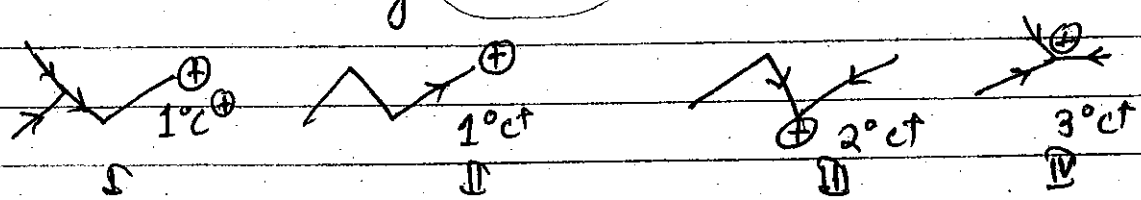
(II)



I II III

Stability (I) < (II) < (III)

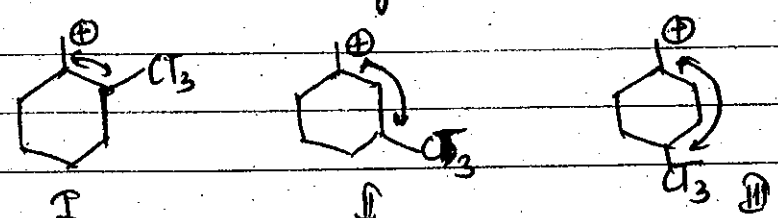
(III)



I II III IV

Stability IV > III > I > II

(IV)



I II III

Stability III < II < I (Distance factor)

(V)

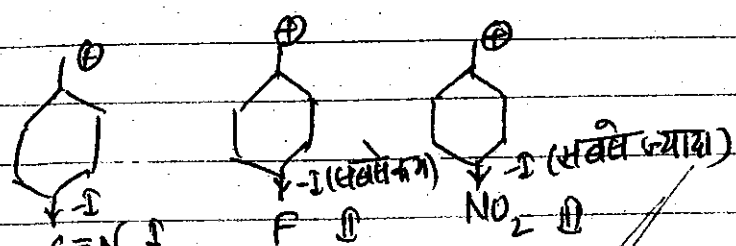
$CH\equiv C^{\oplus}$ $CH_2=CH^{\oplus}$ $CH_3>CH_2^{\oplus}$

3.25 I 2.5 II 2.5 III

saturated cation more stable than unsaturated

Stability III > II > I

(VI)



I II III

Stability II > I > III (-I series)

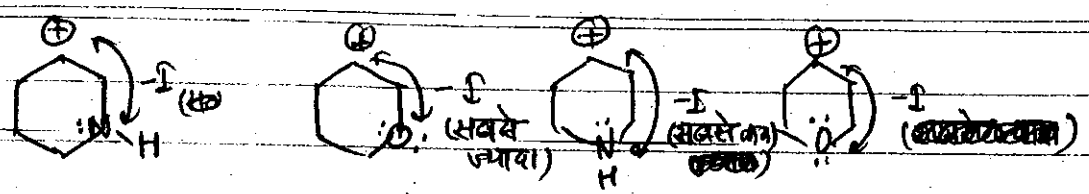
(VII)

$\boxed{CH\equiv C}-CH_2\leftarrow\overset{\oplus}{C}H_2$ $\boxed{CH_2=CH}\leftarrow CH_2\leftarrow\overset{\oplus}{C}H_2$ $CH_3-CH_2>CH_2>\overset{\oplus}{C}H_2$

-I I -I II +I III

Stability III > II > I

(VII)



I II III IV

II > IV > I > III (Distance)

Key Point Stability of carbocation & free radical $\propto \frac{+I \text{ Effect}}{-I \text{ Effect}}$

Stability of saturated cation > Stability of unsaturated cation
Jyada more EN atom -ve charge stable & less EN atom +ve charge stable

NOTE Priority order for stability in Inductive Effect :-
① Distance factor
② No. of groups
③ Power

Distance factor > No. of grp > Power

(IX) $\underset{3^\circ}{(CH_3)_3C^\cdot} > \underset{2^\circ}{(CH_3)_2CH} > \underset{1^\circ}{CH_3-CH_2^\cdot}$

(X) $CT_3-CH_2-\dot{C}H_2 > CD_3-CH_2-\dot{C}H_2 > CH_3CH_2-\dot{C}H_2$
(K.I.E)

Stability Of Anions

KEY POINT Stability of anion $\propto \frac{-I \text{ Effect}}{+I \text{ Effect}}$

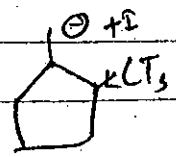
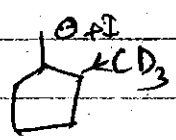
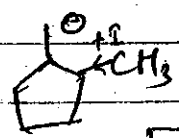
Stability of unsaturated anion > Stability of saturated anions

① $CH_3-\overset{\ominus}{C}(CH_3)_2$ (3°) I $CH_3-\overset{\ominus}{C}H-CH_3$ (2°) II $CH_3-CH_2^{\ominus}$ (1°) III $CH_3^{\ominus}$ IV

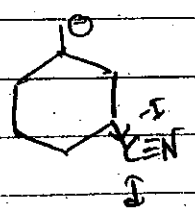
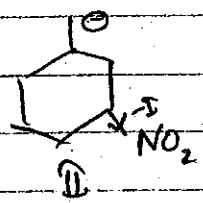
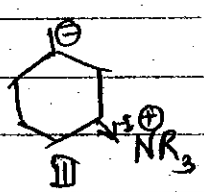
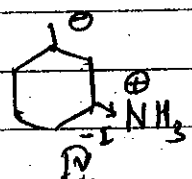
Stability III > II > I

or IV > III > II > I

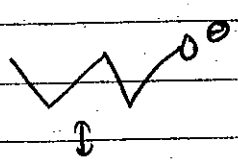
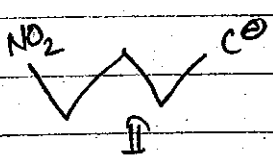
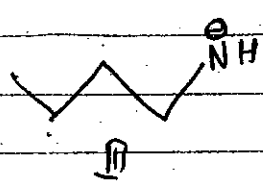
1°C⊖ > 2°C⊖ > 3°C⊖

② 



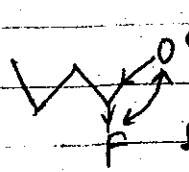
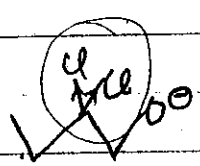
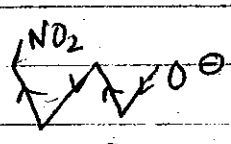
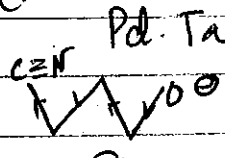
Stability II > III > I

③ 




Stability III > IV > II > I

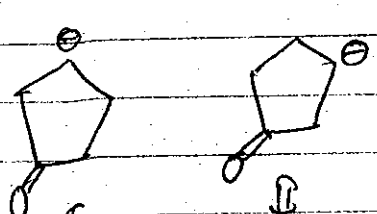
④ 



I > III > II (Acc. to EN Factor/ Pd. Table)

⑤ 




Dist > No. of groups > Power

Stability I > II > III > IV

⑥ 

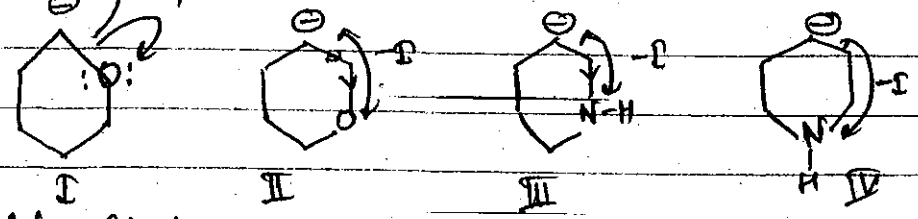
I = II

II > I

Anion always wants to be a base

acid base ⇌ (reaction)

Anion → Base ✓ Nucleophile ✓ But not basic



I II III IV

repulsion But lp is in vacant d orbital (Size same)

Stability ⇒ II > III > IV > I

Acidic & Basic Strength

$$H\text{-}A \rightleftharpoons H^+ + A^-$$

Species which can donate H^+ in aq. medium

$$H\text{-}A \underset{K_a\uparrow}{\rightleftharpoons} H^+ + A^{\ominus}$$

Acid (S.A) — conjugated base (Weak base)

$A^{\ominus}$ ↓ Stabilised by EWG ⇓ equilibrium forward direction ⇓ $[H^+]\uparrow$ Strong Acid

$[H^+]\uparrow$ $K_a\uparrow$ $pK_a\downarrow$ Strong Acid

$[H^+]\downarrow$ $K_a\downarrow$ $pK_a\uparrow$ Weak acid

KEY POINT Acidic Strength ∝ Stability of anion ∝ $\frac{-I \text{ Effect}}{+I \text{ Effect}}$

Acidic Strength ∝ K_a ∝ $\frac{}{pK_a}$

Acidic Strength acc. to periodic table Correlation

I ग्रेड स्टडी सर्कल, NCERT

Acidic strength in period

E.N ⟶ R

CH_4 ⇌ $\overset{\ominus}{C}H_3 + H^{\oplus}$ → Min stable anion → Min acidic

NH_3 ⇌ $\overset{\ominus}{N}H_2 + H^{\oplus}$

H_2O ⇌ $\overset{\ominus}{O}H + H^{\oplus}$

HF ⇌ $F^{\ominus} + H^{\oplus}$ → Max^m stable anion → Max^m Acidic

⟶ E.N ⇑
⟶ Stability of anion ⇑
⟶ Acidic strength ⇑

Acidic strength in group

U.P ⟶ Down

$H\text{-}F \rightleftharpoons H^{\oplus} + F^{\ominus}$ — Max^m repulsion, Min stable

$H\text{-}Cl \rightleftharpoons H^{\oplus} + Cl^{\ominus}$

$H\text{-}Br \rightleftharpoons H^{\oplus} + Br^{\ominus}$

$H\text{-}I \rightleftharpoons H^{\oplus} + I^{\ominus}$ — Min repulsion, Max^m stable

Overlapping ⇓

U.P ⟶ Down

⟶ Size ⇑
⟶ Repulsion ⇓
⟶ Stability of anion ⇑
⟶ Acidic strength ⇑

KEY POINT

Up/L ⟶ A.S ⇑ ⟶ R⁻

A.S ⇑ ⟶ Down

① H_2O, $R\text{-}OH$, $CH \equiv CH$, NH_3,  , CH_4 Best acid??

$OH^{\ominus}$ (0.5) H^+ $R\text{-}O^{\ominus}$ (0.5) H^+ $CH \equiv C^{\ominus}$ (3.25) H^+ $NH_2^{\ominus}$ (3) H^+  (2.75-88) $H^{\oplus}$ $CH_3^{\ominus}$ 2.5 $H^{\oplus}$

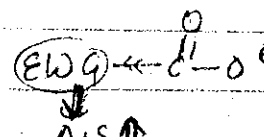
H के साथ Bond बनाने की Tendency ज्यादा होती है Base की होती है। H को खोना → Base

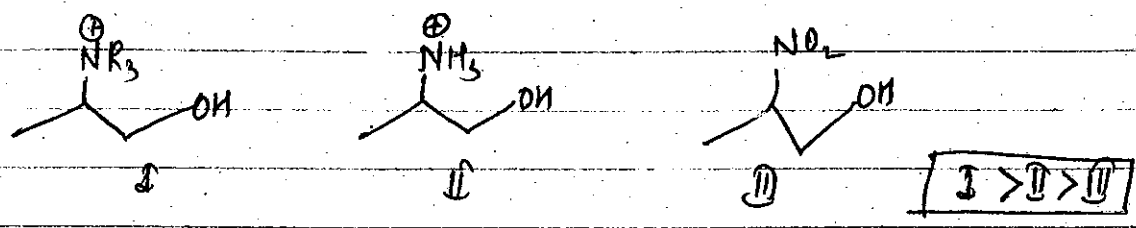
All alcohol have less acidity than water, except CH_3OH (due to solvation)

Acidic Strength $H_2O > R\text{-}OH > CH\equiv CH > NH_3 >$ $> CH_4$

Except $CH_3OH > H_2O$ As

Q.2 $CH_3\overset{+I}{-}CH_2-\overset{O}{\overset{\|}{C}}-OH < CH_3\overset{+I}{-}\overset{O}{\overset{\|}{C}}-OH < H-\overset{O}{\overset{\|}{C}}-OH$

KEY POINT 

Q.3 

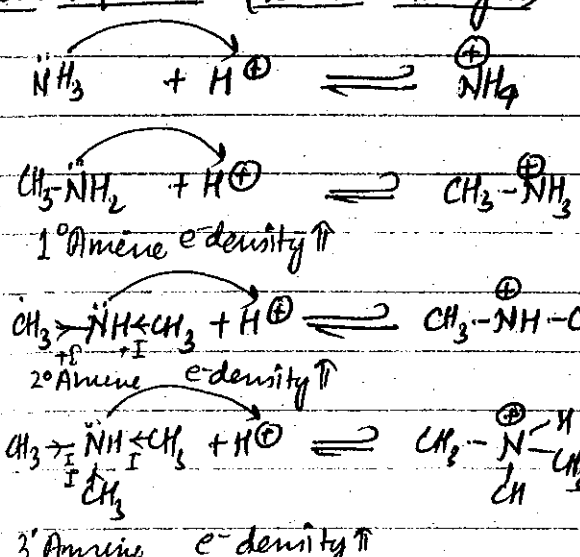
I > II > III

BASE (BASIC STRENGTH)

Species which can donate lone pair or negative charge to H^+.

Basic Strength Of 1° 2° 3° Amine In Various Medium

Gaseous Medium (Basic Strength)



Basic Strength ⇒

3° Amine > 2° Amine > 1° Amine > $\ddot{N}H_3$

Basic Strength in Non-polar Medium (Benzene, Alkane, CCl_4)

3° Amine > 2° Amine > 1° Amine > $\ddot{N}H_3$

Basic Strength in Aqueous Medium

(a) Basic strength of amine in case of methyl group.

$CH_3-\ddot{N}H-CH_3 > CH_3-\ddot{N}H_2 > CH_3-\underset{CH_3}{\underset{|}{\ddot{N}}}-CH_3 > \ddot{N}H_3$

($+I$ & Solvat^n) | | CH_3 (only $+I$) | (only solvat^n)

2° Amine | 1° Amine | 3° Amine | Ammonia

$-CH_3 \Rightarrow$ ठाँटे वाला 213

(b) Basic strength of amine in case of ethyl group

$CH_3-CH_2-\ddot{N}HCH_2CH_3 > CH_3-CH_2-\underset{CH_2CH_3}{\underset{|}{\ddot{N}}}-CH_2CH_3 > CH_3-CH_2-\ddot{N}H_2 > \ddot{N}H_3$

(Solvat^n & $+I$) | CH_2CH_3 ($+I$) | | (Solvat^n)

$-C_2H_5 \Rightarrow$ बड़े वाला 231

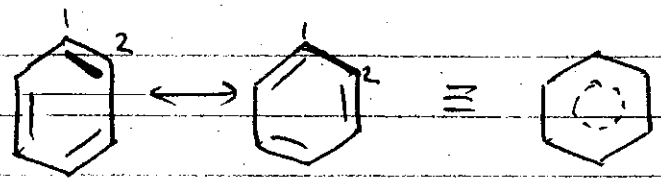
KEY POINTS Basic Strength $\propto \frac{+I \text{ Effect}}{-I \text{ Effect}}$

Basic Strength $\propto$ Tendency to donate $L.p$ to H^+

Basic strength $\propto$ stability of cation $\left[-\overset{\oplus}{N}-\right]$

To show we double bond ē ki possible hain single bond ke in case of reactions ki explain this resonance aaya. Hypothetical concept resonating str. Of conc. o/p Tse, no effect on elk conc

RESONANCE



C_1-C_2 1.34 C_1-C_2 1.54 1.39 (1.4)

Resonating str.
or
Contributing str.
or
Canonical str.

Resonating hybrid
Real str.
lowest energy
Max stable
Explain almost C.P & P.P.

Permanent Effect
Hypothetical Concept
Intramolecular phenomenon.
Resonance is a stablising phenomenon.
In resonance we cannot change position of atom only delocalisat^{n} of π-e$^-$s, lone pair, $\ominus$ve charge, free radical, $\oplus$ve charge

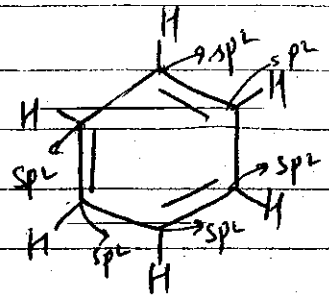
Delocalisat^{n} ⇒ Not fixed ⇒ movable e$^-$ ⇒ energy release ↑ses
localised e$^-$ ⇒ Fixed e$^-$ ⇒ not movable e$^-$ ⇒ energy ↓ses.

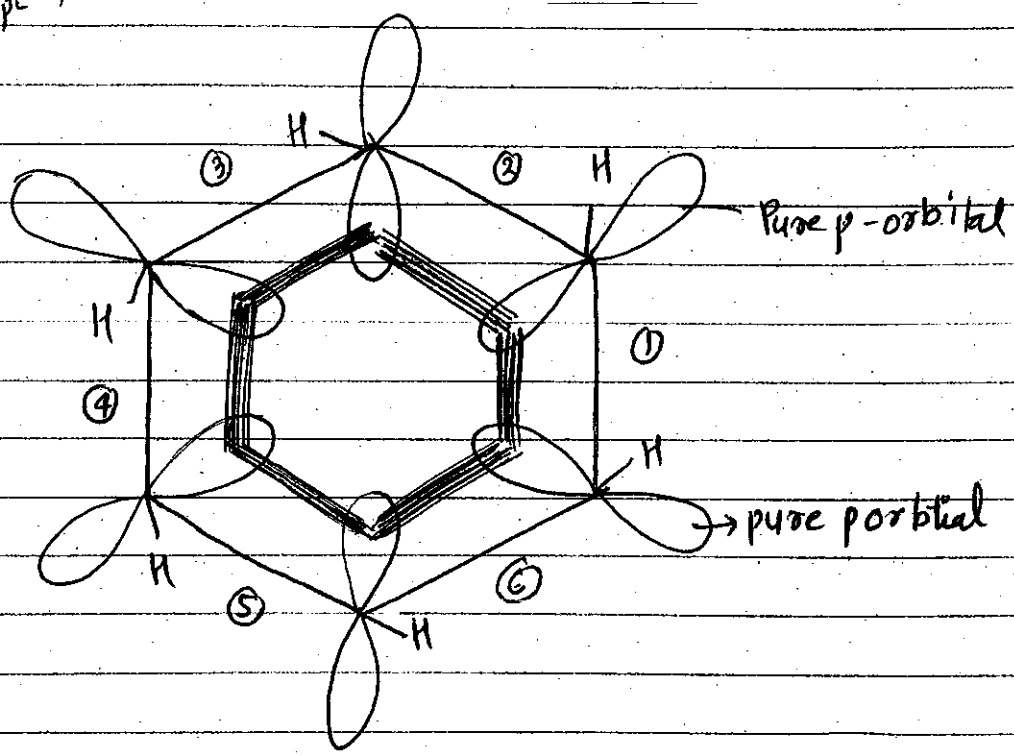
In resonance atoms or orbitals which are participated must be in a same plane.
When properties of a molecule cannot explain by single Lewis dot structure even sometimes we make more than 1 lewis dot structure that all structure is k/a RESONATING STR. But real str. is RESONATING HYBRID that can explain all P.P & C.P of a molecule

"for a resonance compound must have conjugatory system."

Carbocation hoga ke vaha pai lone pair wala ho jaa" effective resonance

out of plane - localised
inside plane - delocalised

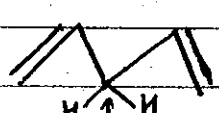




Type of System

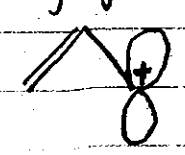
Conjugated sys.
Planer system with pure p-orbital
eg. 
Resonance ✓

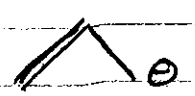
Cumulated sys.
eg. $CH_2=CH=C=C=CH_2$
2 ek khada, ek pada
[Khada khade ke sath pada pade ke sath resonance]

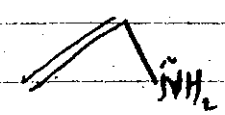
Isolated sys


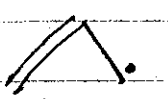
sp^3 ⇒ Non-planar
⇓
Isolated carbon.
No resonance

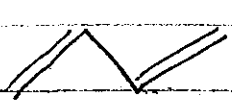
Conjugated Systems

① 

② 

③ 

④ 

⑤ 

⑥ $CH_3-\overset{(+)}{CH}-\ddot{O}-CH_3$

⑦ Vacant d-orbital reso.

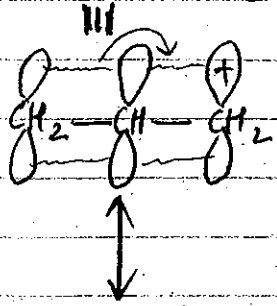
str. ijads Orbital ↑ ↓

Condition for Resonance [Mesomeric Effect]

~~Double bond conjugated with +ve charge.~~

① $CH_2 = CH - \overset{\oplus}{C}H_2$ = shifted towards → ⊕ charge

(T_2 [Allylic C$^\oplus$] T_1 [Double bond])



Migrat^n of 2e$^-$

2e 2e

1e$^-$ migrat^n

1e 1e

[2 Resonating Str.]

$\overset{\oplus}{C}H_2 - CH = CH_2 \equiv \overset{+\delta}{C}H_2 = CH = \overset{+\delta}{C}H_2$ (Resonating Hybrid)

(T_2 T_1)

Double bond conjugated with -ve charge

$CH_2 = CH - \overset{\ominus}{C}H_2$ ⊖ charge shift towards → = bond

(T_2 T_1)

Allylic anion

2 Resonating str.

$\overset{\ominus}{C}H_2 - CH = CH_2 \equiv CH_2 = CH = CH_2$

(T_2 T_1) [Resonating hybrid]

Double bond conjugated with ~~lone~~ lone pair

$CH_2 = CH - \ddot{C}l:$ Lone pair shift towards → = bond

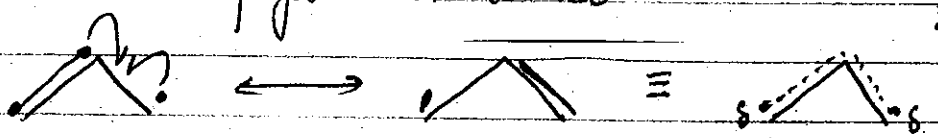
(T_2 T_1) Vinyl chloride

$\ominus CH_2 - CH = \overset{\oplus}{C}l \equiv \overset{-\delta}{C}H_2 = CH = \overset{+\delta}{C}l$

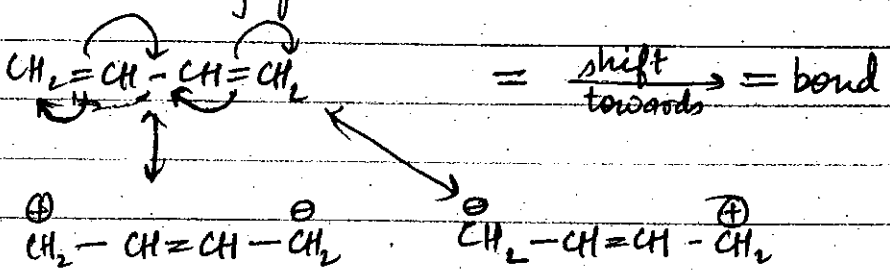
(T_2 T_1) [Resonating hybrid]

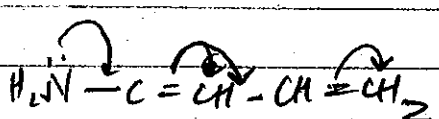
Jaha mesomeric waha resonance
But jaha resonance waha mesomeric not jaroori

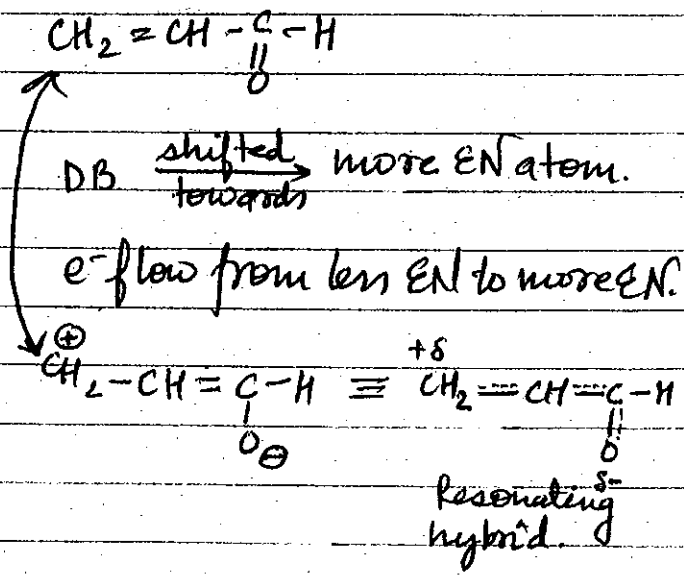
Double bond conjugated with radical



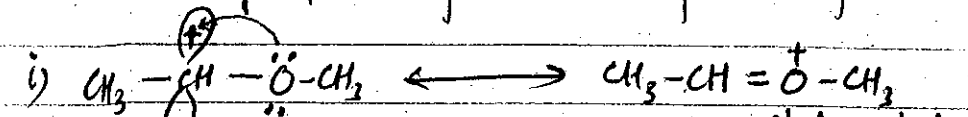
Double bond conjugated with double bond.

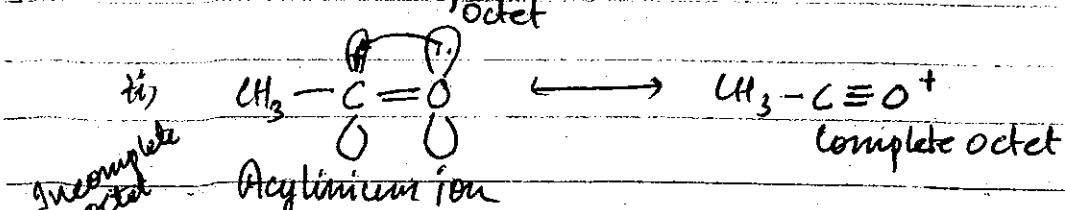






⑥ Positive charge & lone pair at adjacent position





Robin ईs → P, S, Cl
of chemistry अगेजनो ले लेते
Ganko kodte hai

i) $CH_3-\overset{\oplus}{C}H-\ddot{N}H-CH_3 \longleftrightarrow CH_3-CH=\overset{\oplus}{N}H-CH_3$

Vacant d-orbital resonance.

(I) $\overset{\ominus}{C}H_2-\ddot{S}-CH_3 \longleftrightarrow CH_2=\overset{\ominus}{S}-CH_3$

vacant d orbital

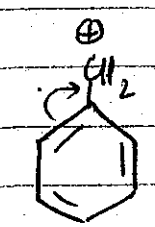
$\overset{\oplus}{C}H_2-\ddot{S}-CH_3 \longleftrightarrow CH_2=\overset{\oplus}{S}-CH_3$

(II) $\overset{\ominus}{C}H_2-\ddot{P}(H)-CH_3 \longleftrightarrow CH_2=\overset{\ominus}{P}(H)-CH_3$

Vacant d orbital

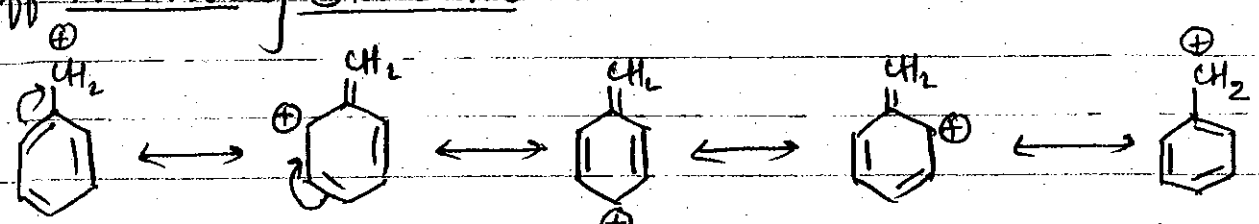
$\overset{\oplus}{C}H_2-\ddot{P}(H)-CH_3 \longleftrightarrow CH_2=\overset{\oplus}{P}(H)-CH_3$

i)

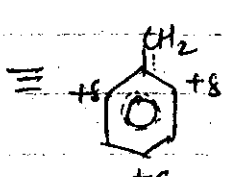


Benzyl cation

Diff. resonating Structure

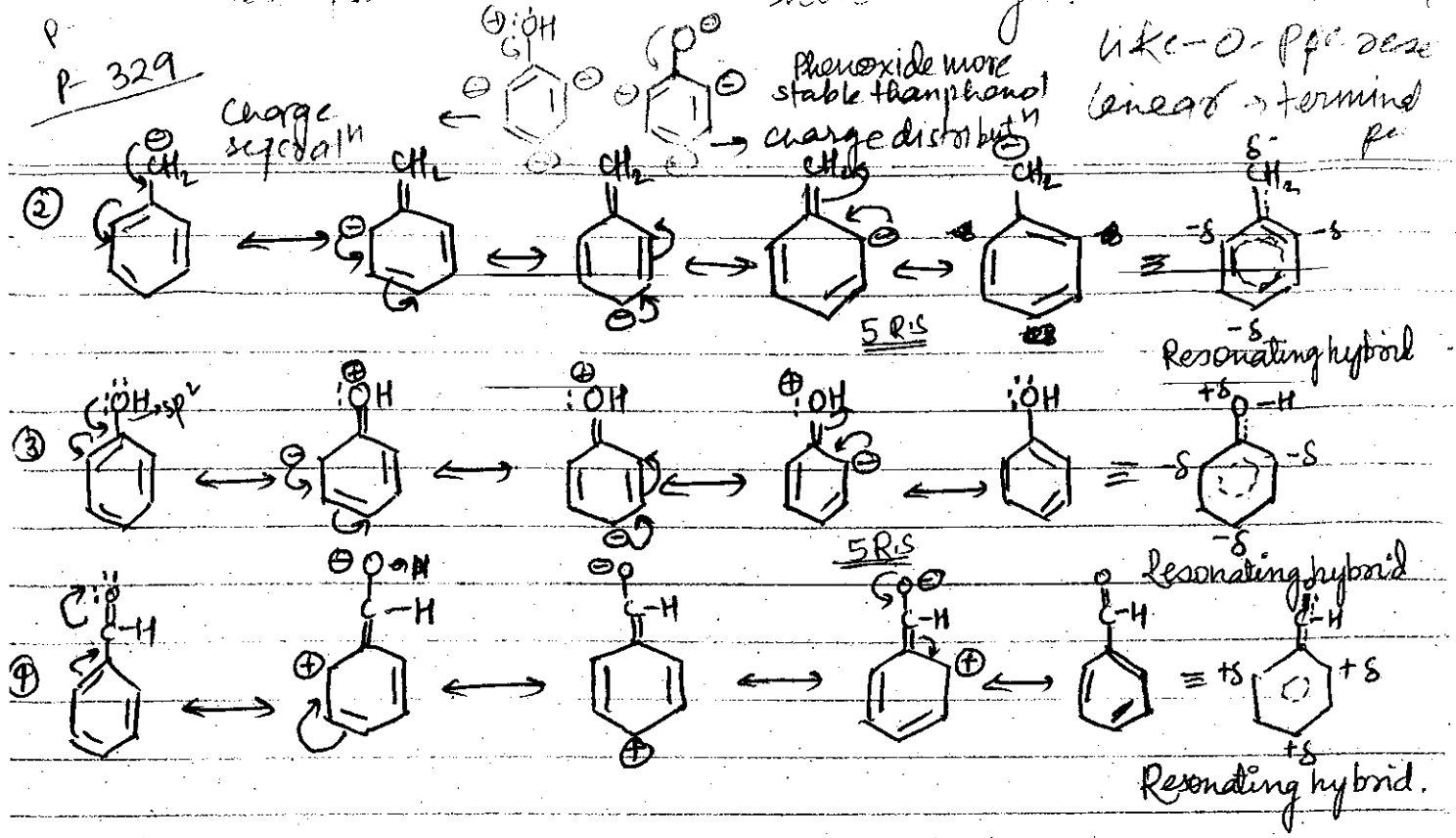


5 Resonating hybrid structure.



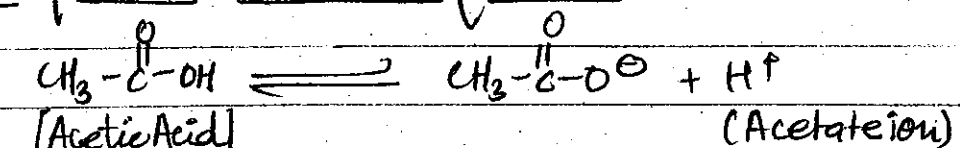
Resonating hybrid

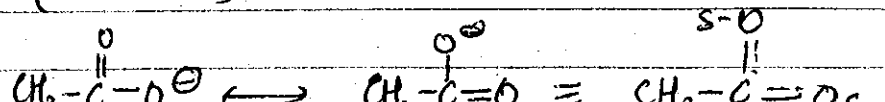
P-329

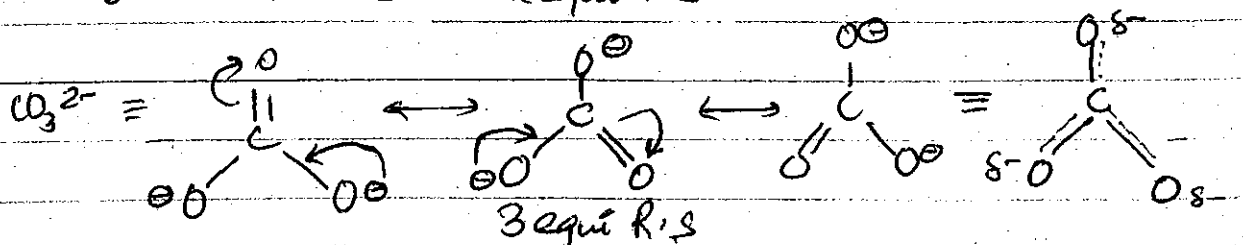


KEY POINT: In linear compound resonance Effect observed at both terminal of a molecule. In benzene like molecule resonance Effect is observed in o- & p- position

EQUIVALENT RESONANCE

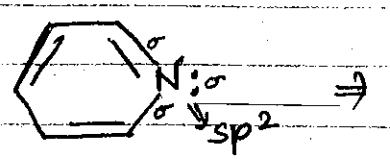


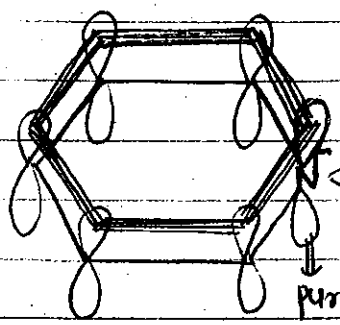


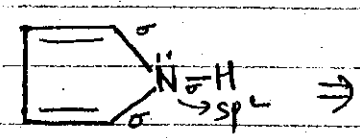


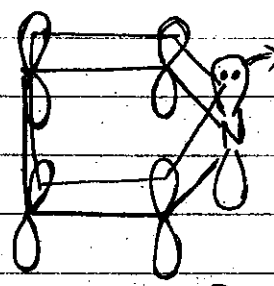
Equivalent Resonance is more effective than normal resonance

LOCALISAT^N & DELOCALISAT^N OF ELECTRON

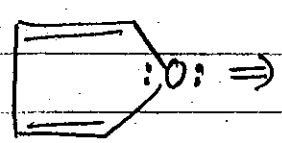
① 

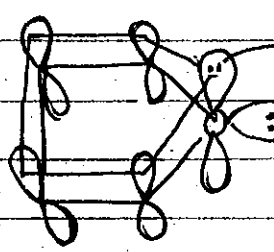
Pyridine ⇒ 

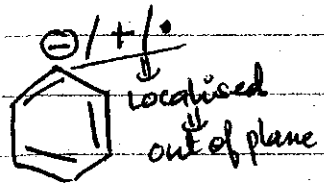
② 

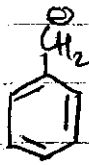
Pyrrole ⇒ 

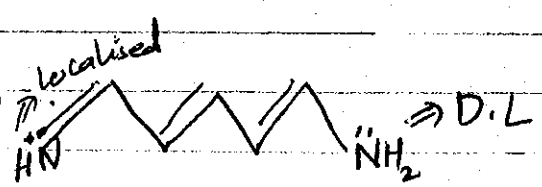
Basic Strength ⇒ Pyridine > Pyrrole

③ 

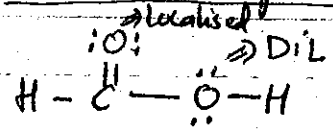
Furan ⇒ 

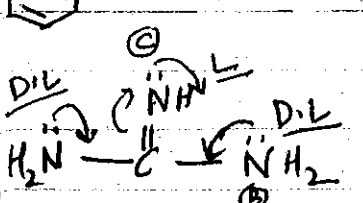
④ 

⑤ 

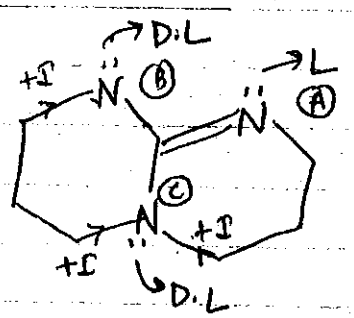
⑥ 

Basic strength ⇒ A > B

⑦ 

⑧ 

Basic strength ⇒ C > A = B

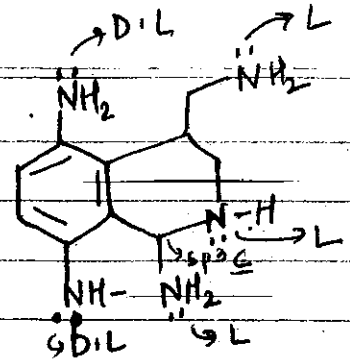
⑨ 

B·S ⇒ A > C > B

Resonance

π bond ↯ Localised
π bond ∄ Next Delocalised

(10)



(11) $CH_2 = \overset{\ominus}{C}H$ } localised

$HC \equiv C^{\ominus}$ }

KeyPOINT When ever ⊖ve charge, lone pair, free radical ⊕ve charge or π bond present at same atom then mostly π bond involved in resonance in this condition ⊖ve charge, l.p, free radical, ⊕ve charge remain localised

Stability Of Resonating Structure

Non-polar R.S > Polar R.S

(Polar)RS with complete octet > Polar R.S with incomplete octet

At more EN atom ⊖ve charge stable

At less EN atom ⊕ve charge stable

DISTANCE FACTOR :-

⊕/⊖ ⇒ Distance ⇓ → Stability ⇑

⊕/⊖ ⇒ Distance ⇑ → Stability ⇓

⊕/⊕, ⊖/⊖ ⇒ Distance ⇑ → Stability ⇑

Distance ⇓ → Stability ⇓

-F⁺
-O⁺
-N⁺

⇒ Incomplete octet ⇒ Highly unstable ⇓ Not exist

Complete octate

$\rightarrow C^{\ominus}$
$- \overset{\oplus}{F} -$
$= \overset{\oplus}{O} -$
$= \overset{+}{N} =$

⇒ Complete octate

Stability

(I) $CH_2=CH-\ddot{Cl}:$ (I) — Neutral

$\overset{\ominus}{C}H_2-CH=\overset{\oplus}{Cl}$ (II)

I > II

(II) $CH_3-\overset{\oplus}{C}H-\ddot{O}-CH_3$ — Incomplete octate (I)

$CH_3-CH=O^{+}-CH_3$ — Complete octate (II)

II > I

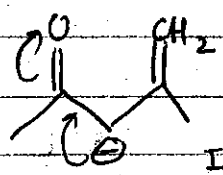
(III) $CH_3-CH=CH-CH=CH-\ddot{O}-CH_3$ (I)

$CH_3-\overset{\ominus}{C}H-CH=CH-CH=\overset{\oplus}{O}-CH_3$ (II) — Distance

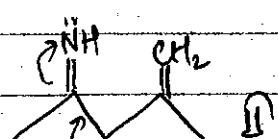
$CH_3-CH=CH-CH=CH-\overset{\oplus}{O}-CH_3$ (III) — Distance

I > II > III

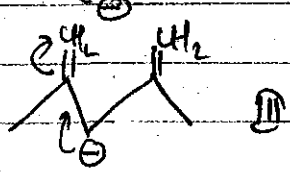
(IV)



(I)



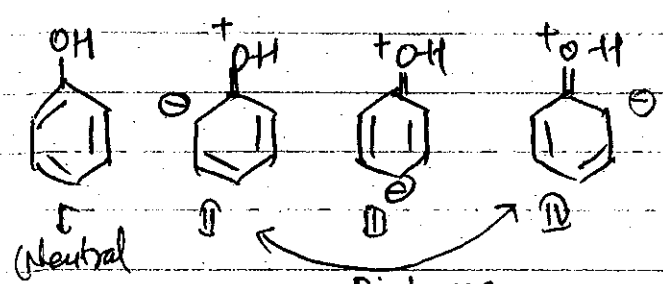
(II)



(III)

I > II > III

(V)



(I) Neutral — (II) — (III) — (IV)

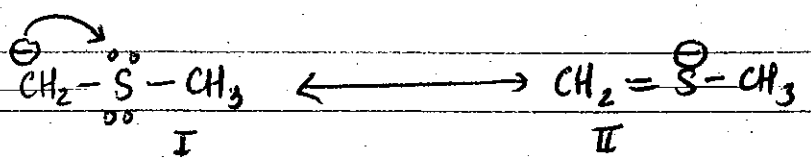
Distance

I > II = IV > III

Sheet 1

STABILITY OF RESONATING STRUCTURE

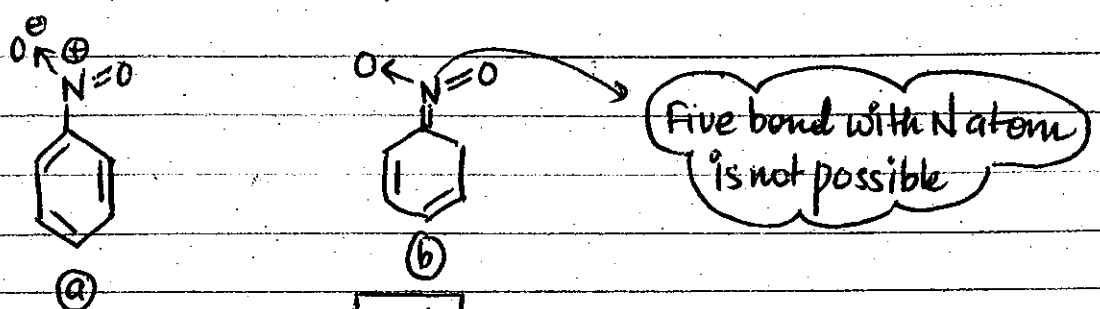
Q.1



I ⟷ II

I < II

Q.2

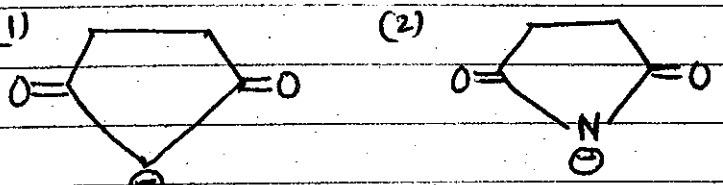


ⓐ ⓑ

a > b

Q.3

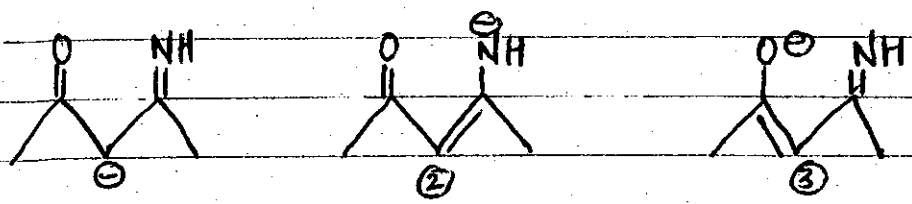
(1) (2)



⊖ve charge at C atom ⊖ve charge at N atom

2 > 1

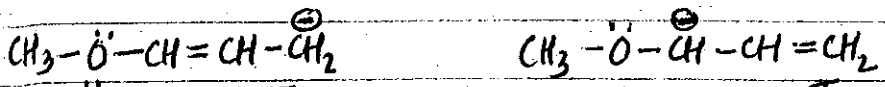
Q.4



① ② ③

3 > 2 > 1 ⊖ve charge

Q.5



I II

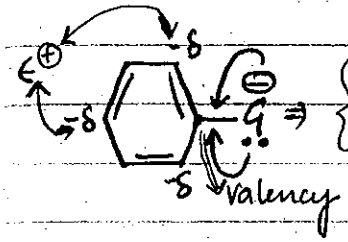
(l.p ⊖ve repulsion)

I > II

TYPE OF RESONANCE

① +R or +M Effect ⇒ Electron releasing group
② -R or -M Effect ⇒ Electron withdrawing group

① +R or +M Group



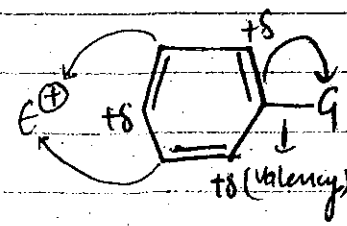
⇒ { All lone pair
+All ⊖ve charge (containing grp) involve in reso.
⇓
+M/+R

⇒ Activated Ring
⇒ All groups are o-, p- directing

+R/+M ⇒ $-\overset{\ominus}{\underset{\text{valency}}{\underset{\|}{C}}}H_2$, $-\overset{\ominus}{N}H$, $-\overset{\ominus}{O}:$, $-N(CH_3)_2$, $-NHCH_3$, $-NH_2$, $-\ddot{O}H$, $-\ddot{O}R$,

$-\ddot{N}H-\overset{O}{\overset{\|}{C}}-R$ $-\ddot{O}-\overset{O}{\overset{\|}{C}}-R$, $-\ddot{X}:$ (halogen)

② -R or -M Group (Effect)



⇒ { All polar π bond
vacant orbital involving reso.
⇓
-M/-R

Deactivated Ring
m-directing groups

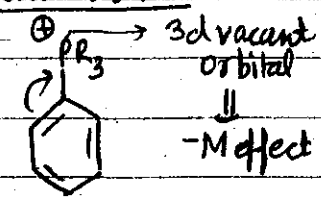
-M/-R ⇒ $-\overset{O^{-\delta}}{\overset{\|}{C}}-H$, $-\overset{O^{\delta-}}{\overset{\|}{C}}-$, $-\overset{O^{\delta-}}{\overset{\|}{C}}-O-R$, $-\overset{O^{\delta-}}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-$, $-\overset{O^{-\delta}}{\overset{\|}{C}}-NH_2$, $-\overset{O^{-\delta}}{\overset{\|}{C}}-OH$,

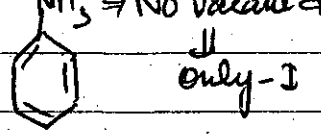
$-\overset{O^{-\delta}}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-OH$, $-\overset{+\delta}{N}\overset{-\delta}{=}O$ (↘O), $-C\equiv N$, $-CH=NH$ $-C\equiv CH$ etc

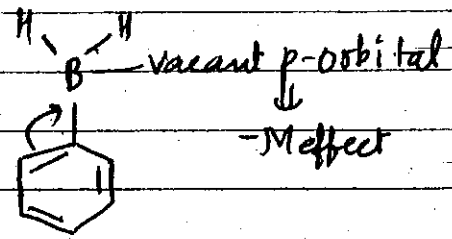
non polar
3.25 (more EN)

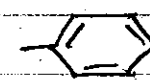
I → e⁻ orbital में e⁻ ...
M → e⁻ orbital में e⁻ ...

Vacant Orbital

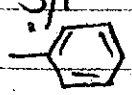
(I) 

(II) 

(III) 

+M/-M → $-\ddot{S}H$, $-\ddot{P}H_2$ (Robin hood)  $-N=\ddot{O}$, $-CH=CH_2$

Find out the diff-electronic Effect in following groups

	+I	-I	+M	-M
① Halogen ($-\ddot{X}:$)		✓	✓	
② Alkyl group	✓			
③ Allanion [$-\overset{\ominus}{C}H_2$, $-\overset{\ominus}{N}H$, $-O^{\ominus}$]	✓		✓	
④ Polar π-bond [$-\overset{+}{C}-H$, $-\overset{+}{C}-OH$]		✓	~~✓~~	✓
⑤ $-\ddot{S}H$			✓	✓
⑥ 		✓	✓	✓
⑦ $-BH_2$				✓

Comparison b/w I-Effect & M Effect.

In general mesomeric Effect is more Effective than inductive effect but in case of two groups (Halogen, $COO^{\ominus}$), inductive effect is more effective than mesomeric Effect.

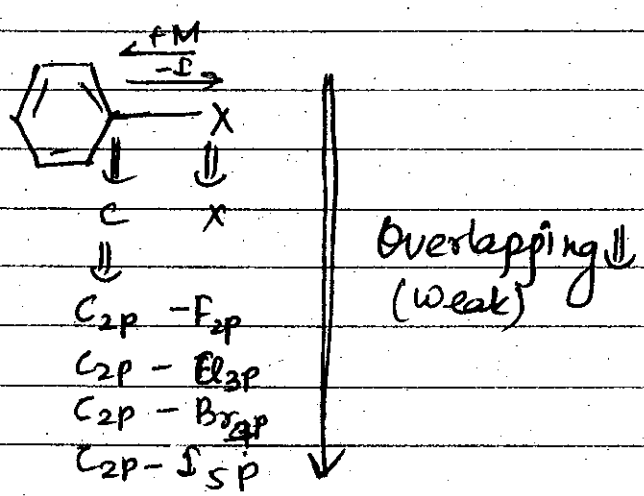
~~-I Effect~~ :-

① $-\ddot{X}:$ [-I/+M] ⇒ Net effect ⇒ e^- withdrawing effect [-I > +M]

-I Effect: $-F > -Cl > -Br > -I$
(10000 each)

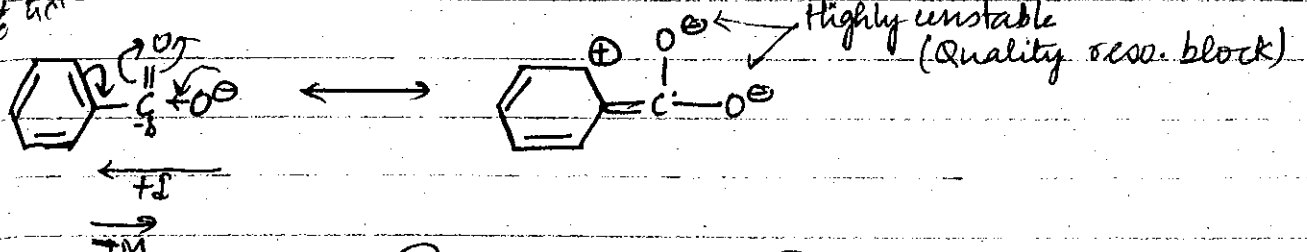
+M Effect: $-\ddot{F}: > -\ddot{Cl}: > -\ddot{Br}: > -\ddot{I}:$
(9000, 8000, 5000, M)

If both Effect (-I/+M) are overlapped then $\boxed{-F < -Cl < -Br < -I}$



② $-\overset{O}{\overset{\|}{C}}-O^{\ominus}$ [+I/-M] ⇒ Net Effect ⇒ e^- Releasing Effect [+I > -M]

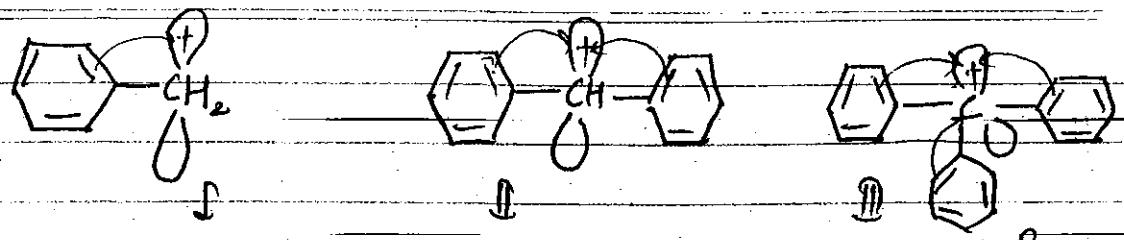
Quality reso. structure



APPLICATION OF RESONANCE

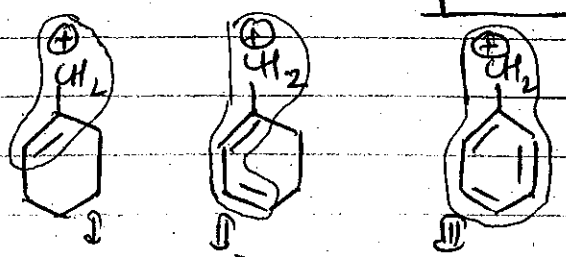
Stability Of Carbocation & Free Radical

KEY POINT: Stability of carbocation & Free radical $\propto \frac{+M/+I}{-M/-I} \propto$ extent of reso.

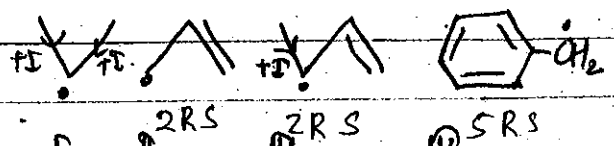
① 

Min Reso — Resonance by π bond — Maxm Reso

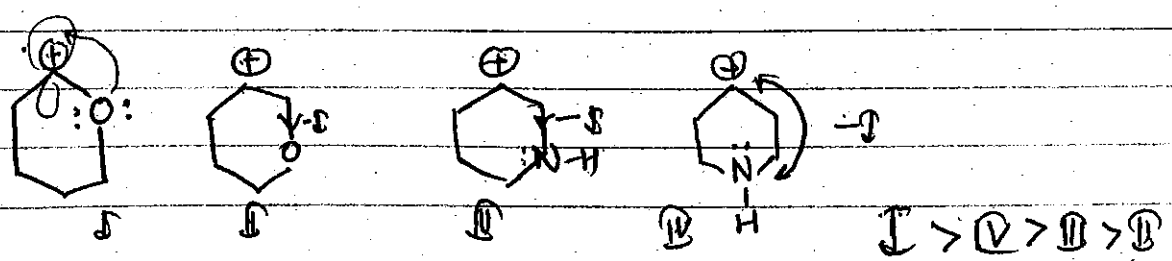
III > II > I

② 

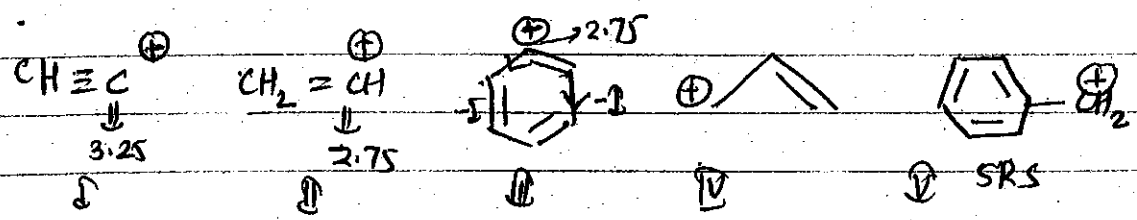
II > I > III

③ 

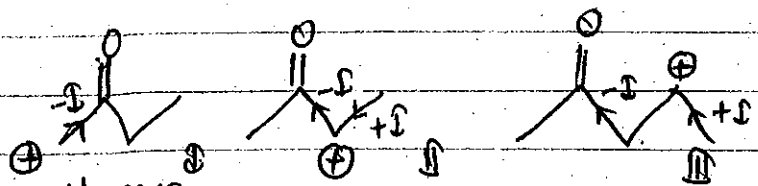
IV > III > II > I

④ 

I > V > III > II

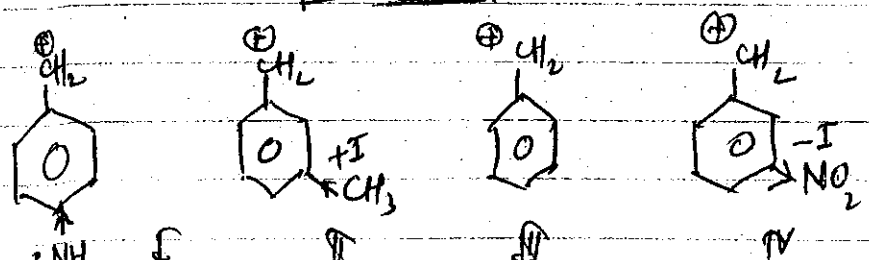
⑤ 

V > IV > II > III > I

⑥ 

No reso.

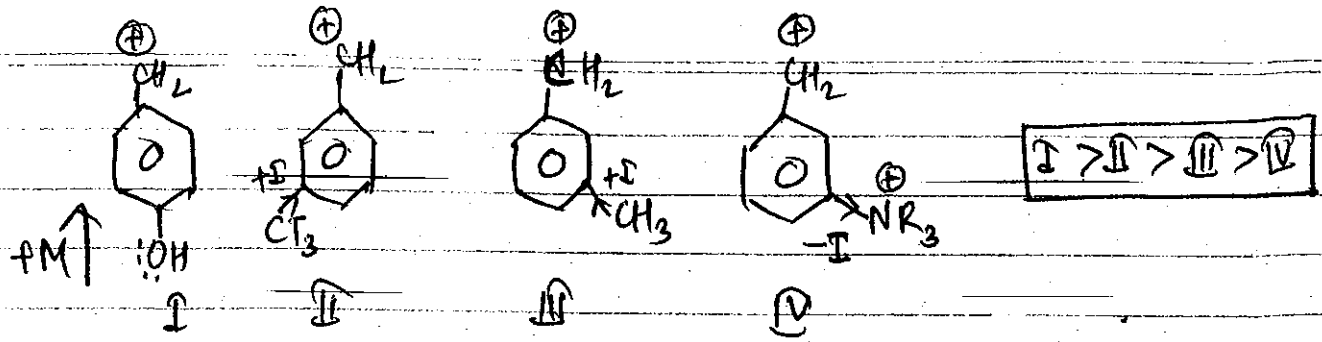
III > II > I

⑦ 

+M ↑

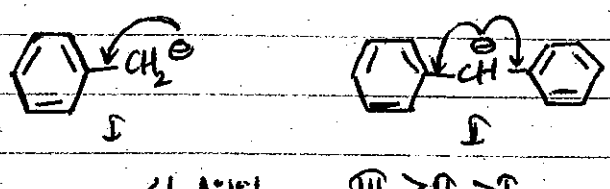
I > II > III > IV

Eq H U Reactant में H Proton Stability
Compound Ester Acidic Enol content



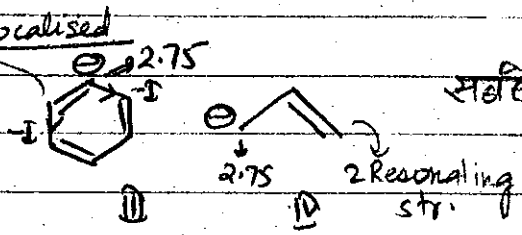
Stability Of Anion

KEY POINT: Stability of anion $\propto \frac{1}{+M / +I}$ $\propto$ extent of resonance

① 

Stability III > II > I

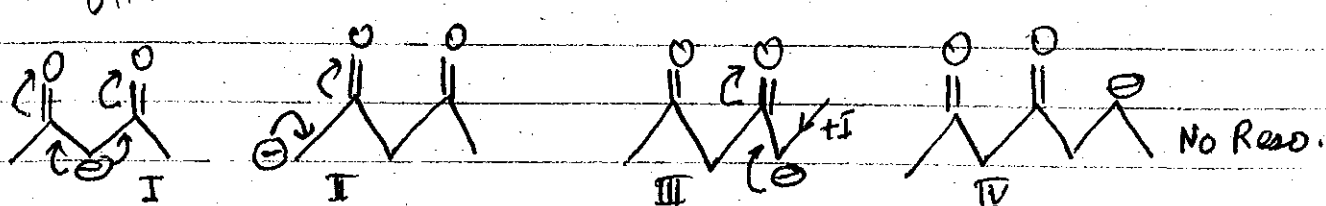
② $CH \equiv C^{\ominus}$ $CH_2 = CH^{\ominus}$ $H_2O^{\ominus}H$ introduced then most stable OH ≠ EN



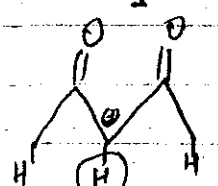
सबसे पहले EN देखेंगे

25 | 2.75 | I | II | III | IV

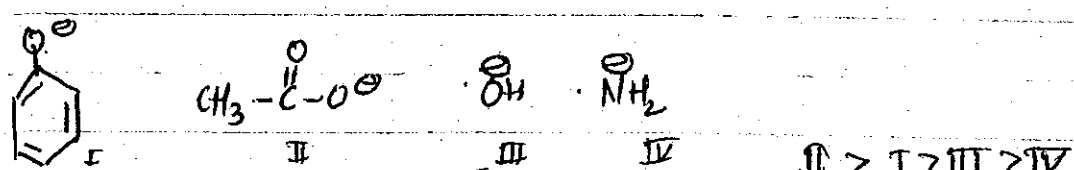
I > IV > III > II

③ 

I > II > III > IV



RDS → fast enol ↑...

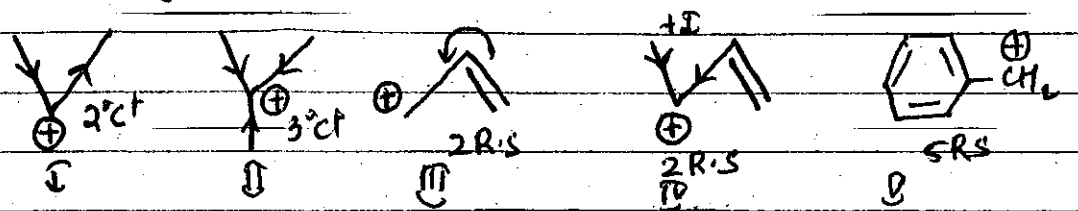
④ 

5 R.S | 2 eq. R.S | EN(3.5) | (3.0) EN

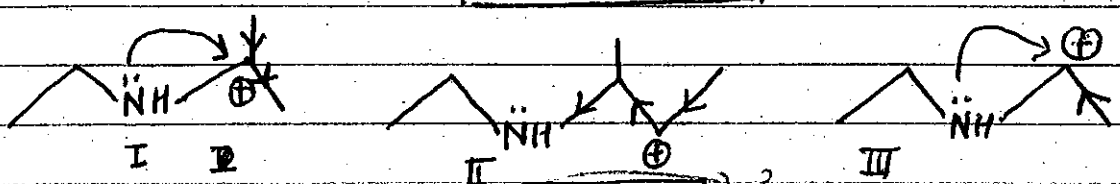
II > I > III > IV

Sheet-2

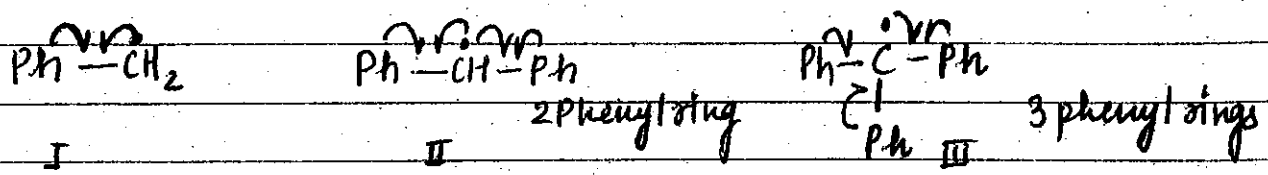
STABILITY OF CARBOCATION AND FREE RADICAL

① 

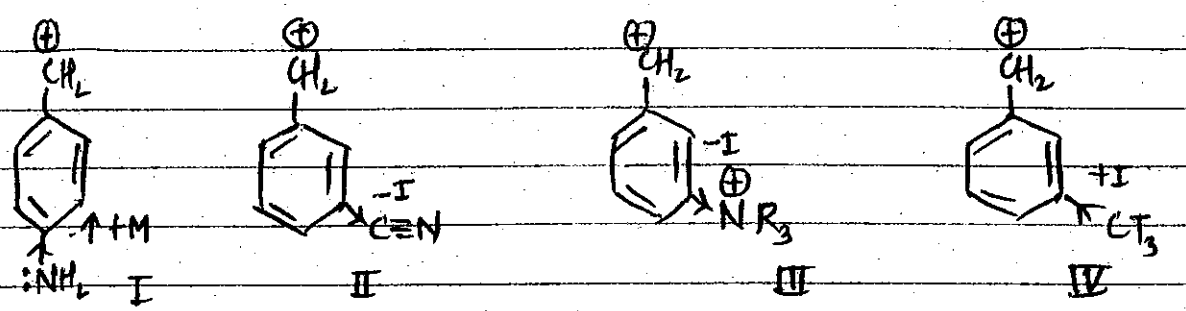
I < II < III < IV < V

② 

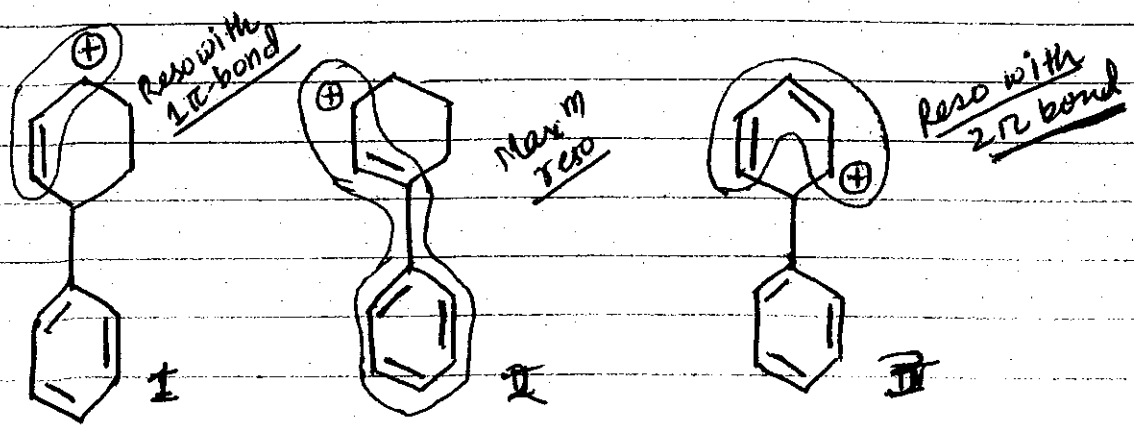
I > III > II

③ 

III > II > I

④ 

I > IV > II > III

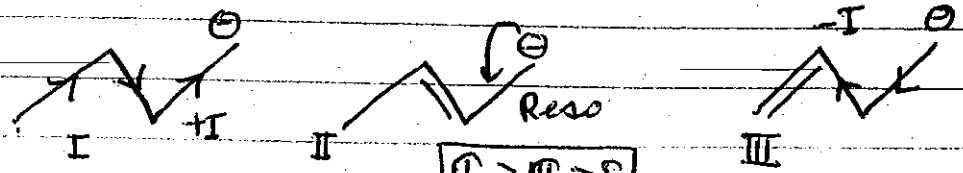
⑤ 

2 > 3 > 1

Sheet-3

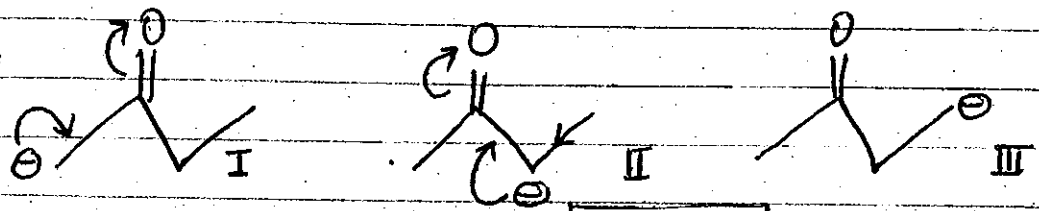
STABILITY OF CARBANION

Q.1



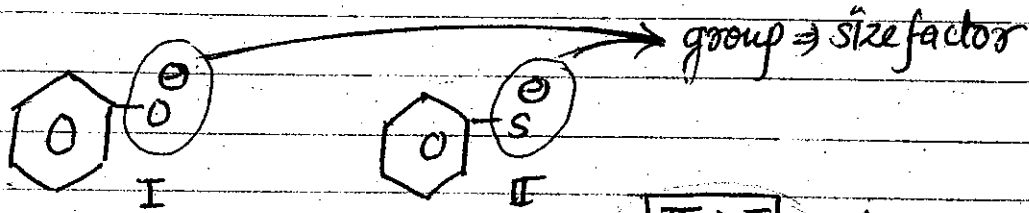
I > III > II

Q.2



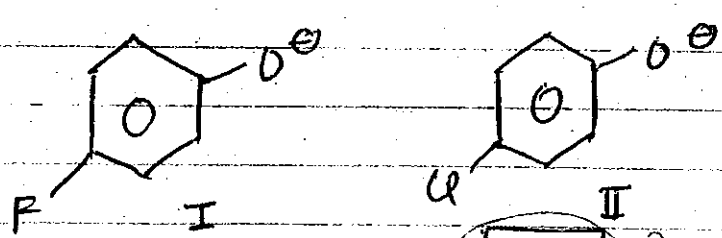
I > II > III

Q.3



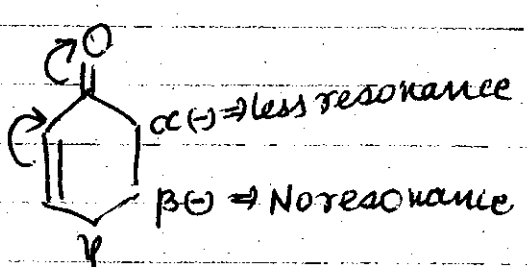
II > I ?

Q.4



II > I ?

Q.5



α(-) ⇒ less resonance

β⊖ ⇒ No resonance

γ

-ve charge more resonance

γ > α > β

Acidic mean anion → anion [illegible] Acid

Acidic Strength

KEY POINT

Acidic strength ∝ Stability of anion ∝ −I/−M ∝ $\frac{1}{+I/+M}$

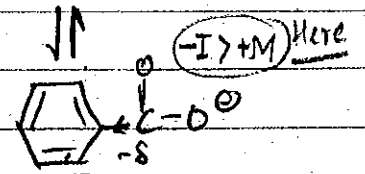
∝ Ka ∝ $\frac{1}{pKa}$

① $H-\overset{O}{\overset{\|}{C}}-O-H$ (I) > $C_6H_5-\overset{O}{\overset{\|}{C}}-OH$ (II) > $CH_3-\overset{O}{\overset{\|}{C}}-OH$ (III)

Formic Acid — Benzoic Acid — Acetic Acid

$H-\overset{O}{\overset{\|}{C}}-O^{\ominus} + H^{\oplus}$

Max^m solvat^n
Max^m charge sep.
Stability of anion ↑
A·S ↑



$CH_3-\overset{O}{\overset{\|}{C}}-O^{\ominus} + H^{\oplus}$

+I

Acc to I-Effect

A·S ∝ I > II > III

② CH_3-OH (I) > H_2O (II) > C_2H_5OH (III)

I > II > III

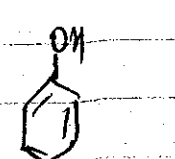
$CH_3-O^{\ominus} + H^{+}$

⇒ charge density ↑
⇒ Steric hindrance ↓
⇒ Solvat^n ↑
⇒ Stability of Anion ↑
⇒ A·S ↑

$OH^{\ominus} + H^{\oplus}$

$C_2H_5-O^{\ominus} + H^{+}$

⇒ charge density ↑
⇒ steric hindrance ↑
⇒ solvat^n ↓
⇒ Stability of anion ↓
⇒ A·S ↓

③  (I) 5 R.S

$CH_3-\overset{O}{\overset{\|}{C}}-OH$ (II) 2 eq. R.S

C_2H_5OH (III) $C_2H_5-O^{\ominus}$ 3.5

$CH\equiv CH$ (IV) $CH\equiv C^{\ominus}$ 3.25

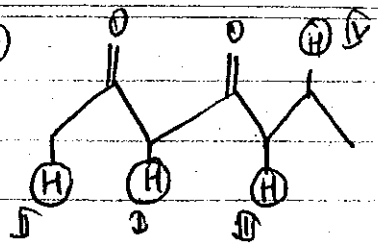
NH_3 (V) $^{\ominus}NH_2$ 3.0

II > I > III > IV > V

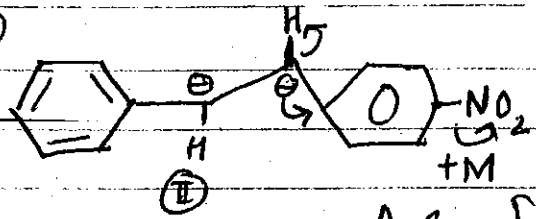
SIR & O-effect only for triangular group

C. Acid of बुला ने Ortho effect PicricAcid > FormicAcid (A·S)

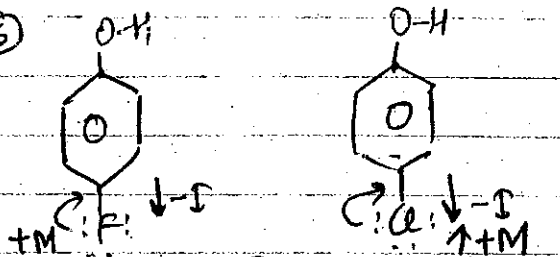
जिसमें ortho का बुला है SIR (Steric Inhibition of reso)

④ 

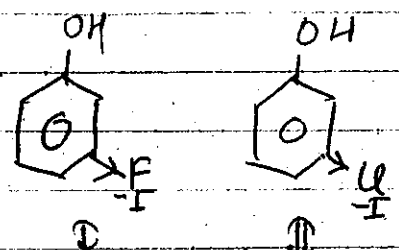
A·S I > II > III > IV

⑤ 

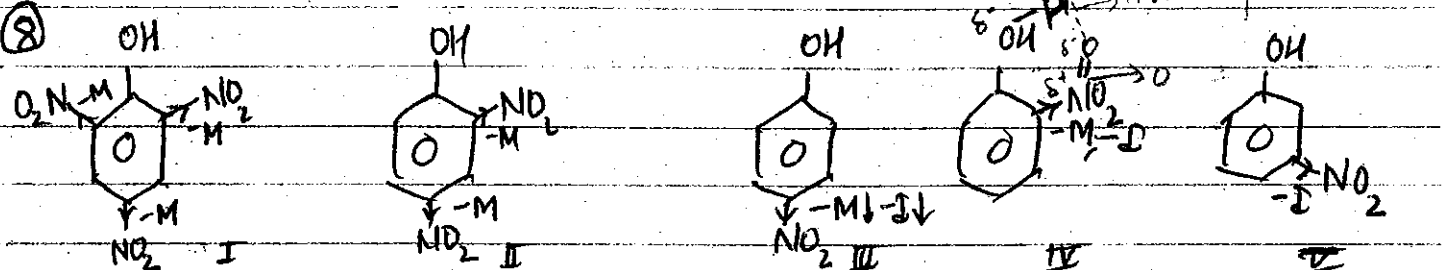
A·S I > II

⑥ 

A·S II > I (Inductive + mesomeric)

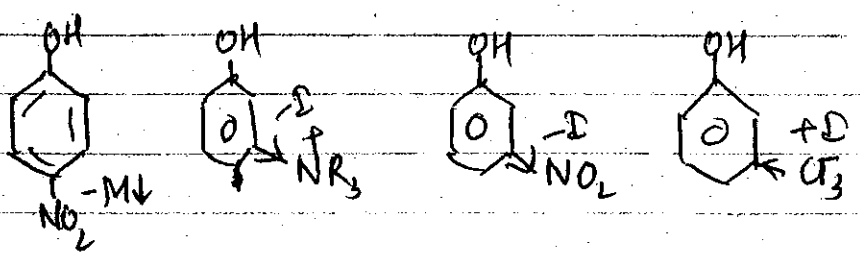
⑦ 

(Only inductive) A·S I > II

⑧ 

PicricAcid p-nitrophenol o-nitrophenol m-nitrophenol

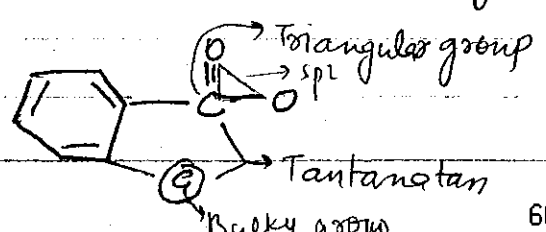
I > II > III > IV > V

⑨ 

I > II > III > IV

O-Effect [Ortho Effect] (Only for aromatic Carboxylic Acid)

Ortho substituted aromatic carboxylic acid is more acidic than p- & m- substituted carboxylic acid this effect is known as ORTHO EFFECT



due to steric hindrance -C(=O)-O change its plane

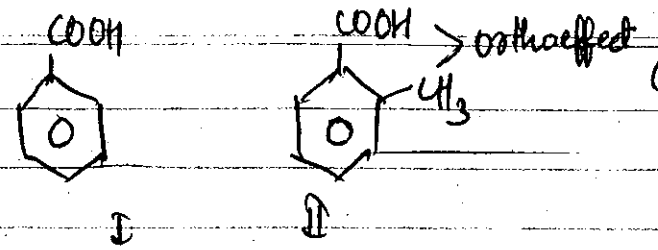
⇓

out of plane

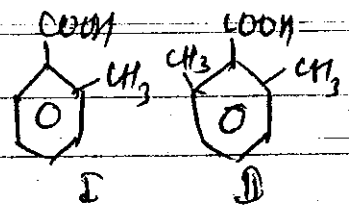
⇓

100% quality reso ⇒ stability of anion ↑

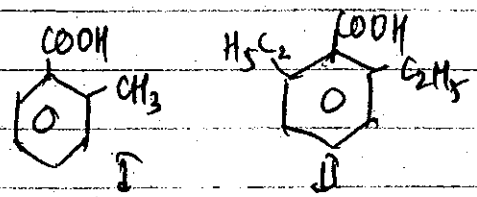
Incase SO_3H → sulphonic acid ⇒ no ortho effect. resonance
sp^3 hybridised.

① 

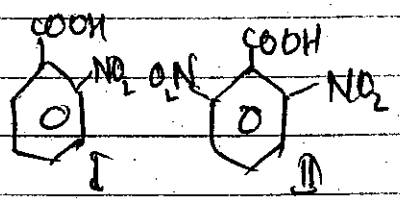
A·S II > I

② 

A·S II > I

③ 

A·S II > I

④ 

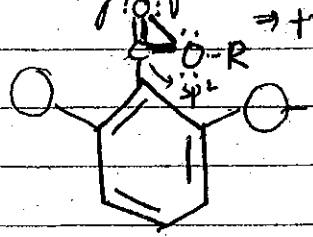
A·S II > I

SIR

➡ O-effect not observed in case of -H, -D, -T, -F, -C≡N

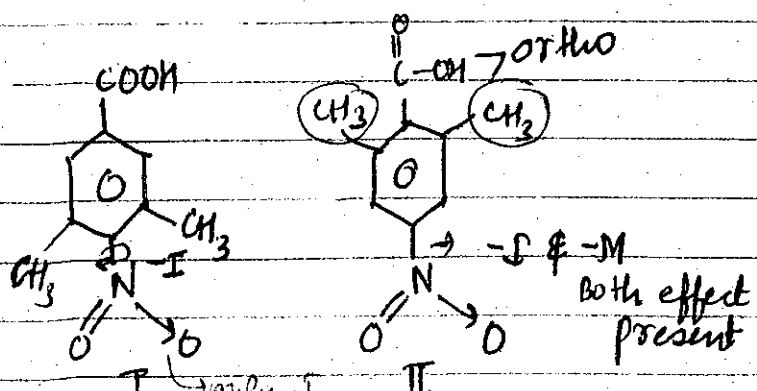
Whenever bulky group present at o-position of triangular group then due to steric repulsion triangular group change its plane (Tendency of reso. ↓) This effect is k/a SIR.

⇒ triangular grp. when present like $R-\overset{O}{\overset{\|}{C}}-OR$ $R-\overset{O}{\overset{\|}{C}}-NH_2$ $-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}$, NO_2, $-\ddot{N}(CH_3)_2$ ... etc



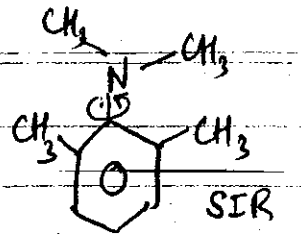
⇓

All triangular grp & all alkyl group ...
$-CH_3$, $-C_2H_5$ ...



I > II Due to SIR so no M effect

N → lone pair sp³ hybrid orbital में है Delocalise नहीं होता है।

② 

SIR

Basic Strength

Keypt Basic strength ① $\alpha \frac{1}{\text{resonance}}$ [L.P → localised More basic; → Delocalised]

② α +I Effect $\alpha \frac{1}{-\text{I effect}}$

③ $\alpha \frac{1}{1}$ $\quad \ddot{N}_{sp^3} > \ddot{N}_{sp^2} > \ddot{N}_{sp}$

④ $\alpha \frac{\%\ s \text{ character of Donar atom}}{1}$

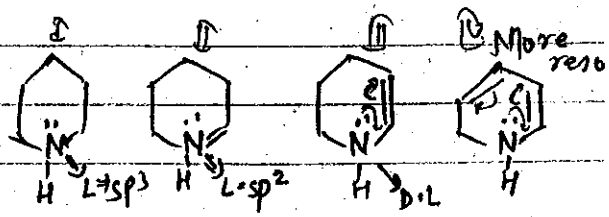
$\alpha \frac{1}{\text{Steric hindrance}}$ [In case of aniline]

1. I $CH_3-CH_2-CH_2-\ddot{N}H_2$ ⇉ L = sp^3

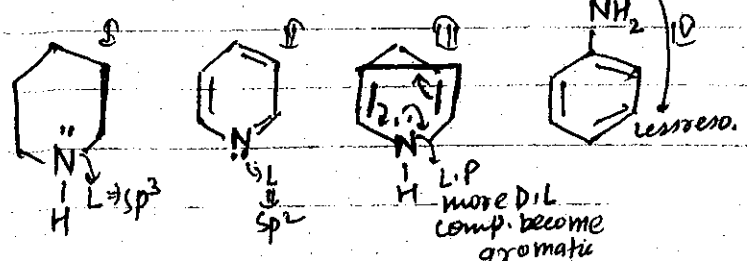
II $CH_3-CH_2-CH=\ddot{N}H$ ⇉ L ⇉ sp^2

III $CH_3-CH_2-C\equiv\ddot{N}$ ⇉ L ⇉ sp

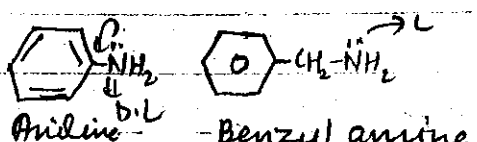
I > II > III

2. 

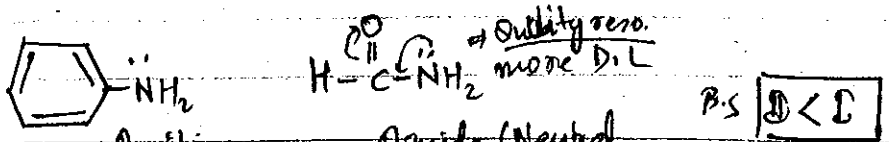
I > II > III > IV

3. 

I > II > IV > III

4. 

B·S II > I

5. 

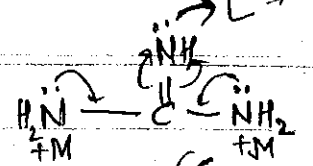
Quality reso.
more D·L

B·S II < I

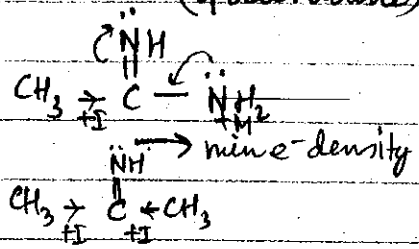
B·S

Schiff's Base

Never gives F.C.R (Friedel craft's Rxn) given only after Schiff's Base



(Guanidine)

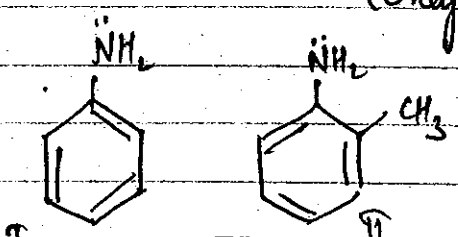


I > II > III

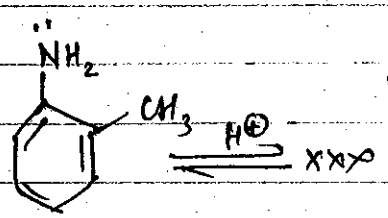
SIP (Steric Inhibition Of Protonation)

(Only for ANILINE)

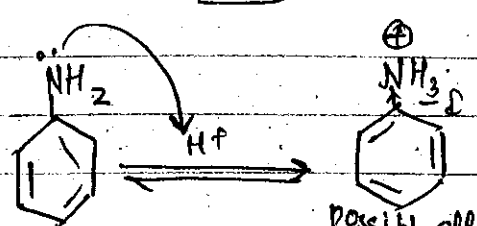
①



B·S ⇒ I > II

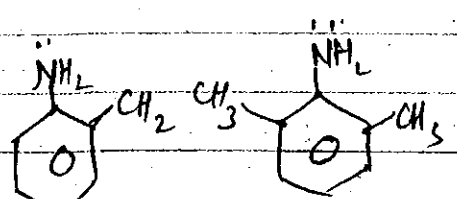


effective collision b/w l.p & H+ Not possible due to tautomerism



possible effective collision b/w l.p & H+

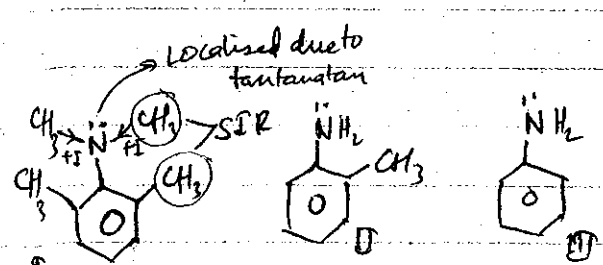
②



B·S I > II

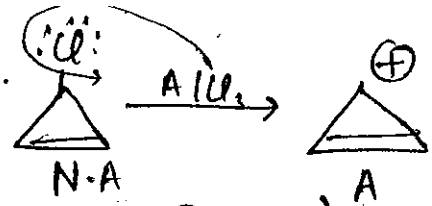
Whenever o-substituted (+)ve at aniline then due to steric repulsion effective collision not possible b/w l.p of Nitrogen atom & H+ so basic strength ↓ses. This Effect is known as SIP

Q.3



I > III > II

LOT → cyclooctatetraene



Aromaticity (HUCKEL'S RULE)

Aromatic
Non-Aromatic
Anti Aromatic

Stability →	Aromatic	Non-Aromatic	Anti Aromatic
	cyclic reso ↑ fullfill confi. (All e⁻ in BMO)	No cyclic reso ↑ fullfill confi (All e⁻ in BMO)	cyclic reso ↑ but not fullfill confi. (e⁻ in A·BMO or e⁻ in NB·MO)

NA ⟶ A बना लें
AA ⟶ NA बना लें
AA ⟶ A बना लें
A ⟶ NA ✗✗✗
NA ⟶ AA ✗✗✓
A ⟶ AA ✗✗✓

Aromatic
① compound must be cyclic
② cyclic resonance (over the entire cycle)
③ comp. must be planar
④ comp. must follow Huckel's Rule ↓

$(4n+2)\ \pi e^-$
$n = 0, 1, 2, 3, 4 \ldots$
$2\pi e^-, 6\pi e^-, 10\pi e^-, 14\pi e^- \ldots$

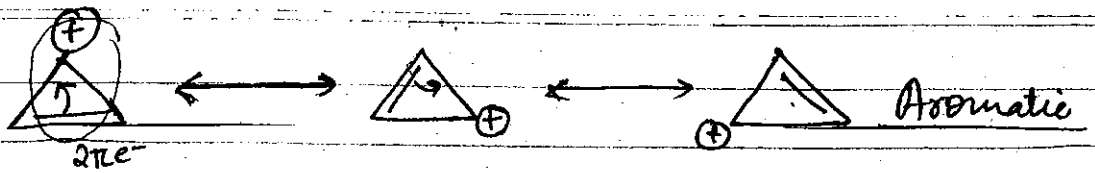
Non Aromatic
out of four any one condition violated then compound behave as a non-aromatic

Anti Aromatic
comp. must be cyclic
cyclic reso. (over the entire cycle)
comp. must be planar
comp. follow Huckel rule ↓

$(4n)\ \pi e^-$
$n = 0, 1, 2, 3, 4 \ldots$
$4\pi e^-, 8\pi e^-, 12\pi e^-, 16\pi e^-$

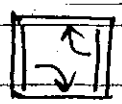
NMR = Nuclear Magnetic Resonance

Q.1



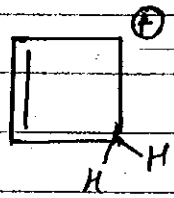
Aromatic

Q. 2



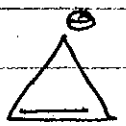
cyclobutadiene Antiaromatic

Q.3



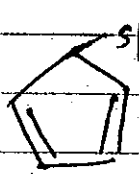
Non-aromatic

Q.4.



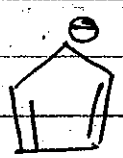
Antiaromatic

Q.5



Non aromatic

Q6



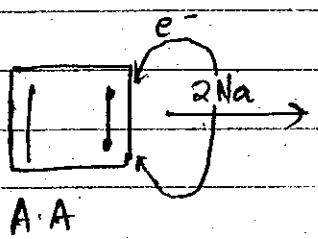
Aromatic

cyclopentadiene anion

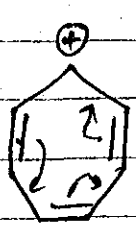
Q.7

Antiaromatic

Q.8

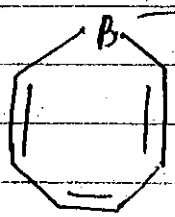


Q.9



Tropolium cation (Aromatic)

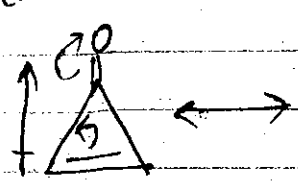
Q.10



→ vacant p-orbital

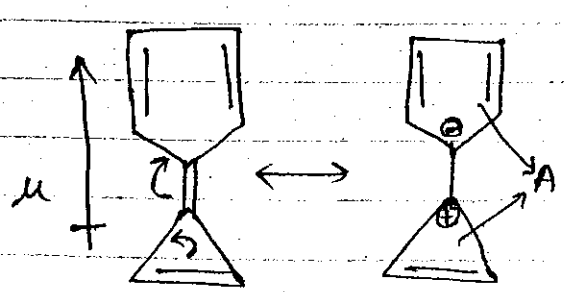
Aromatic

Q.11

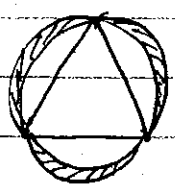


(Q.A) Quasi aromatic (Q.A)

Q.12

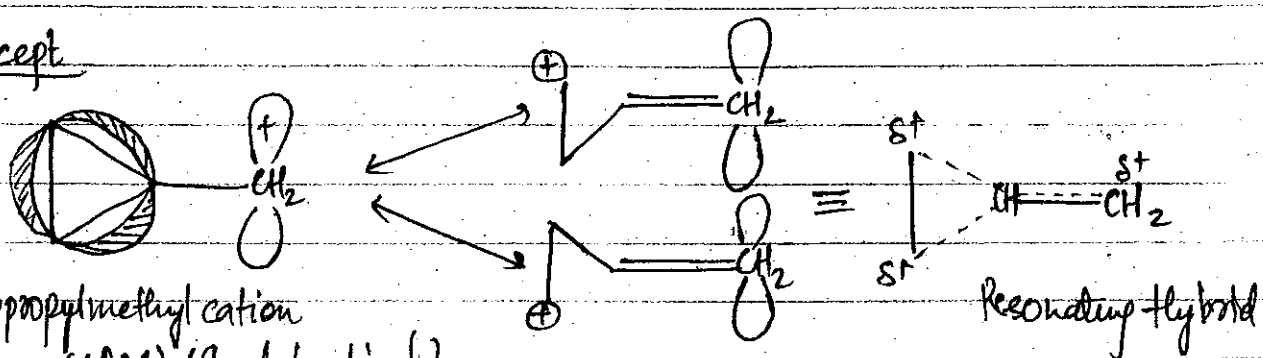


Dancing Resonance (In cyclopropane)



$\Rightarrow \pi$ bond behaves as π-bond

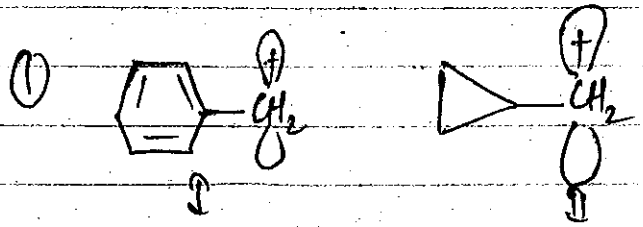
Concept



Cyclopropylmethyl cation (CPM) (4e delocalised)

Resonating hybrid

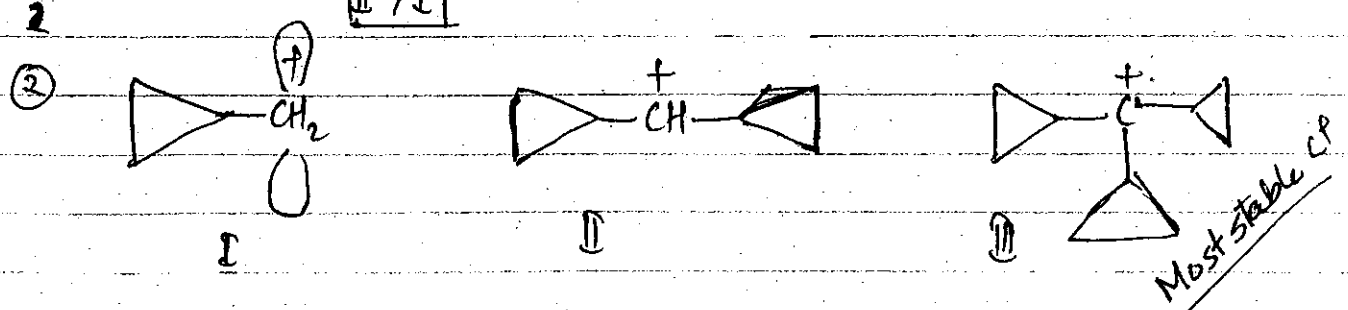
1



I II

II > I

2



I II III

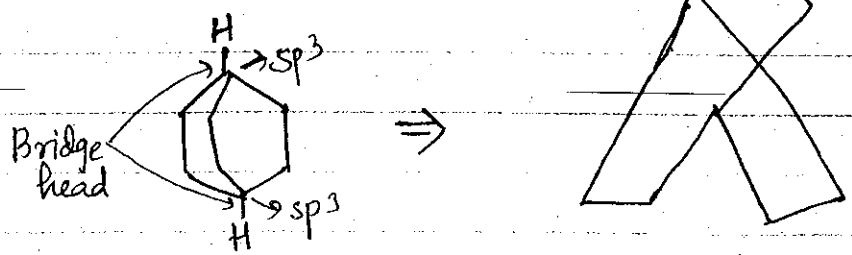
III > II > I

Bond Length

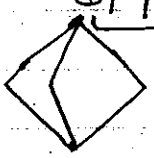
Bond length — > = > ≡

—	=	=	≡
II	II		
100% SB	Partially DB	100% DB	100% TB

Bredt's Rule

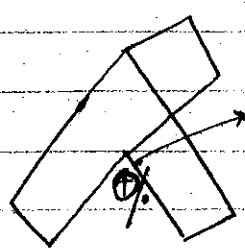


⊕/•/= ⇒ hyb sp^2 ⇒ Bredt's rule voilate ⇒ dash dash -- --

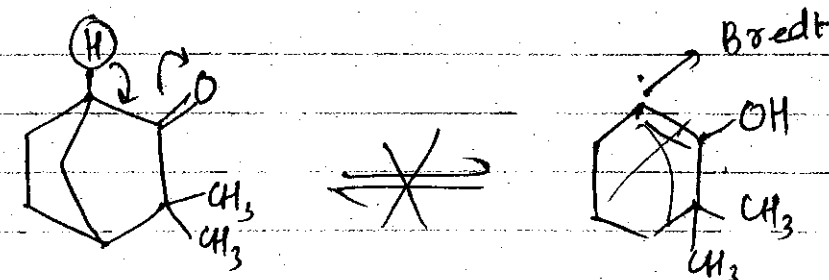


↳ नहीं ये हो नहीं सकता

1.



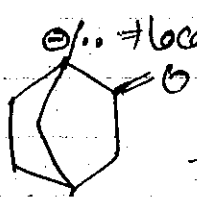
②



Keto form enol form

No tauto XX

③



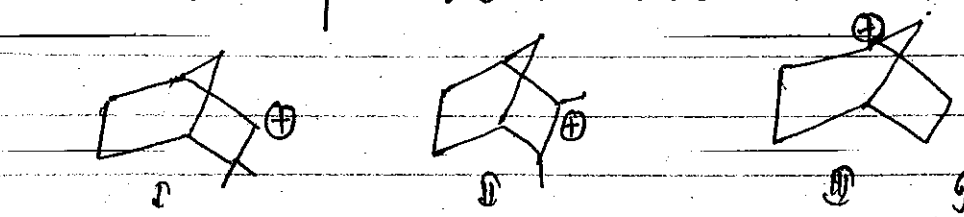
Tautomerism ≠

~~Reason~~ According to Bredt's bridge head planarity cannot be obtained before 8-membered ring

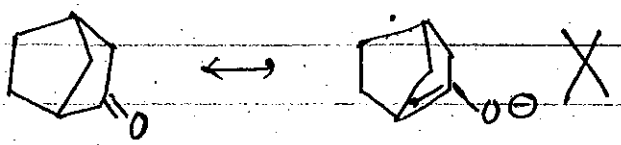
Sheet-8

BREDT'S RULE

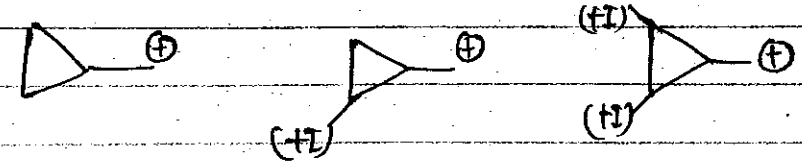
1. In which compound Bredt's rule is violated?

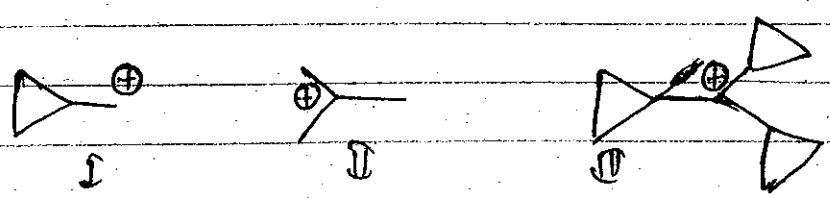


I II III In (III) Bredt's rule violated.

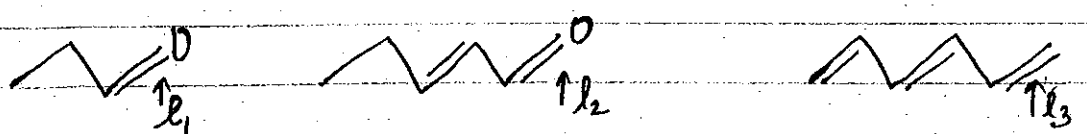
2.  Because sp^2 can't possible at bridge position (Bredt's rule)

DANCING RESONANCE

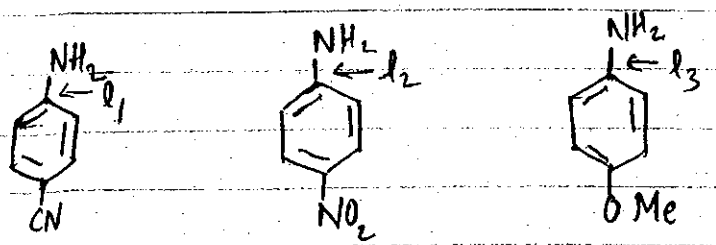
(1)  Stability III > II > I

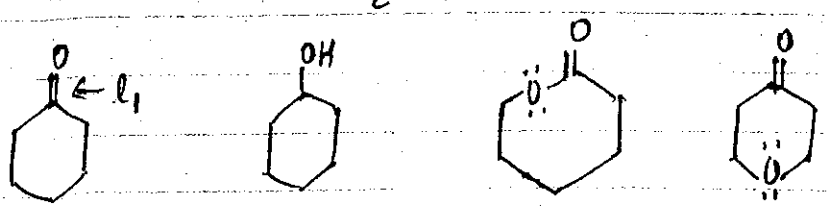
(2)  I II III II > I > III

BOND LENGTH

(1)  $l_3 > l_2 > l_1$

→ max m resonance
→ max m single bond char.

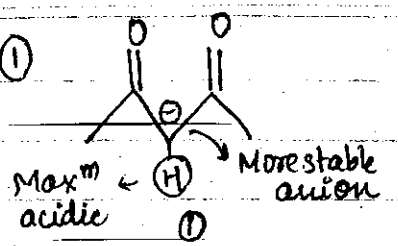
(2)  $l_3 > l_1 > l_2$

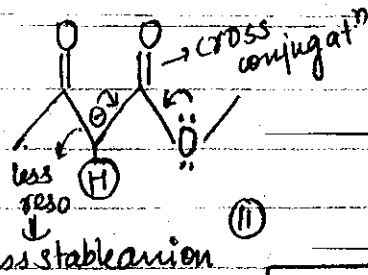
(3)  $l_2 > l_4 > l_3 > l_1$

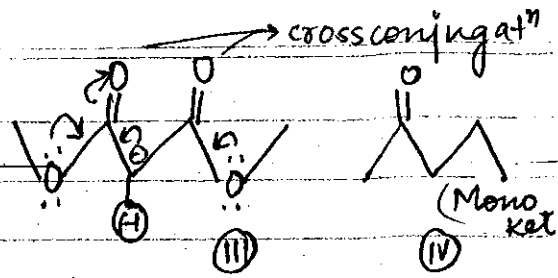
Sheet-7

ENOL CONTENT

(1)





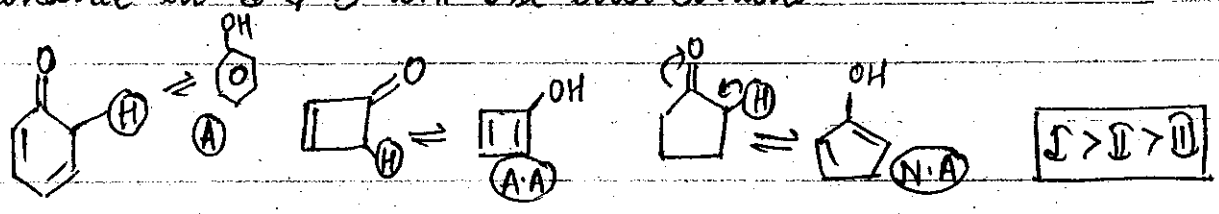


II III IV

$$\text{I} > \text{II} > \text{III} > \text{IV}$$

→ As the diketo has more enol content than mono keto
→ Resonance in III & IV will ↓se enol content

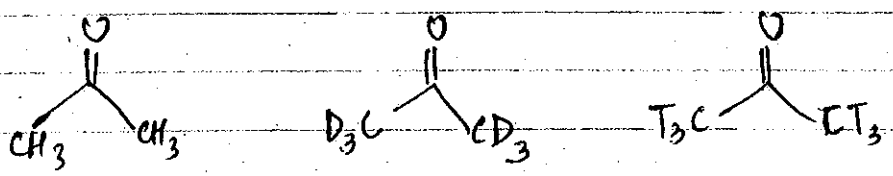
(2)



$$\text{I} > \text{II} > \text{III}$$

→ (I) will form aromatic enol (II) will form antiaromatic enol & III will make non-aromatic enol

(3)

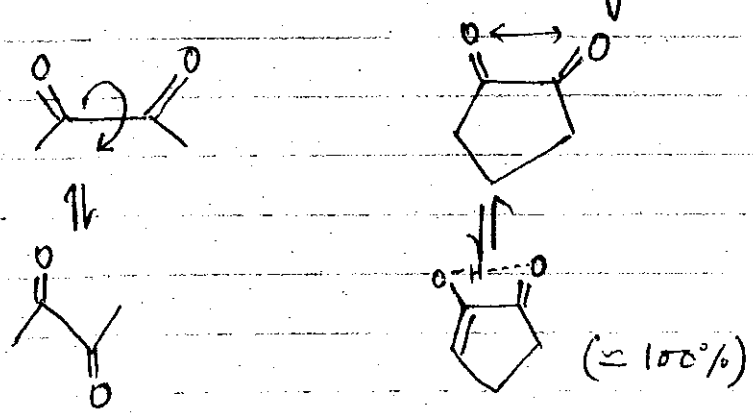


$$\text{I} > \text{II} > \text{III}$$

Acc. to K.I.E

→ C-T > C-D > C-H bond strength So (I) is easy to form enol

(4)

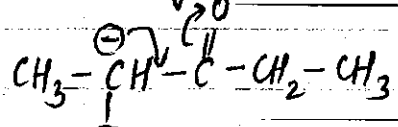


(≃ 100%)

→ Due to open chain in (I), it can rotate & relief strain of Diketo but in 2nd due to ring, it can't rotate so nearly 100% of it will convert in enol form.

Sheet-6

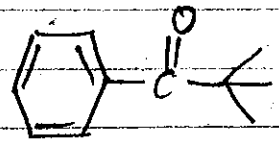
Which one give tautomerism

① 

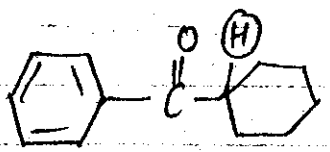
α-H ✓

⊖ Reso ✓

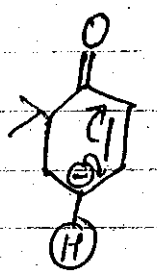
give tauto ✓

② 

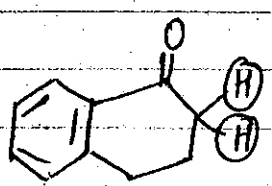
No tauto ✗✗

③ 

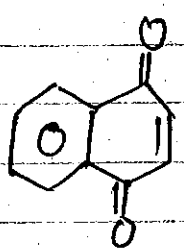
give tauto ✓

④ 

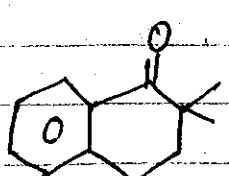
give tauto ✓

⑤ 

give tauto ✓

⑥ 

No tauto ✗✗

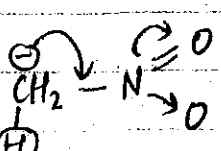
⑦ 

tautomerism ↓↓ Aromaticity Break

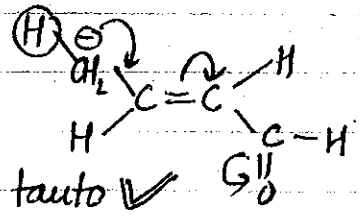
No tauto ✗✗

⑧ 

give tauto ✓

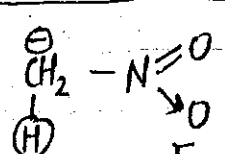
⑨ 

Tauto ✓

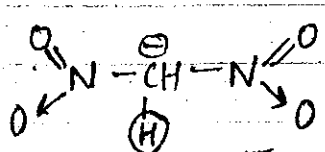
⑩ 

tauto ✓

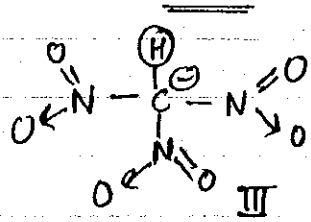
ENOL CONTENT

① 

I



II

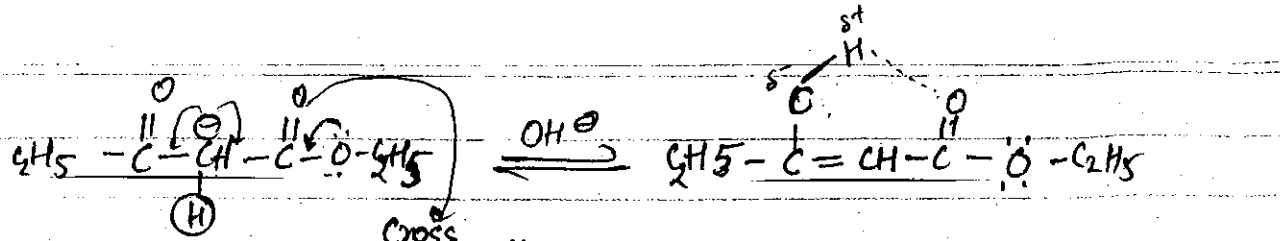


III

enol content III > II > I

Amide ~~and~~ Tautomerism

Q.3



Acetoacetic ester (AAE)

cross conjugat^{n}

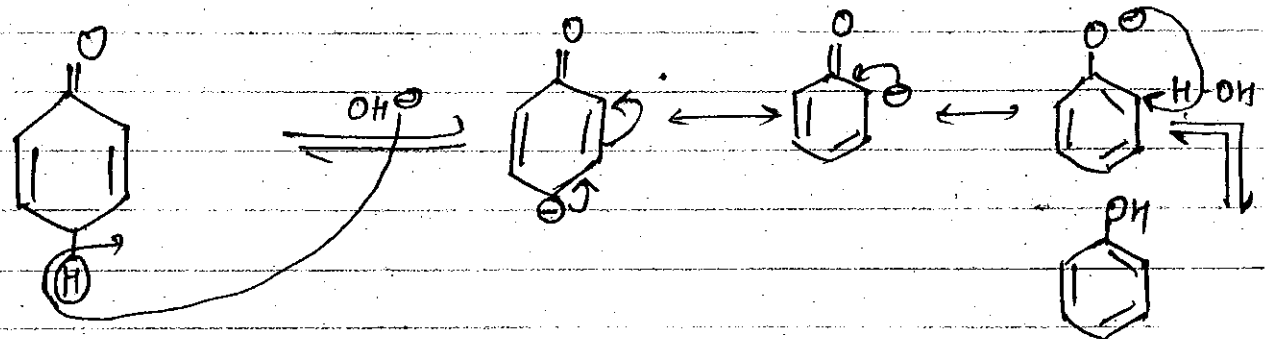
⇒ Acidic character of CH bond ↓
⇒ Stability of anion ↓
⇒ enol content ↓
⇒ RDS ↓

93%

enol content ↓
H-Bonding ✓
Resonance ✓
C-H bond acidic char. ↓ R.D.S ↓

7%

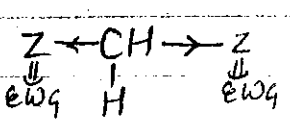
Q.4



p-tautomerism
space tautomerism
Pentaid system

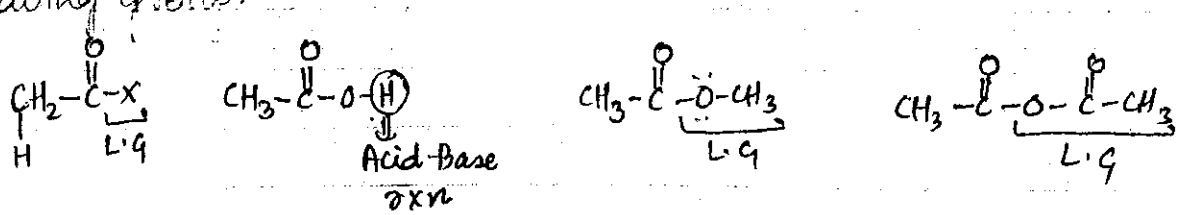
enol form
Aromatic
99.99% (≃100%)

KEY POINT Whenever $-CH_2-$ group having strong EWG then it is a ACTIVE METHYLENE. In case of active methylene. Enol content formed always more than 50%.



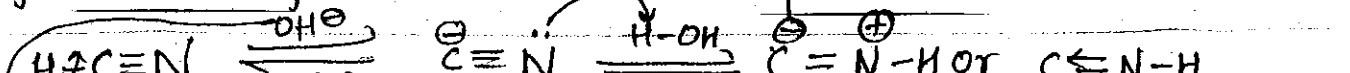
EWG(Z) ⊖ $-\overset{O}{\overset{\|}{C}}-$, $-C\equiv N$, $-NO_2$ etc

NOTE Acid derivatives does not give tautomerism due to presence of leaving group.



No tautomerism

④ CYANO- ISOCYANO TAUTOMERISM



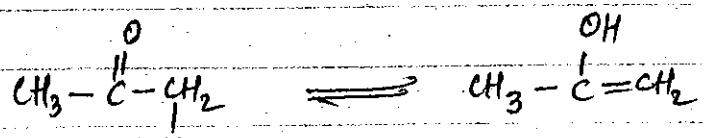
⇒ KETO-ENOL EQUILIBRIUM

Generally keto form is more stable than enol form because C=O is thermodynamically stable bond. It has covalent as well as extra ionic character that's why rxn favours towards formation of C=O.

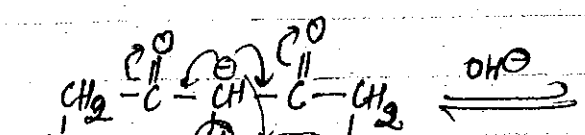
Note enol form may be more stable than keto form if following factors are present in enol form.

① Aromaticity
② Resonance
③ H-bond
④ Acidic character of C-H bond.

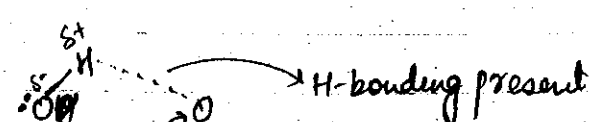
Q.1



②

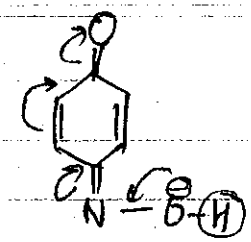


Acidic strength of C-H bond ↑ (-I effect)
R.D.S ↑
Rxn favours forward direct^{n} ↑
keto form 23%



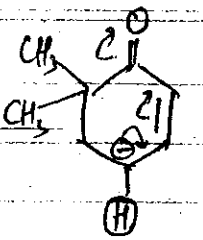
① Reso ✓
② H-bonding ✓
enol content
76%

(11)



tauto

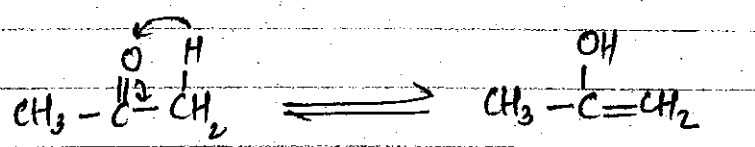
(12)



tauto

Type Of Tautomerism

① KETO-ENOL TAUTOMERISM :-

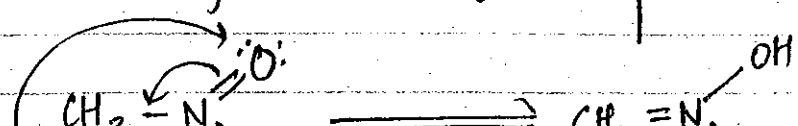


"keto form"

Triad system
[तीन पे चलती है]

"enol form"

② NITRO ACI TAUTOMERISM



"Nitro form"

"Aci form"

③ NITROSO-OXIMO TAUTOMERISM

"Nitroso form"
triad system

"Oximo" tauto

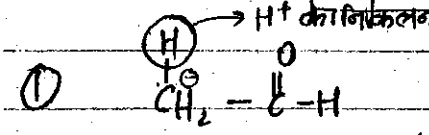
Acidity of C-H ↑
R.D.S - fast
Rxn Favours forward
enol content ↑

KEY PT. enol content ∝ Stability of anion / acidic strength of C-H bond

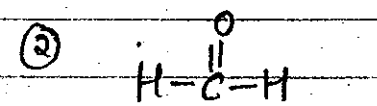
Which one comp. gives tautomerism?

KEY PT → ① Check α-H of given comp.

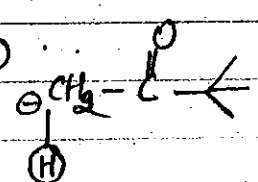
② After checking / trapping H^+ ion if ⊖ve charge involve in resonance then comp. gives tautomerism.



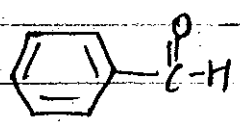
① α-H ✓ tauto ✓
⊖ve charge involve in reso ✓



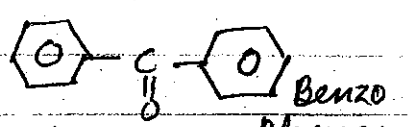
② Formaldehyde
No α-H
No tauto ✗✗



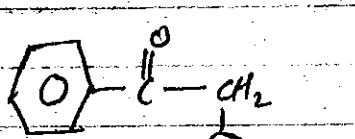
③ ⊖ Reso ✓
α-H ✓
Tauto ✓



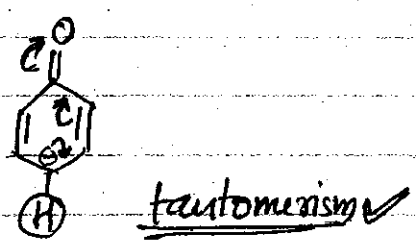
④ No α-H
No tauto ✗✗



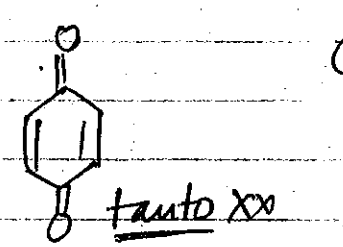
⑤ Benzo phenon
No α-H
No tauto ✗✗



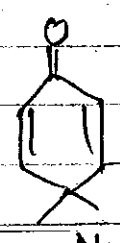
⑥ gives tauto ✓



⑦ tautomerism ✓

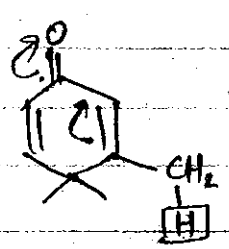


⑧ tauto ✗✗
p-quinone



⑨ No tauto ✗✗

→ para tautomerism
→ space tautomerism
→ pentad "
⑤ atom involved



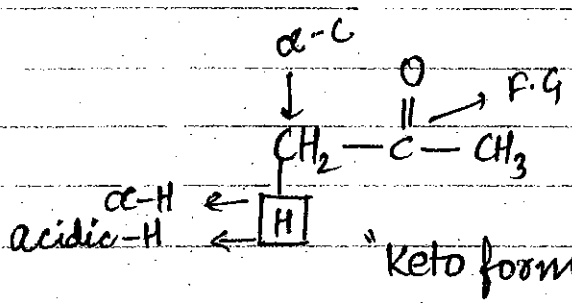
⑩ tauto ✓

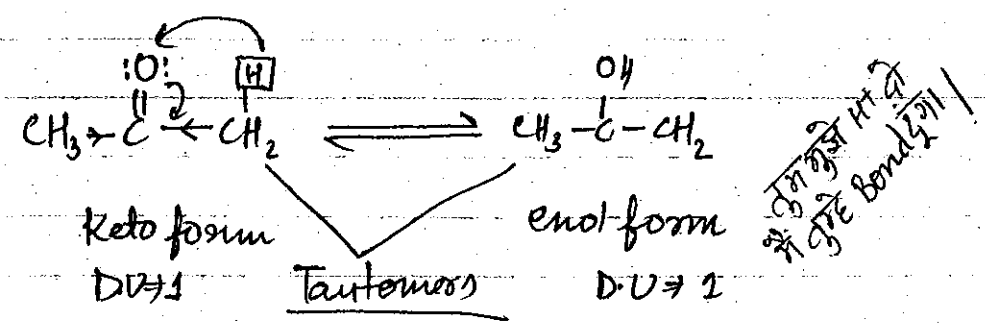
Tautomerism (CHEMISTRY OF α-H.)

Compound having same M.F but diff. structural formula due to transferon of acidic hydrogen is k/a TAUTOMERS & this pheno. is ka TAUTOMERISM

Two tautomers have DYANMIC EQVI. that's why tautomerism is aka DESMOTROPISM.

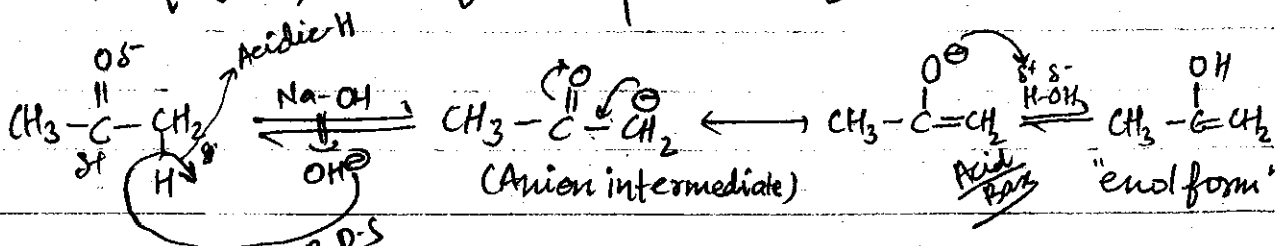
Tautomers also have fxnal group isomerism but priority give to tautomerism.





Rapid shifting of H^+ ion b/w two atoms of a same molecule by acid-base rxn is k/a TAUTOMERISM

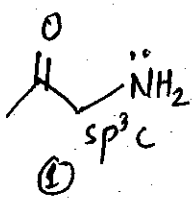
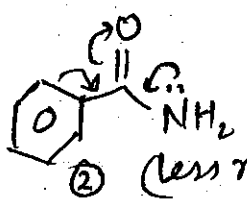
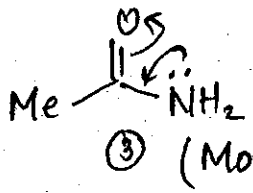
BASE CATALYSED TAUTOMERISM



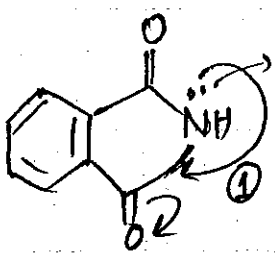
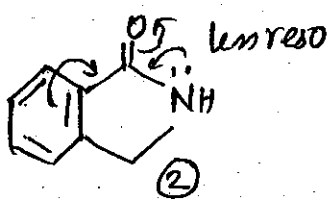
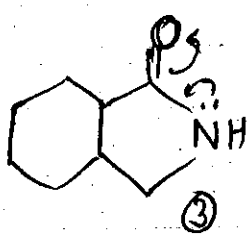
Sheet-5

① $PH_3-\ddot{N}$ ① Max^m reso. $PH_2-\ddot{N}H$ ② $PH-\ddot{N}H_2$ ③ $Ph-CH_2-\ddot{N}H_2$ ④ No reso.

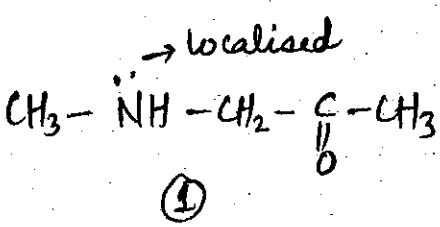
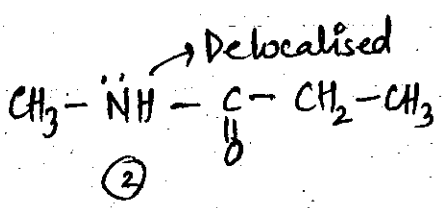
B·S ④ > ③ > ② > ①

②  ① sp^3 C  ② (less reso.)  ③ (More reso.)

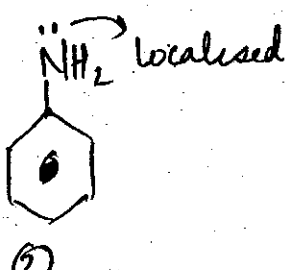
B·S ① > ② > ③

③  Max^m reso.  less reso ②  ③

B·S 2 > 3 > 1

④  ① localised  ② Delocalised

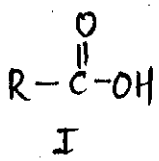
B·S 1 > 2

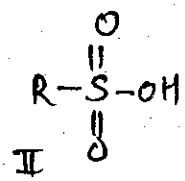
⑤  ①  ② localised

B·S ② > ①

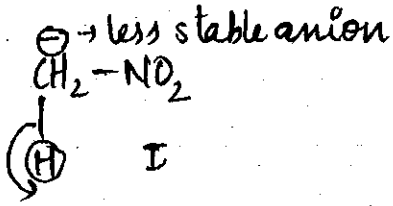
Sheet-4

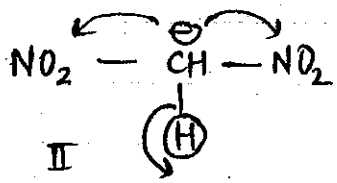
ACIDIC STRENGTH

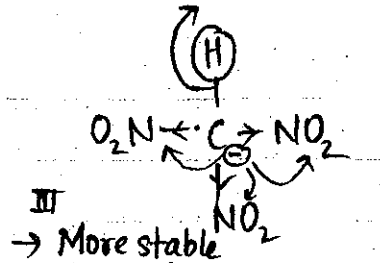
① 
I (2eq. R.S)


II (3eq. R.S) More stable

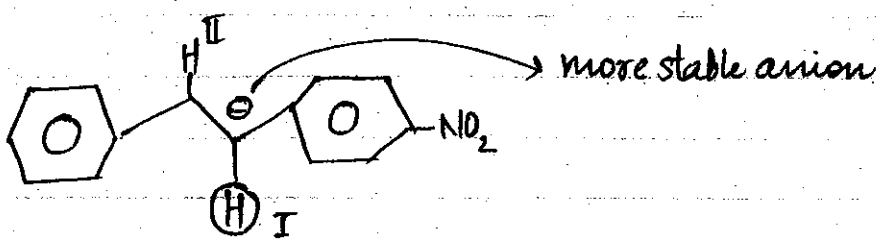
A.S II > I

② 
→ less stable anion
I

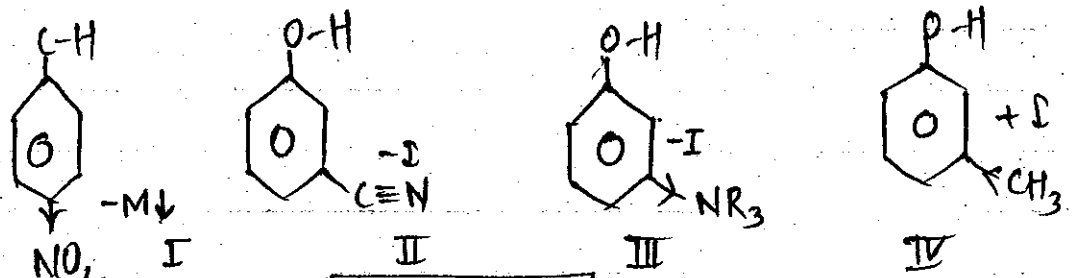

II


III
→ More stable anion
→ Max^m reso. with NO_2

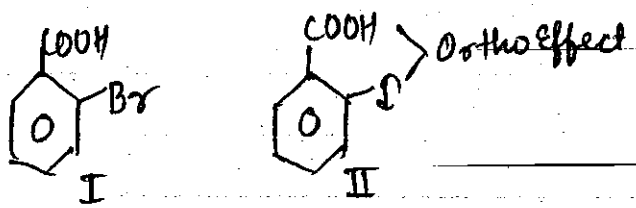
A.S III > II > I

③ 
more stable anion
I

Max^m acidic H ⇒ I > II

④ 
I II III IV

A.S I > III > II > IV

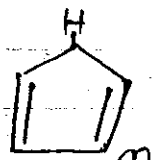
⑤ 
Ortho effect
I II

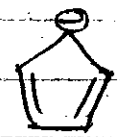
A.S II > I

Induct^{n}

Atom (Aromatic) Eq. reso Reson^{n} Hyperconjugat^{n}

Q.2





Aromatic anion

$CH \equiv CH$ ⇌ (II)

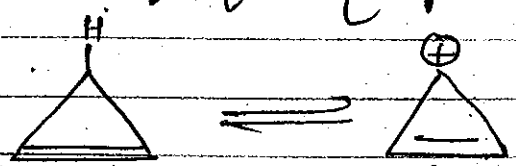
$CH \equiv C^{\ominus} + H^{\oplus}$

3.25

(I) > (II) Acidic Strength

Source Of Anion (Hydride)

(I)



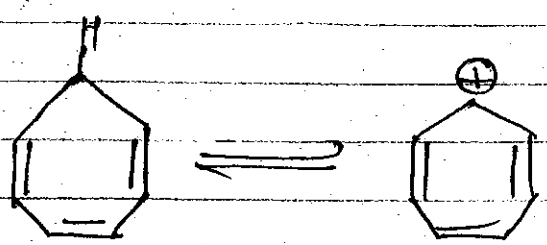
N.A A

$+H^{\ominus}$ → Source of Anion (Hydride ion)

⇓

$H_2 \uparrow$ (in water)

(II)

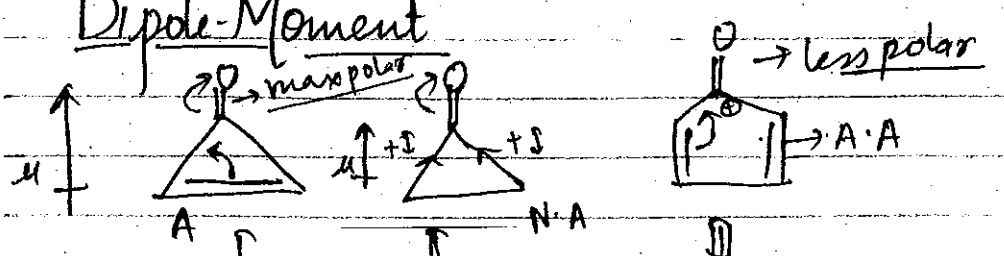


N.A

$+H^{\oplus}$ → source of hydride ion.

→ give H_2 with H_2O.

Dipole-Moment

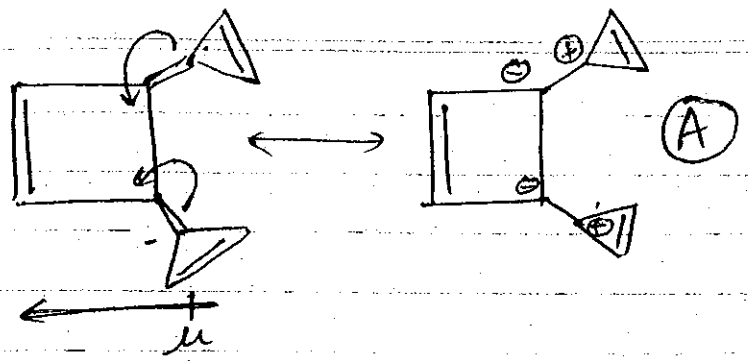


μ · I > II > III

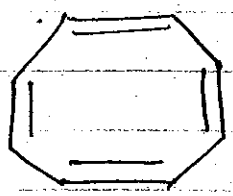
cycle में alternate π bond

8 वाले में π bond Plane से बाहर Plane में है तो Non Planar

Q.13

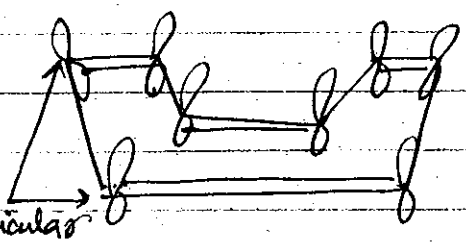


Q.14



Non-Aromatic

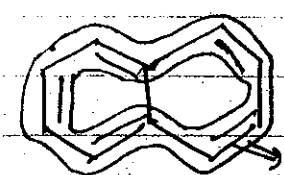
COT → cyclooctatetraene



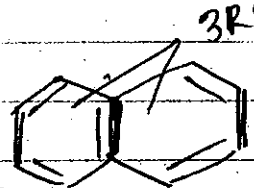
perpendicular

no resonance

Q.15



Aromatic ⟷



3RS (तिहरा जोड़ Bond)

3 तक R-S

more stable

↳ 2 benzoid nucleus

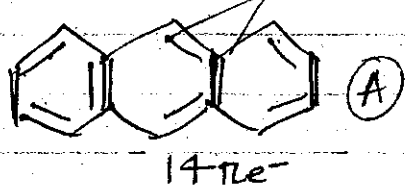
10 π e⁻

↳ 1 benzoid nucleus

⇩ > ⇩

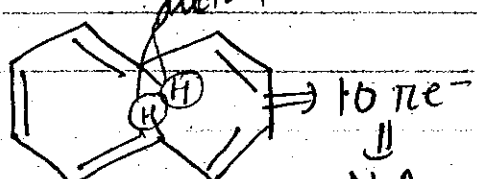
Stable

Q.16



14 π e⁻

Q.17



N.A

Coepulsion में

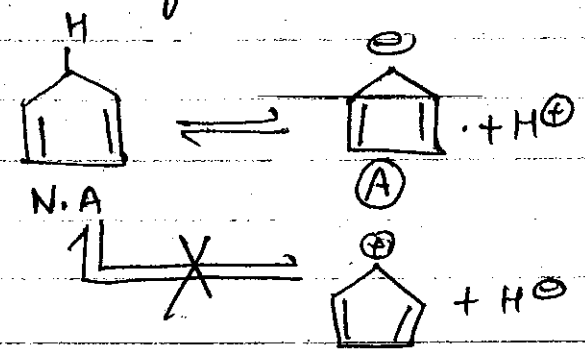
अगर ये 5 या 7 या 30 10 Annulene

जाता है Hence N. Planar Hence N.A

Application Of Aromaticity

Acidic Strength

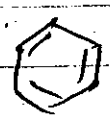
Q.1



1,3 cyclopentadiene ⇒ Acidic

① — → Reso. ⇑ → D.B character B.L ⇓

② = → Reso ⇑ → S.B character B.L ⇑

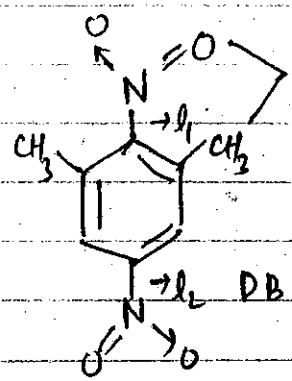
Q.1. CH_3-CH_3 $CH_2=CH_2$ $CH\equiv CH$  → Partially D.B

$\downarrow l_1$ $\downarrow l_2$ $\downarrow l_3$

100% SB 100% DB 100% TB

B.L $l_1 > l_4 > l_2 > l_3$

Q.2

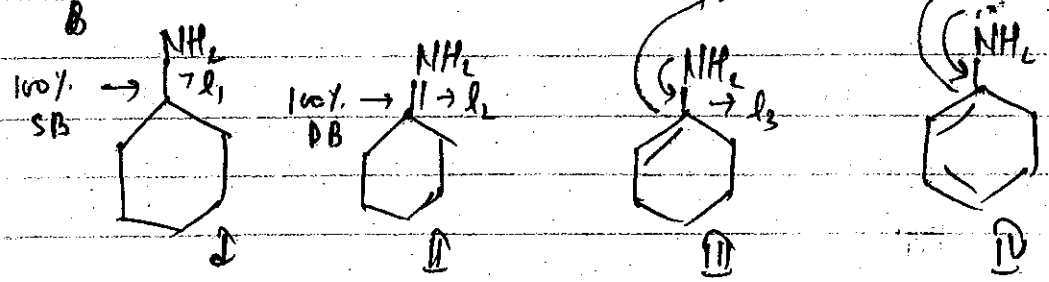


SIR (Group घूम नहीं पाता out of plane No reso)

B.L $\boxed{l_1 > l_2}$

$\rightarrow l_2$ DB character

Q.3



100% SB → l_1 (I)

100% DB → l_2 (II)

less reso → less D.B character → l_3 (III)

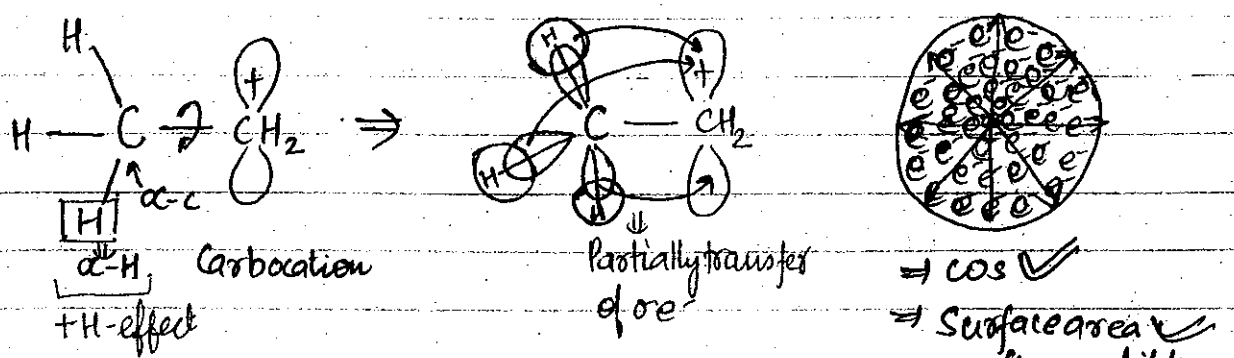
more reso → more DB character (IV)

$l_1 > l_3 > l_4 > l_2$

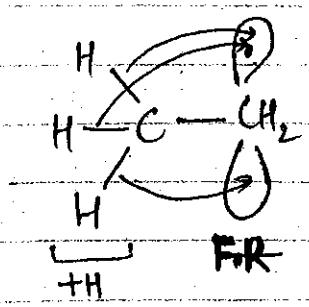
Hyperconjugation

① Permanant Effect
② Involve C-H σ e⁻ / C-X σ e⁻
③ In hyperconjugat^{n} effect partially transfer of σ e⁻s
④ Following conjugated system give hyperconjugat^{n} effect.

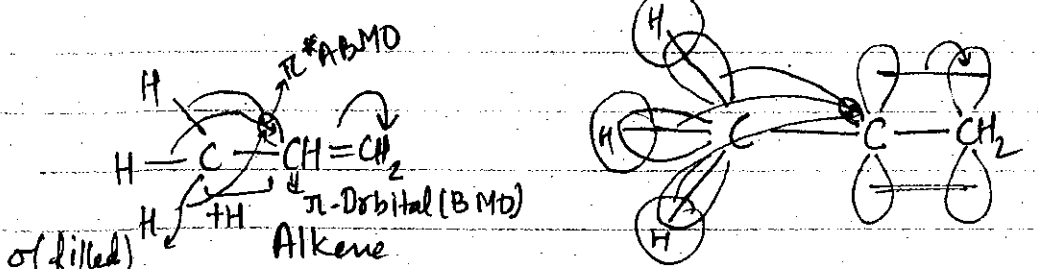
①



②



③



④

$CX_3-CH=CH_2$

CX_3 ⇒ -H effect

⑤

CX_3 ⇒ -H effect

① Hyperconjugation effect observed in CARBOCATION, FREE RADICAL, ~~ALKENE & ALKYNE~~ having α-H.

② Hyperconjugation effect not observed in CARBANION due to repulsion factor

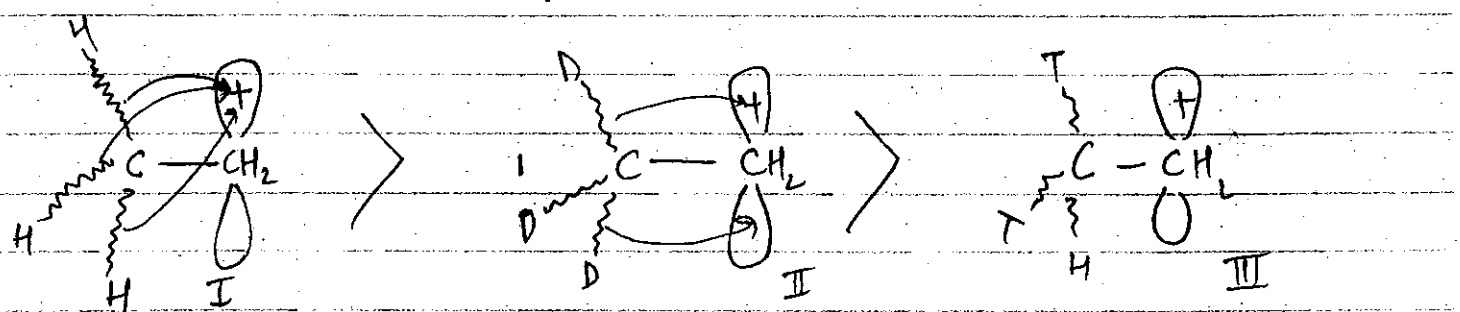
③ H.C Effect is also K/a

→ σ-π conjugation

→ No bond resonance

→ Nathan Baker Effect

KIE In Hyperconjugation Effect



C-H bond
weak bond
More break
H.C ↑

C-T bond
Strong bond
less break
less H.C ↓↓

Stability I > II > III

Order of +H Effect $-CH_3 > -CD_3 > -CT_3$

Acc. to K.I.E

Application

Stability Of Carbocation & Free Radical

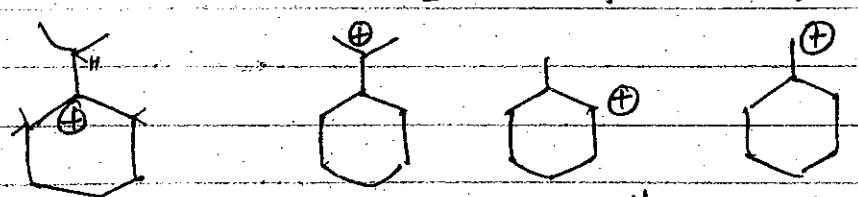
Key pt → Stability of Carbocation & Freeradical ∝ No. of α-H

① $CH_3-\overset{\oplus}{C}H-CH_3$ (I, 6α-H) $\qquad$ $CH_3-CH_2-CH_2-CH_2-\overset{\oplus}{C}H-CH_2-CH_2-CH_2-CH_3$ (II, 4α-H)

I > II Stability

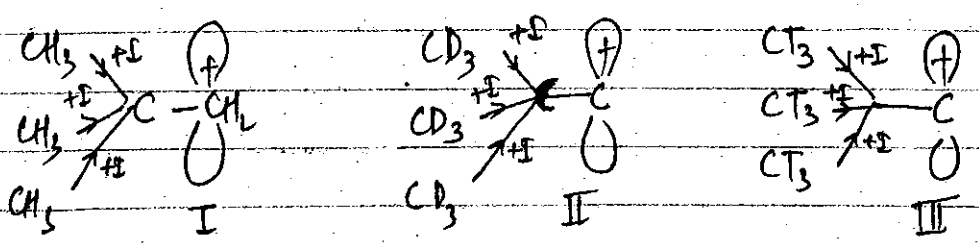
② $CH_3-\overset{\oplus}{C}H_2$ (3α-H) $\qquad$ $CH_3-\overset{\oplus}{C}H-CH_3$ (6α-H) $\qquad$ $CH_3-\overset{\oplus}{C}(CH_3)-CH_3$ (9α-H)

III > II > I Stability

③ 

I 5α-H $\qquad$ II 7α-H $\qquad$ III 3α-H $\qquad$ IV 1α-H

II > I > III > IV

④ 

I $\qquad$ II $\qquad$ III

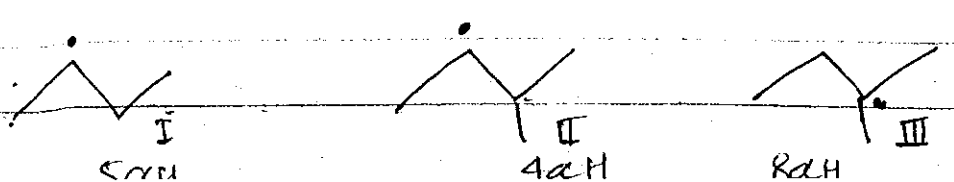
→ No α-H
→ No Hyperconjugation

III > II > I

Hyperconjugation Effect not observed in C–C bond (Strong bond)

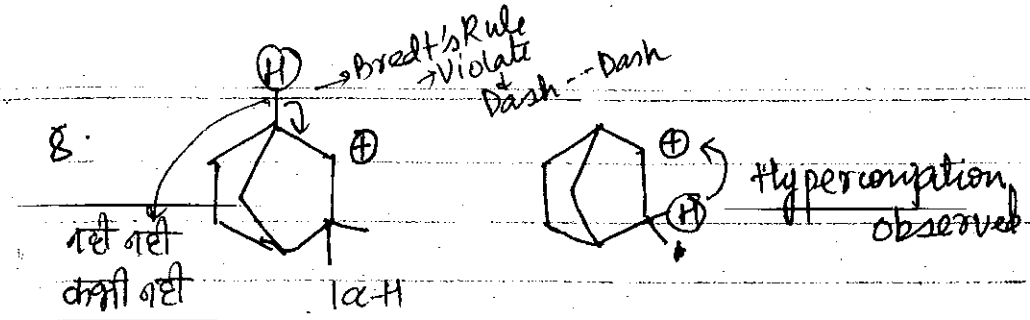
⑤ $CH_3-\overset{\oplus}{C}(CH_3)-CH_3$ (I) $\qquad$ $CD_3-\overset{\oplus}{C}(CD_3)-CD_3$ (II) $\qquad$ **I > II**

⑥ $CH_3-\dot{C}H$ (I) $\qquad$ $CH_3-\dot{C}H-CH_3$ (II) $\qquad$ $CH_3-\dot{C}(CH_3)-CH_3$ (III) $\qquad$ **III > II > I**

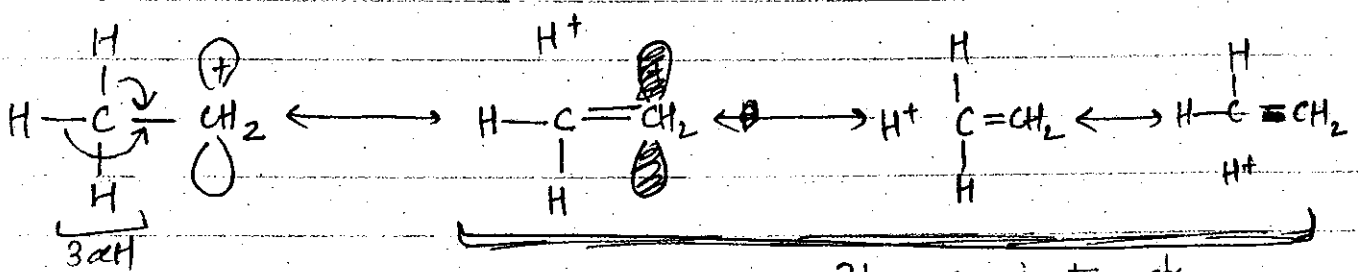
⑦ 

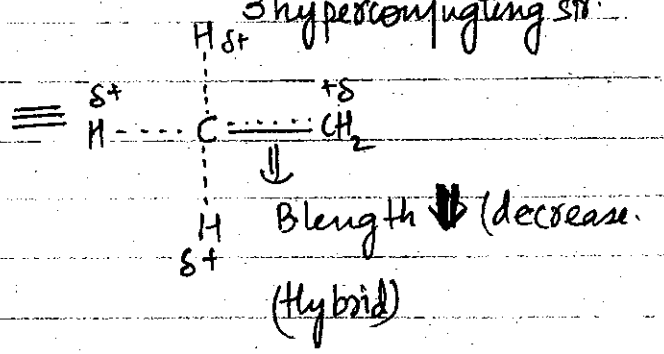
I 5α-H $\qquad$ II 4α-H $\qquad$ III 8α-H

III > I > II



HYPERCONJUGATING STRUCTURE

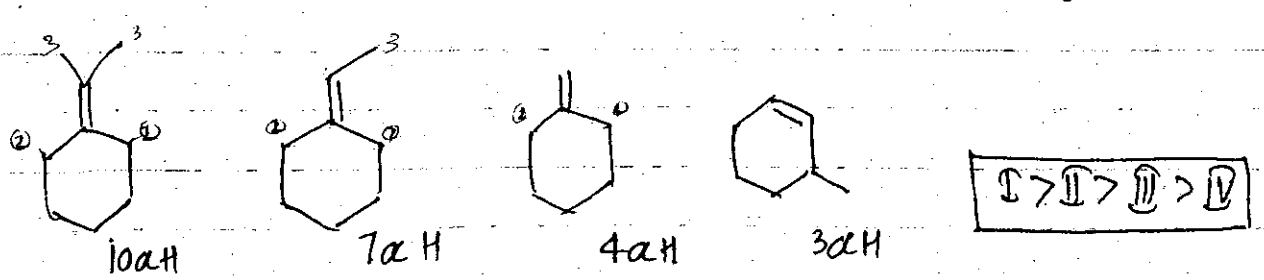




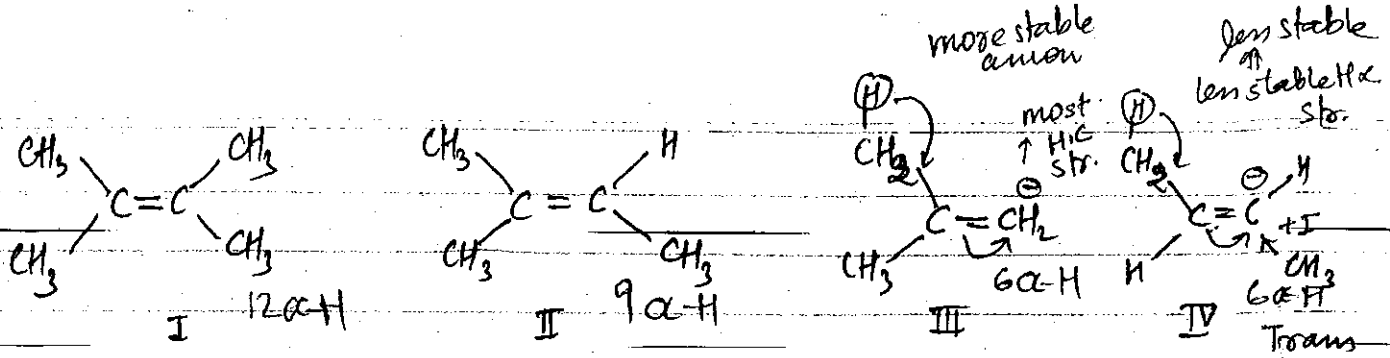
Stability Of Alkene

No. of hyperconjugating str = No. of α-H.

① $CH_2=CH_2$ (I) $CH_3-CH=CH_2$ (II) — II > I Stability

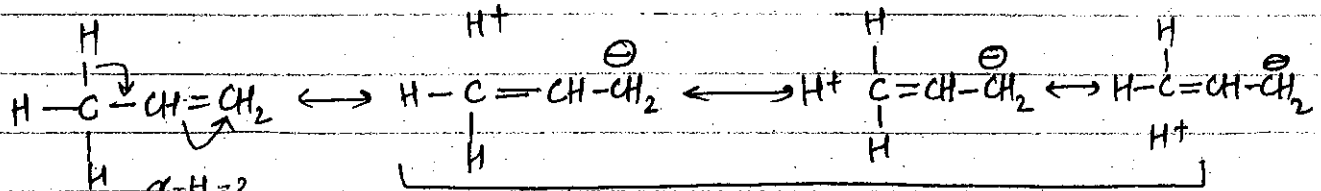


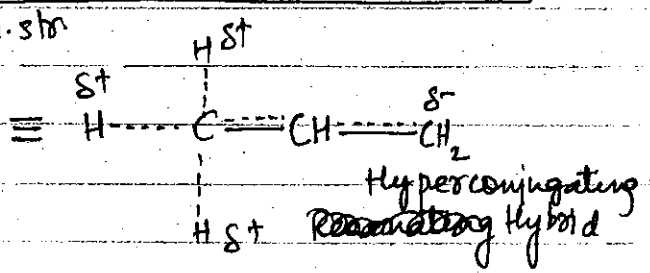
KEYPT: Stability of alkene ∝ No. of α-H.



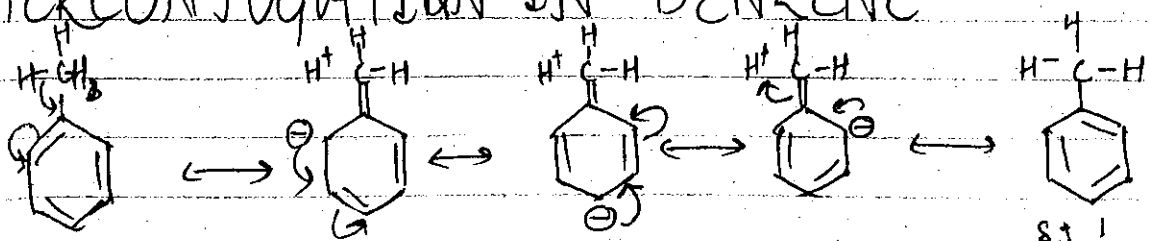
I > II > III > IV > V > VI > VII

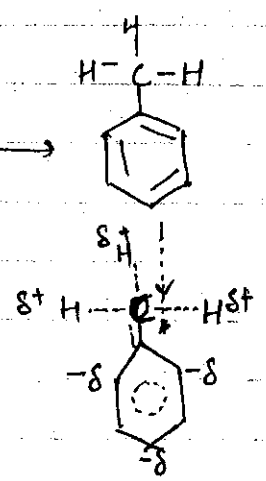
HYPERCONJUGATING STR. OF ALKENE





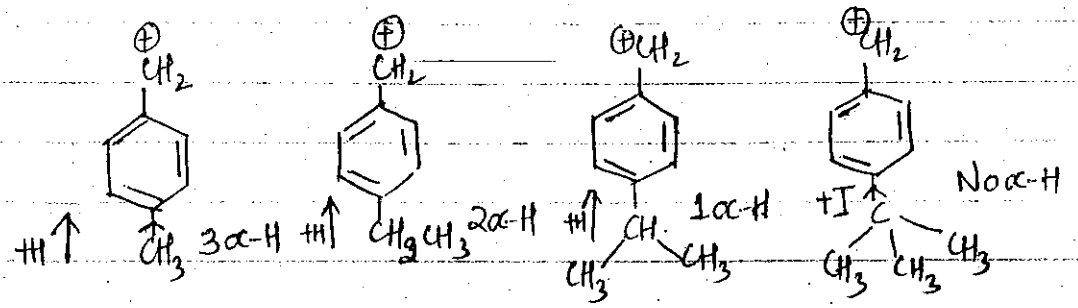
HYPERCONJUGATION IN BENZENE





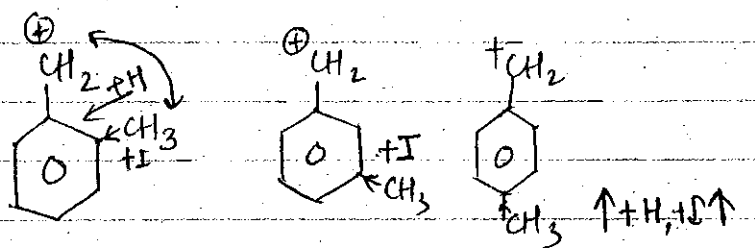
Hyperconjugation effect observed at o- & p- position in benzene like molecule.

Q.1



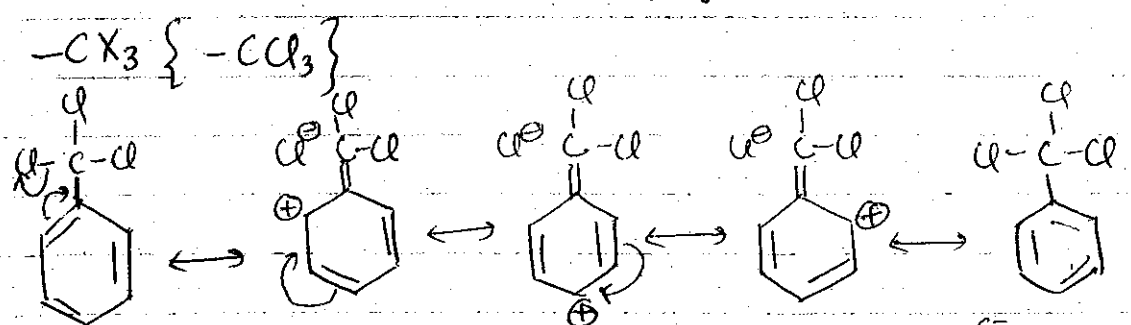
I > II > III > IV

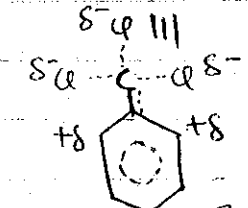
Q.2



I > III > II

-H Effect (Reverse Hyperconjugation)



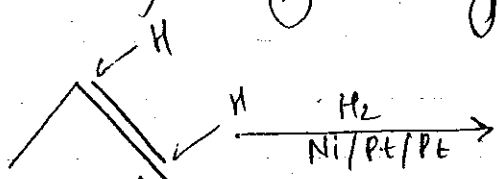


Deactivated Ring

V. Imp ++

Heat Of Hydrogenation [REDUCTION RXN]

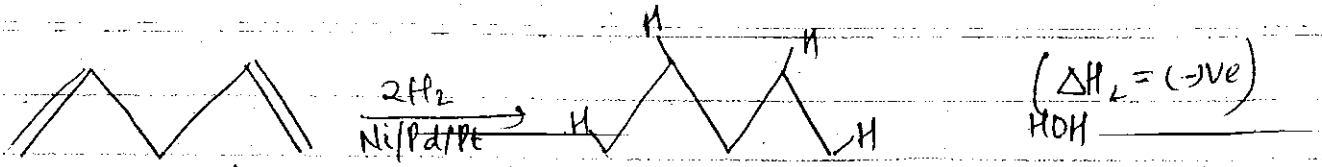
1.



1π-bond (weak bond) DU=1

2σ-form Strong form [DU=0]

ΔH1 ∝ +ve
HOH



$(\Delta H_2 = (-)ve)$

2π-bond — 90-bond form

HOH

$\boxed{\Delta H_2 > \Delta H_1}$

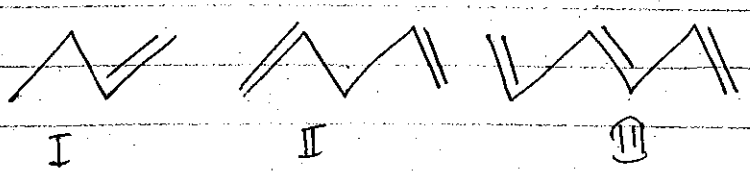
Amount of heat released when one mole unsaturated fl.c completely hydrogenated into saturated compound.

KEY PT :- Heat of hydrogenat^n $\propto$ No. of π bond. [except aromatic comp]

If π-bonds are equal then HOH

$HOH \propto \frac{1}{\text{Stability of comp.}}$

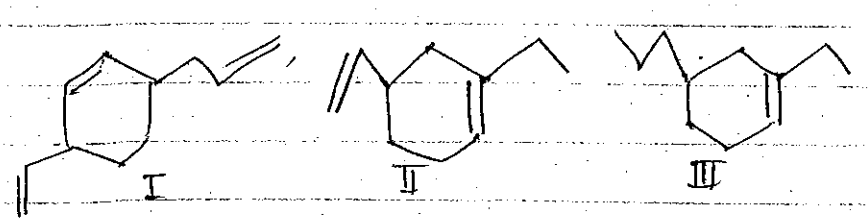
①



I II III

HOH → $\boxed{III > II > I}$

②



I II III

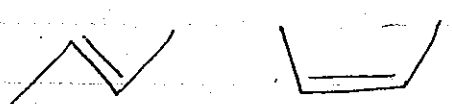
HOH $\boxed{I > II > III}$

③ $CH_3-CH=CH_2$ (I) — 3α-H

$CH_2=CH_2$ (II) — zero

HOH $\boxed{II > I}$

④

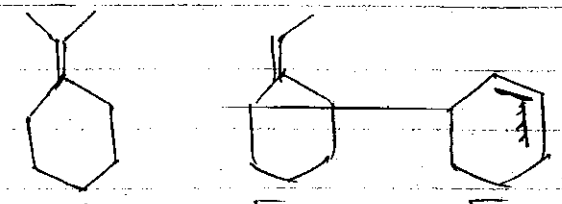


trans cis

HOH $\boxed{cis > trans}$

cyclohexane more stable than benzene
(Very much stable)

5.



I II III

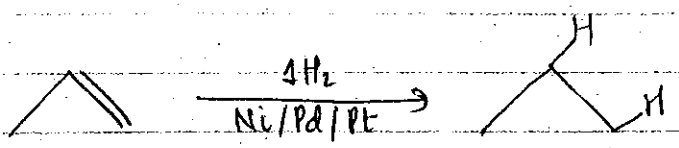
10 α-H 7 α-H 4 α-H

HOH: III > II > I

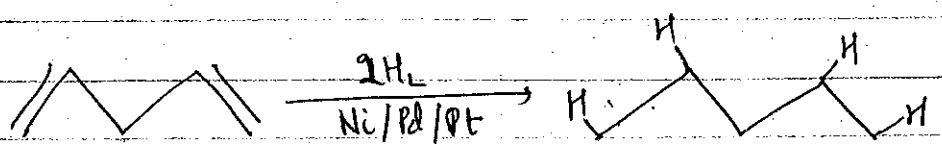
Stability: I > II > III

6.

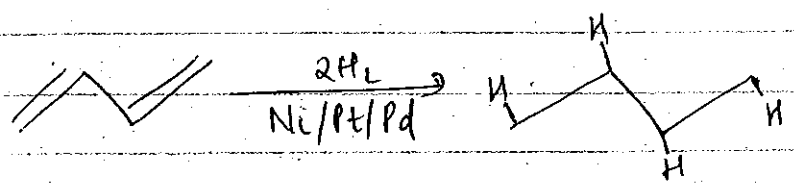
Calculat^{n} Of Resonance Energy On The Basic of HOH

① 

$\Delta H = -28.6$ Kcal/mol

② 

$\Delta H = -57.2$ Kcal/mol

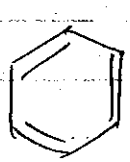
③ 

$\Delta H = -54.2$ Kcal/mol

RE = Theo HOH − Pract. HOH

= 57.2 − 54.2

RE = 3 Kcal/mol

④ 

1π → −28.6 Kcal/mol

3π → −85.5 Kcal/mol (Theo. HOH)

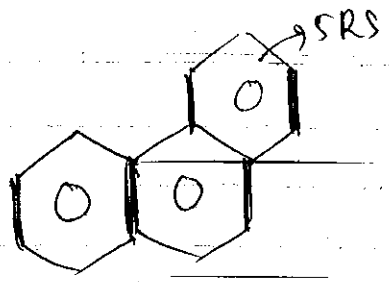
−49.8 Kcal/mol (Practical HOH)

RE = Theo HOH − Pract. HOH

= 85.8 − 49.8

RE = 36 Kcal/mol

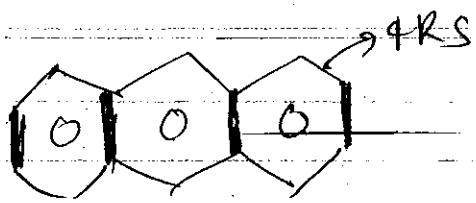
(5)



Phenanthrene

More Stable

RE = -92 Kcal/mol

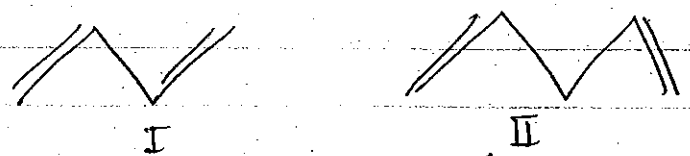


Anthracene

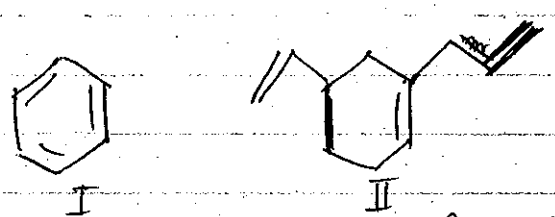
less stable

RE = -84 Kcal/mol

(1)

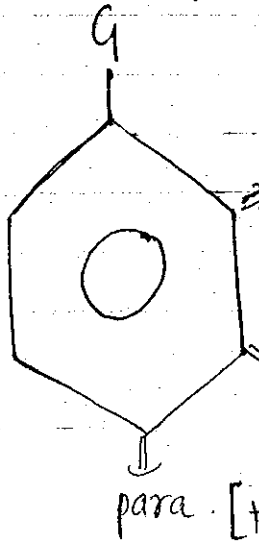


Per mole HOH / per π-HOH / per mol H_2 ⇒ **II > I**



Per π bond / per mol H_2 ⇒ **II > I**

Various Effect At o m & p position



⇒ ortho [+R/-R / +H/-H / +I/-I / ortho effect or SIF or SIR / H-bonding]

⇒ meta [+I/-I]

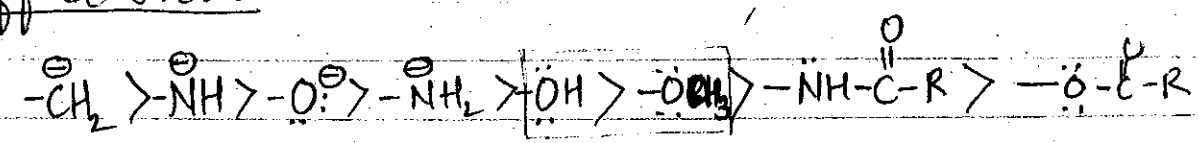
para [+R/-R/+I/-I]

A E R H I

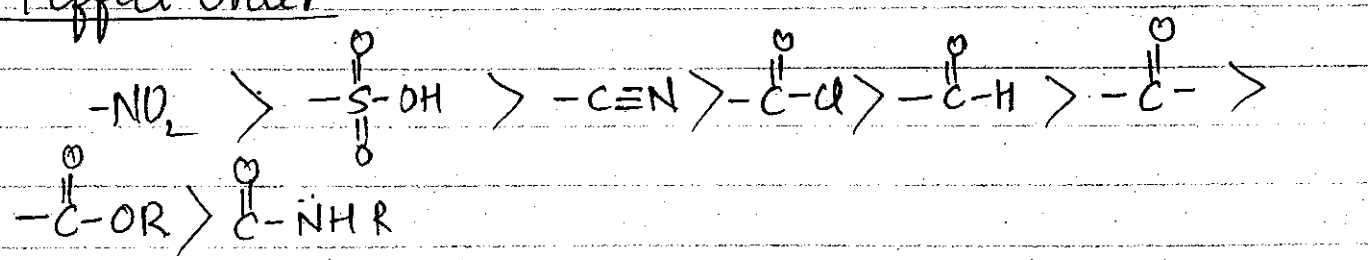
~~Aromatic~~ Atom or (C,N,O,F) | Equi Reso | Normal Reso | ~~Hyper~~ conjugat^{n} | Inductive Effect

Order of effect | Reso > Hyperconjugat^{n} > Inductive

+M Effect Order



-M Effect Order



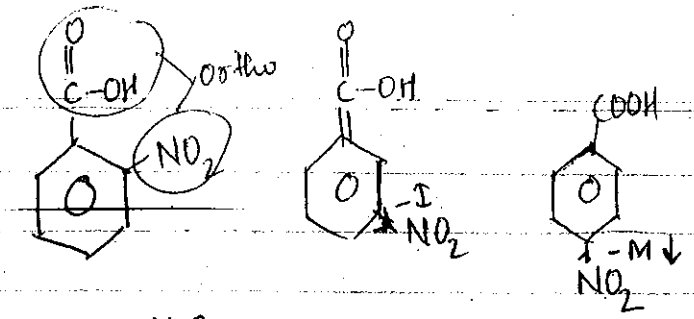
+H Effect Order

$CH_3 > CD_3 > CT_3$

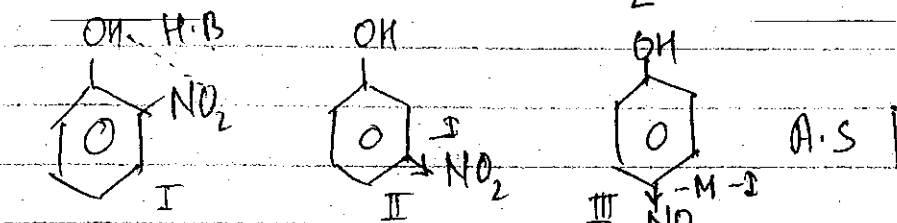
-H-Effect Order

$-CH_3$

1

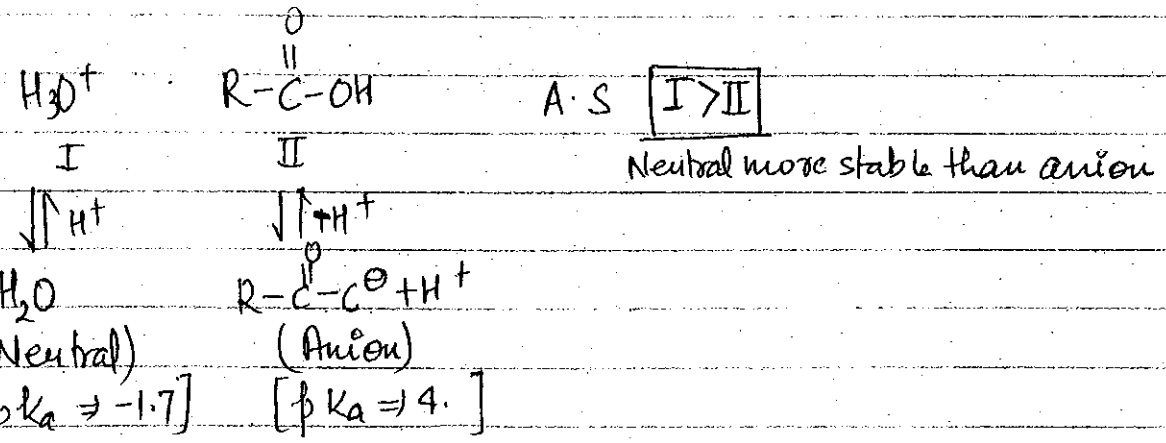


2.

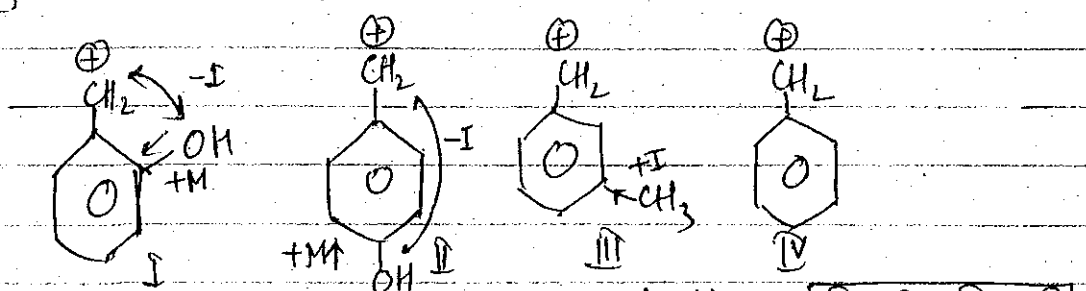


O-nitrophenol m-nitrophenol p-nitrophenol

3.



4.



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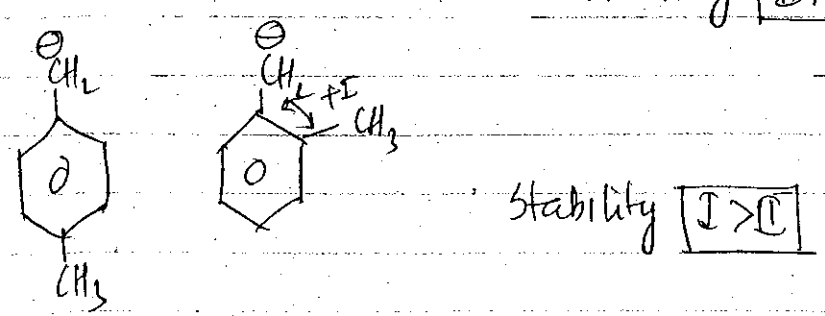


Bond Energy (B·E)

Keypt: $BE \propto \frac{1}{\text{Stability of free Radical}}$

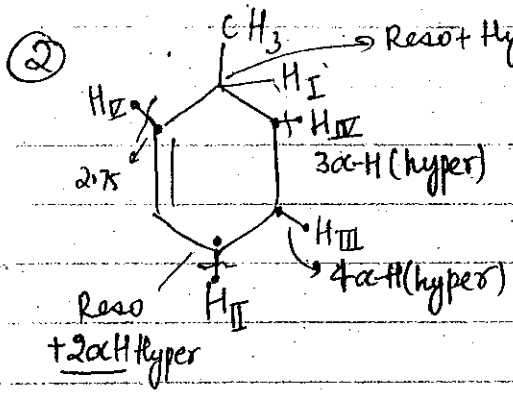
① $CH_2 \equiv \overset{\curvearrowright}{C}\overset{\curvearrowleft}{H}$ $CH_2=CH-H$ CH_3-CH_2-H

I II III B.E I > II > III

I: $CH \equiv C^{\bullet}$ — II — 3·25 — highly unstable, more B.E

II: $CH_2=\dot{C}H$ — II — 2·75

III: $CH_3 \rightarrow \dot{C}H_2$ + II — more stable, less B.E

② 

V > IV > III > II > I B.E

Heat Of Combustion (HOC)

KEY PT :- $HOC \propto$ No. of Carbon

$HOC \propto \frac{1}{\text{Stability}}$

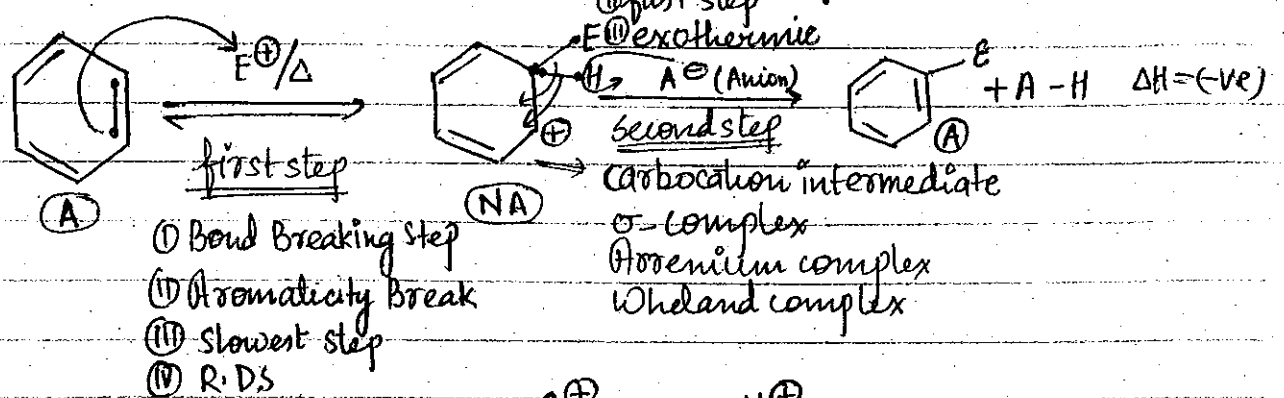
Some Rxn

Reactivity of Aromatic Comp.

(1) Electrophilic Substitut^{n} Rxn

Rea:

Reactivity of Aromatic Compound for Electrophilic Substitut^{n} Rxn.



① Bond forming step
② fast step
③ exothermic

① Bond Breaking step
② Aromaticity Break
③ Slowest step
④ R.D.S

Carbocation intermediate
σ-complex
Arrenium complex
Wheland complex

H or D or T ⇒ no effect on rxn
as RDS is first step
not removal of H/D/T

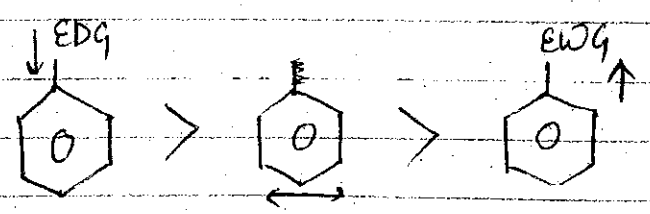
KEY POINT Reactivity of aromatic comp ∝ Stability of carbocation inter.

α +M/+H/+I

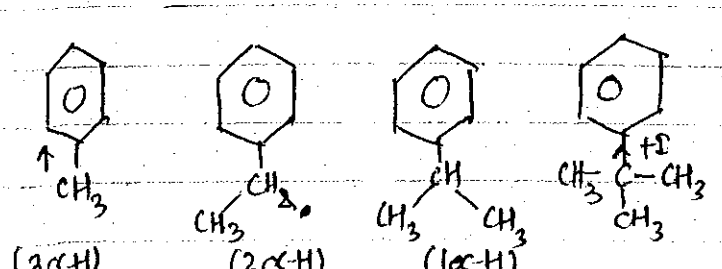
α 1

-I/-M/-H

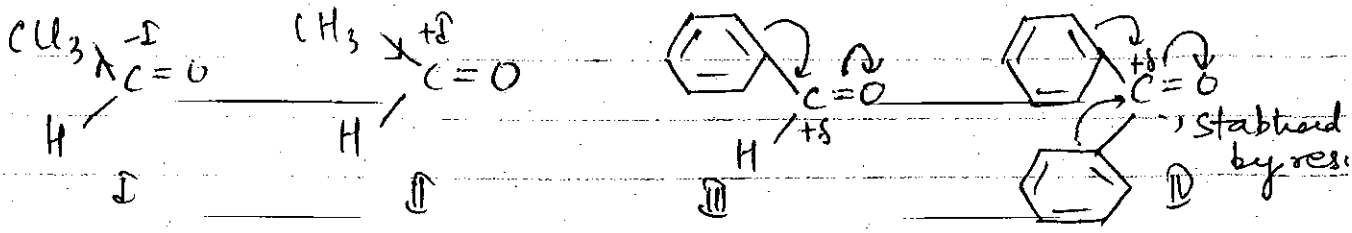
KEY POINT

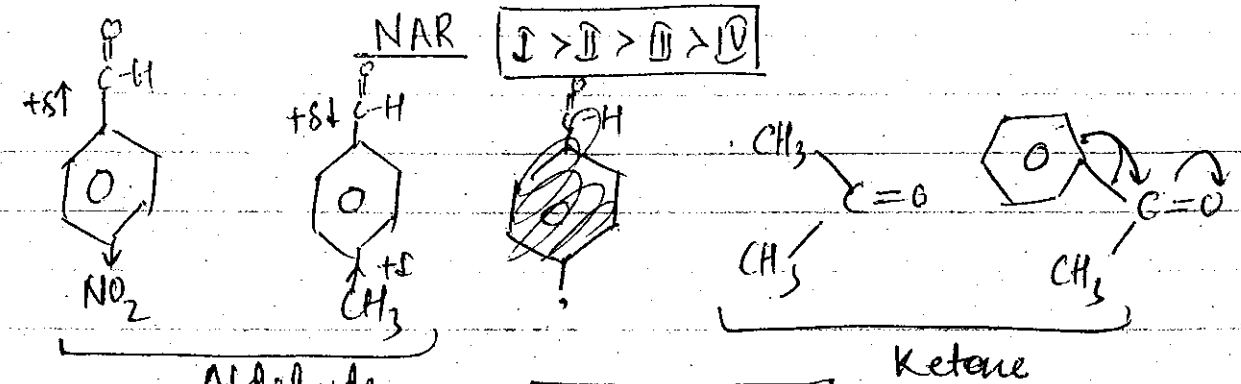


①



Reactivity ESR $\boxed{\text{I} > \text{II} > \text{III} > \text{IV}}$

(2) 

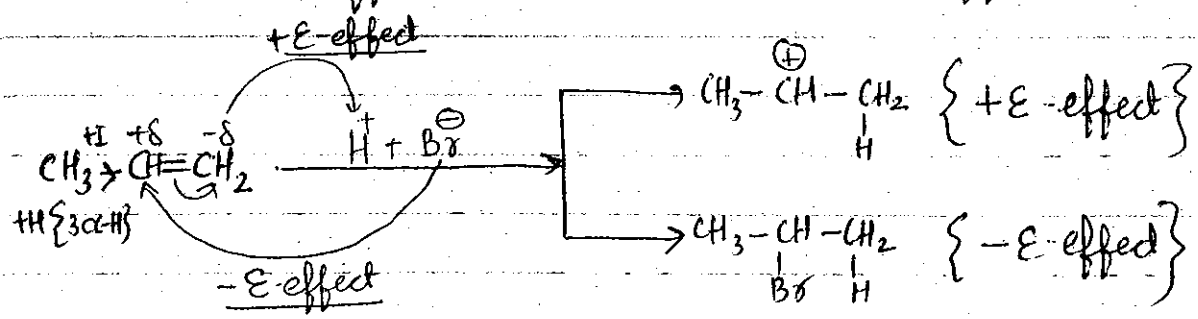
(3) 

I > II > III > IV

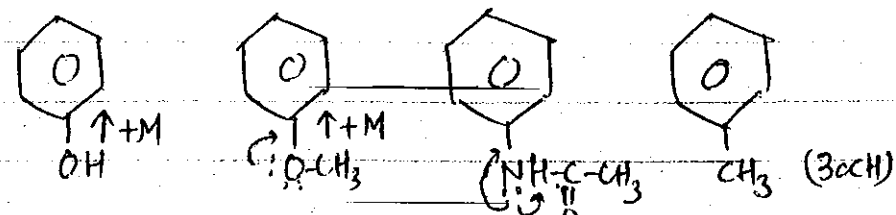
ELECTROMERIC EFFECT

Temperory Effect

It involve completely delocalisation of π-electron. Whenever π-e⁻ completely delocalised in presence of attacking reagent then this effect is K/a Electromeric Effect

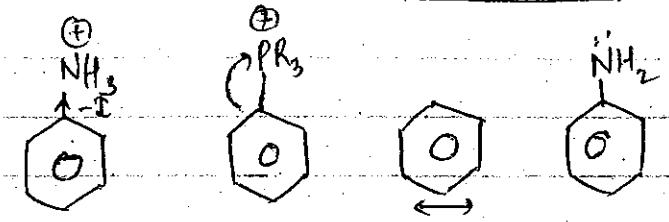


(2)



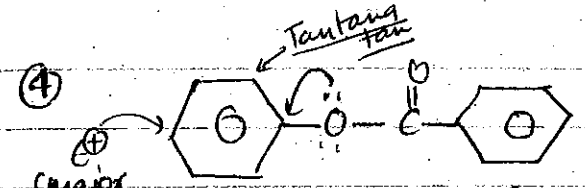
I > II > III > IV

(3)



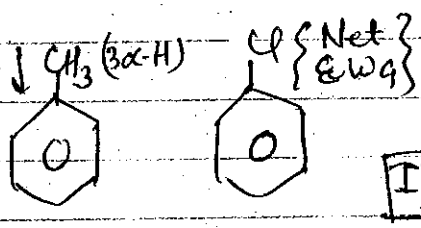
ESR IV > III > I > II

(4)



(Activated ring) A > B

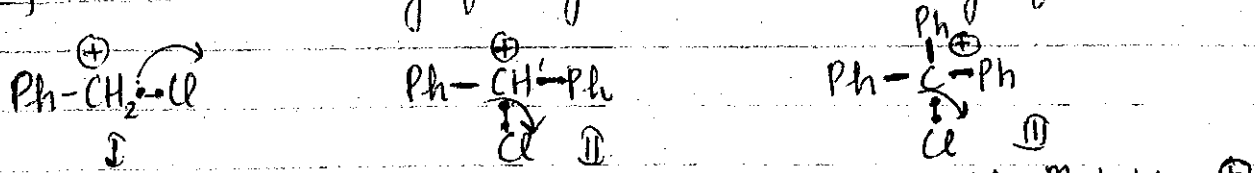
(5)



I > II ESR.

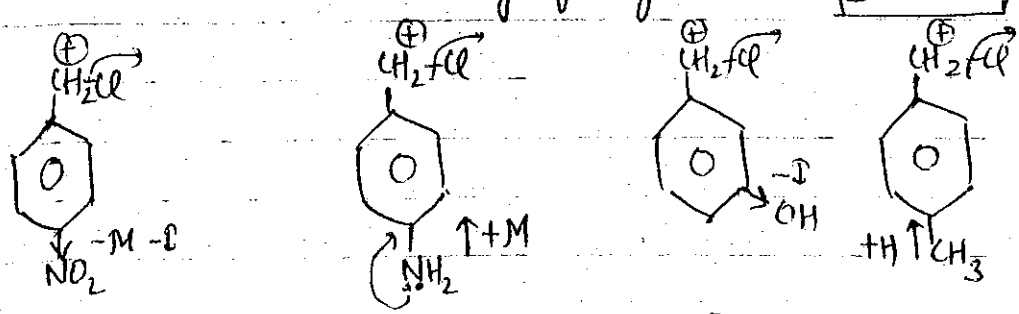
Reactivity of Alkyl halide Rxn Involve Carbocation Intermediate

KEY POINT Reactivity of alkyl halide ∝ Stability of carbocation



Max^m stable C⊕

Reactivity of alkyl halide III > II > I



Reactivity II > IV > III > I

Product racemic mixture if chiral centre is gen. यदि chiral केंद्र बनता है, तो racemic मिश्रण बनता है

107° पर Attack hence steric hindrance matters although planer

Sterichindrance ↓ Aldehyde > Ketone (NAR)

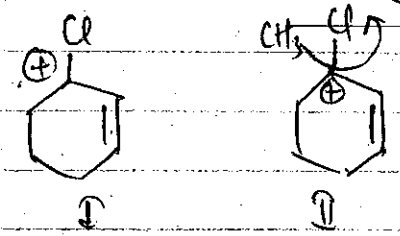
C=O पर hyper conjugation नहीं होगा

③ $CH_3-CH_2-\overset{\oplus}{O}(-CH_2-Cl) \rightarrow CH_3-CH_2-\overset{\oplus}{O}(-CH(CH_3)_2)$

I — II — {3α-H

Reactivity II > I

④

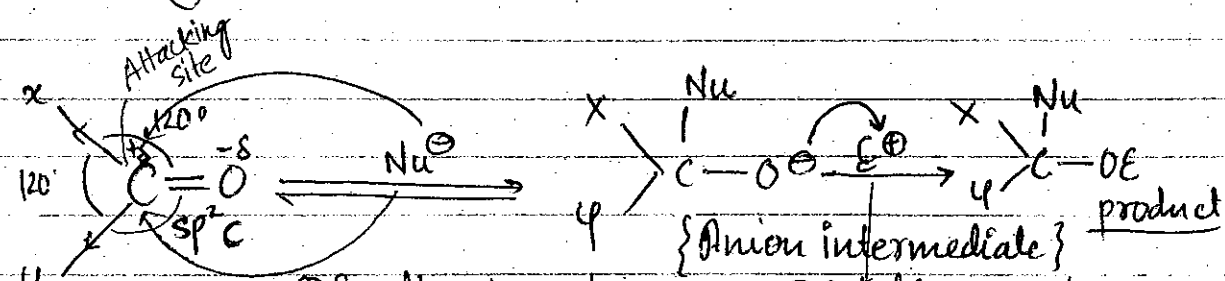


I II

Reactivity II > I

Reactivity Of Carbonyl Compound for Nucleophilic Addition Reaction

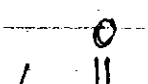
#



① Bond breaking step
② Slowest step
③ RDS

If EWG present
⇓
+δ (charge ↑ ⇒ R·O·R ↑)

① Bond forming step
② fast step

KEYPOINT Reactivity of NAR ∝ Charge on sp^2 Carbon ()

∝ 1

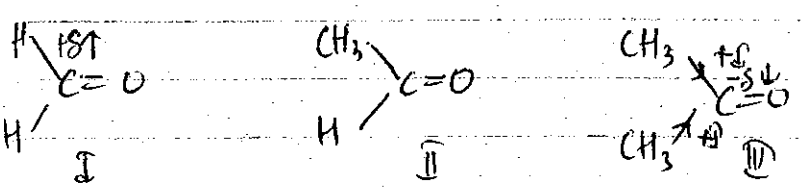
Sterichindrance

∝

Reactivity of NAR ⇒ Aldehyde > Ketone

(Both aromatic & aliphatic)

①

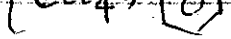


I II III

Reactivity NAR I > II > III

Reaction Mechanism

SOLVENT

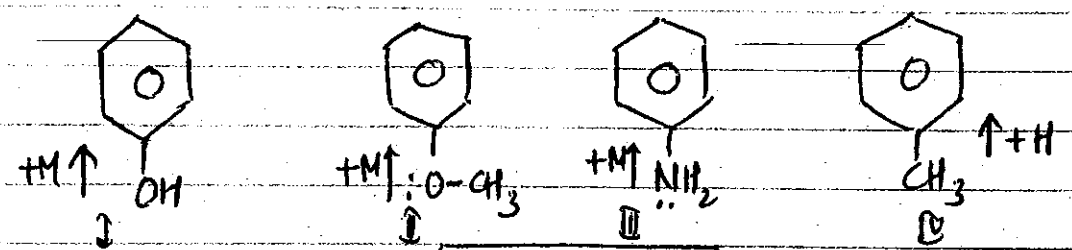
- Polar solvent ($\mu \neq 0$)
  - Polar Protic Solvent
  - Polar Aprotic Solvent
- Non-Polar Solvent ($\mu = 0$)
  - { CCl_4,  , CS_2, ... etc }

Polar Protic Solvent

Solvent which are polar in nature

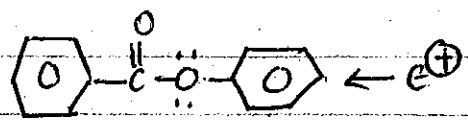
SHEET-9

Reactivity for E·SR

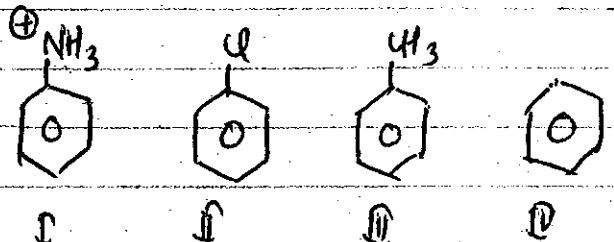
① 

I II III IV

Rate of ESR III > I > II > IV

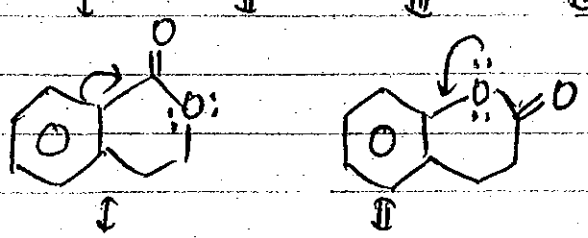
② 

Ring Deactivate (A) Ring Activate (B) B > A

③ 

I II III IV

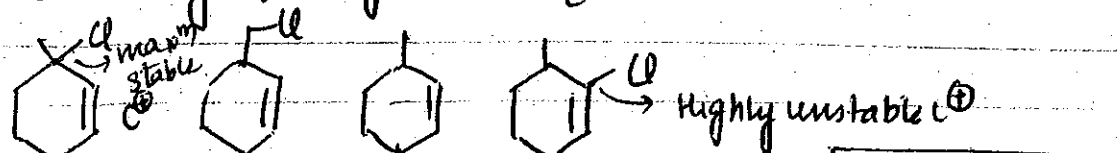
E·SR III > IV > II > I

④ 

I II

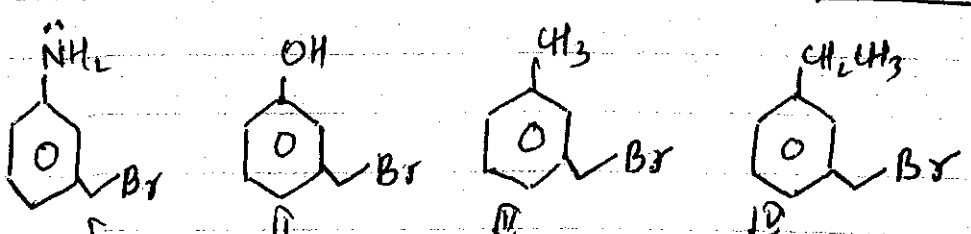
ESR II > I

Reactivity of Alkyl Halide { $C^{\oplus}$ intermediate }

① 

I II III IV

I > II > III > IV

② 

I II III IV

IV > II > I > III

③ $CH_3-NH-CH_2-\overset{\oplus}{C}H_2 \; Cl$ → min stable C⊕ form

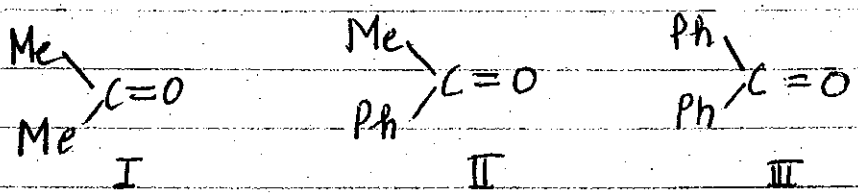
$CH_3-CH_2-\overset{\oplus}{N}H-CH_2 \; Cl$ (only reso)

$CH_3-NH-\overset{\oplus}{C}(Cl)-CH_2-CH_3$ → max stable C⊕ form (reso + hyper)

Reactivity III > II > I

Reactivity Of N.A.R

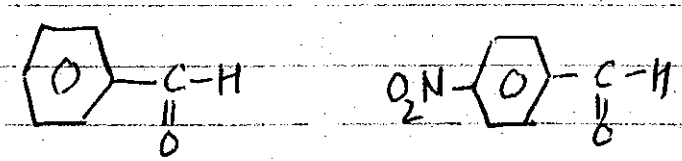
①



I II III

R.O.R III > II > I

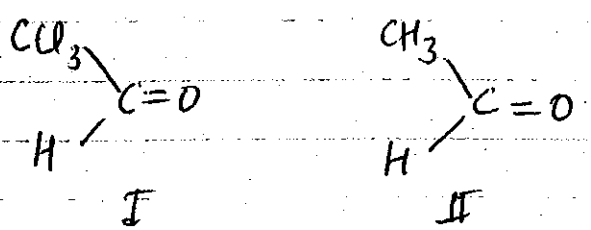
②



I II

NAR II > I

③



I II

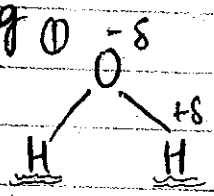
NAR ⇒ I > II

Reaction Mechanism

SOLVENT

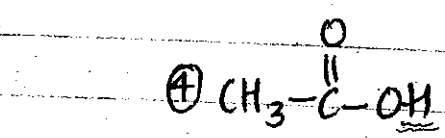
- Polar Solvent ($\mu \neq 0$)
  - Polar Protic
  - Polar Aprotic
- Non-Polar Solvent ($\mu \neq 0$)

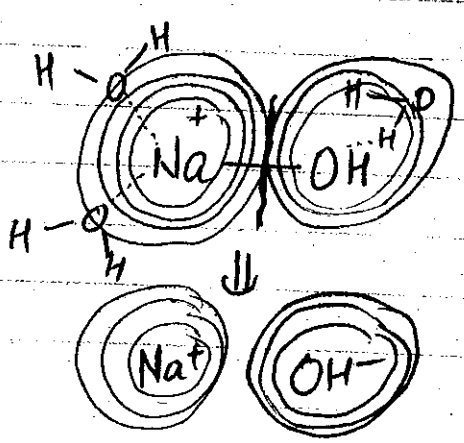
Polar Protic Solvent Solvent which is polar in nature

eg ① 

② R-OH

③ NH_3 { $R-NH_2$ $R-NH-R$ ... etc }

④ 



PPS solvate the cation as well as anion part of a reagent

Polar Aprotic Solvent Solvent which are polar in nature & do not have active H.

short form → PAS
DMF DMA etc.

① $R-\overset{-\delta}{O}-\overset{+\delta}{R}$ {Alkether)

② $CH_3-\overset{+\delta}{C}(=O^{-\delta})-CH_3$ {Acetone)

③ $CH_3-\overset{+\delta}{S}(=O^{-\delta})-CH_3$

④ DMF

⑤ DMA

⑥ THF()

Polar
+
But Noactive-H

Na^+ + $\overset{\ominus}{O}H$ ⇒ No solvatn of anion

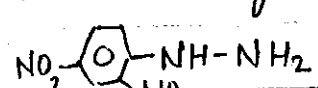
PAS solvate only cation part of a reagent

Nucleophile Sps. donate pair of e⁻ to other than H⁺.
complete octet
Electron efficient sps
behave as a lewis base

Type of Nucleophile

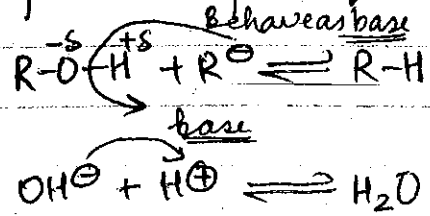
Anionic $R^{\ominus}$ $\overset{\ominus}{C}\equiv N$, $R-\overset{\ominus}{S}$, $H^{\ominus}$, $OH^{\ominus}$, $\overset{\ominus}{S}H$, $\overset{\ominus}{F}$, $\overset{\ominus}{Cl}$, $\overset{\ominus}{Br}$, $\overset{\ominus}{I}$, $R-\overset{\ominus}{O}$ etc

Neutral $\ddot{N}H_3$ $R-NH_2$ $R-NH-R$ $R-\underset{R}{N}-R$, H_2O $H-\ddot{O}-\ddot{O}-H$ (H_2O_2) NH_2-NH_2 (hydrazine)

$R-OH$, $NH_2-\ddot{O}H$ (hydroxyl)  (Phenyl hydrazine)  2,4 DNP

Base

Sps donate pair of e⁻ to $H^{\oplus}$



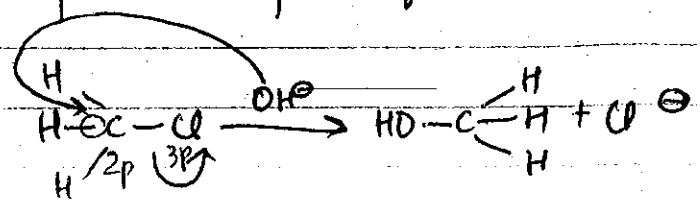
$$R\text{-}O^{-\delta}\text{-}H^{+\delta} + R^{\ominus} \rightleftharpoons R\text{-}H$$

$$OH^{\ominus} + H^{\oplus} \rightleftharpoons H_2O$$

No significance of steric hindrance.

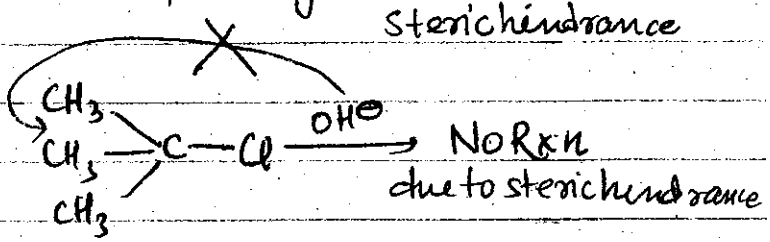
Nucleophile

sps donate pair of e⁻ to other than $H^{\oplus}$



Nucleophilicity depends on steric hindrance.

$$\text{Nucleophilicity} \propto \frac{1}{\text{steric hindrance}}$$



Some Imp. Point

Anion is better nucleophile than its conjugate

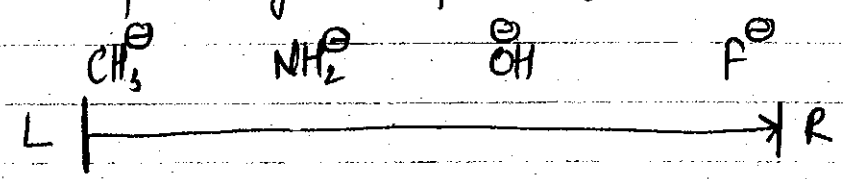
$OH^{\ominus} > H_2O$

$NH_2^{\ominus} > NH_3$

$SH^{\ominus} > H_2S$

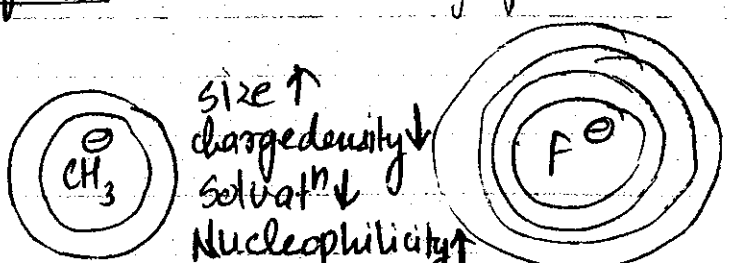
Nucleophilicity acc. to pd table correlation

@ Nucleophilicity in a period (PPS)



① EN factor ↑ EN ↑ Stability of anion ↑ Nucleophilicity ↓

②



Base $CH_3^{\ominus} > NH_2^{\ominus} > OH^{\ominus} > F^{\ominus}$

$Nu^{\ominus}$ $CH_3^{\ominus} > NH_2^{\ominus} > OH^{\ominus} > F^{\ominus}$

Non-Polar $I^{\ominus} > Br^{\ominus} > Cl^{\ominus} > F^{\ominus}$ $Nu^{\ominus}$

PPS of same P ER
chalu grp chalu pd

(b) Nucleophilicity in a group.

i) Nucleophilicity in P.P.S

up Na-f ⇒ Na^{+} + $F^{\ominus}$

size ↓
Chargedensity ↑
solvatn ↑
nucleophilicity ↓

→ size ↑
→ Chargedensity ↓
→ solvatn ↓
→ $Nu^{\ominus}$ ↑

down Na-I ⇒ Na^{+} + $I^{\ominus}$

size ↑
Chargedensity ↓
solvatn ↓
nucleophilicity ↑

$Nu^{\ominus}$ $I^{\ominus} > Br^{\ominus} > Cl^{\ominus} > F^{\ominus}$

Base $F^{\ominus} > Cl^{\ominus} > Br^{\ominus} > I^{\ominus}$

ii) Nucleophilicity in PAS

up Na-F ⇒ Na^{+} $F^{\ominus}$

No solvatn of anion

down Na-I Na^{+} I^{-}

$Nu^{\ominus}$ $F^{\ominus} > Cl^{\ominus} > Br^{\ominus} > I^{\ominus}$

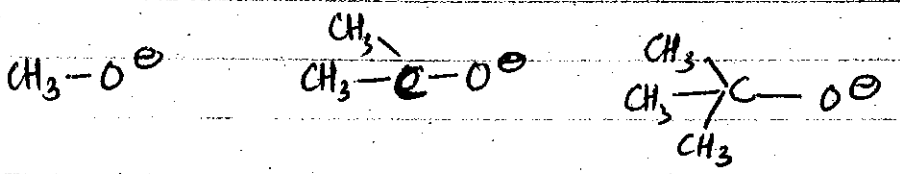
Acc to PAS

Q.1 $R-O^{\ominus}$, $R-S^{\ominus}$

$Nu^{\ominus}$ $R-S^{\ominus} > R-O^{\ominus}$

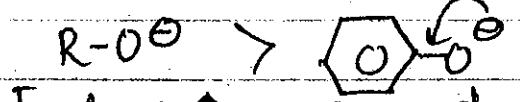
Base $R-O^{\ominus} > R-S^{\ominus}$

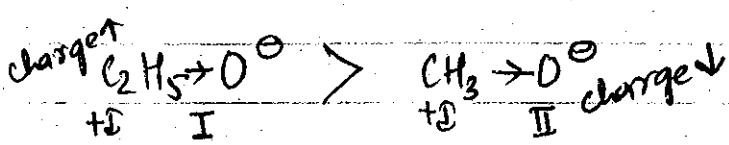
Nucleophilicity $\propto \frac{1}{\text{Steric hindrance}}$



I > II > III

Nucleophilicity depends on charge magnitude





Leaving Group

Species which can eliminate in the form of ⊖ve charge from a organic compound or substrate is kla leaving grp.

Ability of leaving grp directly proportional to stability of anion

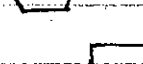
Weaker base are better leaving grp.

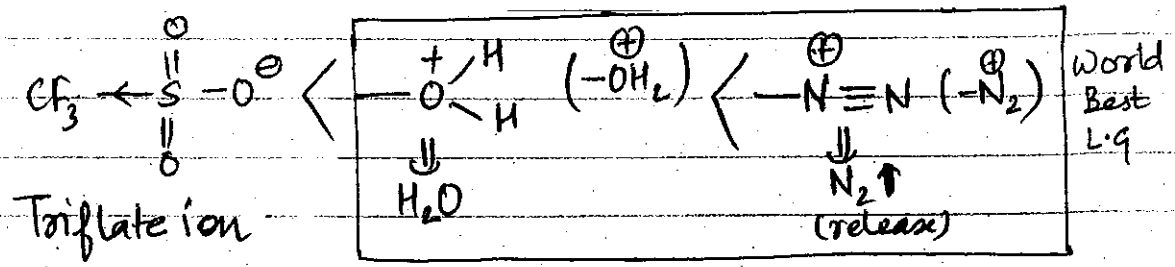
$F^{\ominus} < Cl^{\ominus} < Br^{\ominus} < I^{\ominus}$

Stability of anion ↑ L.G ↑

Lewis Acid ⇒ cation होता है जो e⁻ ले

② $\overset{\ominus}{N}H_2 < \overset{\ominus}{O}H$ (LG)

③ $R-O^{\ominus} <$  (LG)

④ 

Electrophile Sps having low energy vacant orbital is K/a Electrophile
↓
(Organic comp/intermediate)

Types

① **Cationic Electrophile**

R^+ {$\overset{\oplus}{C}H_3$}, $R-\overset{O}{\overset{\|}{C}}\oplus$ $\overset{\oplus}{N}=O$ $\overset{\oplus}{N}O_2$ $\overset{\oplus}{S}O_3H$ $\overset{\oplus}{Cl}$ $\overset{\oplus}{Br}$ $\overset{\oplus}{I}$ ... etc

NOTE $\overset{\oplus}{N}H_4$ ~~$H_3O^{\oplus}$~~

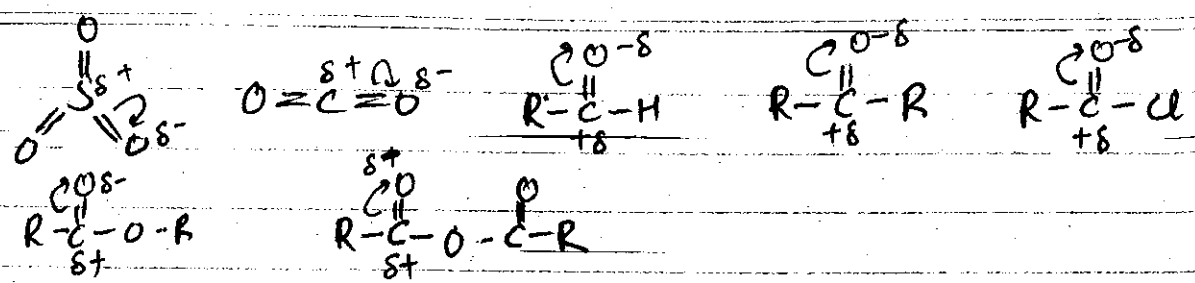
↓

Not E⊕ ⇒ No vacant orbital

② **Neutral Electrophile**

$\dot{C}H_3$ {neutral} $BeCl_2$ BF_3
$AlCl_3$ $ZnCl_2$ $GaCl_3$ $SnCl_4$
PCl_3 PCl_5 $SbCl_5$

NOTE, All lewis acid behave as a electrophile
All polar π-bond behave as a electrophile.



Type Of Rxn

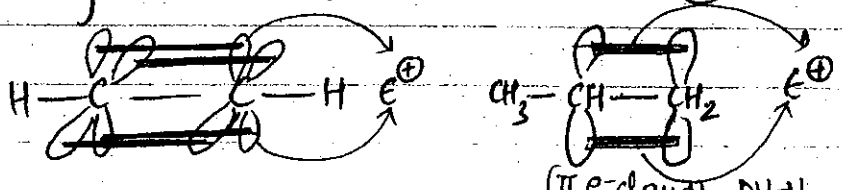
Reagent

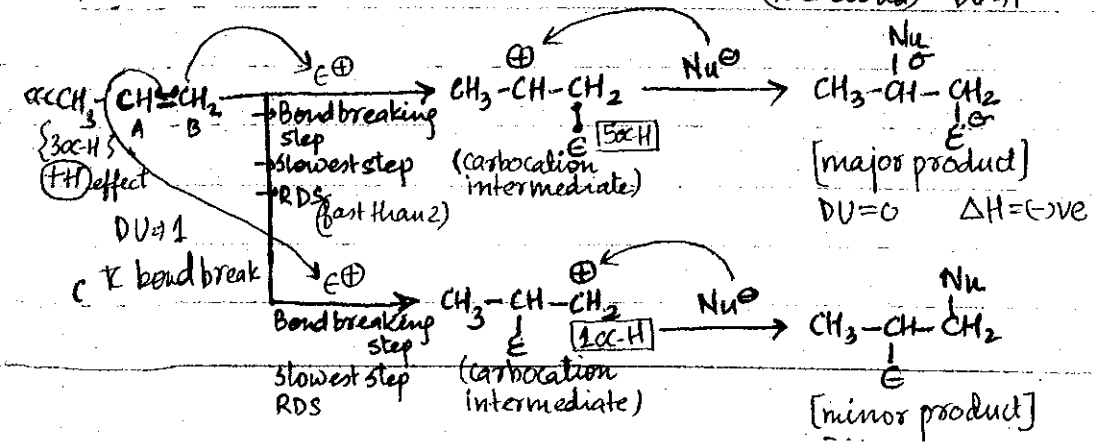
(A–B)

- Heterolysis ($A^{\delta+}$–$B^{\delta-}$)
  - $A^{\oplus}$ {$E^{\oplus}$, Electrophile} {Carbocation}
    - ① Electrophilic Addition Rxn {EAR}
      - eg. Alkene, Alkyne
    - ② Electrophilic Substitution Rxn {ESR}
      - eg. Aromatic Compound
  - $B^{\ominus}$ {Anion} {Nucleophile $Nu^{\ominus}$}
    - ① Acid-Base Rxn
    - ② Nucleophilic Addition Rxn
      - eg. Carbonyl comp. (Aldehyde & Ketone)
    - ③ Nucleophilic Substitut^{n} Rxn
      - eg. Alkyl halide
- Homolysis (A–B)
  - F·R· (demerisation mainly) ← Disproportionat^{n} rxn. (आओ Bond तोड़ें)
    - ① Free radical Addition Rxn (FRSR)
      - eg. Addition of HBr in presence of peroxide
    - ② Free radical sub. rx^{n} (FRSR)
      - eg. Alkane

Electrophilic Addition Rxn Of Alkene & Alkyne

(Carbocation Inter.)

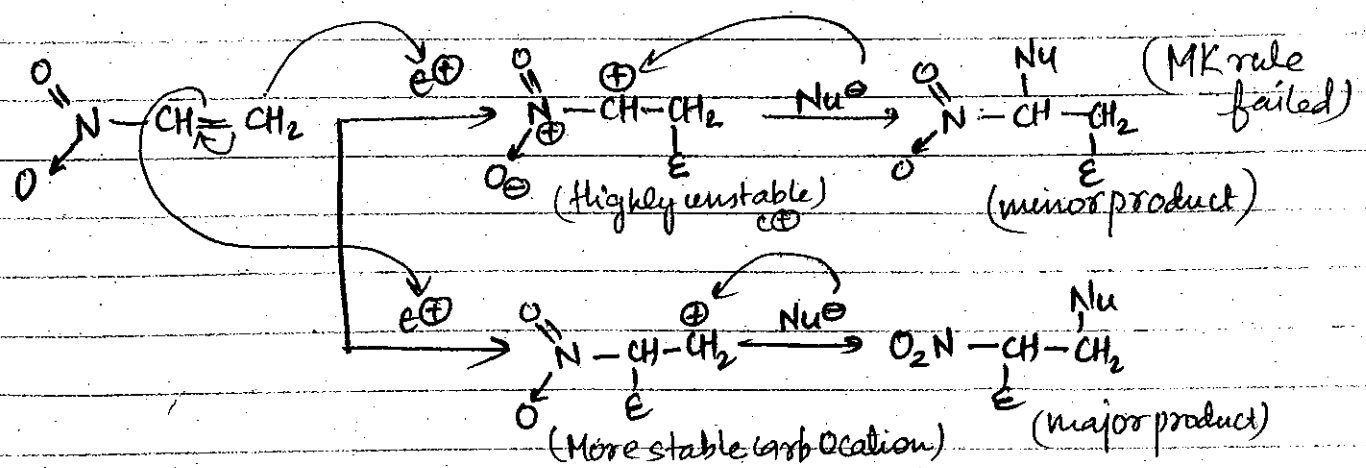




① Carbocation intermediate is formed in this rxn
② Formation of C^+ is RDS of rxn.
③ Reactivity of rxn ∝ stability of carbocation
④ Carbocation rearrangement is possible.
⑤ Reaction also k/a Markonikov Addition Rxn.

Markonikov's Rule :-

During EAR of alkene & alkyne -ve part of a reagent always goes to that unsaturated C that have least no. of H atom.



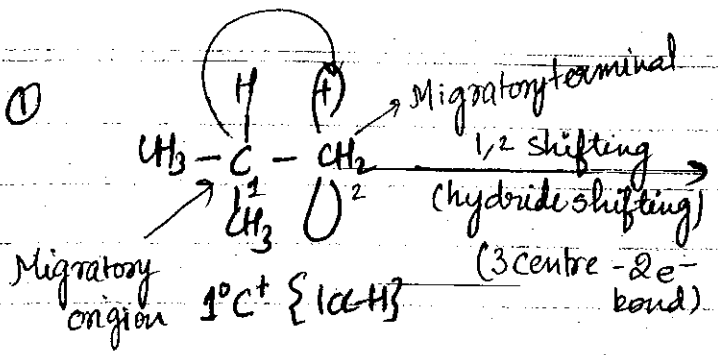
$H_3N-CH=CH_2 \xrightarrow{E-Nu}$ MK rule failed

$R_3\overset{+}{N}-CH=CH_2 \xrightarrow{Nu^\ominus}$ MK rule failed

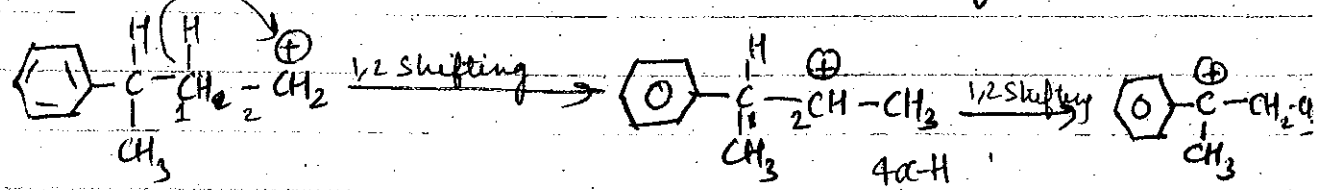
$\dot{C}Cl_3-CH=CH_2 \xrightarrow{Nu^\ominus}$ MK rule failed

Carbocation Rearrangement

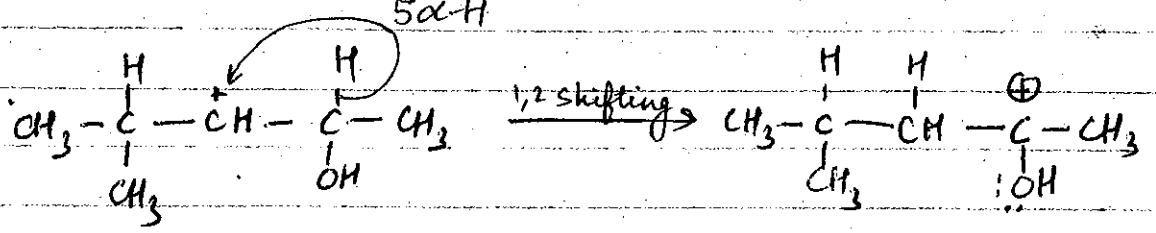
Before product formation carbocation have general tendency to rearrange themselve.
Carbocation rearrangement not observed in unsaturated carbocation
C-R is an exothermic process & energy available at room temp.

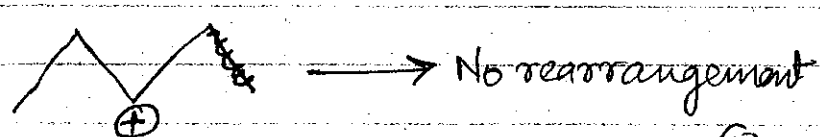
① 

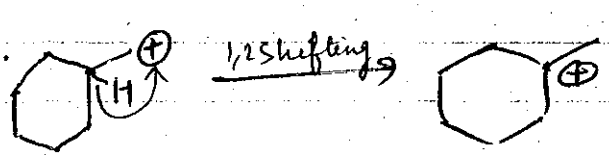
② $CH_3-CH=\overset{\oplus}{C}H$ ⟶ unsaturated $C^{\oplus}$ ⇒ No rearrangement.

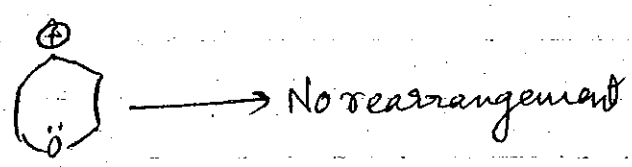
③ 

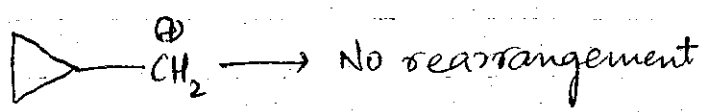
④ $CH_3-\ddot{O}-CH_2-CH_2-\overset{\oplus}{C}H-CH_3$ ⟶ No rearrangement

⑤ 

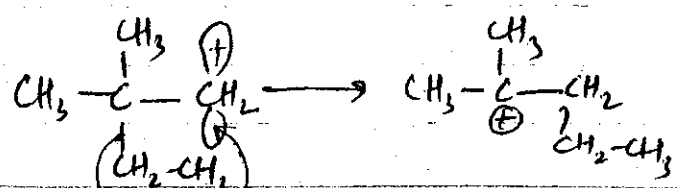
⑥  ⟶ No rearrangement

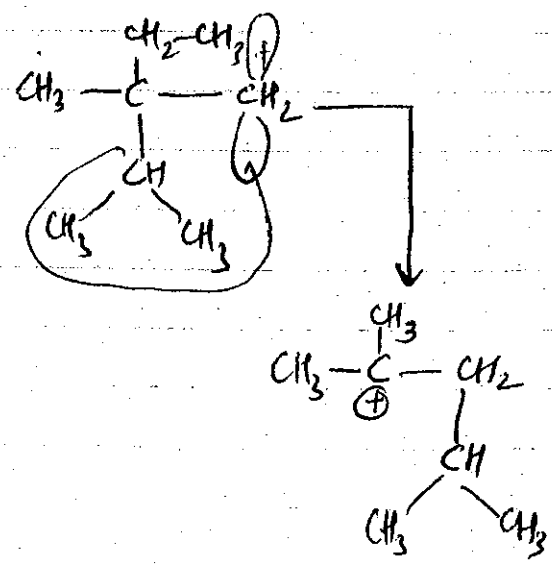
⑦ 

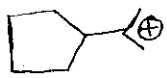
⑧  ⟶ No rearrangement

⑨  ⟶ No rearrangement

(Dancing resonance)

⑩ 

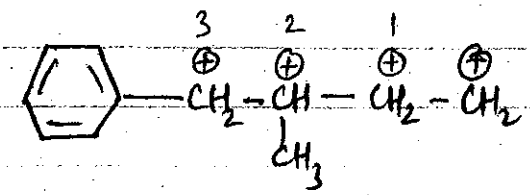
⑪ 

H.W 

Migratory Aptitude

Tendency to shift diff unit during carbocation rearrangement is K/a Migratory Aptitude

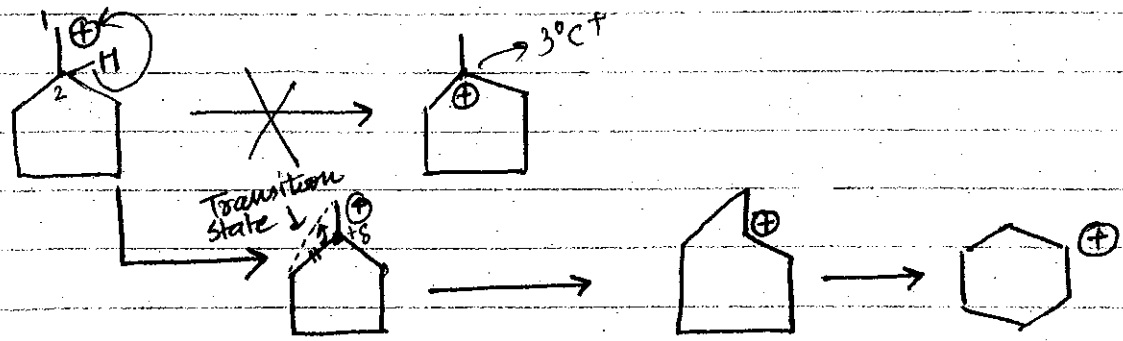
$H^{\oplus} > 3^{\circ}$ Alkyl $> 2^{\circ}$ Alkylgrp $> 1^{\circ}$ Alkylgroup $> -CH_3$

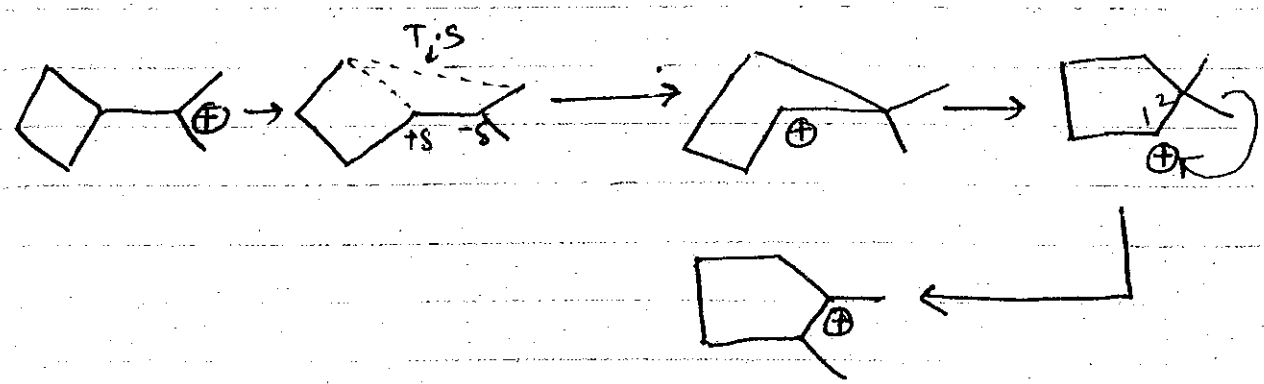


3 times 1,2 shifting.

Ring Expansion

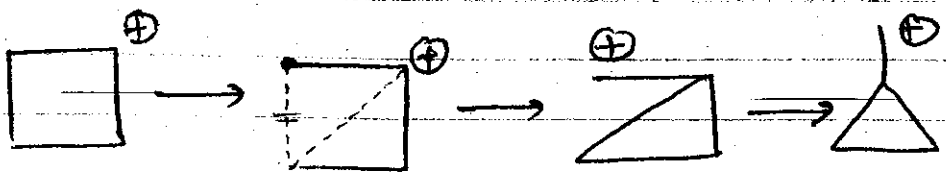
Ring expansion is more effective than Carbocation rearrangement during ring expansion the whole molecule stable because angle strain ↓ses

1. 

2. 

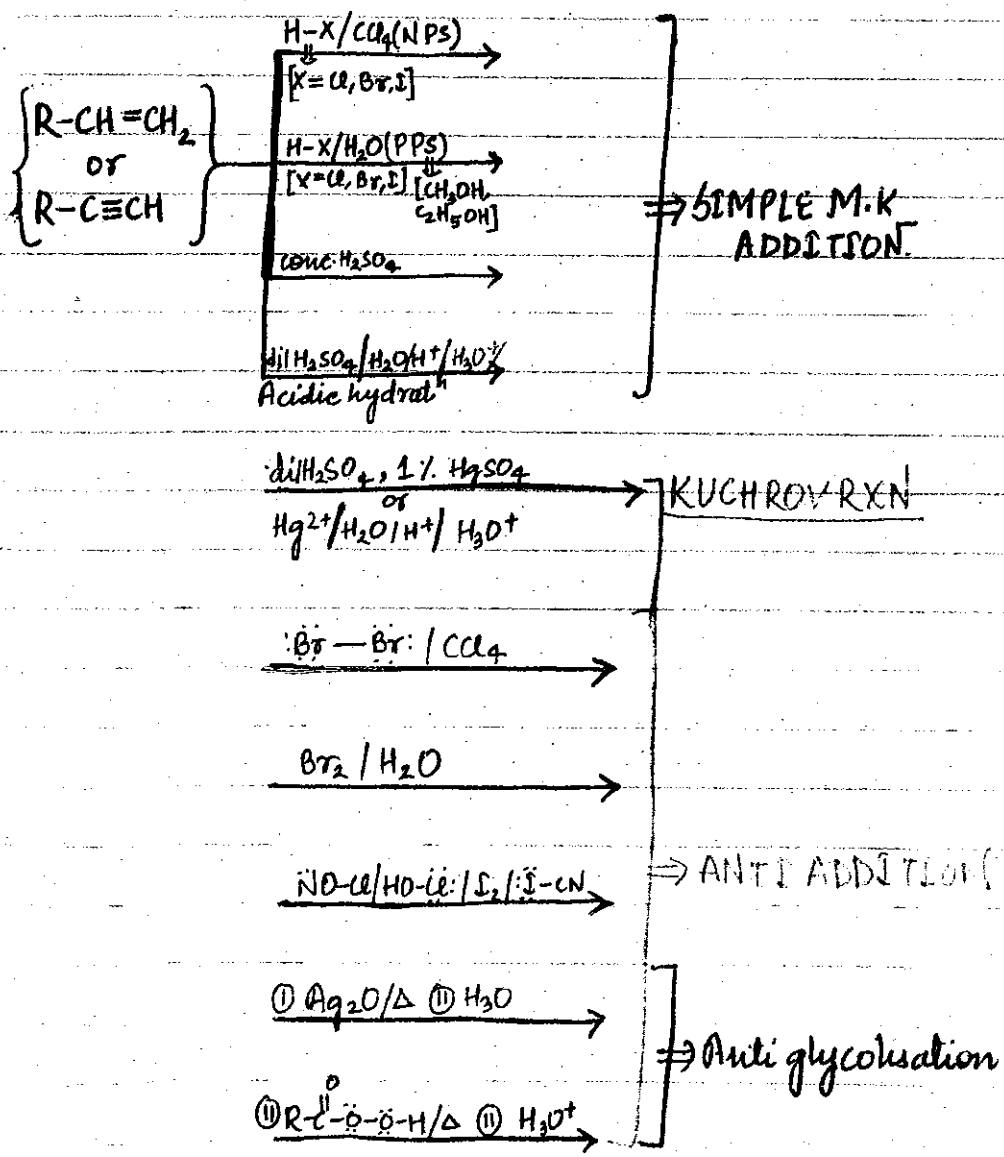
NPS → Non-Polar Solvent.
PPS → Polar Protic Solvent

Ring Contraction



Due to Dancing Res

Different EAR



HBr → source of electrophile
H+ ... Electrophilic attack ... generate ... in HBr

$(CH_3COO)Hg \cdot H_2O$ / $NaBH_4$ → (OMDM)

syn Addition:
- BH_3-THF / H_2O_2/OH^- → (H·B·O)
- syn hydroxylation: ① 1% alkaline $KMnO_4$ (cold) ② OsO_4

1. Addition Of H-X in Three of CCl_4 (NPS)

[X = Cl, Br, I]

i) Alkene

Net Rxn: $CH_3-CH=CH_2 \xrightarrow{HBr/CCl_4} CH_3-\underset{\underset{H}{|}}{\overset{\overset{Br}{|}}{CH}}-CH_2$ (2° Alkyl halide)

- → 1 π e⁻ cloud
- → DU = 1

- → 2 σ bond formed
- → Strong bond
- → DU = 0

Mech:

$CH_3-CH=CH_2 + H-Br \rightarrow CH_3-\overset{\oplus}{C}H-CH_2-H + Br^-$

① Bond breaking step
② RDS

$CH_3-\overset{\oplus}{C}H-CH_2-H + Br^- \rightarrow CH_3-\underset{\underset{H}{|}}{\overset{\overset{Br}{|}}{CH}}-CH_2$

carbocation intermediate → 2° Alkyl halide

$E^\oplus$ (1s H) + $Nu^\ominus$ (4p Br): σ filled BMO, B.O.↓ ⇒ $E^\oplus$

Carbocation intermediate formed in this rxn
Formation of carbocation is RDS of this rxn
Reactivity of rxn directly proportional to stability of carbocation
Simple M.K Addition takes place.
Carbocation rearrangement possible

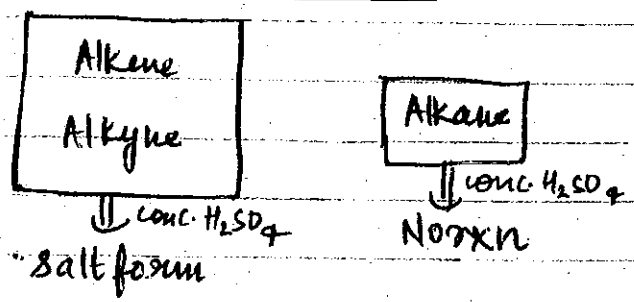
ii) Alkyne

Net Rxn: $CH_3-C\equiv H \xrightarrow{H-Br-CCl_4} CH_3-\underset{\underset{Br}{|}}{\overset{\overset{Br}{|}}{C}}-CH_3$

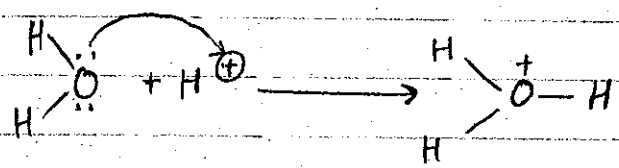
GEM Dihalide

Rxn used in practical organic chemistry

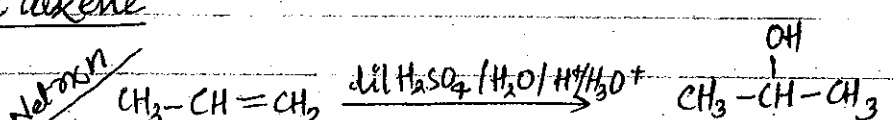
Generally alkene & alkyne give ~~rxn~~ with conc. H_2SO_4 & form salt while alkane do not react with conc. H_2SO_4 at room temp

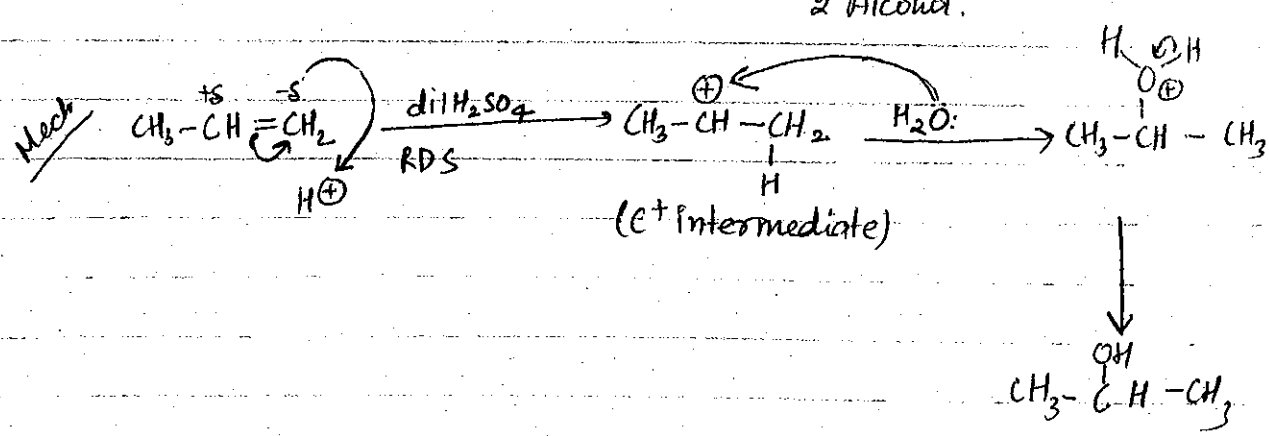


① Reaction with dil. H_2SO_4 / H_2O / H^+ / Acidic Hydration



i) At alkene





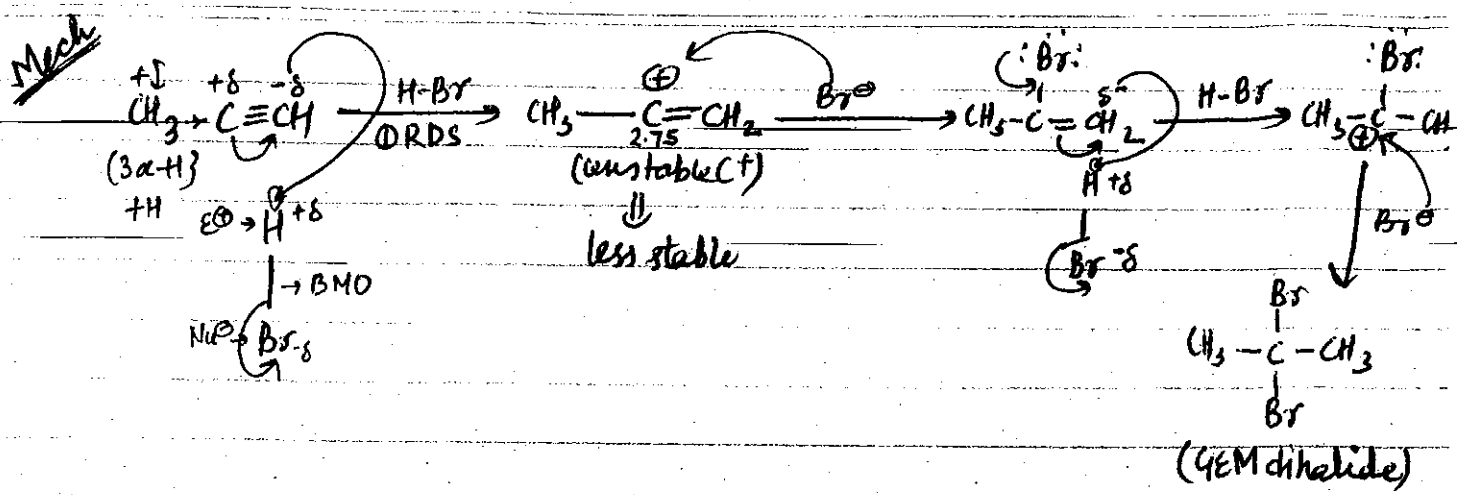
Carbocation intermediate formed in this rxn

Formation of C^+ is RDS of rxn

Reactivity of rxn ∝ Stability of C^+

C^+ rearrangement possible.

Mech



Reactivity of rxn

Alkene > Alkyne

saturated C⁺ more stable — unsaturated C⁺ less stable C⁺

② Addition Of H-X/H₂O (Polar Solvent)

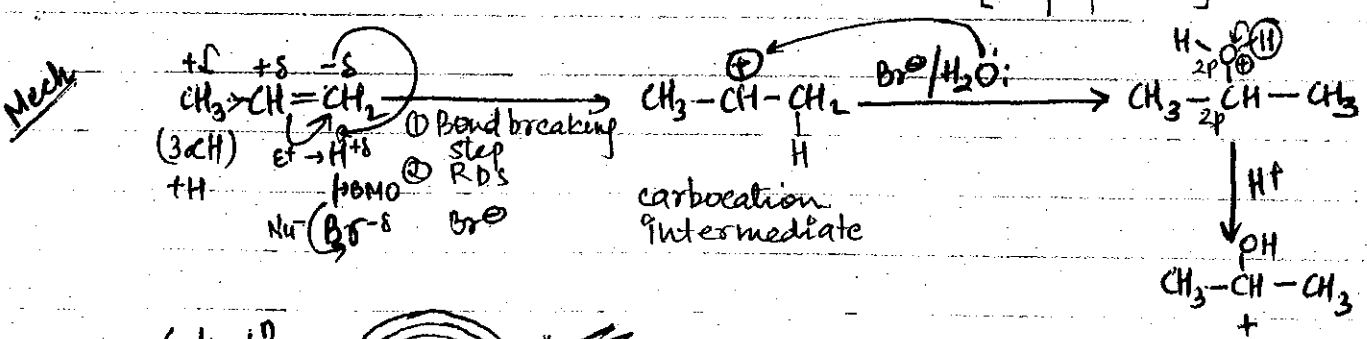
[X = Cl, Br, I] [CH₃OH, C₂H₅OH]

i) At alkene

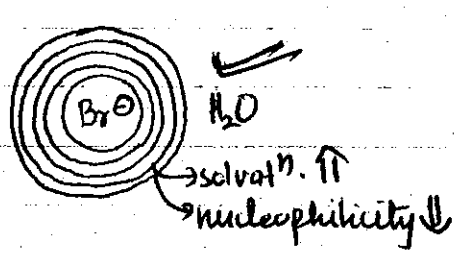
Net rxn

$CH_3-CH=CH_2 \xrightarrow{HBr/H_2O} CH_3-\underset{OH}{CH}-CH_3$ [2° Alcohol] [major product]

Mech



Solvat^n



HBr worked as catalyst.

- Carbocation intermediate formed in this rxn
- Formation of C⁺ is RDS of rxn.
- Reactivity of rxn ∝ Stability of carbocation
- Carbocation rearrangement possible

Alcohol का [illegible]

***Keypoint Whenever rxn is carried out in ⊕nce of polar protic solvent then due to solvation of anion its nucleophilicity ↓ses in this condition solvent addition takes place.

** Amount of solvent more than amt of anion that is why solvent addition takes place.

ii) Of alkyne

(A) $CH_3-C\equiv CH$ (+H) $\xrightarrow[RDS]{HBr/H_2O}$ $CH_3-\overset{+}{C}=CH_2$ (unsaturated C⊕) $\xrightarrow{Br^{\ominus}/H_2O:}$ $CH_3-C(OH)=CH_2$ (enol form) ⇌ $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ (Ketone form)

(B) $CH\equiv CH$ (acetylene) $\xrightarrow{H-Br/H_2O}$ $CH=CH$ (H) (unsaturated C⊕) $\xrightarrow{Br^{\ominus}/H_2O:}$ $CH(OH)=CH_2$ enol form ⇌ $H-\overset{O}{\overset{\|}{C}}-CH_3$ Aldehyde

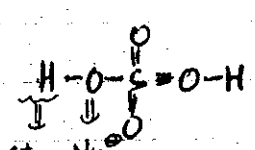
Keypoint ⇒ In case of alkyne all alkyne give ketone product while acetylene give aldehyde product during addition of HX/H_2O

③ Reaction With Conc. H_2SO_4

$CH_3-CH=CH_2$ (3α-H, +H) $\xrightarrow{conc.\ H_2SO_4}$ $CH_3-\underset{O-SO_3H}{CH}-CH_3$

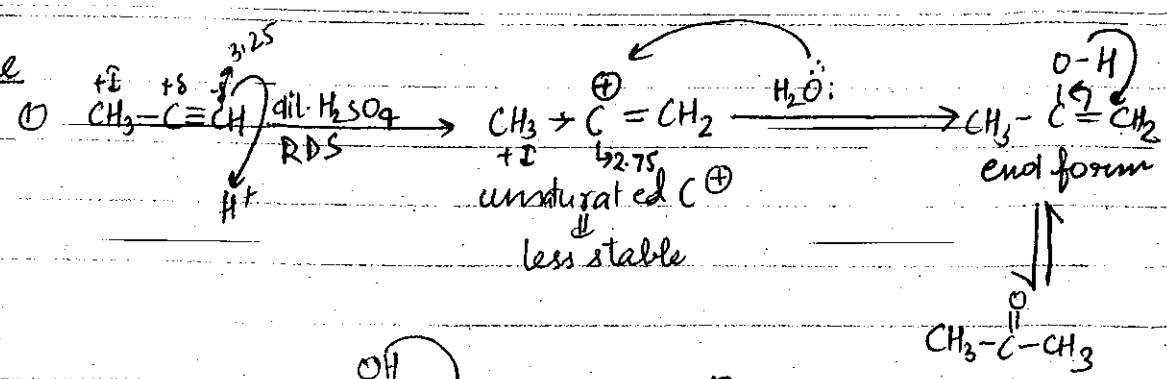
"Bisulphate salt"

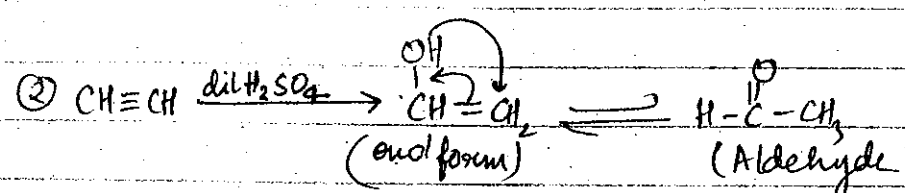
alkane alkyne ये नहीं देते



Kucherov used the rxn of hydration on alkyne

ii) At alkyne

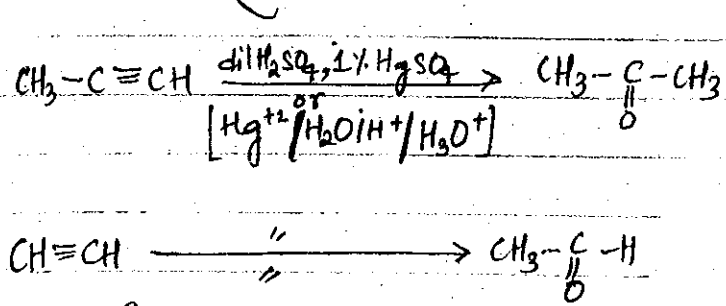




Whenever hydration rxn is carried ~~to carri~~ out at alkyne the rate of hydration rxn is very slow because unsaturated C^{+} form as a rxn intermediate

**NOTE Whenever rxn is carried out in presence of dil H_2SO_4, 1% $HgSO_4$ or Cu^{+2} then rate of hydration rxn at alkyne is very fast because rxn follow anti-addition mechanism.

KUCHEROV RXN



⇒ Rate of hydration rxn ⇑
⇒ becoz Hg^{+2} ⇒ high ϕ

Anti Addition

KEYPT: If $E^{\oplus}$ having l.p the rxn always completes with anti addition mechanism.

① Addition of Br_2/H_2O

→ Br_2/H_2O ⇒ Brown colour.
→ Bromine water test
→ Test of unsaturation

Net rxn

$CH_3-CH=CH_2 \xrightarrow[\text{Brown colour}]{Br-Br/H_2O} CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-Br$ [50%] | $CH_3-\underset{Br}{\underset{|}{CH}}-CH_2-OH$ [50%]

Colourless

R.M

enantiomers

Mech

$CH_3-CH=CH_2 \xrightarrow[RDS]{Br-Br/H_2O} CH_3-\overset{+}{C}H-CH_2-Br$

$\epsilon^{\oplus}$ → Br ⇒ BMO ⇒ $\epsilon^{\oplus}$

Nu → Br

(Rapid step)

Synergic bonding

ring में open chain की तरह stable होगा।

3 memb cyclic ion formed as (Bromonium) ion

$CH_3-\overset{a}{CH}-CH_2$ (BMO)

octet com

a–b=c → B·L

Non classical ct (NCC)

Thermody

Br^-/H_2O:

$CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-Br$ | $CH_3-\underset{Br}{\underset{|}{CH}}-CH_2-OH$

Colourless

Racemic Mix.

ϵ^+ have l.p that's why rxn completed with anti addition mech.

3 memb. cyclic halonium ion (Bromonium) formed as a rxn intermediate

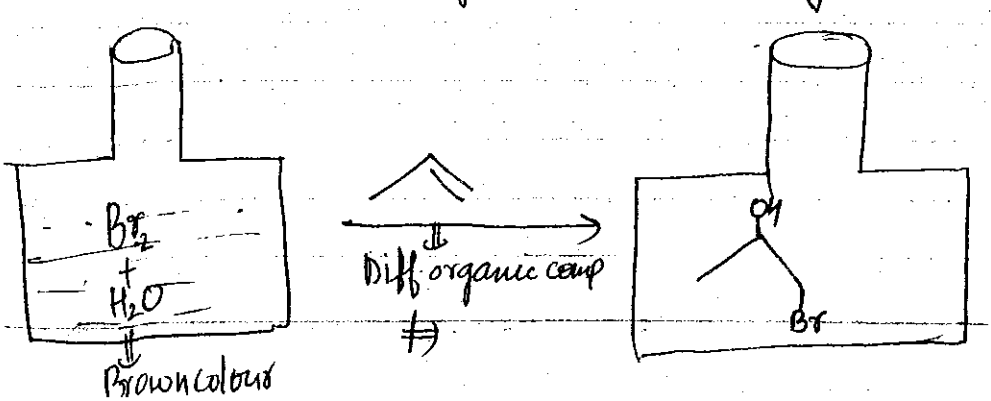
Format^n of cyclic halonium ion is RDS of rxn

C^+ rearrangement not possible

Rxn used in practical org. chem.

Rxn aka Br_2 water test or test of unsaturat^n

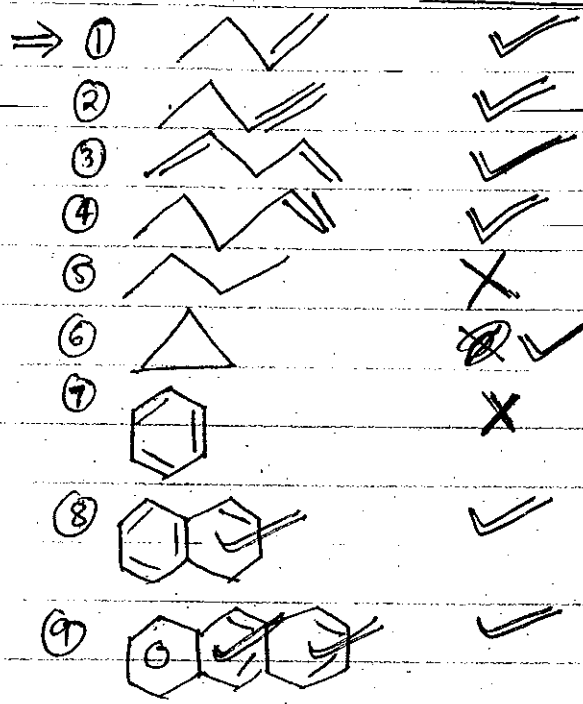
POC (Practical Organic Chemistry)



Cl>CH-CH$_2$-Cl (Westrosol

Perfect benzoid वाला भी देगा
बाकी नहीं देंगे

Colourless



cyclopropane give test of unsaturation.
No test of unsaturat^n.
↓
Aromaticity break

② Addition Of Br_2 / CCl_4

Br_2 ⇒ Brown colour
test of unsaturat^n

Hetero

① $CH_3-CH=CH_2 \xrightarrow{Br-Br/CCl_4} CH_3-\underset{*}{CH}(Br)-CH_2(Br)$ / $CH_3-\underset{*}{CH}(Br)-CH_2(Br)$ (colourless)

vic. dihalide

⑪ $CH_3-C\equiv CH \xrightarrow[(2\,eq.)]{Br-Br/CCl_4} CH_3-C(Br)_2-CH(Br)_2$

Bihar PMT

⑪ $CH\equiv CH \xrightarrow{Cl_2/CCl_4} H-C(Cl)_2-C(Cl)_2-H$ (Westrosol)

③ Addition Of Br_2 / water in brine sol^n

Brine sol^n ⇒ conc-sol^n of NaCl

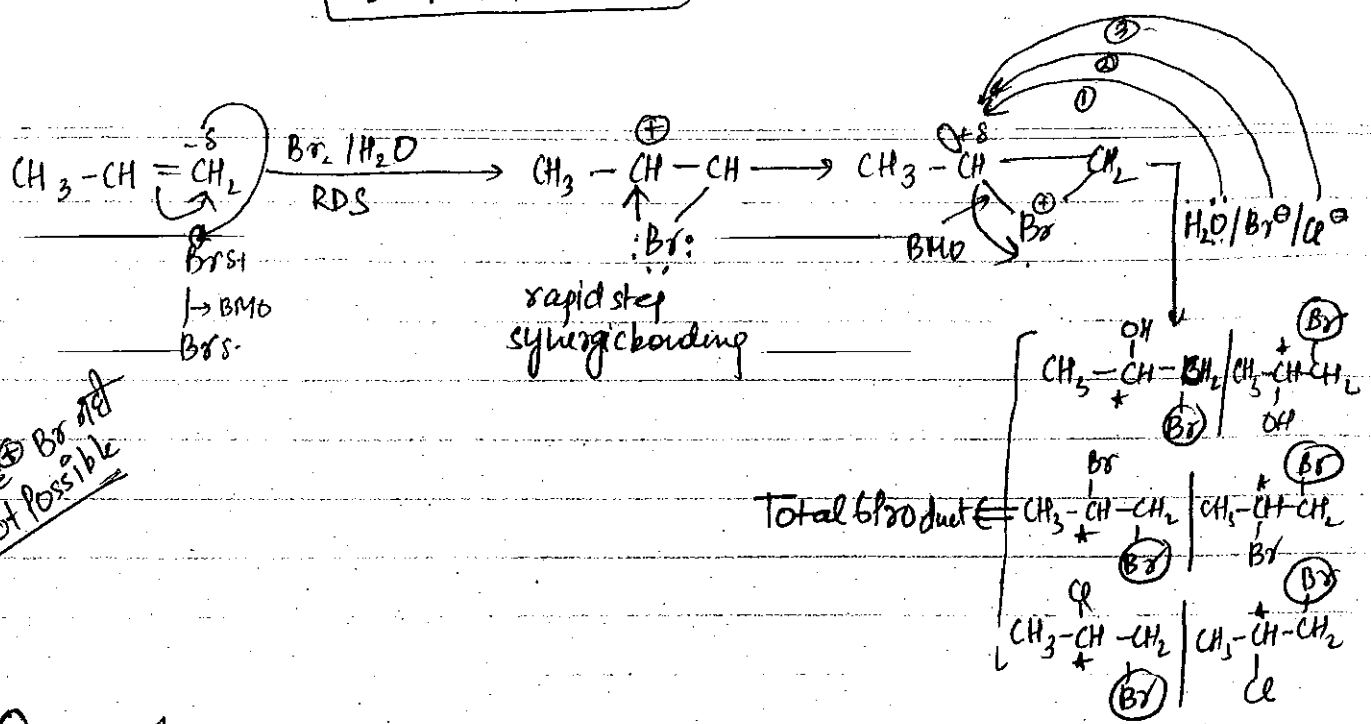
Hetero

$CH_3-CH=CH_2 \xrightarrow[\text{in Brine sol}^n]{Br_2,\text{water}}$ Total no. of product? ⑥

① $E^{\oplus}$ Br_2 ($Br^{\oplus}$) [only 1 $E^{\oplus}$] Na^+ ⇒ Not $E^{\oplus}$

⑪ $Nu^{\ominus}$ H_2O $Br^{\ominus}$ $Cl^{\ominus}$ ↑ Three $Nu^{\ominus}$

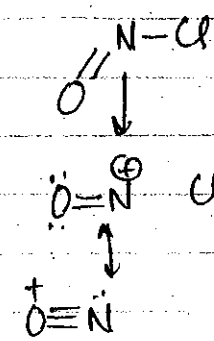
$Br_2\ H_2O \rightarrow$ Br, OH लेगेगा
$Br_2\ CCl_4 \rightarrow$ Br, Br लेगेगा
anti



Ozonolysis

① Addition of NO-Cl / HO-Cl / I-Cl / I-CN / CCl_4

Ⓐ Addition of NO-Cl



Nitroso

$$CH_3-CH=CH_2 \xrightarrow[+N=O/Cl^{\ominus}]{NO-Cl/CCl_4} CH_3-\underset{\underset{NO}{|}}{CH}-CH_2 \;\Big|\; CH_3-\underset{\underset{Cl}{|}}{CH}-CH_2-NO$$

Ⓑ Addition of HO-Cl / CCl_4

$HO-Cl \rightarrow OH^{\ominus} + Cl^{\oplus}$

Nitroso

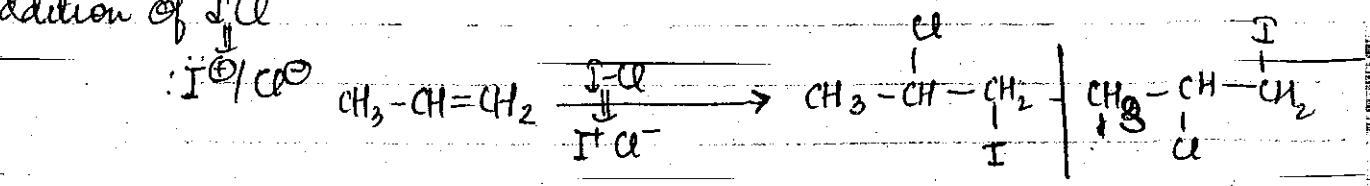
$$CH_3-CH=CH_2 \xrightarrow[Cl^{\oplus}/OH^{\ominus}]{HO-Cl} CH_3-\underset{\underset{OH}{|}}{CH}-CH_2 \;\Big|\; CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-Cl$$

50% 50%

Ag_2O/Δ → nascent O_2 ⇒ इसमें से opp-side 2 OH लगता है

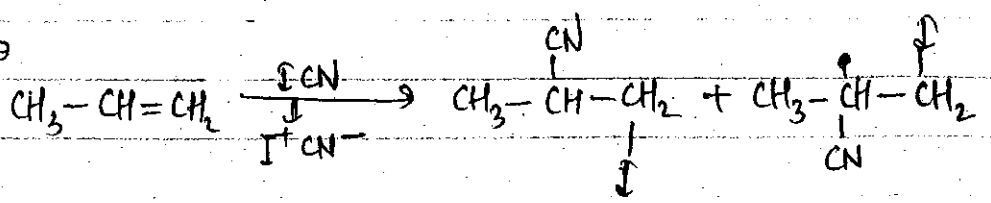
Addition of ICl

$I^{\oplus}/Cl^{\ominus}$

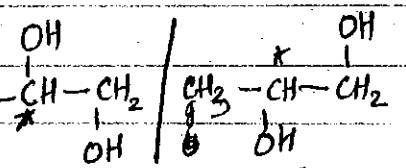


Addition of ICN

$I^{+}/CN^{\ominus}$

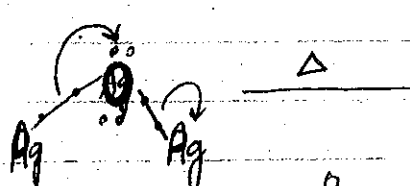


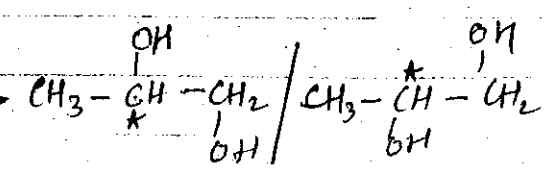
Anti Hydroxylation Rxn (Glycolisation Process)

① $CH_3-CH=CH_2 \xrightarrow[ii)\ H_3O^+]{i)\ Ag_2O/\Delta}$ 

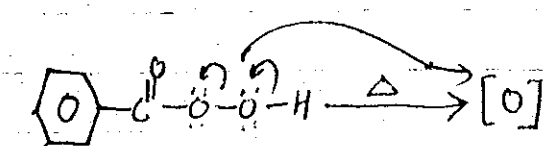
⇒ glycol product [racemic mix] optically inactive

⇒ Anti glycolysat^n Product



② $CH_3-CH=CH_2 \xrightarrow[ii)\ H_3O^+]{i)\ R-\overset{O}{\overset{\|}{C}}-O-O-H/\Delta}$ 

racemic mixture



MCPBA
(Meta chloro per benzoic acid)
give nascent oxygen

Oxymercuration Demercuration Reaction (OMDM)

~~only 1st~~ step ⇒ Anti Addition ~~Product~~ M·K

Reagent ⇒ $(CH_3-\overset{O}{\overset{\|}{C}}-O)_2Hg/H_2O$ / $Hg(OAc)_2/H_2O$

OAc (leaving grp) — Acyl grp (Ac)

$NaBH_4$ (Sodium Borohydride) (SBH) / $NABH_4$

→ Three kam

→ Reducing agent (give $H^\ominus$ (hydride) in medium → best nucleophile

→ Acid halide, Aldehyde & Ketone ke $\overset{O}{\overset{\|}{C}}$ or Ko $\overset{OH}{C}$ me change karta Hai

Ne·oxy

$CH_3-CH=CH_2 \xrightarrow[NaBH_4]{Hg(OAc)_2/H_2O} CH_3-\underset{OH}{\overset{\ddots}{CH}}-\underset{H}{CH_2}$ (Acc to M·K) (No rearrangement)

Mechanism

$CH_3-\overset{+H}{CH}=\overset{+\delta}{CH_2}$ (-δ) $\xrightarrow{Hg(OAc)_2}$ $CH_3-\overset{+}{CH}-CH_2$ ⟷ $CH_3-CH-CH_2$ (octate complete, BMO)

$:Hg-OAc$ (attacks the more substituted carbon)

$:Hg-OAc$ (bridged) ⇒ NCC form

→ cyclic mercurinium ion form as a non intermediate

⇒ No carbocation rearr.

$H_2\ddot{O}:$ attacks the more substituted carbon

$CH_3-\underset{sp^3}{CH}(OH)-CH_2-HgOAc$ (BMO)

FIRST STEP ⇒ Anti Addition

$Na^+[H_3B-H]^\ominus \rightleftharpoons H^\ominus$

$CH_3-CH(OH)-CH_2-H$

SECOND STEP ⇒ M·K

2° Alcohol

Simple M·K Addition Product

~~$CH_3-CH_2-C\equiv$~~

In OMDM reaction ~~first step~~ is completed with anti addition mech. but overall rxn give Markonikov addition product.
3 memb. cydic mercurium ion formed as a rxn intermedia
Carbocation rearrangement not possible.
In OMDM rxn all alkyne give ketone product while acetyle give aldehyde product

At alkyne

① $CH_3-C\equiv CH \xrightarrow[NaBH_4]{Hg(OAc)_2/H_2O} CH_3-\underset{OH}{C}=\underset{H}{CH} \rightleftharpoons CH_3-\underset{O}{\overset{\|}{C}}-CH_3$

(enol form) (Keto form)

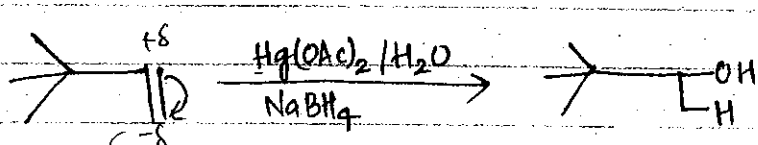
② $CH_3-C\equiv C-CH_3 \xrightarrow{OMDM} CH_3-\underset{H}{\overset{OH}{C}}=C-CH_3 \rightleftharpoons CH_3-CH_2-\underset{O}{\overset{\|}{C}}-CH_3$

(enol form) Keto form)

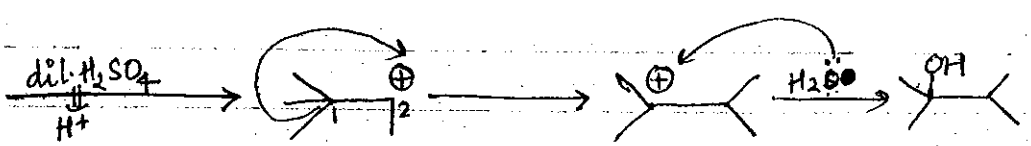
③ $CH\equiv CH \xrightarrow{OMDM} CH_3-\underset{O}{\overset{\|}{C}}-H$

Aldehyde

Q.1

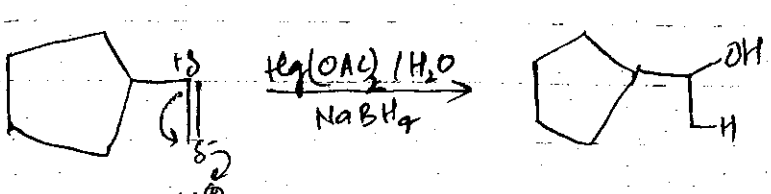


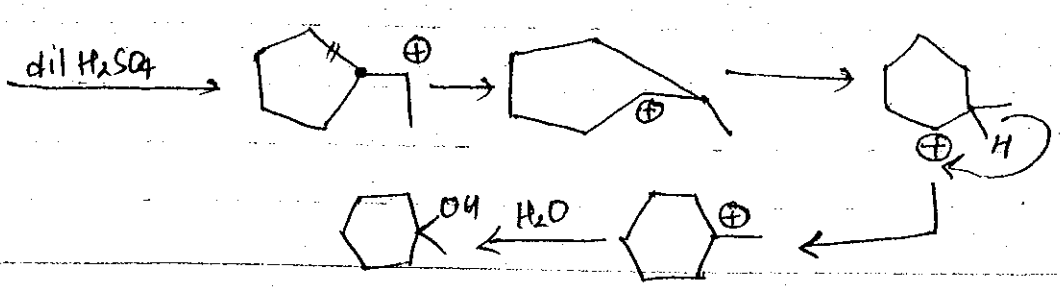
No Rearrangement



With rearrangement

Q.2





KEYPOINT ①

① $Br_2/CCl_4 \Rightarrow$ ~~2Br~~

② $Br_2/H_2O \Rightarrow Br.OH$

③ $NOCl/CCl_4 \Rightarrow$ ~~$\overset{+}{N}O/Cl^-$~~

④ $HOCl/CCl_4 \rightarrow \overset{\ominus}{O}H/Cl^-$

⑤ $Ag_2O/\Delta/H_3O^+ \Rightarrow 2OH$

⑥ $R-\overset{O}{\overset{\|}{C}}-O-O-H/\Delta/H_3O^+ \Rightarrow 2OH$

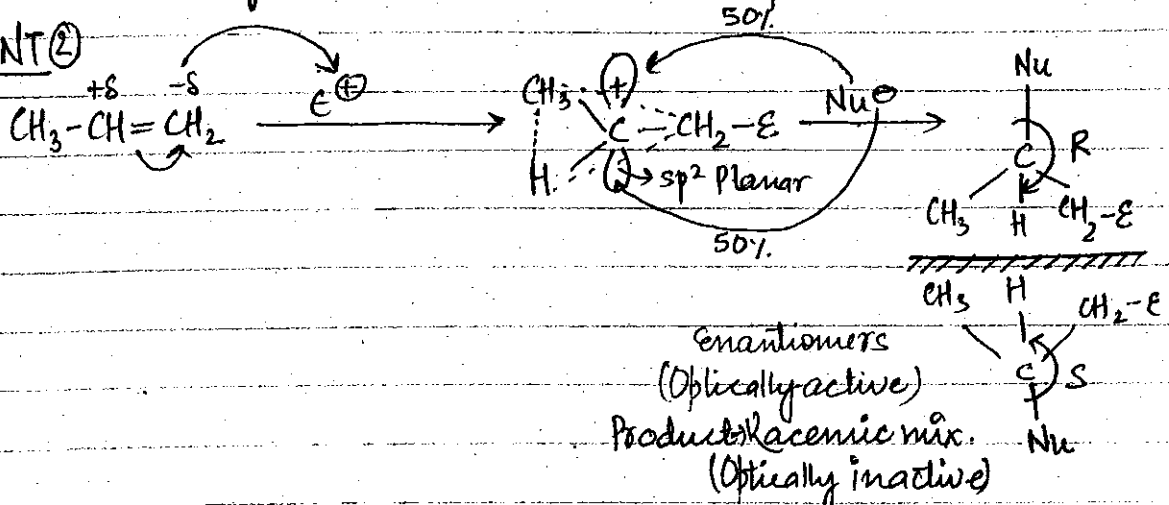
⑦ $\dfrac{Hg(OAc)_2/H_2O}{NaBH_4} \Rightarrow H., OH$

⇒ Electrophile have lone pair that's why rxn completed with ANTI ADDITION mech.

⇒ Three membr cyclic ring form as a Reaction intermediate

⇒ Carbocation ~~reagent~~ rearrangement not possible

KEYPOINT ②



Whenever chiral centre is generated during attack of nucleophile then equimolar mixture of a compound having R-S configuration w.r.t their c.c obtain as a product

KEYPOINT ③ Reactivity of ~~Alkyl~~ halide

$$\boxed{H\text{-}I > H\text{-}Br > H\text{-}Cl > H\text{-}F}$$

@MDM without rearrangement 2° ROH
HBO rearrangement ✗ 1° ROH

4MCTS ⇒ 4 Memb. Cyclic T.S

KEYPOINT ④ Reactivity of dihalogen for anti addition (Tendency to form cyclic halonium ion)

$$F_2 > Cl_2 > Br_2 > I_2$$

↳ small size
good overlapping

Syn Addition

① Hydroboration - Oxidation Rxn

Reagent ⇒ $\frac{BH_3\,THF}{H_2O_2/OH^\ominus}$ → Basic medium
→ oxidising agent (OA)

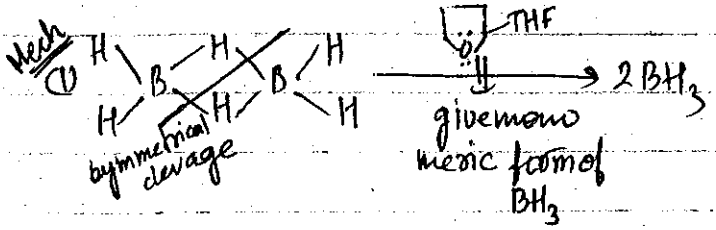
Net Rxn

$$CH_3-CH=CH_2 \xrightarrow[H_2O_2/OH^\ominus]{BH_3,THF} CH_3-\underset{H}{CH}-\underset{OH}{CH_2}$$

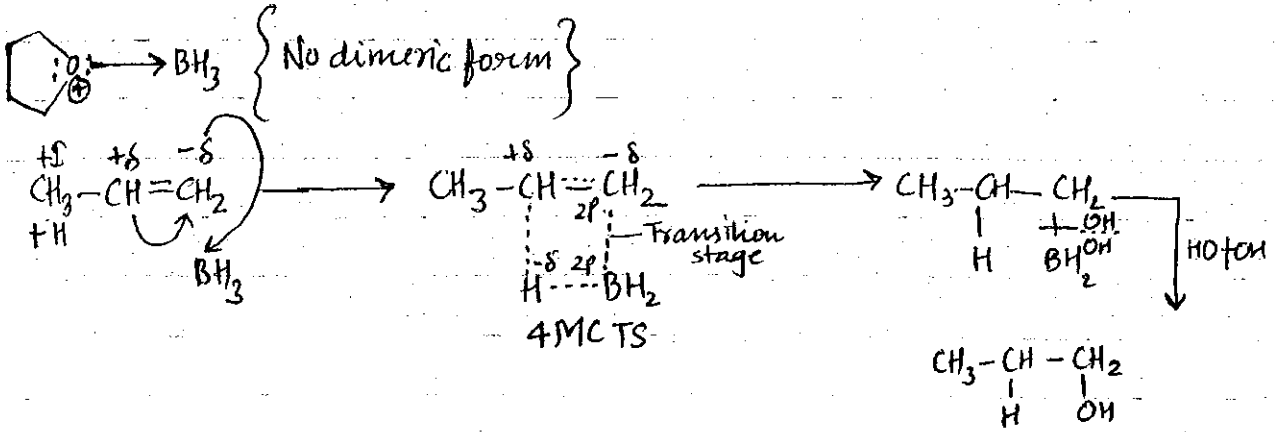
⇒ 1° Alcohol
⇒ Syn addition
⇒ Anti markovnikov addition

Mech

(I)



(II)



⇒ 1° Alcohol
⇒ Syn addition
⇒ Anti M.K Addition product

~~Extreme~~ Internal alkyne ⇒ ~~Alcohol~~

HBO rxn < Internal alkyne - ketone
Terminal alkyne - aldehyde

After Hyper

In HBO rxn anti M·K product is obtained

~~Syn addn~~

In HBO rxn, rxn completed with syn addn
carbocation rearrangement not possible
4 MCTs formed
used in practical organic chem.

In HBO rxn all terminal alkyne & acetylene give aldehye product while all internal alkyne give ketone product. Thats why rxn used for identification of terminal & internal alkyne

① $CH_3-CH_2-C\equiv CH$ (Terminal Alkyne) $\xrightarrow[H_2O_2\ OH^-]{BH_3.THF}$ $CH_3CH_2-CH=CH_2 \rightleftharpoons CH_3CH_2-CH_2-CHO$ (Aldehyde)

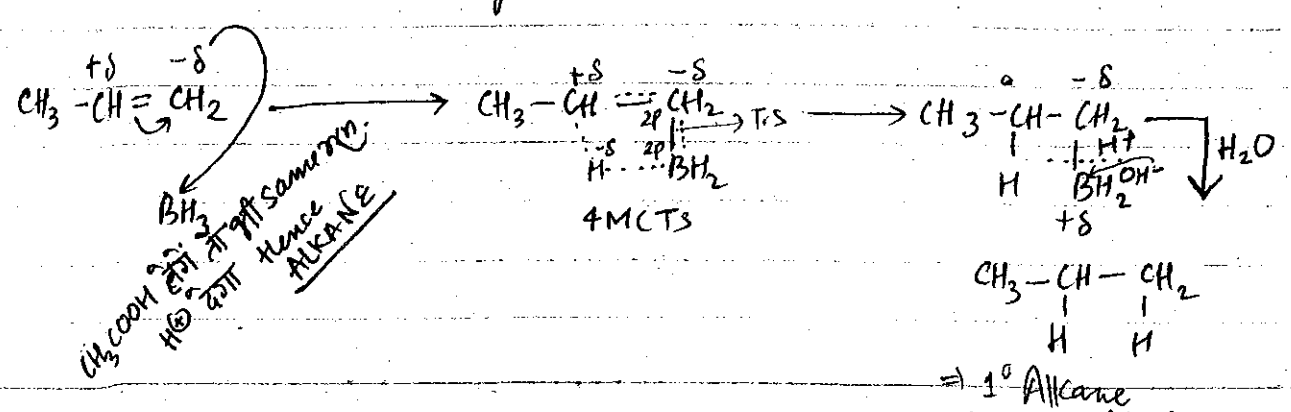
② $CH_3-C\equiv C-CH_3$ (Internal Alkyne) $\xrightarrow{HBO}$ $CH_3-C(H)=C(OH)-CH_3$ (enol) $\longrightarrow CH_3-CH_2-C(=O)-CH_3$

③ $HC\equiv CH \xrightarrow{HBO} CH_3-C(=O)-H$

Hydroboration Reduction (H·B·R rxn)

Not rxn $CH_3-CH=CH_2 \xrightarrow[H_2O]{BH_3,\ THF} CH_3-CH_2-CH_3$

⇒ Alkane
⇒ syn addition

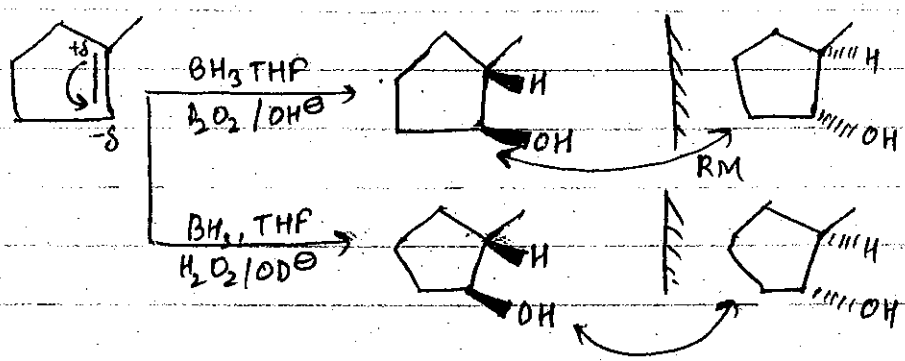


$KMnO_4$ ⇒ pink colour ⇒ charge transfer spectrum

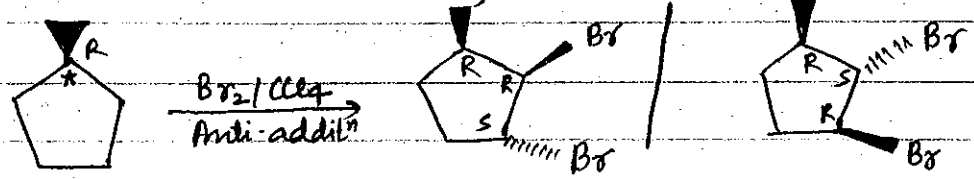
② $CH_3-CH=CH_2 \xrightarrow[CH_3-\overset{O}{\overset{\|}{C}}-O-H \ (T)]{BH_3\ THF} CH_3-\underset{H}{CH}-\underset{H\ (T)}{CH_2}$

⇒ Alkane
⇒ Syn-addition

Q.1



Q.2



Not mirror images
⇓
Diastereomers

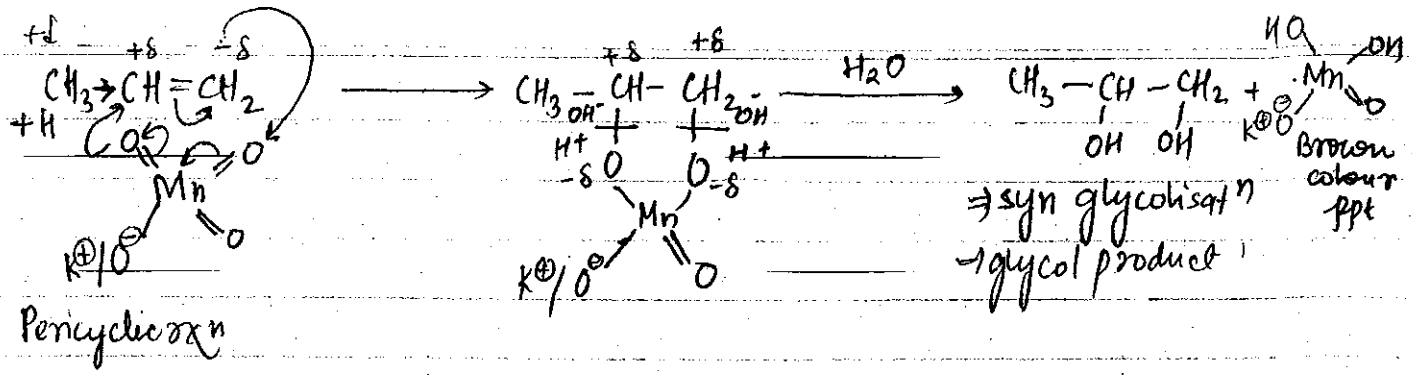
③ Reaction With 1% Alkaline $KMnO_4$ (Syn-Hydroxylat^n) (Cold)

1% alk. $KMnO_4$ is K/a Baeyer's Regent.
Read^n aka test of π-bond & test of unsaturat^n.
1% alk. $KMnO_4$ is a PINK colour solution. But after compled^n of rxn change into BROWN colour ppt.
Syn Glycolysat^n obse
Cyclic Magnese ester formed as a rxn intermediate

Net rxn

$CH_3-CH=CH_2 \xrightarrow[KMnO_4]{1\%\ alkaline} CH_3-\underset{OH}{CH}-\underset{OH}{CH_2}$

glycol product
Syn-glycolisat^n



Pericyclic rxn

⇒ syn glycolisation
⇒ glycol product

Rxn with OsO_4 (Osmium Tetraoxide)

$$CH_3 - CH = CH_2 \xrightarrow{OsO_4} CH_3 - \underset{OH}{CH} - \underset{OH}{CH_2}$$

glycol product

KEYPT

(HBO) $\frac{BH_3, THF}{H_2O_2 / OH^{\ominus}}$ H OH (Anti M·K Addition)

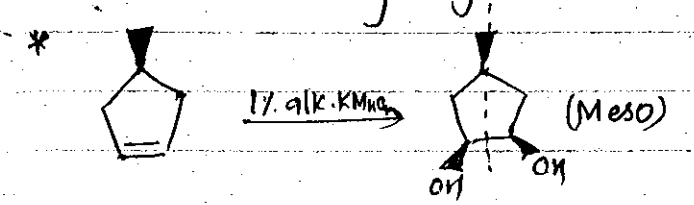
(HBR) $\frac{BH_3\ THF}{H_2O}$ H, H

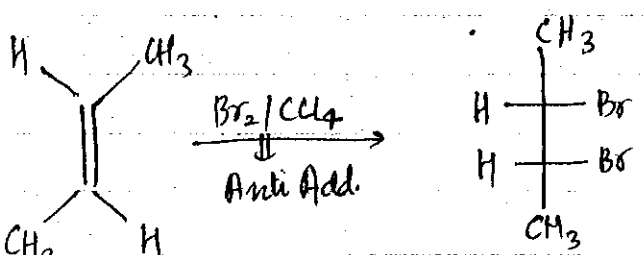
(BAEYER'S REA.) 1% Alkaline $KMnO_4 \Rightarrow$ OH, OH

$OsO_4 \Rightarrow$ OH, OH

(RUREADY) $Ni/Pt/Pd/H_2 \Rightarrow$ H, H

Stereochemistry Of Electrophilic Add. Rxn

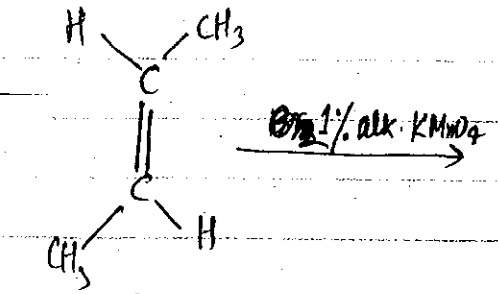




Trans-2-butene

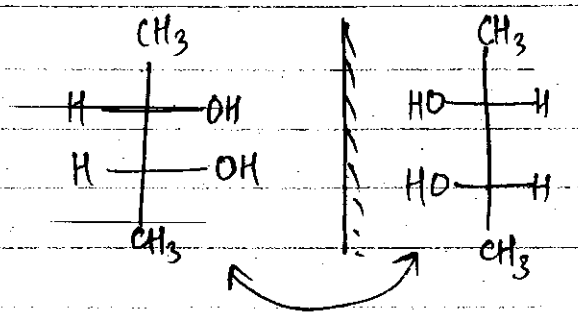
Meso

Optically inactive due to COS not due to POS

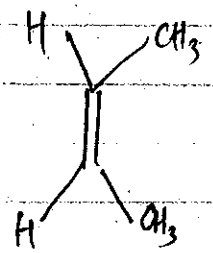
② 

Trans - Alkene.

Br_2 1% alk. $KMnO_4$ →

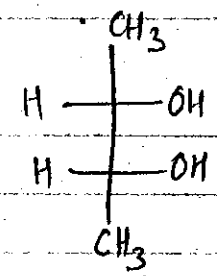


R·M (Racemic mix.)

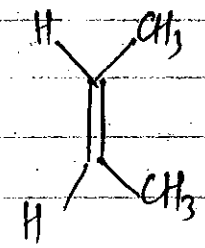
③ 

(cis - Alkene)

1% alk. $KMnO_4$ →

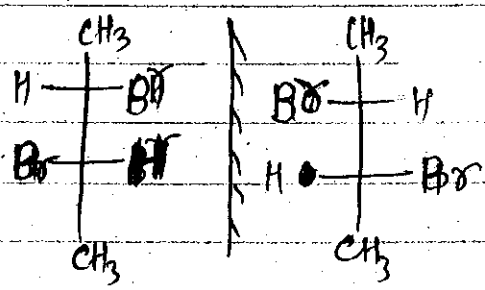


Meso (POS)

④ 

cis - Alkene

Br_2 / CCl_4 →

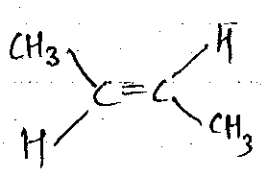


KEY PT

T $\xrightarrow{A}$ M
T $\xrightarrow{S}$ R
C $\xrightarrow{S}$ M
C $\xrightarrow{A}$ R

TAM scientist ⇒ TSR tech. CSM khayi CAR me ni baithenga

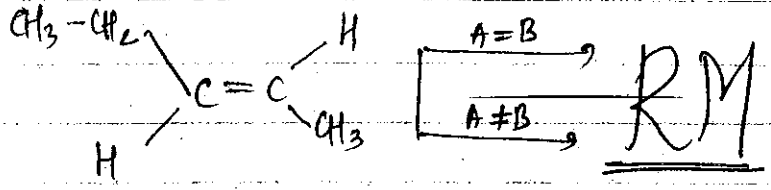
CASE-II

① 

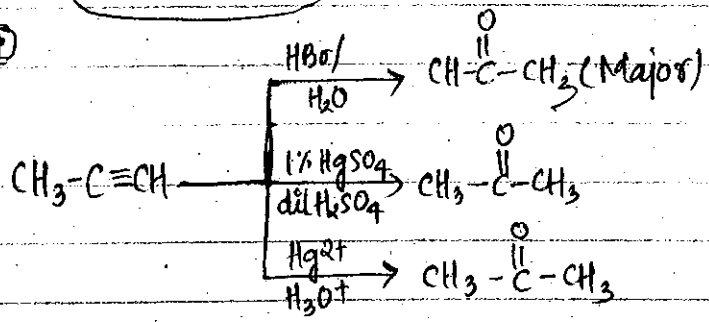
Trans alkene

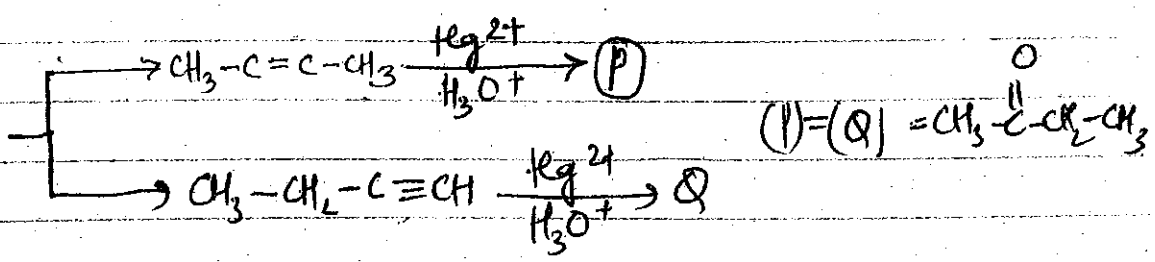
Br_2 / CCl_4 → MESO (A = B)

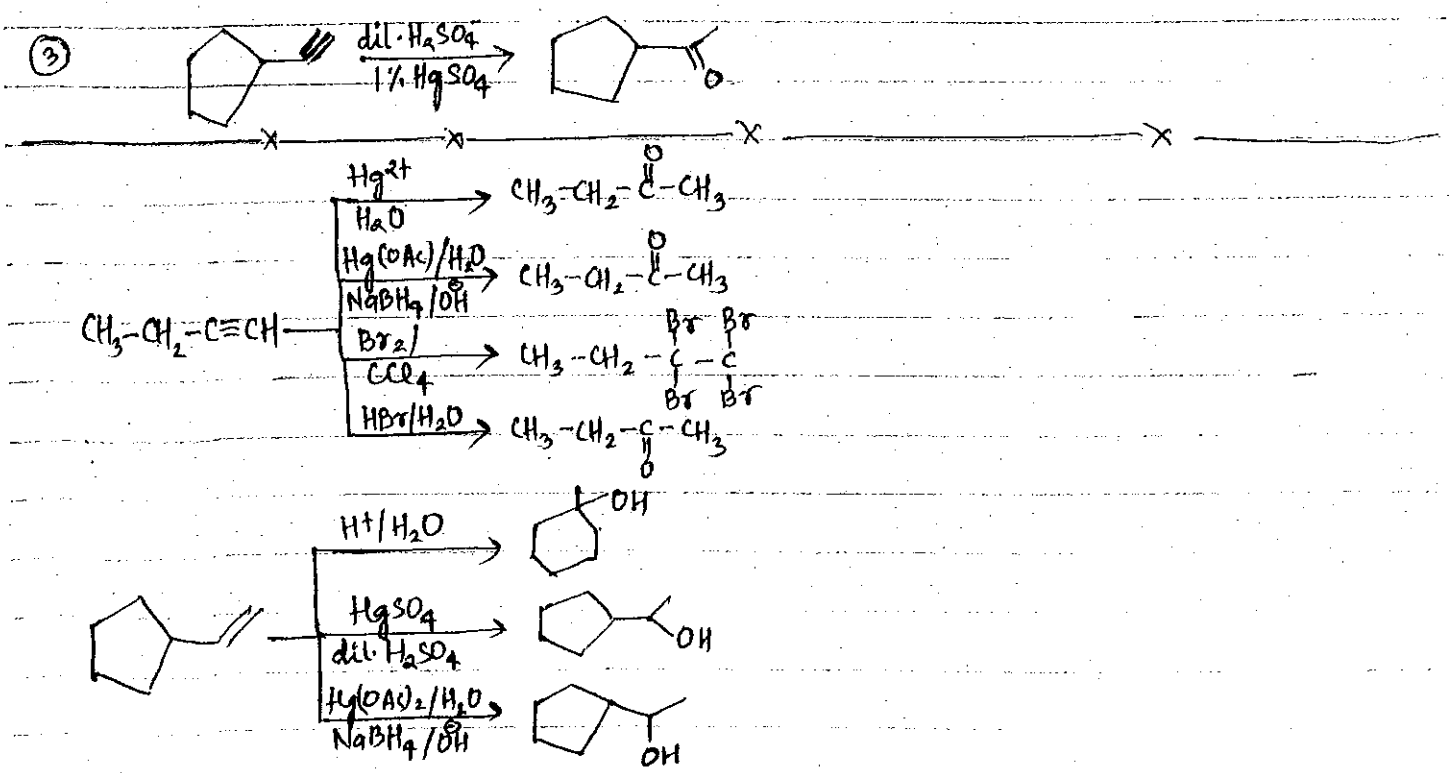
HO-Cl / CCl_4 → R·M (A ≠ B)

② 

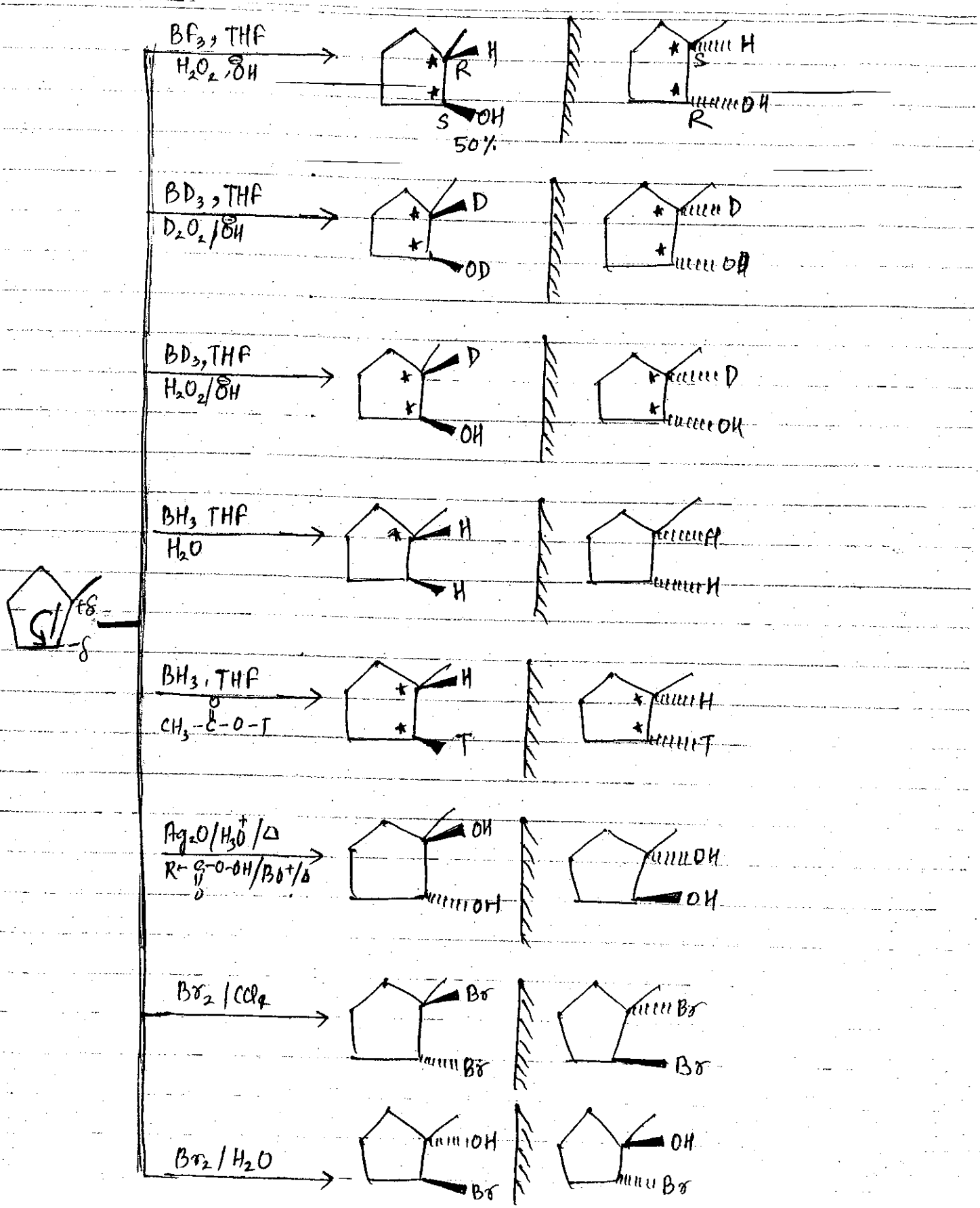
SHEET-11

① 

② 

③ 

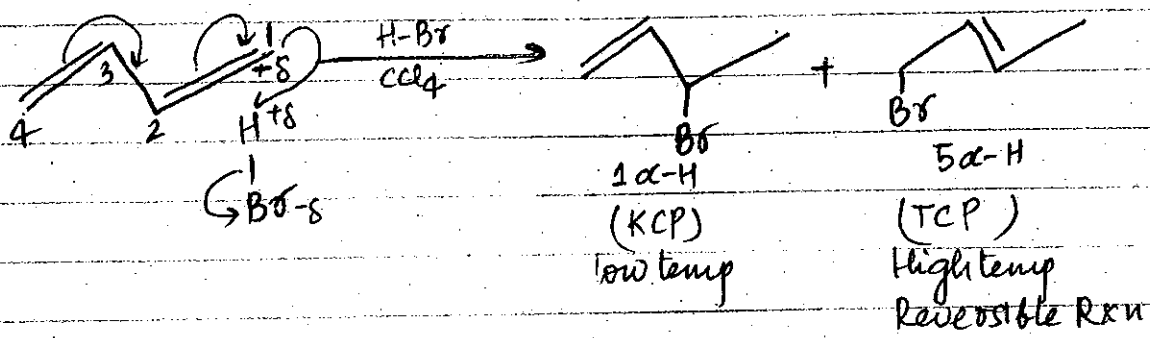
SHEET-12


BF3, THF
H2O2, ⊖OH
R
H
S
OH
50%
S
H
R
OH
BD3, THF
D2O2/⊖OH
D
OD
D
OD
BD3, THF
H2O2/⊖OH
D
OH
D
OH
BH3 THF
H2O
H
H
H
BH3, THF
CH3-C(=O)-O-T
H
T
H
T
Ag2O/H3O+/Δ
R-C(=O)-O-OH/B6+/Δ
OH
OH
OH
OH
Br2/CCl4
Br
Br
Br
Br
Br2/H2O
OH
Br
OH
Br

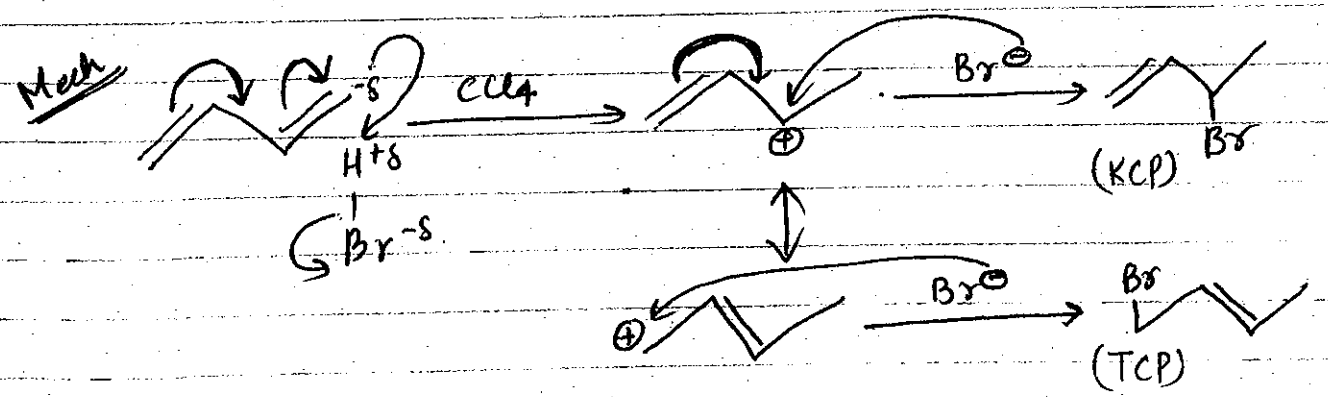
TCP = Thermodynamically Stable Product | 1,2 addition ⇒ KCP product
↓ if more stable than
KCP = TCP product

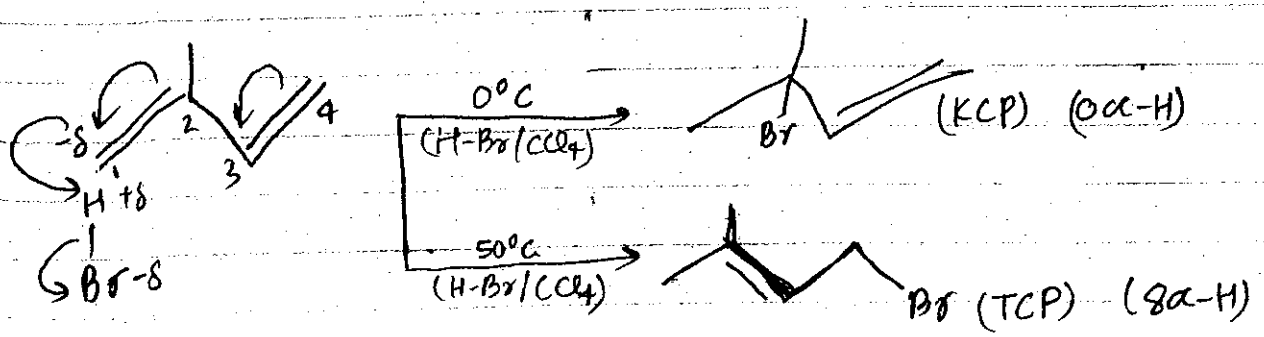
KCP & TCP Product

Kinetically Controlled Product ↔ Thermodynamically Controlled Product



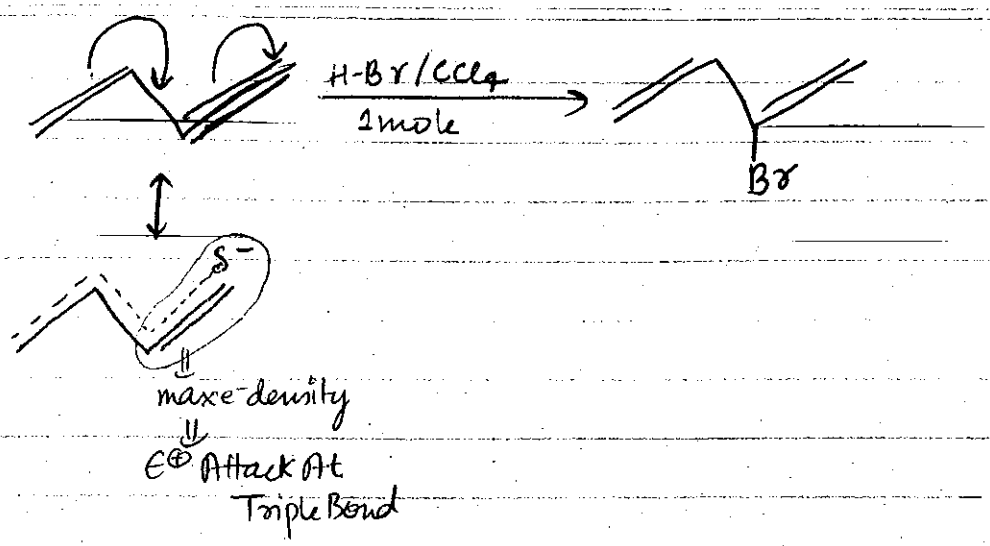
⇒ Whenever two double bond present at conjugated position then we decide KCP & TCP product
⇒ 1,2 addition always give KCP product
⇒ TCP product is thermodynamically stable product & rxn carried out at higher temp. & reversible rxn.



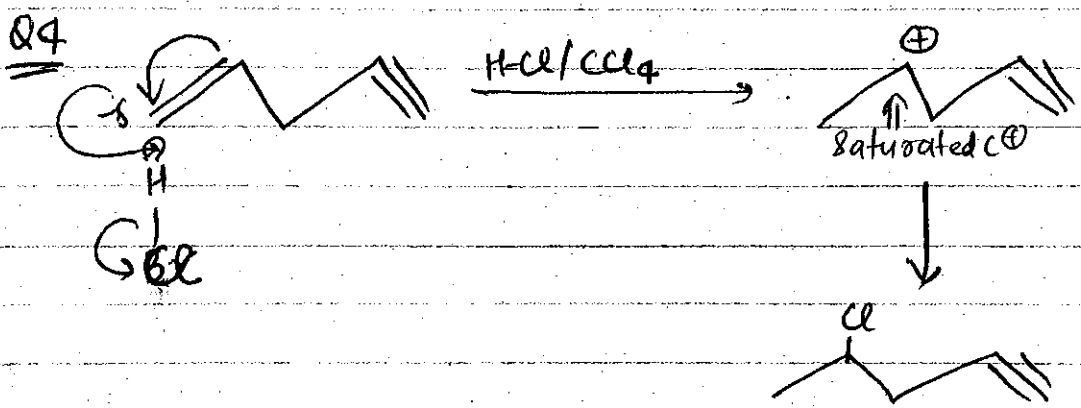


=, ≡ conjugated attack on T.B
=, ≡ non-conjugated attack on D.B
↓
as saturated cation formed

Q.3



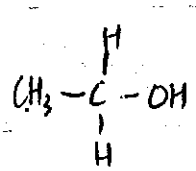
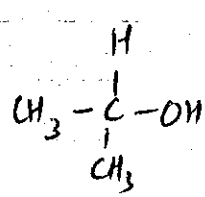
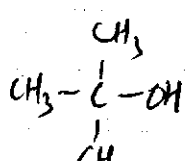
Q4



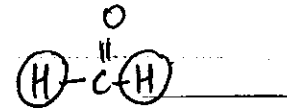
When =, ≡ bond present at conjugated position the E⊕ attack at ≡ bond due to more electron density.

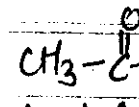
General Oxidation Of Organic Comp/ Chemistry

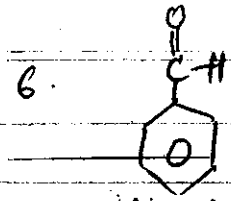
C-H ⟶ C-OH
↳ Oxidisable H

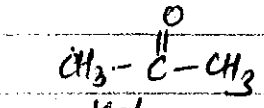
		
1° Alcohol	2° alcohol	3° Alcohol
Oxidisable H ✓	Oxidisable H ✓	Oxidisable H ✗
Oxidat" ✓	Oxidat" ✓	No Oxidat"

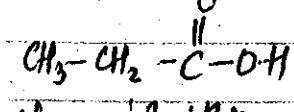
Oxidisable H C–H C এর সাথে O থাকলে তাকে বলে

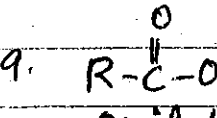
4. 
Formaldehyde
Oxidisable H ✓
Oxidatn ✓

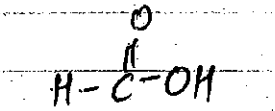
5. 
Acetaldehyde
Oxidisable H ✓
oxidatn ✓

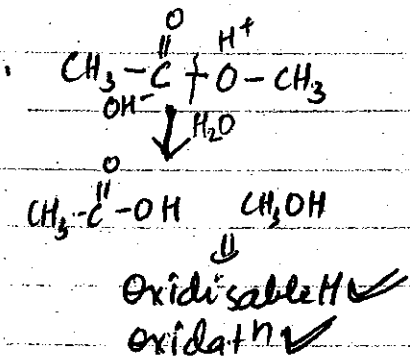
6. 
Oxidisable H ✓
Oxidatn ✓

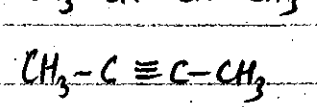
7. 
Ketone
No oxidatn ✗✗

8. 
No oxidatn ✗✗

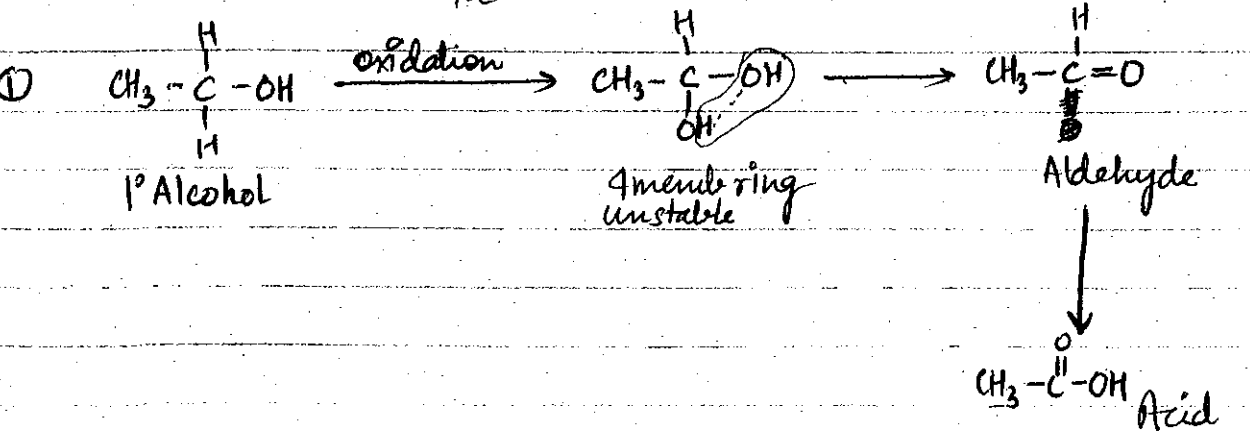
9. 
Oxidatn ✗✗

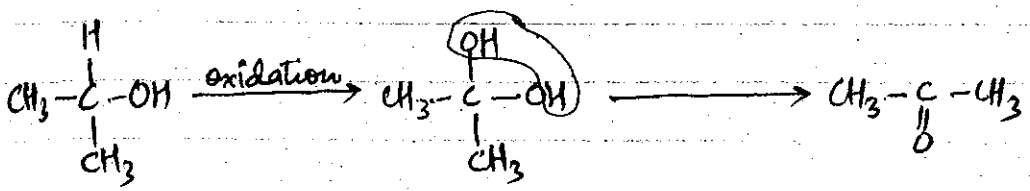
10. 
(Formic Acid)
Oxidisable H ✓
Oxidatn ✓

11. 
Oxidisable H ✓
oxidatn ✓

12. 

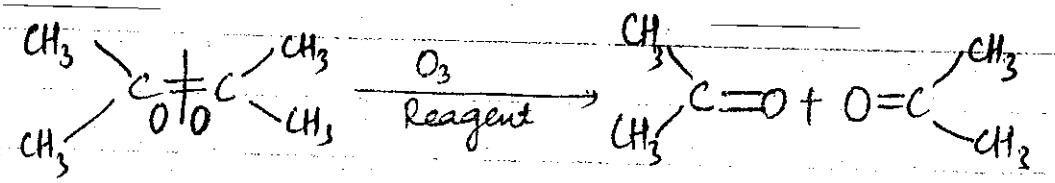
Oxidisable-H ⇒ H attach that C having min. one oxygen then the H is called Oxidisable-H

① 

② 

Ozonolysis Reaction

~~It is a kind of~~ Electrophilic Addition rxn



1 nascent Ox remain there hence Zn / dmp reagent used to prevent further oxi°.

Reagent → H_2O/Zn ⇒ Aldehyde / Ketone (Reductive ozonolysis)

H_2O/xxx ⇒ Acid / Ketone (Oxidative ozonolysis)

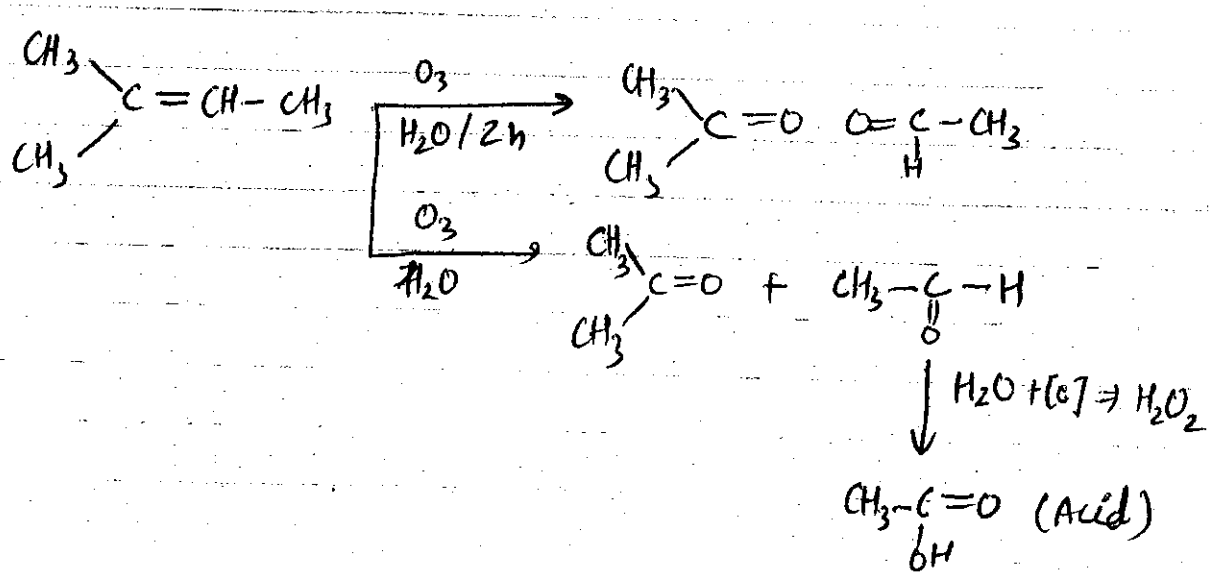
3rd oxygen or O_3

$[O] \longrightarrow [O] \xrightarrow{H_2O} H_2O + [O] \longrightarrow H_2O_2$ oxidising agent ⇓ Again oxidat^n No oxidat^n

$[O] \xrightarrow{Zn} Zn^{+2} + [O^{-2}] \Rightarrow ZnO$

Zinc remove third oxygen of ozone from rxn medium & inhibit further oxidat^n process

Q.1



Q.2 $CH_3-CH_2-CH=CH_2$

$\xrightarrow[H_2O/Zn]{O_3}$ $CH_3-CH_2-CH=O + CH_2O$

$\xrightarrow[H_2O]{O_3}$ $CH_3-CH_2-\underset{H}{\underset{|}{C}}=O + H-\overset{O}{\overset{\|}{C}}-H$

$\downarrow H_2O + [O] \rightarrow H_2O_2$

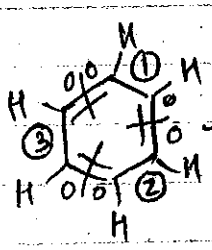
$CH_3-CH_2-\underset{OH}{\underset{|}{C}}=O$ $\quad H-\overset{O}{\overset{\|}{C}}-OH$

$\downarrow$

$HO-\overset{O}{\overset{\|}{C}}-OH$

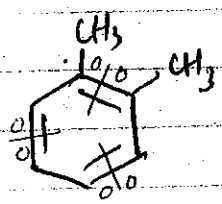
$\rightarrow O=\overset{O}{\overset{\|}{C}} \uparrow + H_2O$

Q.3



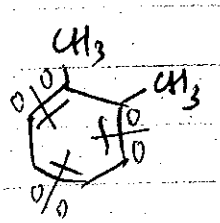
$\xrightarrow[H_2O/Zn]{O_3}$ $3\ H-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H$ Oxaldehyde.

Q.4



$\xrightarrow[H_2O/Zn]{O_3}$ $2(CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H)$ ① + $CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H$ ②

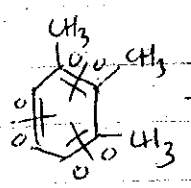
Q.5



$\xrightarrow[H_2O/Zn]{O_3}$ $CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$ ③ + $2\ H-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H$

Total three product evidence of resonance

Q.6.



$\xrightarrow[H_2O/Zn]{O_3}$ $CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H + H-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H + CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$

SHEET-13

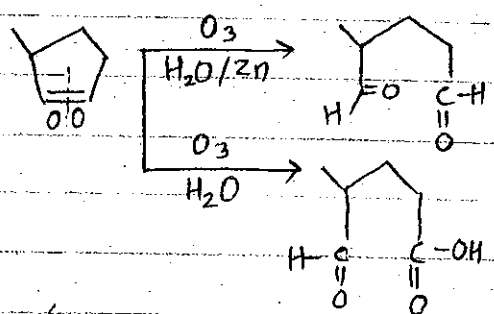
① $(CH_3)_2C=CH-CH_3$ → $(CH_3)_2C=O + O=CH-CH_3$

$(CH_3)_2C=O + O=CH-CH_3 \xrightarrow{[O]+H_2O,\ H_2O_2} CH_3-COOH$

② $CH_3-CH=O + H-CHO$ → CH_3-COOH

$CH_3-CHO \xrightarrow{H_2O_2} CH_3-COOH$

$H-CHO \xrightarrow{H_2O_2} H-COOH \xrightarrow{H_2O_2} H_2O + CO_2\uparrow$

③ 

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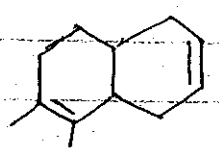
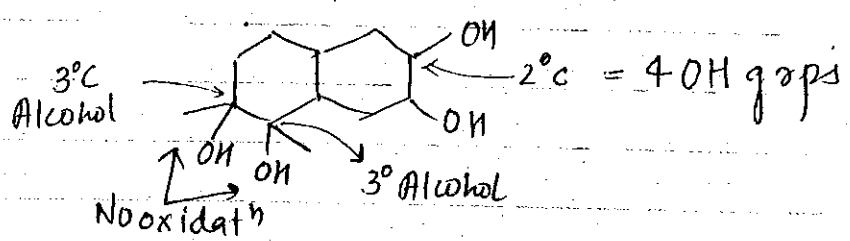
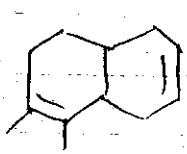
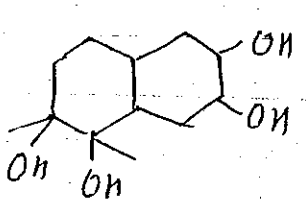
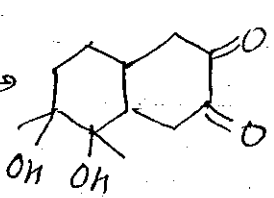
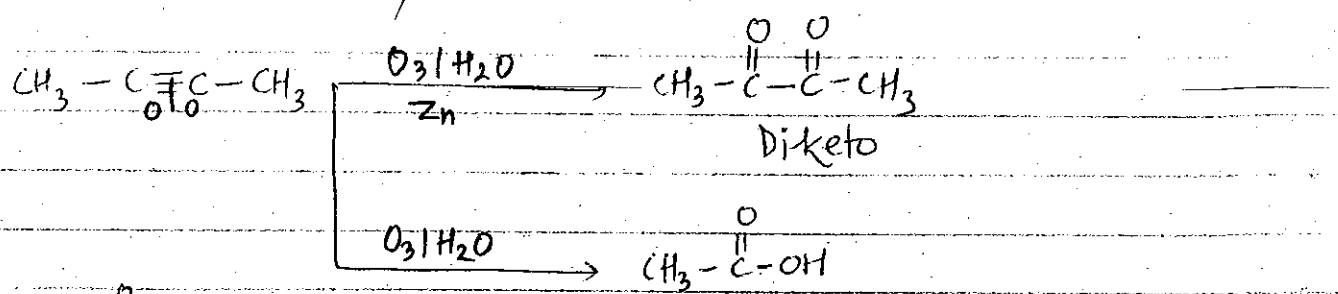
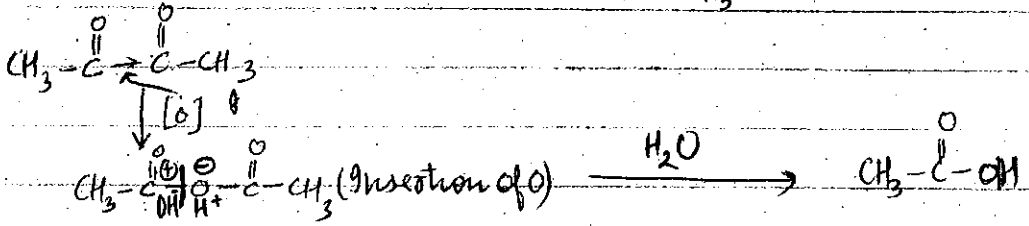
④  $\xrightarrow[KMnO_4]{1\%\ Alkaline}$ Total no. of OH grps in product



⑤  $\xrightarrow[KMnO_4]{1\%\ Alkaline}$  $\xrightarrow{KMnO_4}$ 

Ozonolysis Of Alkyne





Strong Oxidising Agent

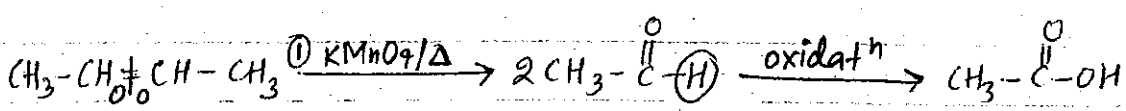
1. $KMnO_4/\Delta$
2. $K_2Cr_2O_7/\Delta$

$\Rightarrow$ Strong oxidising agent

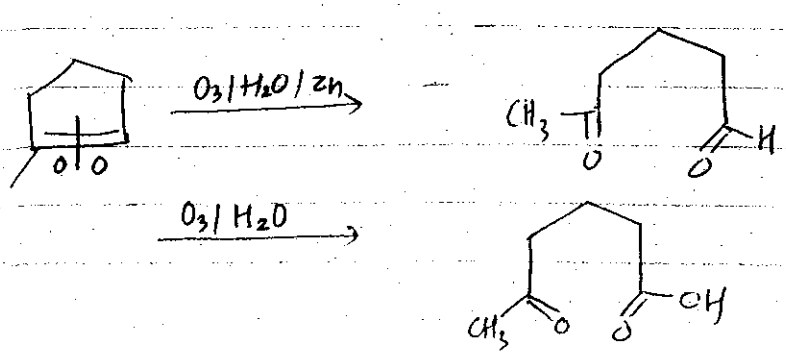
Keypoint

$KMnO_4/\Delta$
$K_2Cr_2O_7/\Delta$
$\Rightarrow O_3/H_2O \Rightarrow$ same oxidation in organic chem. (At alkene)

Q.1



Q.2



$KMnO_4/\Delta$ →

$K_2Cr_2O_7/\Delta$ →

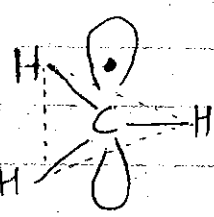
I/ Alkaline →

① $CH_3-C\equiv CH \xrightarrow[H_2O_2\ \bar{O}H]{BH_3,\ THF}$ A $\xrightarrow{K_2Cr_2O_7/\Delta}$ $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH$

A = $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H$

② $CH\equiv CH \xrightarrow{Hg^{+2}/H^+/H_2O} CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow{KMnO_4/\Delta} CH_3-\overset{O}{\overset{\|}{C}}-OH$

Free Radicals



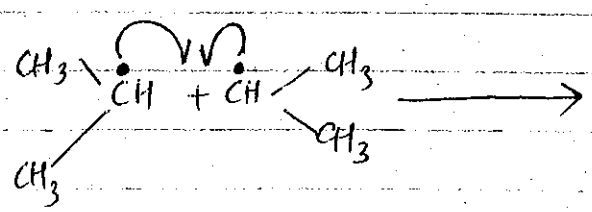
⇒ highly unstable
⇒ more reactive

Radical mainly give dimerisat^n combind^n rxn. During dimerisat^n rxn there is no requirm of activat^n energy bcoz σ bond formin pro When 2 same type radical dimerise then only single product is obtained

① $CH_3 + CH_3 \longrightarrow CH_3-CH_3$ $\quad \Delta H = -Ve$

only single product
% of yield ↑

② $CH_3-CH_2 + CH_2-CH_3 \longrightarrow CH_3-CH_2-CH_2-CH_3$

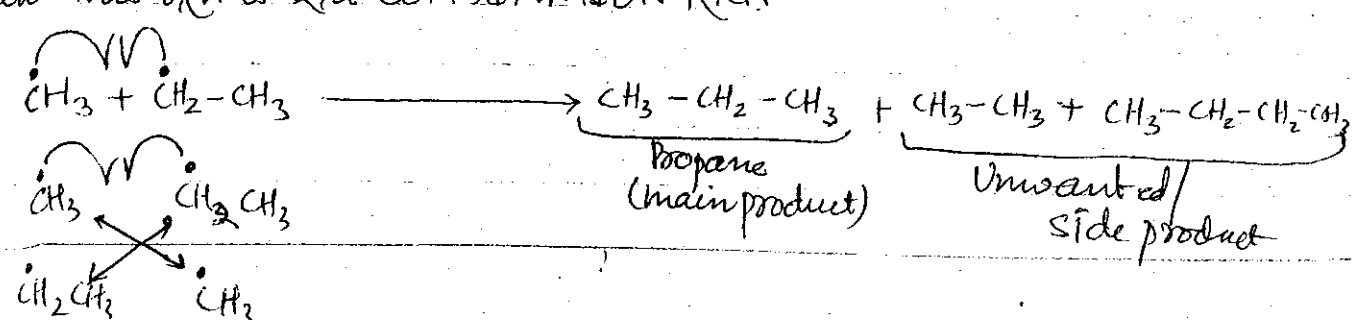
③ 

Up
⇒ Size of F·R ↑
⇒ Steric hindrance ↑
⇒ Rate of Dimerisa decrease ↓
⇒ % of yield ↓
Down.

KEY POINT

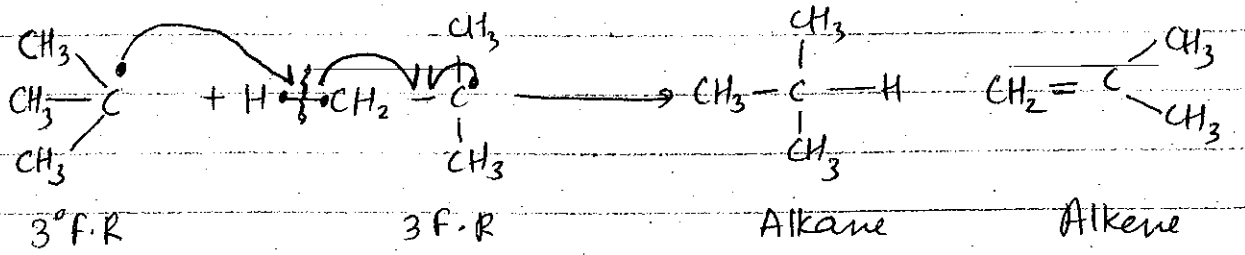
$$\text{Rate of dimerisat}^n \propto \frac{1}{\text{Steric hindrance}}$$

Whenever two different radical are dimerise then mixture of product obtain this rxn is k/a COMBINATION RXN.



$CH_3 + CH_2-CH_3 \longrightarrow \underbrace{CH_3-CH_2-CH_3}_{\text{Propane (main product)}} + \underbrace{CH_3-CH_3 + CH_3-CH_2-CH_2-CH_3}_{\text{Unwanted / Side product}}$

Disproportionation Rxn



Whenever 3° free radical or sterically hindered radical are dimerise then effective collision b/w 3° free radical not possible. In this condition, 3° free radical give disproportionate product

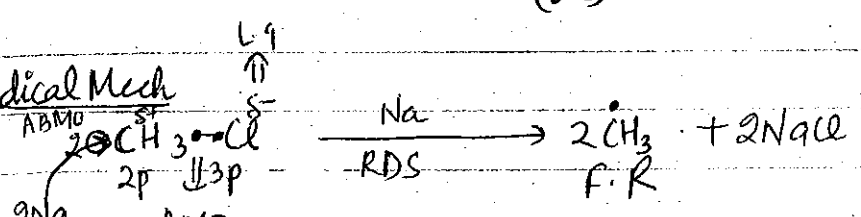
Generation Of Free Radical

① Formation Of free radical by metal

WURTZ REACTION

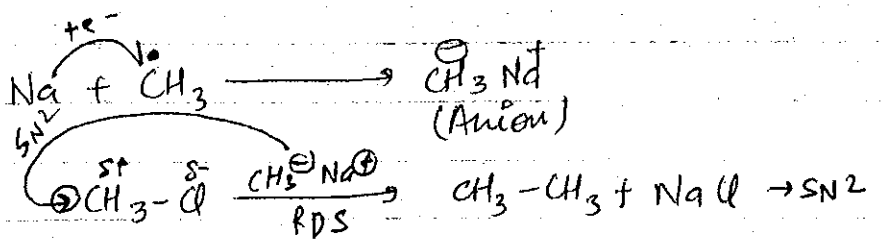
Net Rxn: $CH_3 + Cl + 2Na + Cl + CH_3 \xrightarrow[(D\cdot E)]{\text{Dry ether}} CH_3 - CH_3 + 2NaCl$

Mech: Radical Mech



$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3 - CH_3 \quad [\Delta H = -ve]$$

Ionic Mech



- Wurtz rxn is used to Inc no of carbon in hydrocarbon.
- C-C bond formed in this rxn
- Wurtz rxn completed with radical & ionic both mechanism.
- R-X bond breaking step in RDS of rxn
- Reactivity of rxn $\boxed{R\text{-}I > R\text{-}Br > R\text{-}Cl > R\text{-}F}$ Acc. to L.G.

Type Of Wurtz Rxn

① Simple Wurtz

When two same type alkyl halide participated in wurtz rxn then it is Ya SIMPLE WURTZ.

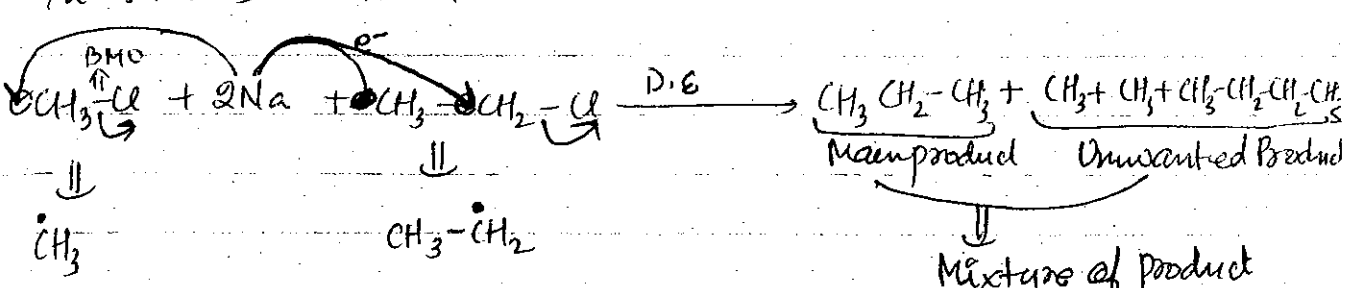
eg. $CH_3\text{-}Cl + 2Na + CH_3\text{-}Cl \xrightarrow[(D.E)]{\text{Dry ether}} CH_3\text{-}CH_3 + NaCl$

$\downarrow$ $\quad\quad$ $\downarrow$

$\dot{C}H_3 \quad\quad \dot{C}H_3$

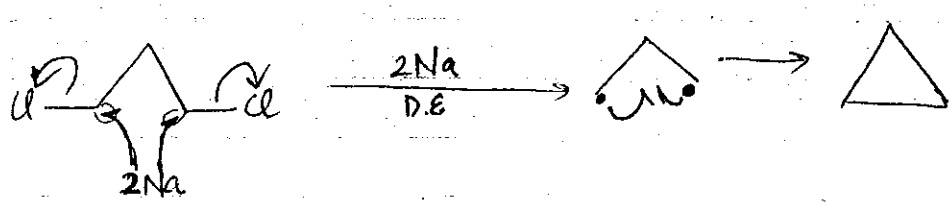
② Mixed Wurtz

When two diff type alkyl halide participated in Wurtz rxn then it is Ya MIXED WURTZ.



③ Intramolecular Wurtz

Q.1



Wurtz Reaction

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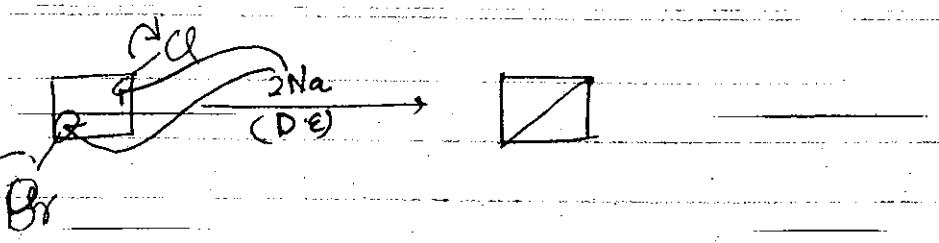
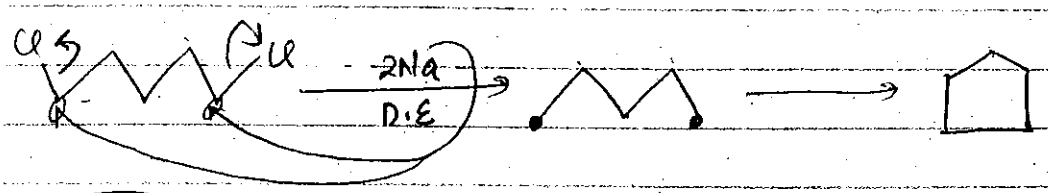
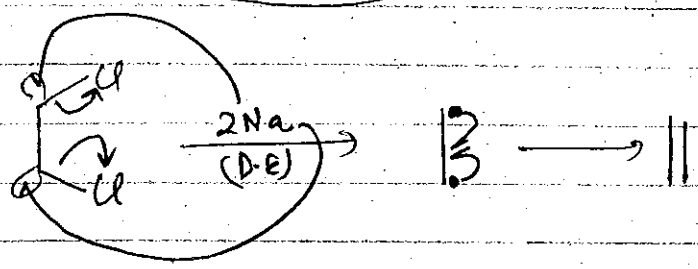
Q2



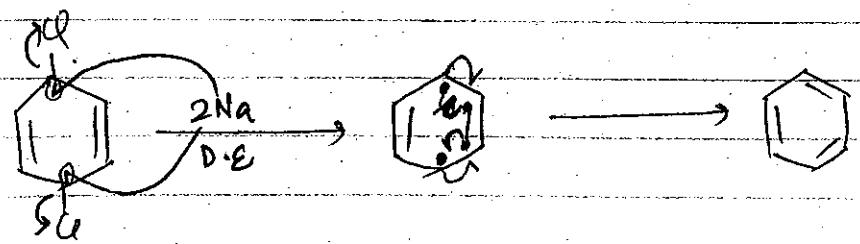
Q.3



Q.4



Q.5



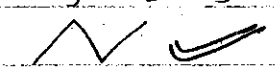
Disadvantages

Odd no. C containing alkane does not formed by Wurtz Rxn because mixture of product is obtained.

CH_4 cannot formed by Wurtz Rxn.

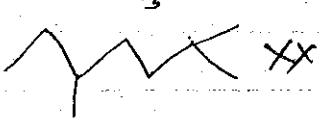
CH_3-CH_3 ✓

$CH_3-CH_2-CH_3$ XX



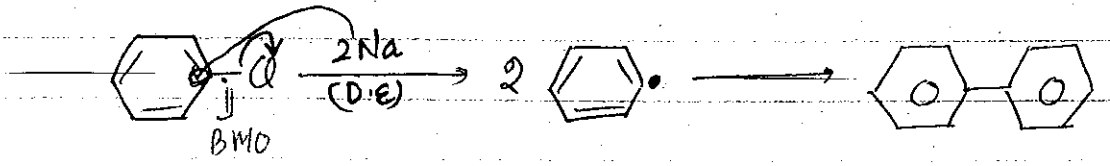
XX

$CH_3-\underset{CH_3}{\overset{}{C}}-CH_3$ XX

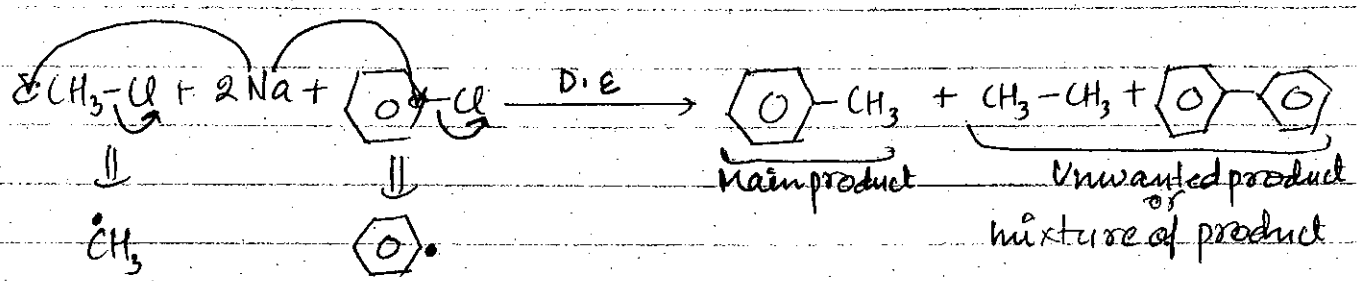


XX

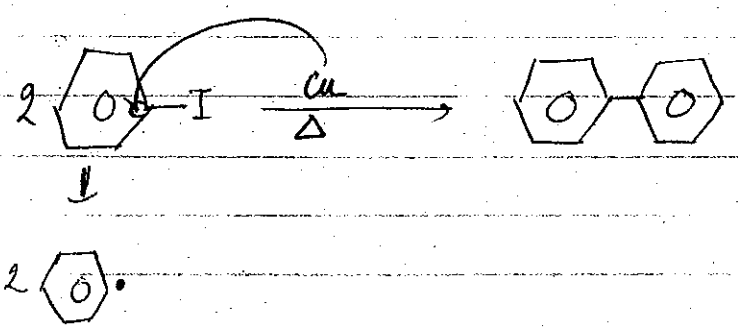
(2) Fittig Rxn



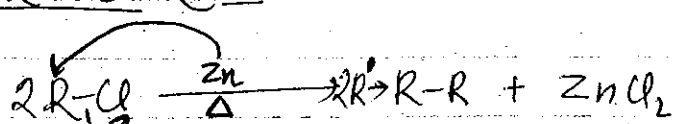
(3) Wurtz Fitting Rxn



④ Ullmann's Condensation



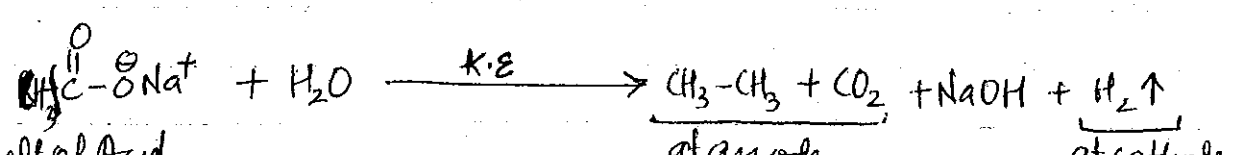
⑤ Frankland Rxn



② Formation Of Free Radical By Using Of Current

Kolbe's Electrolysis (K·E)

Net Rxn



Mech At ANODE $2CH_3-\overset{O}{\overset{\|}{C}}-O^{\ominus} \longrightarrow 2CH_3\cdot + \overset{O}{\overset{\|}{C}}-O\cdot + 2e^-$

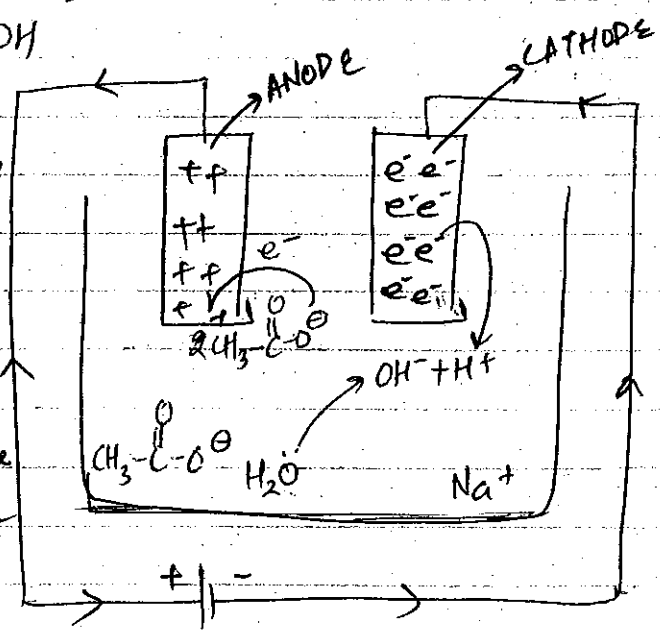
$2CH_3\cdot + \overset{O}{\overset{\|}{C}}=O\uparrow$

At Cathode $CH_3 + CH_3 \longrightarrow CH_3-CH_3$ (At anode)

$H_2O \rightleftharpoons H^+ + \bar{O}H$

$2H^+ \longrightarrow 2H\cdot \longrightarrow H_2\uparrow$

$Na^+ + OH^- \longrightarrow NaOH$



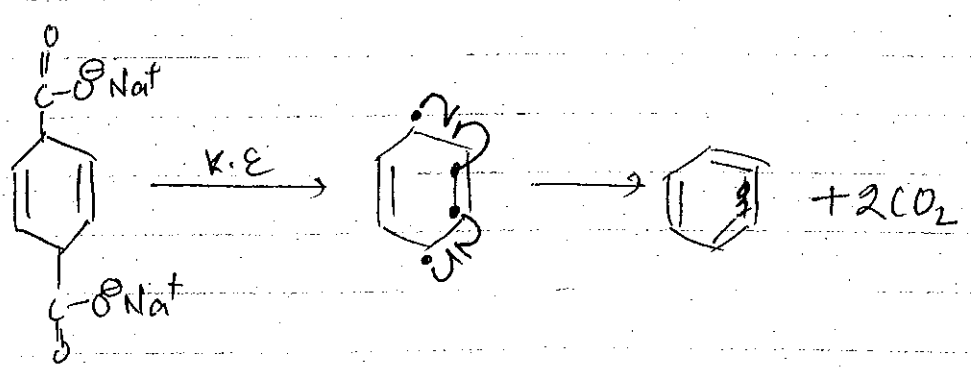
→ During K·E ethane gas evolved at anode by elimination of CO_2

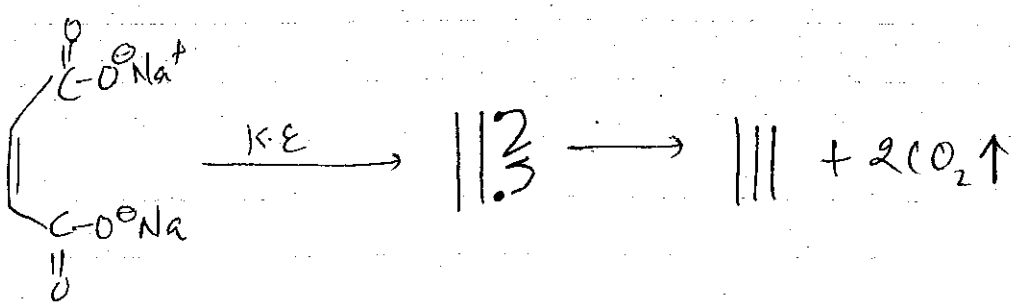
→ H_2 gas eliminate at cathode

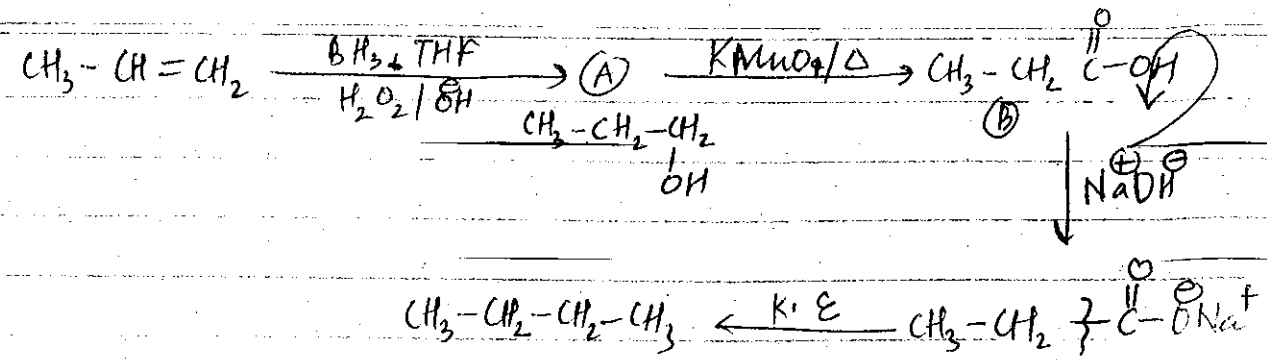
→ If salt of formic acid used in K·E then H_2 gas evolved at both electrode

→ If K·E NaOH formed in medium so pH of medium ↑ses

→ CH_4 cannot formed by K·E

① 

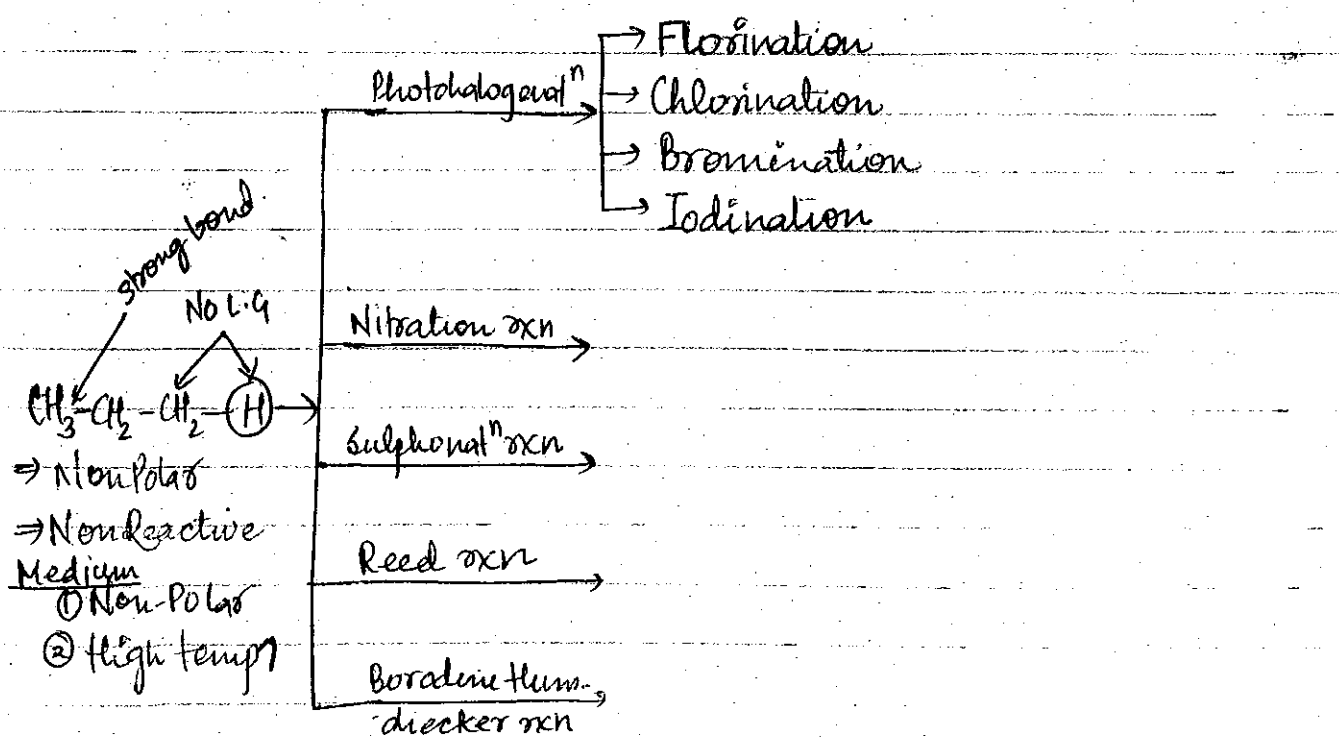
② 



③ Formation Of Free Radical By Use Of Photon

FREE RADICAL SUBSTITUTION RXN (FRSR)

formation of reactive alkane



Formation of reactive alkane

Photohalogenation

Net rxn

$$\underbrace{R-H}_{\text{alkane non-reactive}} + X_2 \xrightarrow{h\nu} \underbrace{R-X}_{\text{reactive}} + H-X$$

highly reactive

Gen. Mech. of F.R.SR.

Mech F.R follow chain rxn

① Chain initiation (C.I) ⇒ hν / Δ / R_2O_2 {Chain Initiator}

② Chain Propagation (C.P) ⇒ product forming step

③ Chain Termination (C.T) ⇒ Max^m dimerisat^n (most exothermic step)

① Chain Initiator (C.I)

$X\!-\!X \xrightarrow{h\nu} 2X^{\bullet}$; ΔH = ⊕ve (endothermic step)

5000 5000 (Trace amt) 500

→ highly unstable, more reactive 1000

② Chain Propagation (C.P)

i) $R\!-\!H + X^{\bullet} \xrightarrow[RDS]{} R^{\bullet} + H\!-\!X$ (Rxn give K.I.E)

F.R. intermediate

ii) $R^{\bullet} + X\!-\!X \longrightarrow R\!-\!X + X$ (Product forming step)

③ Chain Termination (C.T)

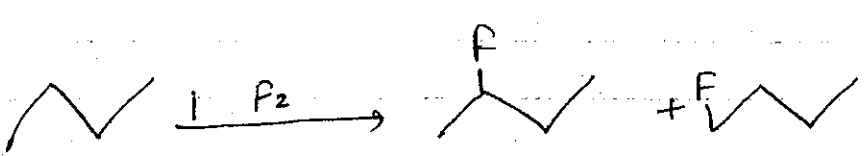
$R^{\bullet} + {}^{\bullet}X \longrightarrow R\!-\!X$

$R^{\bullet} + {}^{\bullet}R \longrightarrow R\!-\!R$ ⇒ max^m Dimerisat^n ⇓ max. exothermic rxn.

ⓐ Florination Rxn

$CH_4 + F_2 \xrightarrow{h\nu} C_{black} + H\!-\!F$; ΔH = ⊖ve highly exothermic & explosive rxn.

(1C = coke) Strongbond



Imp Point

Florination rxn ~~is highly exothermic & explosive rxn~~
highly reactive & non selective
does not depends on stability of free radical
possible even in dark
C black obtained as a product.

Reactivity-Selectivity concept

Reactivity ⇑ → Selectivity ⇓
Selectivity ⇑ → Reactivity ⇓

Per H selectivity Ratio

$3^\circ H : 2^\circ H : 1^\circ H$
1 : 1 : 1

⑥ Bromination Rxn

$$\underset{\text{(Non reactive)}}{R-H} + Cl_2 \longrightarrow \underset{\text{(Reactive)}}{R-Cl} + H-Cl$$

① Chain Initiator (C·I)

$Cl\cdot\!\!\cdot Cl \longrightarrow 2Cl^\bullet$ $\quad \Delta H = (+)ve$ endothermic step
(Sun's rays)
(Trace amt.)
↳ Highly unstable
↳ more reactive

$\Delta H = Cl_2 > F_2$
(more endothermic rxn)

② Chain Propagation (C·P)

i) $R\cdot\!\!\cdot H \xrightarrow{Cl^\bullet} R^\bullet + H-Cl$ (Rxn give K·L·E)
(F.R intermediate)
(ΔH = slightly exothermic rxn)

ii) $R^\bullet + Cl\cdot\!\!\cdot Cl \longrightarrow R-Cl + Cl^\bullet$ (Product forming step

③ Chain Termination (C·T)

$R^\bullet + Cl^\bullet \longrightarrow R-Cl$
$Cl^\bullet + Cl^\bullet \longrightarrow Cl-Cl$
$R^\bullet + R^\bullet \longrightarrow R-R$

} ⇉ Mass Dimerisation ⇓ mass endothermic rxn

Per H- selectivity ratio

3°H :	2°H :	1°H
5	3.8	1

Chlorination rxn is slightly exothermic rxn
may depend on stability of free radical (मौना ई)

Bromination Rxn

$$\underbrace{R\text{-}H}_{\text{Non-reactive}} + Br_2 \xrightarrow{h\nu} \underbrace{R\text{-}Br}_{\text{Reactive}} + H\text{-}Br$$

① Chain Initiator Rxn

$$Br\text{-}Br \xrightarrow{h\nu} 2Br^{\bullet} \qquad \Delta H = +ve \text{ (endothermic rxn)}$$

Br–Br: 5a⁰⁰ Str⁰⁰ (Trace amt)

$2Br^{\bullet}$ → highly unstable
→ more reactive

② Chain Propagation (C.P)

i) $R\text{-}H + Br^{\bullet} \xrightarrow[RDS]{} R^{\bullet} + H\text{-}Br$ (Rxn give K.I.E)

$R^{\bullet}$: F.R intermediate

(ΔH = +slightly endothermic rxn)

ii) $R^{\bullet} + Br\text{-}Br \longrightarrow R\text{-}Br + Br^{\bullet}$ (Product forming step)

③ Chain Termination (C.T)

① $R^{\bullet} + Br^{\bullet} \longrightarrow R\text{-}Br$

② $Br^{\bullet} + Br^{\bullet} \longrightarrow Br\text{-}Br$

③ $R^{\bullet} + R^{\bullet} \longrightarrow R\text{-}R$

} ⇒ Max^m dimerisat^n
⇓
max^m exothermic rxn

Per H- Selectivity Ratio

$3°H : 2°H : 1°H$

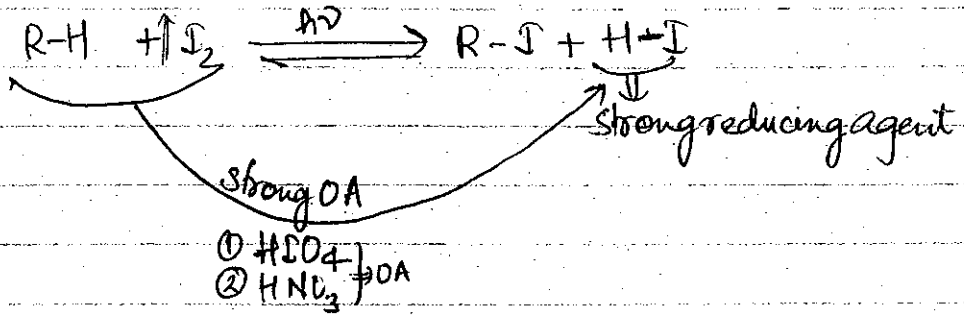
$1600 : 82 : 1$

Bromination rxn is slightly endothermic rxn.

highly selective & non-reactive rxn.

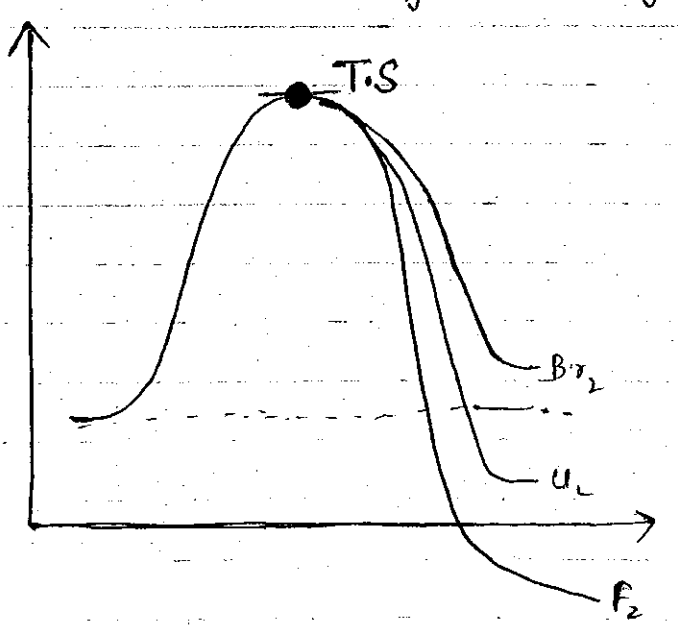
100% depends on stability of free radical

④ Iodination Rxn



$$\underset{(OA)}{HIO_4} + \underset{(RA)}{HI} \longrightarrow I_2\uparrow + H_2O$$

Iodination rxn is highly endothermic & reversible rxn we use strong oxidising agent.



Q.1 $CH_4 \xrightarrow[(excess)\ -HCl]{Cl_2} CH_3-Cl \xrightarrow[-HCl]{Cl_2} Cl-CH_2-Cl \xrightarrow{Cl_2} CHCl_3 \xrightarrow{Cl_2} CCl_4$

(Methylidene chloride) (Chloroform) (Pyrene)

CH_4 ⇓ Firedamp (explosive)

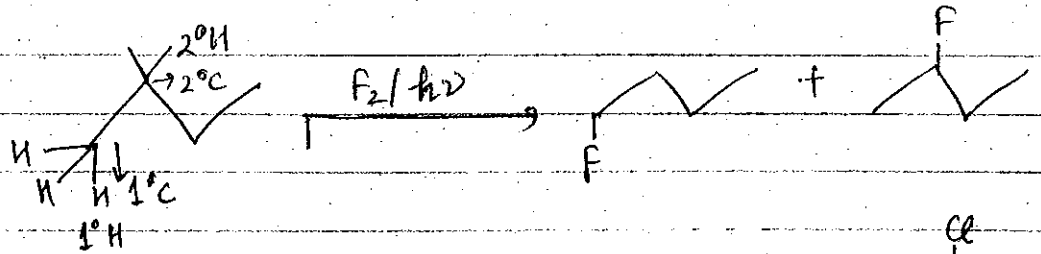
Q.2 CH_4 (excess) $+ Cl_2 \longrightarrow CH_3-Cl$ (major)

BSL ⇒ Bright sunlight
DSL ⇒ Diffused sunlight

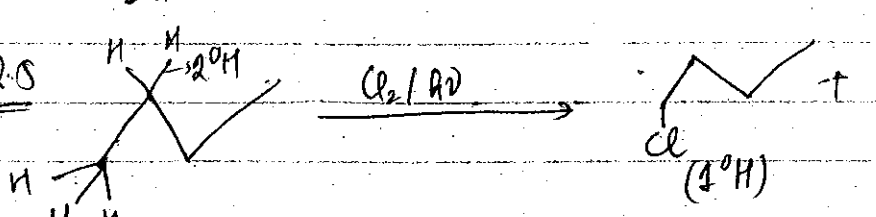
Q.3 $CH_4 + Cl_2$

- $\xrightarrow[excess]{Cl_2/h\nu} CH_3-Cl$ ....
- $\xrightarrow{Cl_2/BSL}$ C (Black)
- $\xrightarrow{Cl_2/DSL} CH_3-Cl$ ----

Q.4



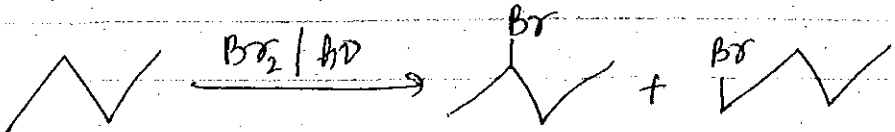
Q.5



No. of 1° H ⇒ 6 ⇐ No. of 2° H 4

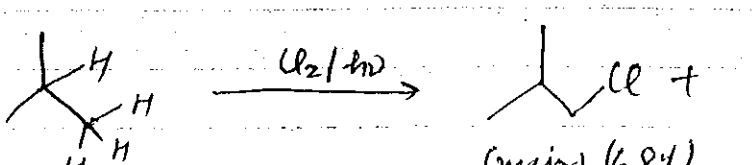
Per H-selectivity ratio	1	3.8
Productivity ratio	1 × 6 = 6	3.8 × 4 = 15.2 (major)

Q.6



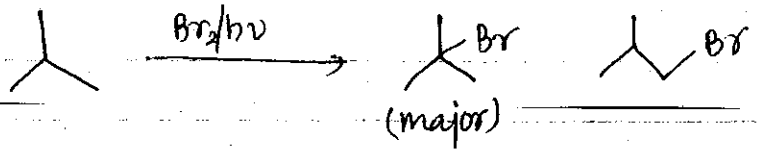
(more stable 3°R) (Major)

Q.7



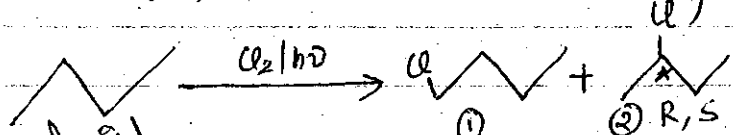
(major) (68%) (minor) (32%)

	1° H	3° H		1° H	3° H
No. of H atom	9	1	Productivity ratio	9	5
Per H-selectivity	9 × 1	1 × 5			



No. of possible monochloro product

Q.1



fractional distillation

① Total product ⇒ 3 (monochloro)

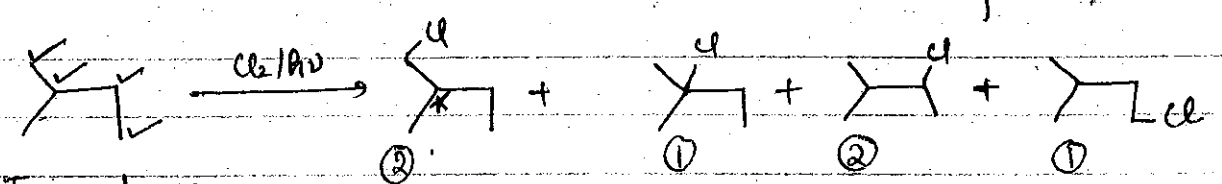
② Total no. of monochloro product (Including stereo) ⇒ ③

③ " excluding (stereo) ⇒ ②

④ Total no. of fractional distilled product ⇒ ②

as enantiomers cannot be seperated.

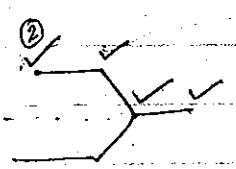
Q. 2



Isopentane

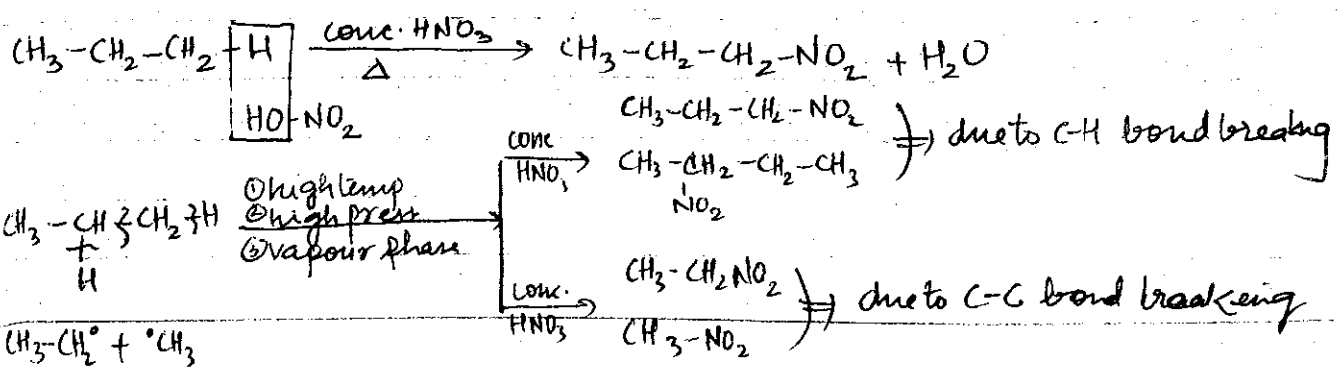
① 6 (Total)
② 6 (excluding stereo)
③ 4 (including stereo)
④ 4 (distilled product)

Q.3



Total ⑧

② Nitration Rxn



अगर $SOCl_2$ होगा तो DARZEN RXN

Benzene पे लगाना है तो $E^{\oplus}$
↳ और Next पे Radical

(II), (III) rxn be selective go acc. to stability.

Ketone O_3 Zn H_2O → same product
O_3 H_2O

Nitration rxn is carried out at higher temp, higher press. & in vapour phase condition it involve breaking of C-C & C-H bond & give mix. of product

(III) Sulphonation Rxn

$CH_3-CH_2-CH_2-H$ —(i) conc. H_2SO_4, (ii) Δ (High temp)→ $CH_3-CH_2-CH_2-SO_3H$ & $CH_3-CH(SO_3H)-CH_3$

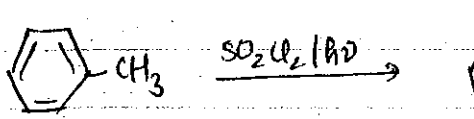
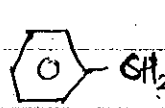
Alkane Aliphatic Benzene
Normal cond.ⁿ
Alkane → Aromatic (cond.ⁿ)

$SO_3 + H_2O \longrightarrow H_2SO_4$

(IV) Reed Rxn

i) $R-H$ —(i) SO_2, (ii) Cl_2, (iii) hν→ $R-SO_2Cl + HCl$
Alkyl suphonyl chloride.

ii) $R-H + SO_2Cl_2 \xrightarrow{40-80^\circ C} R-Cl + S(=O)=O\uparrow + H-Cl$
Suphonyl chloride

Q.1  CH_3 —SO_2Cl_2/hν→  CH_2Cl

(V) Borodine Hunsdiecker Rxn

$CH_3-\overset{O}{\overset{\|}{C}}-OH$ —(i) AgOH, (ii) Br_2/CCl_4→ $CH_3-Br + CO_2\uparrow + AgBr\downarrow$ (ppt)

(I) $2CH_2=CH_2$ —BH_3, THF, H_2O→ $2CH_2(H)-CH_2(H)$ (A) —Br_2/hν→ $2CH_3-CH_2-Br$ (B) —2Na/DE→ $CH_3-CH_2-CH_2-CH_3$ (C) —Br_2/hν→ $CH_3-CH_2-CH(Br)-CH_3$ (D)

(2) $2CH\equiv CH \xrightarrow[1\%\ HgSO_4]{dil\ H_2SO_4} 2CH_3-\underset{\underset{O}{\|}}{C}-H \xrightarrow{KMnO_4} 2CH_3-\underset{\underset{O}{\|}}{C}-OH \xrightarrow{NaOH} 2CH_3-\overset{O}{\overset{\|}{C}}-O^-Na^+$

(A)

CH_3-CH_3 ← (KI, $AgOH, Br_2/CCl_4$) ← CH_3-Br

④ Formation Of Free Radical by using heat (Δ)

FREE RADICAL ADDITION REACTION (FRAR) / PEROXIDE EFFECT / KHARASH EFFECT / ANTI-M. EFFECT (RX

Net rxn

$CH_3-CH=CH_2 \xrightarrow[\Delta]{H-Br/R_2O_2} CH_3-CH_2-CH_2-Br + R-OH$

Mech ① C.I →

(i) $R-\ddot{O}-\ddot{O}-R \xrightarrow{\Delta} 2\,R-O^{\bullet}$ ΔH = (+)ve (endothermic)

Peroxy linkage

(Trace amt.)

(ii) $R-O^{\bullet} + H-Br$ (1s, 4p)

→ $Br^{\bullet} + R-O-H$ (2p, 1s) ΔH = (−)ve (exothermic)

→ $R-\ddot{O}-\ddot{Br}: + H^{\bullet}$ (2p, 4p) ΔH = Endothermic XXX

② C.P →

i) $CH_3-\overset{A}{CH}=\overset{B}{CH_2} + Br^{\bullet}$ → $CH_3-\dot{C}H-CH_2-Br$ (2°) more stable FR (5 α-H) (ΔH = (−)ve)

→ $CH_3-CH(Br)-\dot{C}H_2$ less stable F.R (1°) (1 α-H)

In case of H.I this rxn is ENDOTHERMIC

I → CP ⇒ 1st step endothe exo
Cl → CP ⇒ 1st step exo 2nd endo

(ii) $CH_3-\dot{C}H-CH_2 + H-Br \longrightarrow CH_3-\underset{Br}{\overset{H}{CH}}-CH_2 + Br^{\bullet}$ [Product forming step]
Br H (Product)

In case of HCl this step is ENDOTHERMIC

(iii) C.T

$R-\overset{\curvearrowright}{O}\cdot + \cdot O-R \longrightarrow R_2O_2$

$Br^{\bullet} + Br^{\bullet} \longrightarrow Br_2$

Imp Point
Peroxide effect completed with FRA Mechanism
In peroxide effect Anti-M product is obtained
*Among all H-X only HBr give peroxide effect. Rest like HI, HCl, HF) give simple Markonikov addn oxn with peroxide
In case of HI first step of chain propagation is endothermic
In case of HCl second step of C.P is endothermic

$CH_3CH=CH_2 \xrightarrow{HBr,\ R_2O_2} CH_3-\underset{Br}{CH_2}-CH_2$ (Peroxide Effect)

$\xrightarrow{HI,\ R_2O_2} CH_3-\underset{I}{CH}-CH_3$ (Simple M addition)

$\xrightarrow{HCl,\ R_2O_2} CH_3-\underset{Cl}{CH}-CH_3$ "

$\xrightarrow{HBr,\ CCl_4} CH_3-\underset{Br}{CH}-CH_3$ "

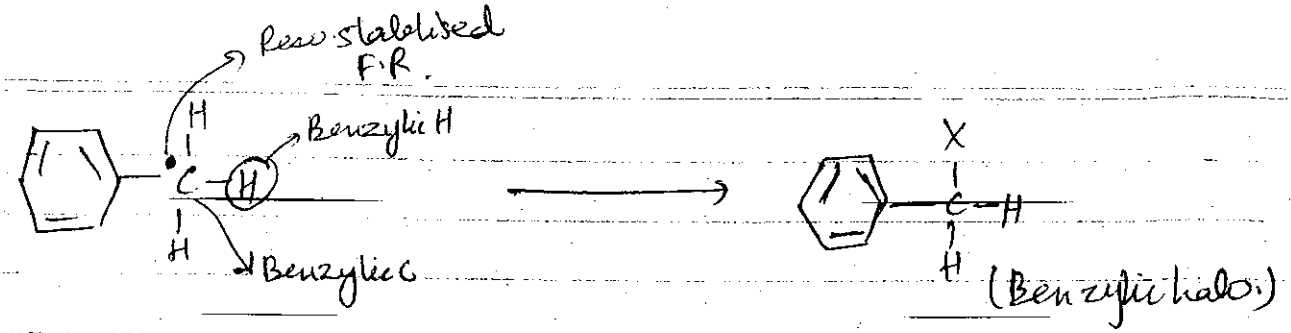
Allylic & Benzylic Halogenation (Selective Halogenation)

(1) $H-\underset{H}{\overset{H}{C}}-CH=CH_2 \longrightarrow H-\underset{H}{\overset{X}{C}}-CH=CH_2$

(H) → Allylic hydrogen
→ Reso Stabilised FR
Allylic Carbon

(Allylic halogenation)

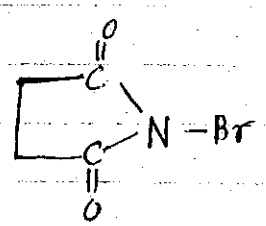
Radical always zero stable



Reagent used for allylic & benzylic halogenat^{n}.

Bromination

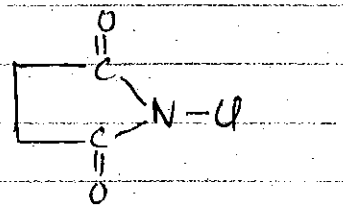
① NBS [N-Bromosuccinimide]



② Br_2/hν/high temp (Δ)

Chlorination

NCS [N-Chloro succinimide]



Cl_2/hν/Δ (high temp)

NBS & NCS form always reso stabilised F.R.

NBS in Organic chemistry

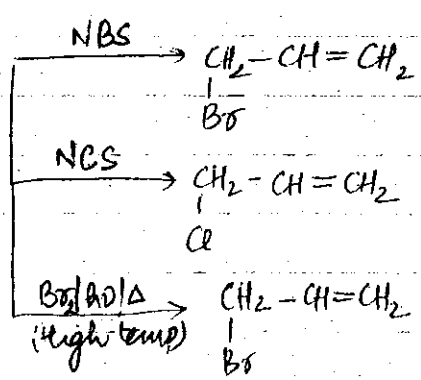
Halogenation at allylic & benzylic position.

Oxidise 1° & 2° alcohol into their respective aldehyde & ketone

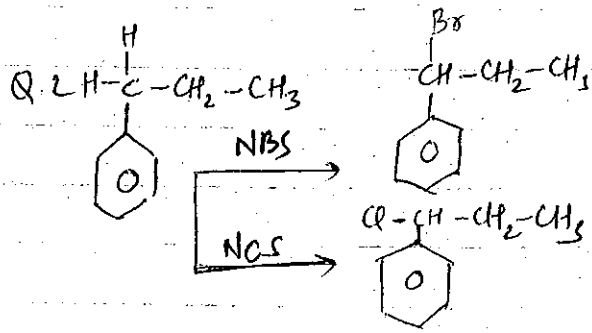
1° Alcohol $\xrightarrow{NBS}$ Aldehyde

2° Alcohol $\xrightarrow{NBS}$ Ketone

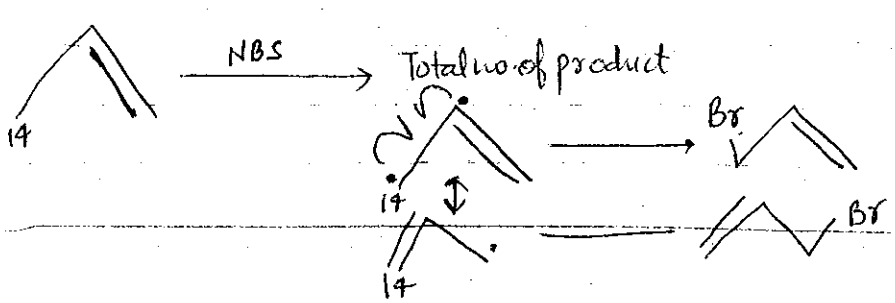
Q.1 $CH_3-CH=CH_2$



Q.2

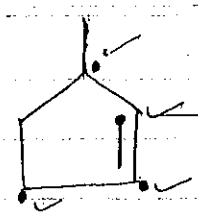


Q.3



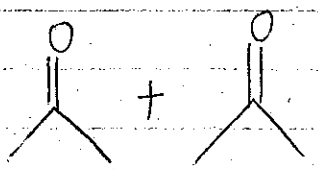
Mg का प्रयोग
↳ Pinacolone diol में
↳ Grignard reagent में

4

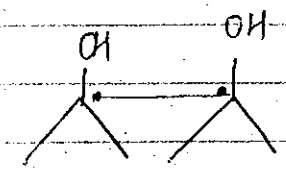


NBS → 4 Total No. of product without stereo

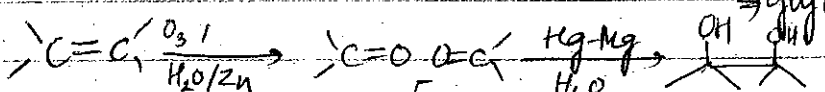
5. Pinnacolone Rxn



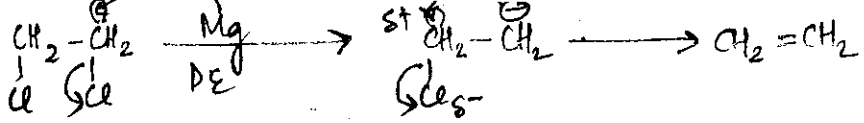
$\xrightarrow[H_2O]{Hg-Mg}$



⇒ Pinacolone product
→ diol product
→ glycol product



(Anion) Nucleophile.



For 1,3 dihalide → △

for 1, 4 & above G.R formed.

Anion / Nucleophile ($Nu^{\ominus}$)

Anion mainly give three rxn:

(I) Acid base rxn

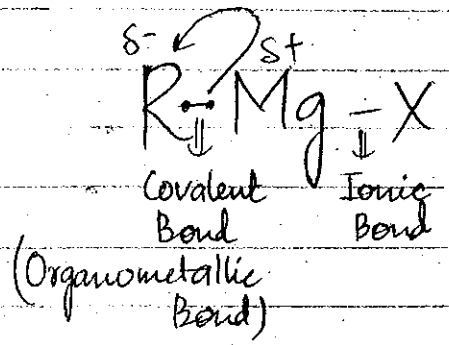
(II) Nucleophilic Addition Rxn (NAR)

(III) Nucleophilic Substitution Rxn (NSR)

Acid base Rxn Of Anion

Grignard reagent is a ORGANOMETALLIC COMP.

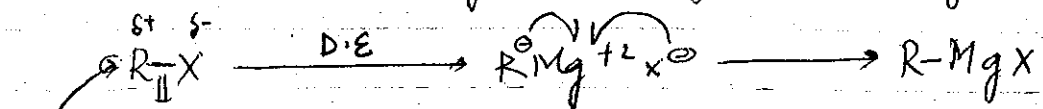
Grignard reagent is SOURCE OF CARBANION (Not carbanion intermediate)

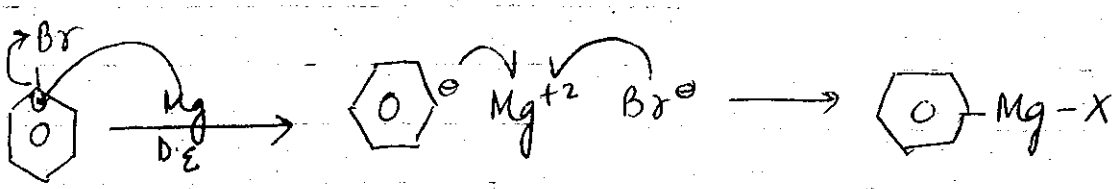


Alkyl Magnesium Halide (R-Mg-X)

Aryl Magnesium Halide (Ar-Mg-X)

Formation Of Grignard Reagent (R-Mg-X)

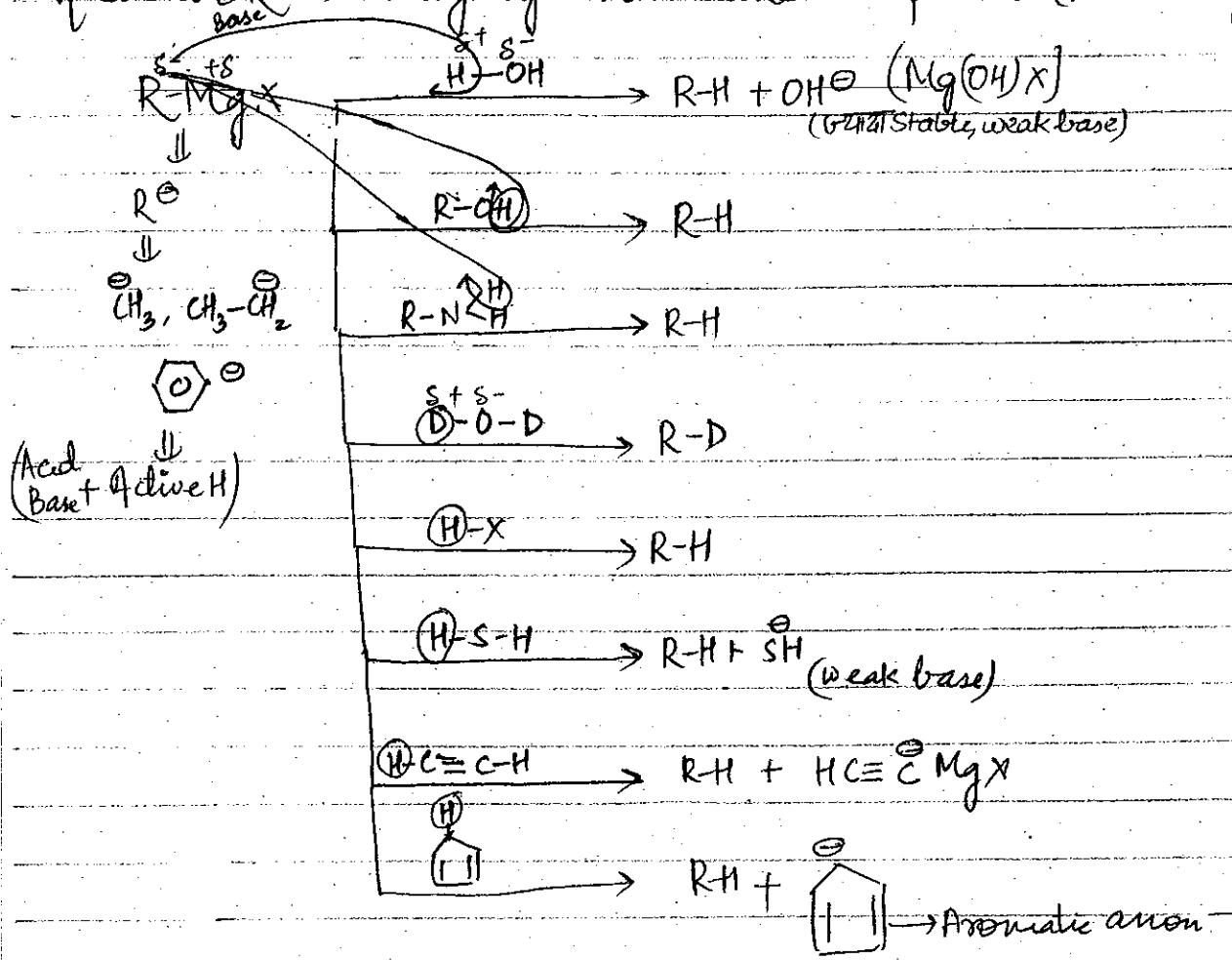




Reactivity ⇒ R-I > R-Br > R-Cl > R-F

Acid Base Rxn Of G.R with Active-H

Acid Base Rxn always goes to weaker component (stability of anion)



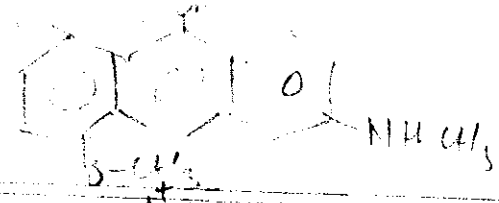
Some Acid base Rxn

① $CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\delta+\ \delta-}{O}H \xrightarrow{Na,\ e^-} CH_3-\underset{\underset{CH_3}{|}}{CH}-O^-Na^+ + \frac{1}{2}H_2\uparrow$

② $CH_3-\underset{\underset{CH_3}{|}}{CH}-OH \xrightarrow[\Downarrow\ Na^+\ H^-]{Na-H} CH_3-\underset{\underset{CH_3}{|}}{CH}-O^- + H_2\uparrow$

③ $CH_3-CH-C\equiv CH$

- $\xrightarrow{Na} CH_3-CH_2-C\equiv C^-Na^+ + \frac{1}{2}H_2\uparrow$
- $\xrightarrow{Na-H/K-H} CH_3-CH_2-C\equiv C^-Na^+ + H_2\uparrow$
- $\xrightarrow{Na^+\ \&\ NH_2^-} CH_3-CH_2-C\equiv C^-Na^+ + NH_3\uparrow$



3 most C.F. o.c. formed
Rxn at 3 C

$CH_3-CH_2-C\equiv CH \xrightarrow[3.5]{NaOH} \text{No Rxn}\ (CH_3-CH_2-C\equiv C^{\ominus})$ (3.25) } XXX

Terminal Alkyne	Internal Alkyne
① Na ② Na-H ③ $Na-NH_2$	① Na ② Na-H ③ $Na-NH_2$
↓	↓
	XXX (No rxn)

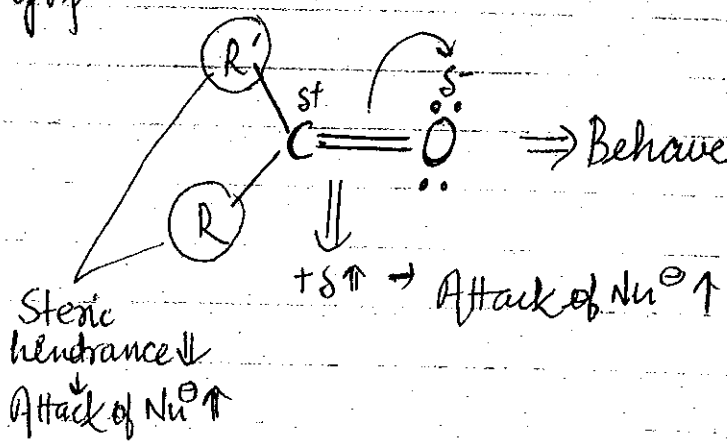
$R-\overset{\delta-}{Mg}-X \xrightarrow[\text{Chloramine}]{Cl-NH_2} R-NH_2 + R-H$ (major)

(NH_2 – L.g)

2OH

Nucleophilic Addition Rxn

Carbonyl compound give nucleophilic addition rxn because there is no leaving grp.

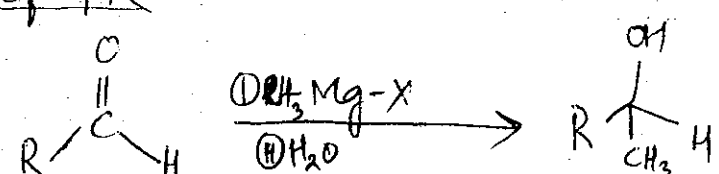


⇒ Behave as both E⊕ & Nu⊖

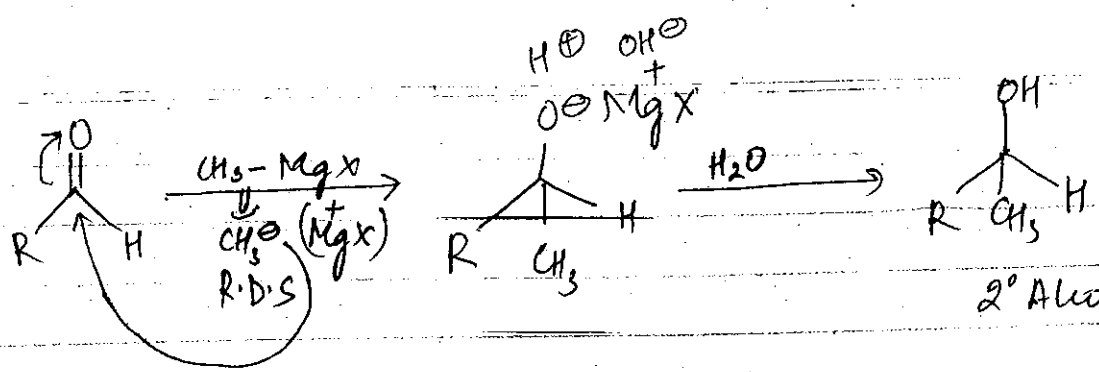
NAR with anionic Nucleophile

① Addition of G.R

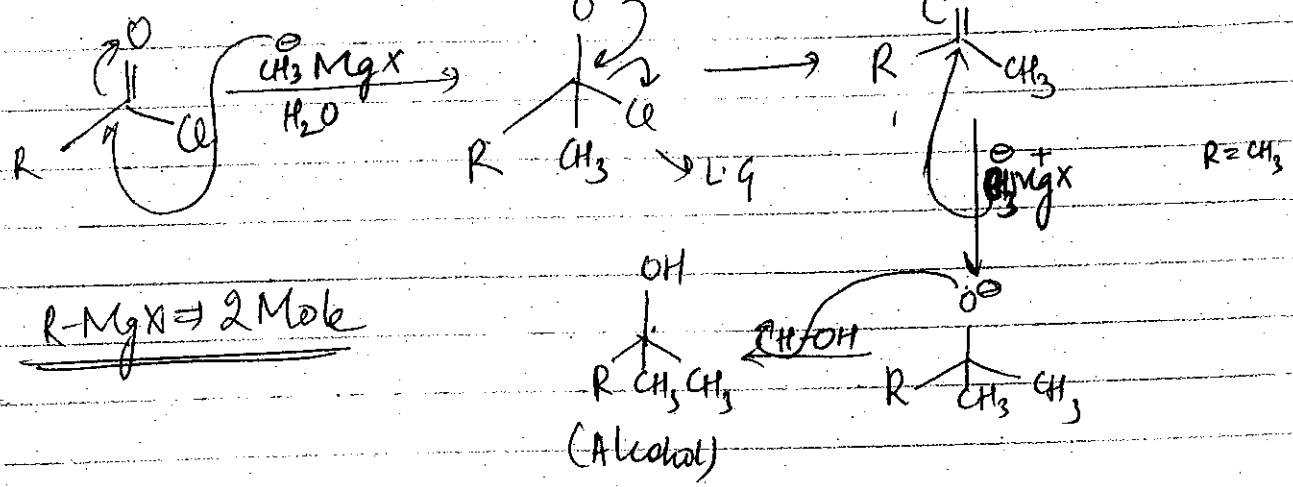
Net Rxn



2° Alcohol

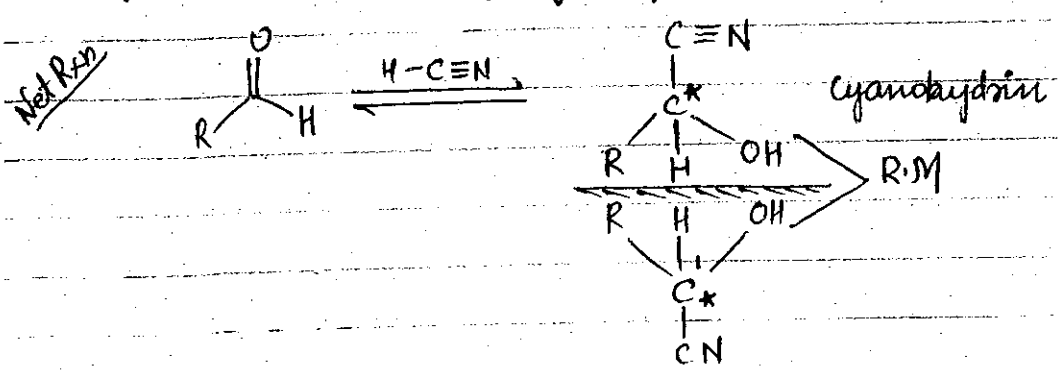


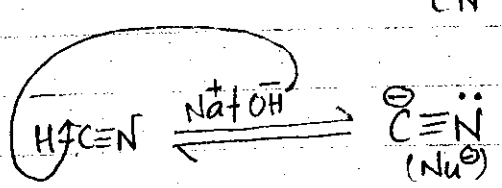
R-MgX ⇒ 1 mol consumed

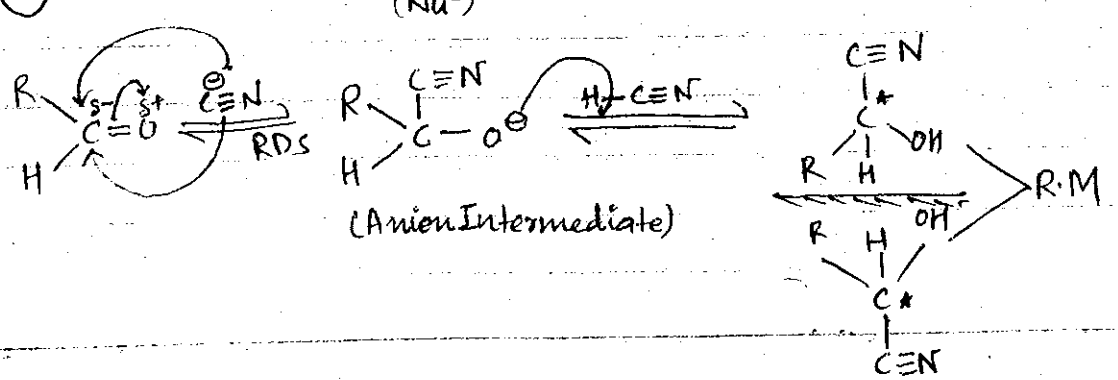
② 

R-MgX ⇒ 2 Mole

Addition Of HCN (Hydrogen Cyanide)

Net Rxn 

Mech STEP-1 

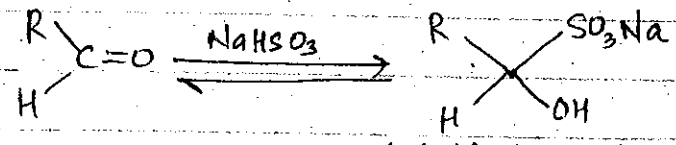
STEP-2 

Formation of cyanodrin is NAR

Whenever Nu⁻ AR ~~carried out~~ in (+)nce of HCl then all aldehyde except formaldehyde & all unsymmetrical ketone give equimolar mix of product (पूरी NAR R(Gn) ~~Hetero~~ Chiral centre gen. होती)

Addition of $NaHSO_3$ (Sodium Hydrogen Sulphite)

Net Rxn



Sod. bisulphite Add. Product

⇓

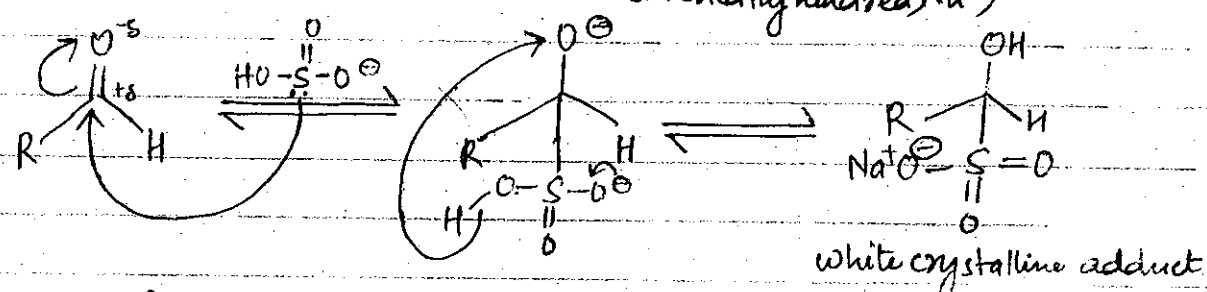
white crystalline solid / adduct

Mech

Step-I $NaHSO_3 \rightleftharpoons Na^+ + HO-\overset{\overset{O}{\|}}{S}-O^{\ominus}$

→ Attacking site (sterically hindred Nu⁻)

Step-II



white crystalline adduct

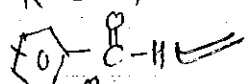
Rxn used in PDC

All aromatic & Aliphatic aldehyde give white crystalline adduct with $NaHSO_3$

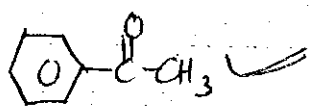
In case of Ketone only methyl Ketone give white crystalline adduct with $NaHSO_3$

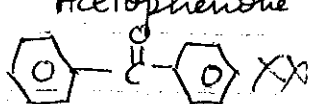
In following compounds, which one give white crystalline adduct with $NaHSO_3$

① $R-\overset{\overset{O}{\|}}{C}-H$

② 

③ $CH_3-\overset{\overset{O}{\|}}{C}-(CH_3)$ → Methyl Ketone

④  Acetophenone

⑤  Benzophenone

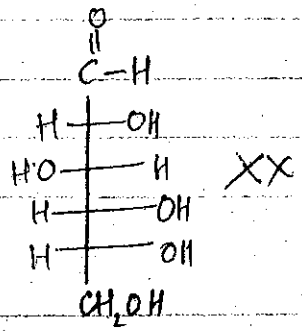
} Both can be seperated by $NaHSO_3$

⑥ $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_3$ 2-pentanone

⑦ $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$ XX 3-pentanone

⇒ Both can be sep. by $NaHSO_3$

⑧



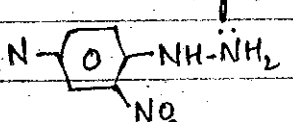
XX

No rxn with $NaHSO_3$ because glucose exist in cyclic hemiacetyl form.

NAR with Neutral Nucleophile

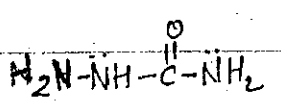
Neutral Nu: $R-\ddot{O}H$, $H_2\ddot{O}$, $\ddot{N}H_3$, $R-\ddot{N}H_2$, NH_2-OH (Hydroxylamine), $\ddot{N}H_2-\ddot{N}H_2$

$Ph-\ddot{N}H-\ddot{N}H_2$



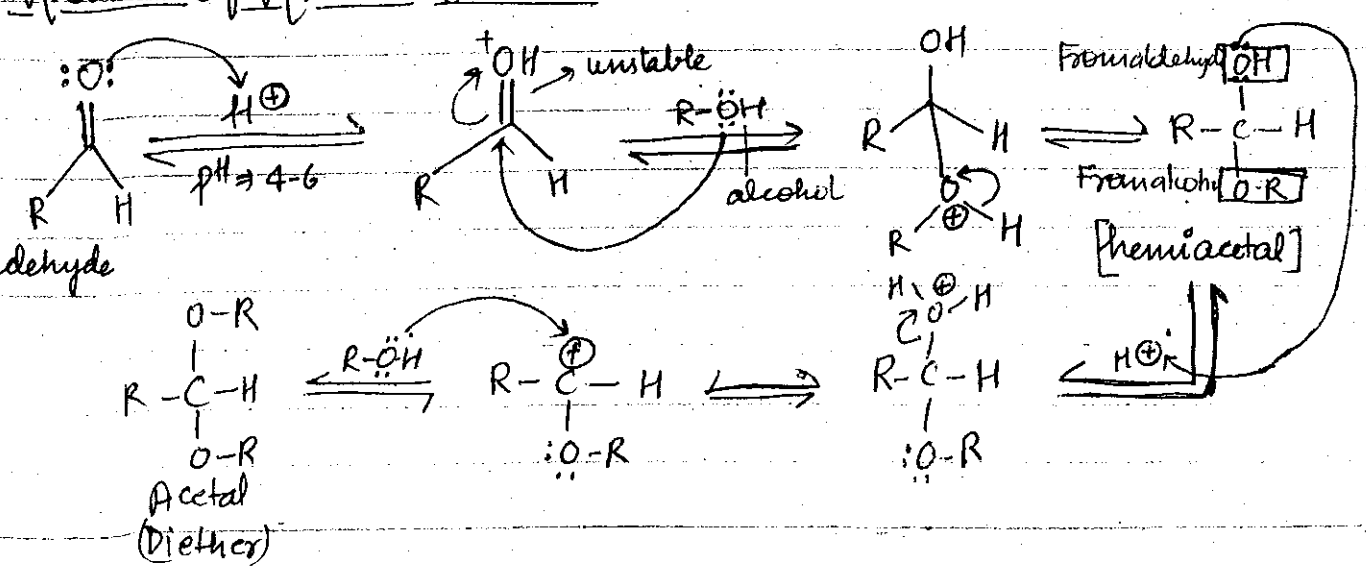
(2,4-DNP)

[Brady's Reagent]



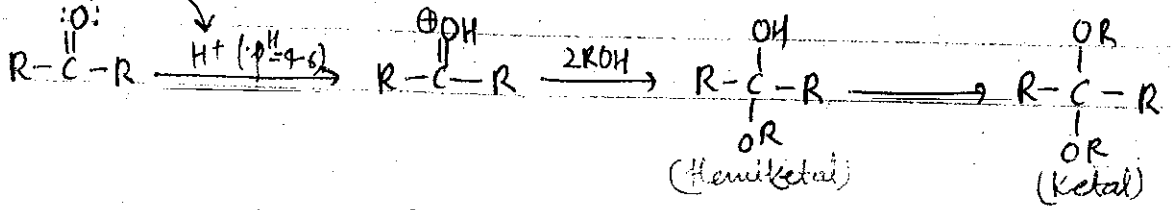
(Semicarbazide)

(A) Addition Of Alcohol (R-OH)



Aldehyde + 1° Alcohol ⟶ Hemiacetal

Ketone + 1° Alcohol ⟶ Hemiketal

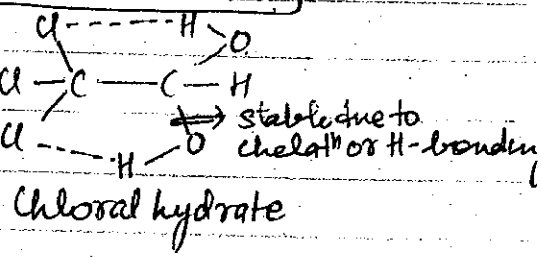
(2) 

Whenever 1 OH & 1 OR gop present at same atom then hemi prefix used.

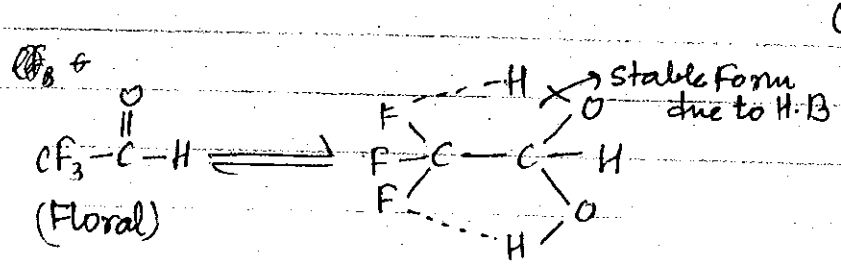
Whenever aldehyde reacted with alcohol in slightly acidic medium then hemiacetal is formed

Hemiacetal is highly unstable in acidic as well as basic medium but in *basic medium it give all reactn of aldehyde

Addition Of H_2O [only few comp. give like Chloral & Floral]

(1) $CCl_3-C(=O)-H$ (Chloral) $\rightleftharpoons$ (H+, pH ⇒ 4-6) $\rightleftharpoons$ $CCl_3-C(=OH^+)-H$ $\rightleftharpoons$ (H_2O:) $\rightleftharpoons$ 

Chloral hydrate

(2) 

(Floral)

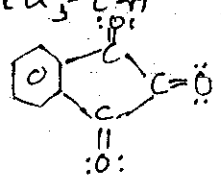
Floral hydrate

Following compounds have (Keq > 1) during add^n of H_2O on aldehyde & Ketone

① $H-C(=O)-H$ (form urotropine (diuretic) on rxn with NH_3)

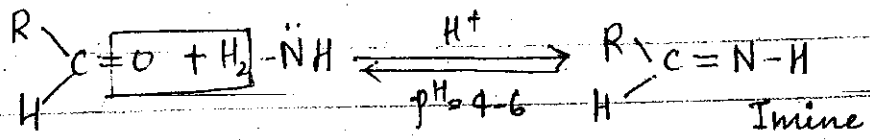
② $CF_3-C(=O)-H$

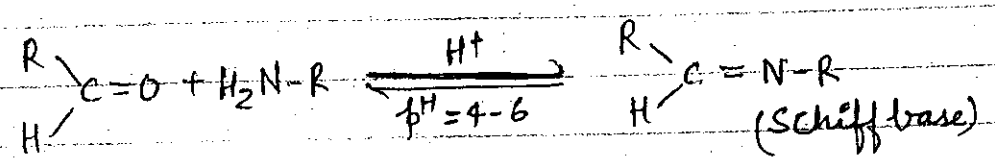
③ $CCl_3-C(=O)-H$

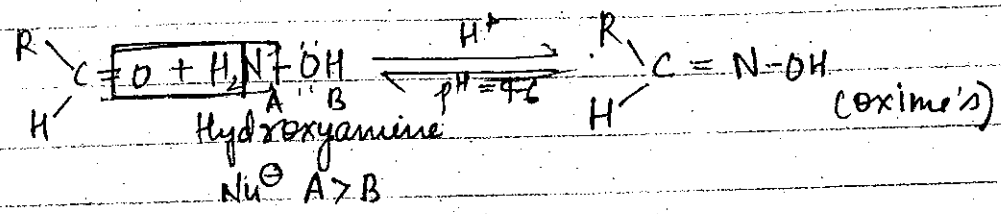
④ 

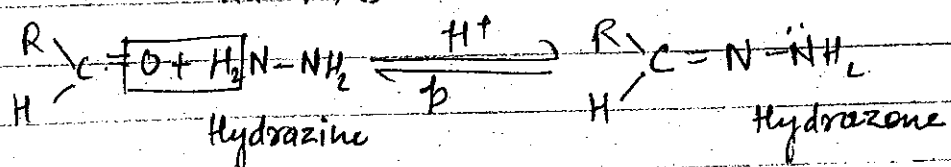
Brady Reagent : Aldehyde & Ketone ko identify karne ke liye
Glucose ke equivalent : Ph-NH-NH$_2$ Phenyl hydrazine ko identify karne ke liye

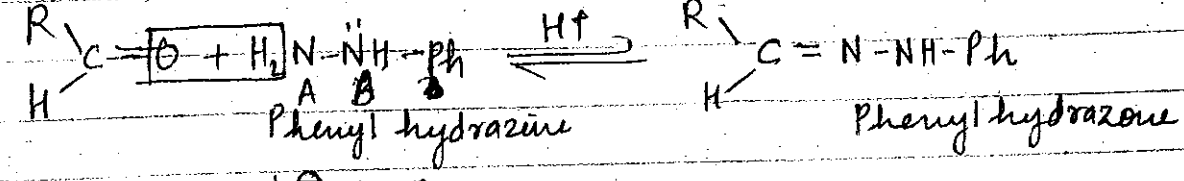
Addition Of Ammonia & Ammonia Derivatives

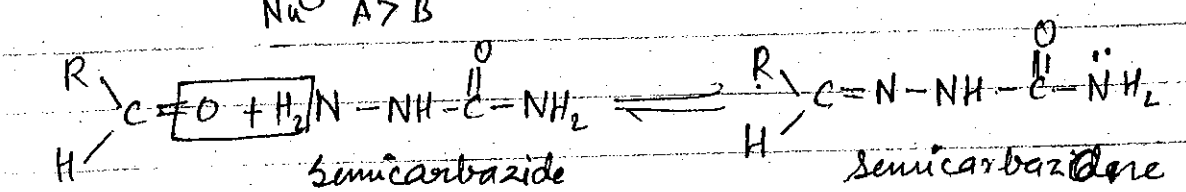
① 

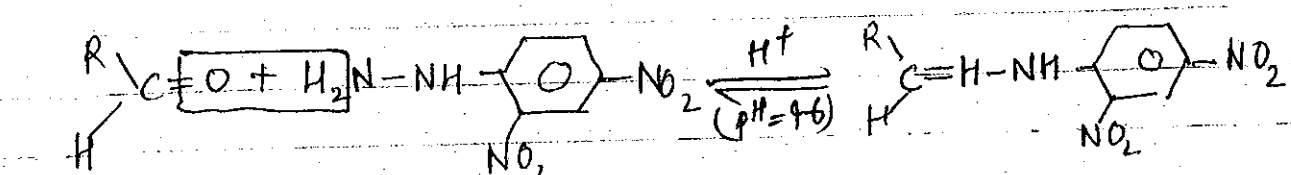
② 

③ 

④ 

⑤ 

⑥ 

⑦ 

All aldehyde & Ketone give yellow orange ppt with 2,4 DNP
It is qualitative test of Aldehyde & Ketone

Nucleophilic Substitution Rxn [NSR / S_N-Rxn]

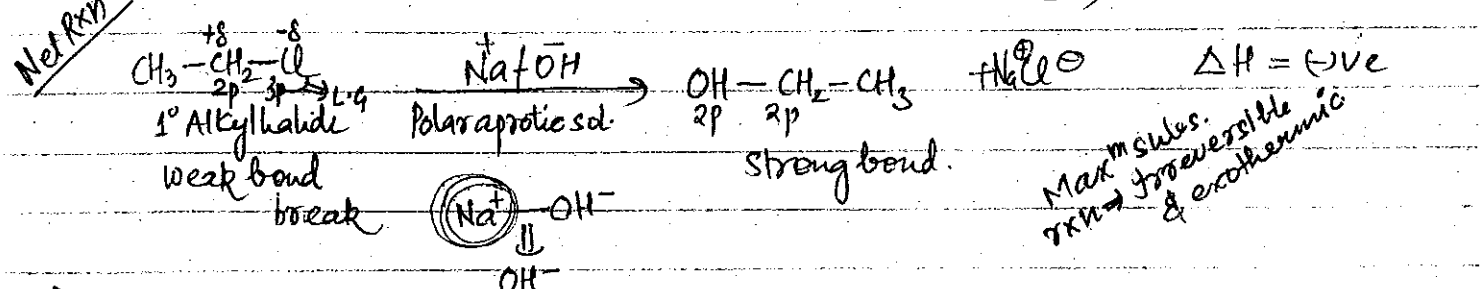
NSR

- Direct Sub
  - S_N^2-Rxn
  - S_N^1-Rxn
  - S_N^i-Rxn
  - ⇒ Alkyl halide (R-X)
  - ⇒ Alcohol (R-OH)
  - ⇒ Ether (R-O-R)
- Indirect Sub
  - S_N^{AE}-Rxn — Nucleophilic Substitution through Addition followed by Elimination Rxn — Acid & Acid Derivative
  - S_N^{Ar}-Rxn — Hydrolysis of aryl halide

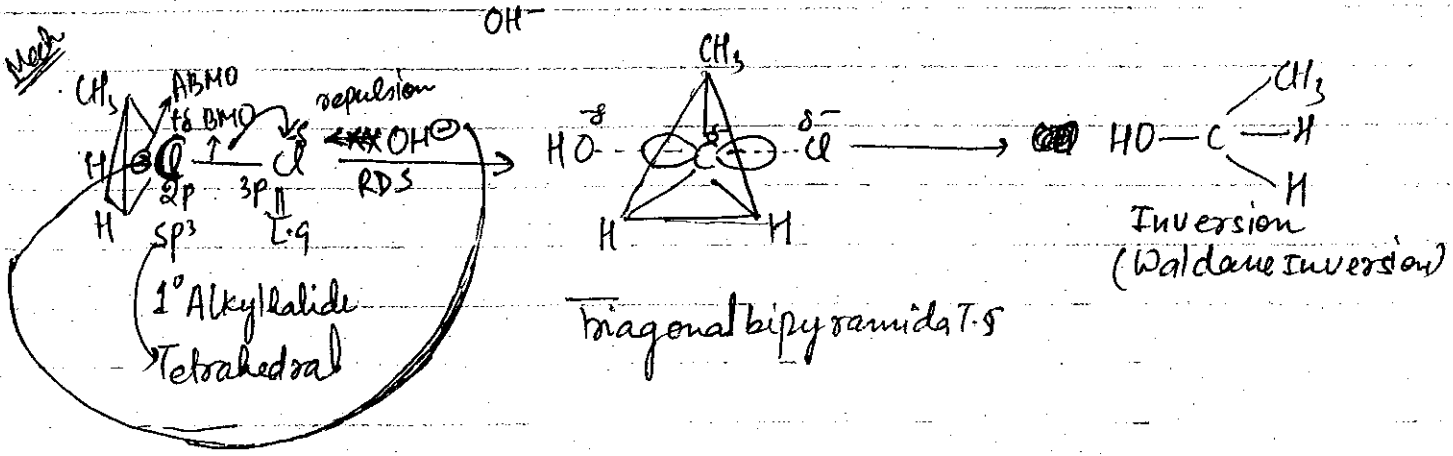
DIRECT

S_N2 Rxn (Nucleophilic Substitution Bimolecular Rxn)

Net Rxn



Mech



One step reaction

Rate expression $r = [CH_3-CH_2-Cl]^1[OH^-]^1$

Molecularity of rxn ②

Order of rxn ②

S_N2 rxn is carried out in PAS

L.G on side lage ⇒ Retention
Opposite side lag ⇒ Inversion

R-X bond breaking step is RDS of rxn.
~~Pentavalent~~ trigonal bipyramidal T.S formed in this rxn.
Anion like character developed in T.S.
In S_N^2 rxn inversion phenomenon observed.
Whenever Nucleophile attack at antiposition of leaving group then inverted anti product is obtained.

Reactivity of S_N^2 rxn

$CH_3-CH_2-Cl > CH_3-\underset{CH_3}{\underset{|}{CH}}-Cl > CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-Cl$

1° Alkyl Halide 2° 3°

No S_N^2 rxn

S_N^2 rxn depends on ability of L.G

$$\boxed{R-I > R-Br > R-Cl > R-F}$$

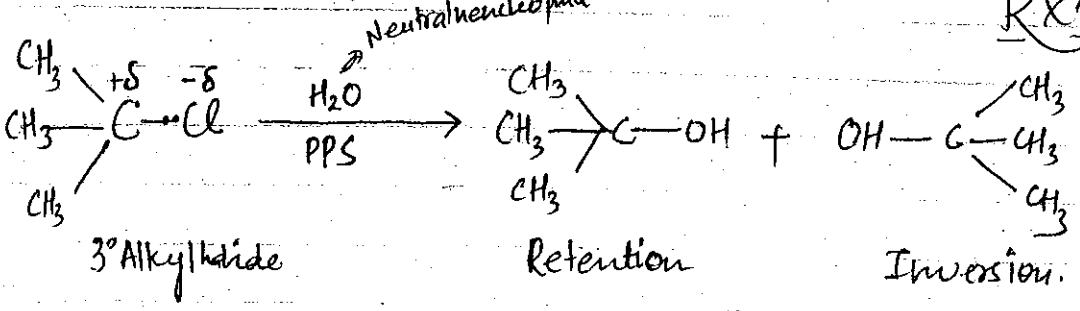
KEY POINT

Reactivity of S_N^2 Rxn ∝ Electron Withdrawing Group.

∝ Nucleophilicity

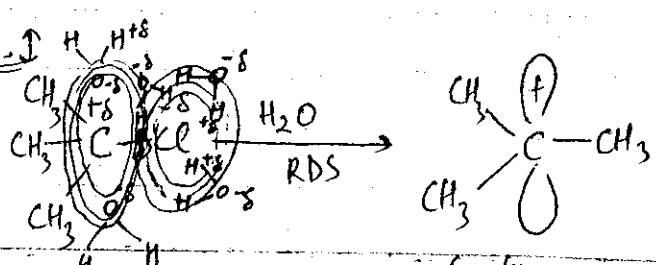
$$\propto \frac{1}{\text{Steric hindrance}}$$

S_N^1 Rxn (Nucleophilic Substitution Unimolecular Rxn)



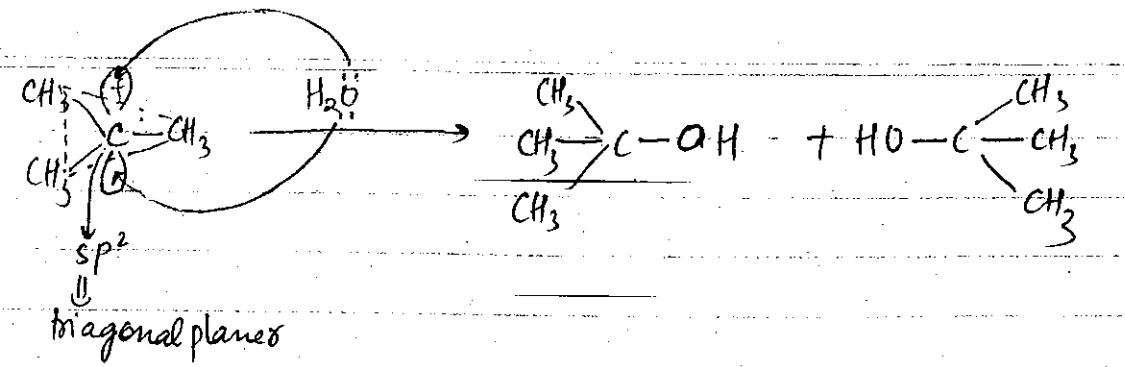
Mech

Step-I



(C^+ Intermediate)

Dispute on any molecule
S_N1 वाले में ☺



① 2 step rxn
② Rate expression $r = K\left[\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\!\!>\!C\!-\!Cl\right]^1$
③ Molecularity (1)
④ Order (1)
⑤ C^+ intermediate formed in this rxn.
⑥ Formation of carbocation is RDS of Rxn.
⑦ Carbocation rearrangement possible.
⑧ Reactivity of rxn & Stability of C^+
⑨ S_N1 rxn carried out in PPS.
⑩ In S_N1 rxn retention & inversion both phenomenon observed
⑫ In S_N1 rxn 100% racemisat^n not occur due to intimate ion-pair mechanism. In intimate ion-pair mech. tendency of inversion more than retetention
⑬ S_N1 rxn is more exothermic than S_N2 rxn
⑭ Reactivity of S_N1 rxn

3° Alkyl halide > 2 Alkyl halide > 1° Alkyl halide
No S_N1 rxn

⑮ Acc. to leaving group reactivity of rxn

$$\boxed{R\text{-}I > R\text{-}Br > R\text{-}Cl > R\text{-}F}$$

No SN^1 rxn

Conclusion Of SN^1 & SN^2 Rxn

1° Alkyl halide S_N2 rxn
2° Alkyl halide PAS → SN^2 Rxn
PPS → S_N1 Rxn

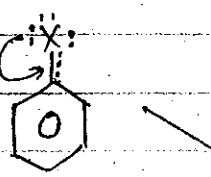
3° Alkyl halide S_N1 Rxn

Determination Of S_N^1 & S_N^2 Rxn

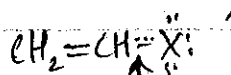
S_N^2 Rxn	S_N^1 Rxn
PAS	PPS
Anion Present	Anion Absent
Small Substrate {1° & 2° Alkyl halide}	Large Substrate {3° & 2° Alkyl halide}

Explain aryl & vinyl halide do not give S_N^1 & S_N^2 rxn while benzylic & allylic position is favourable condition for S_N^1 & S_N^2 rxn.

(I)



Aryl halide



Vinyl halide

→ due to reso. of lp partially double bond character dev.

⇓

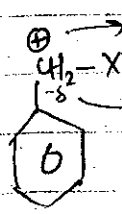
Poor L.G

⇓

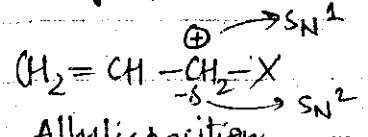
No S_N^1 & S_N^2 rxn

(II) R–F ⇒ No S_N^1 & S_N^2 (strong bond)

(III)



Benzylic position



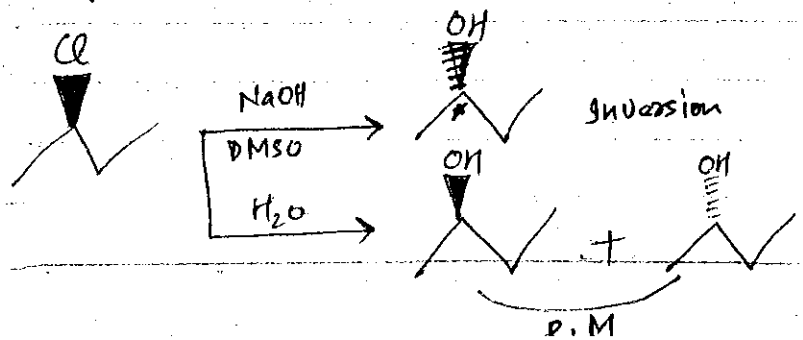
Allylic position

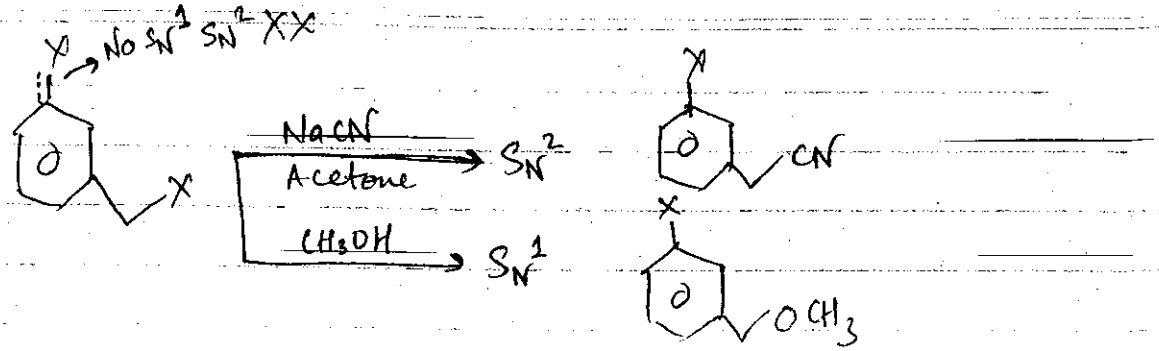
→ Both rxns are favourable at allylic & benzylic position

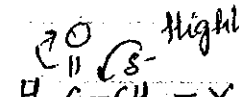
S_N^1 Rxn

S_N^2 Rxn

(I)





Q.  highly stable C.S

I

CH_3-X

II

S_N2 I > II

Various Rxn Based On S_N1 & S_N2 Mech.

1. Fenkelstein Rxn

$$R-Cl + \underset{\text{Acetone}}{NaI} \rightleftharpoons R-I + \underset{\text{(ppt)}}{NaCl\downarrow} \text{ (Ionic comp.)}$$

It is a kind of S_N2 rxn.

Rxn also k/a halogen exchange Method.

② Swart's Rxn

$$R-Cl + \underset{DMF}{AgF} \rightarrow R-F + \underset{\text{(white ppt)}}{AgCl\downarrow}$$

CoF_2 HgF_2 can also be taken

It is a kind of S_N2 rxn

Reaction also k/a as Halogen exchange Method.

③ Darzen Rxn

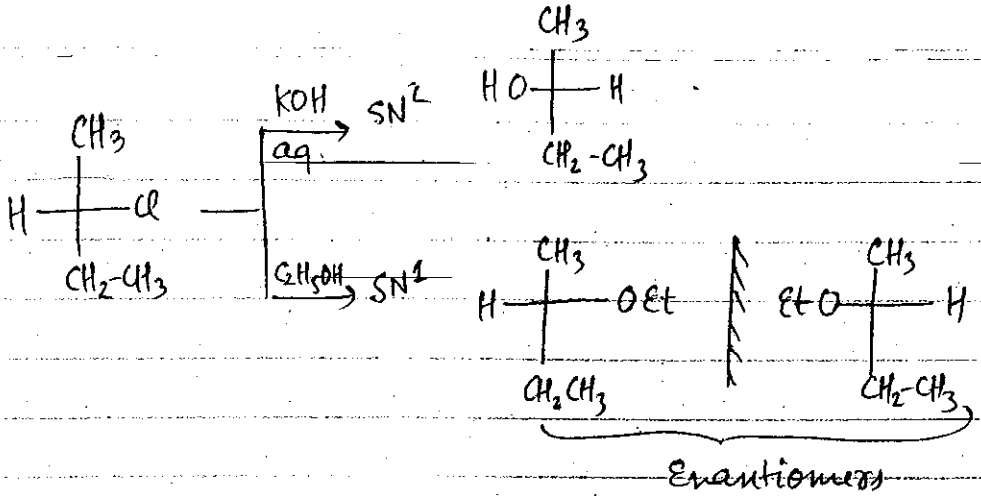
Net Rxn

$$R-OH + \underset{\text{Thionyl chloride}}{SOCl_2} \longrightarrow R-Cl + SO_2\uparrow + HCl.$$

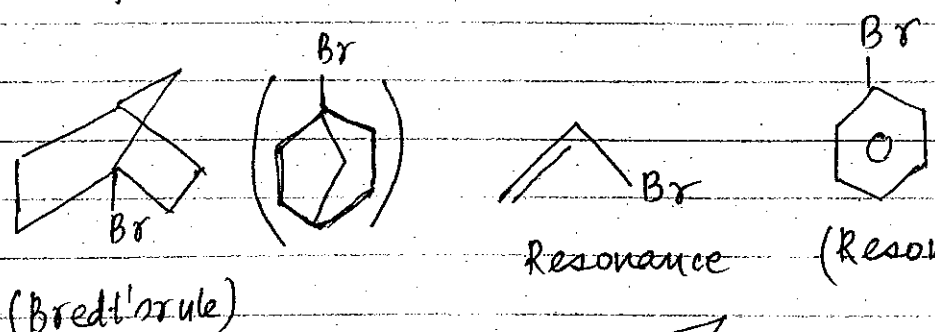
2nd Next Page →

Level-

SHEET-14



Compound which do not show S_N1 as well as S_N2



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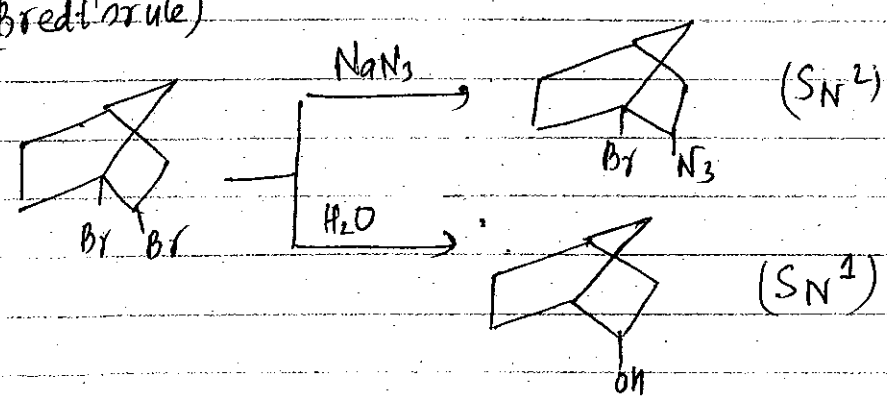

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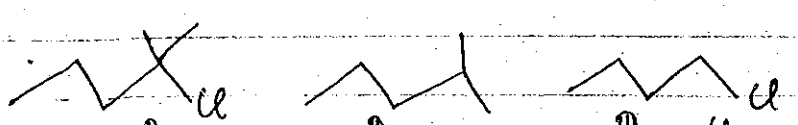
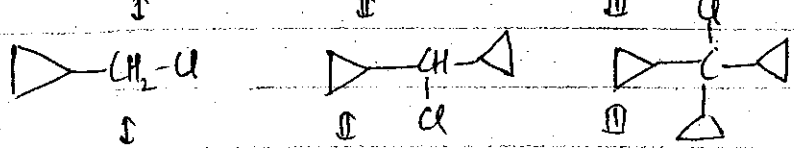


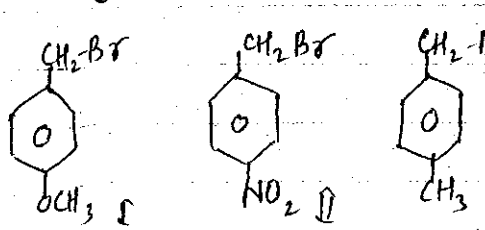
rate of S_N2 : III > II > I

*



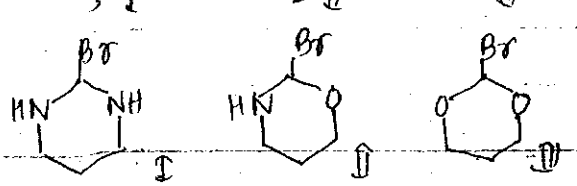
rate of S_N1 : III > II > I

*



rate of S_N1 : I > III > II

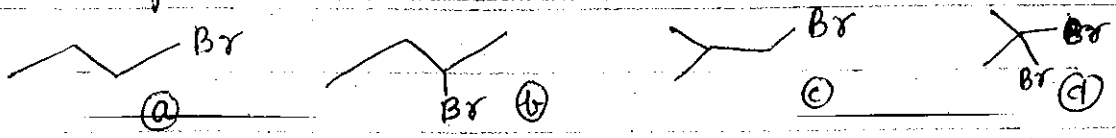
*



rate of S_N1 : I > II > III

SHEET - 15

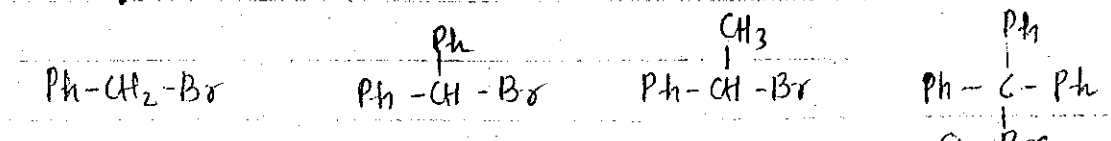
NCERT Pg-295

\# 

(a) (b) (c) (d)

rate of S_N1 (d) > (b) > (c) > (a)

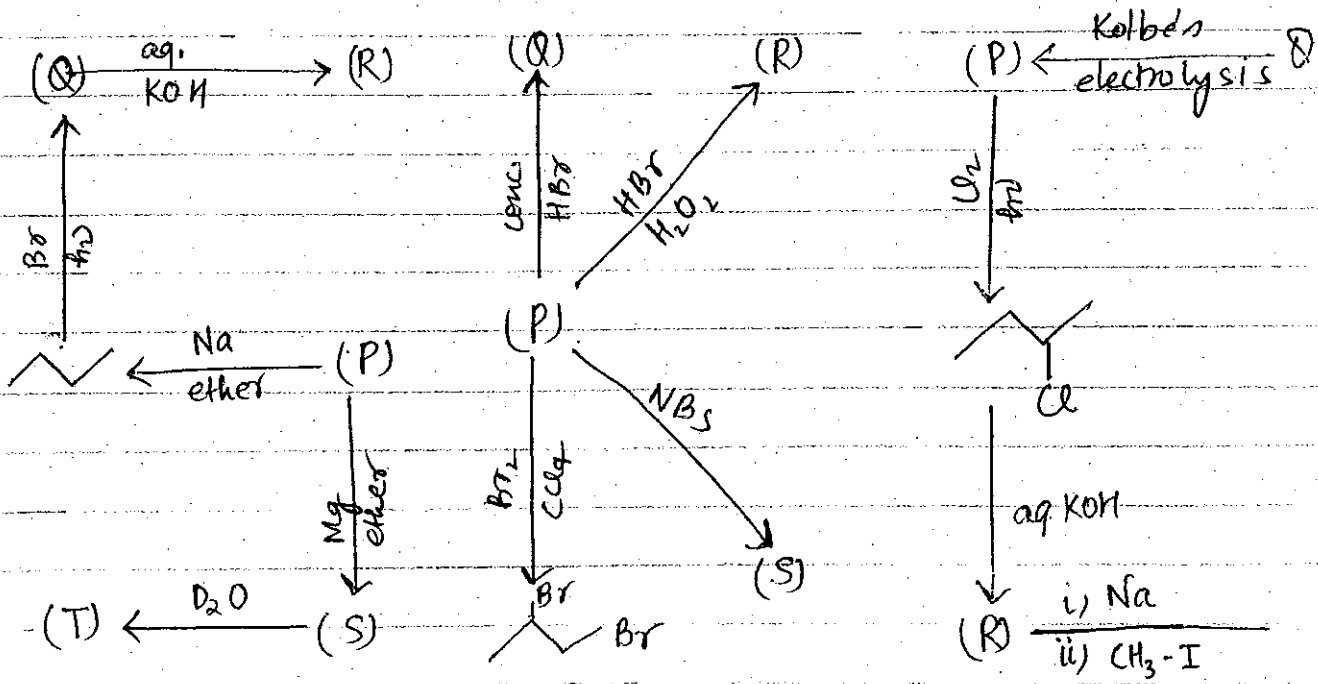
rate of S_N2 (a) > (c) > (b) > (d)

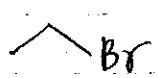
\# 

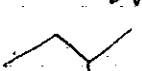
(a) (b) (c) (d)

rate of S_N1 (d) > (b) > (c) > (a)

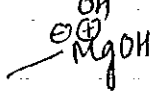
rate of S_N2 (a) > (c) > (b) > (d)



P = 

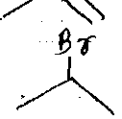
Q = 

R 

S 

T 

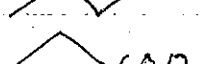
P = 

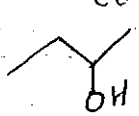
Q = 

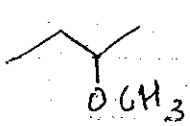
R = 

S 

P = 

Q = 

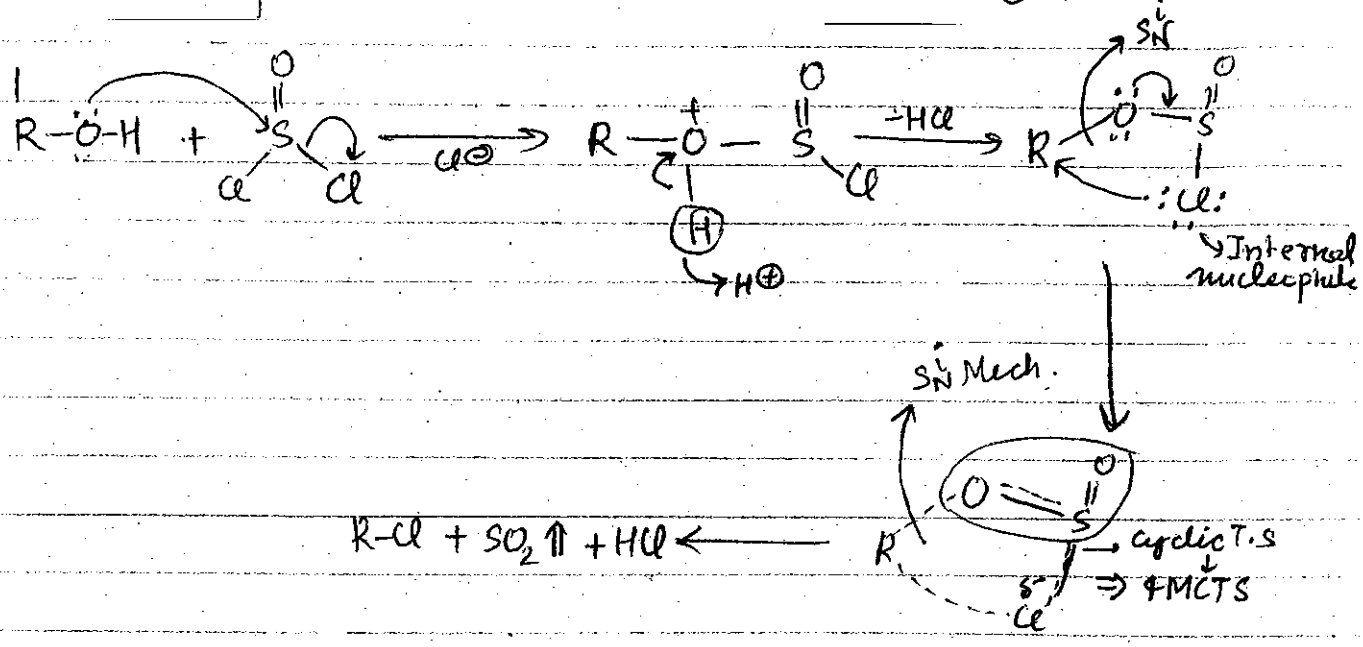
R = 

S = 

cont.

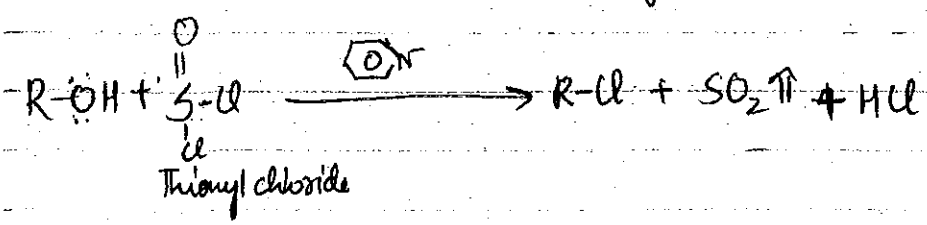
Mech

S_N^i (Nucleophilic Substitution Intramolecular Rxn)

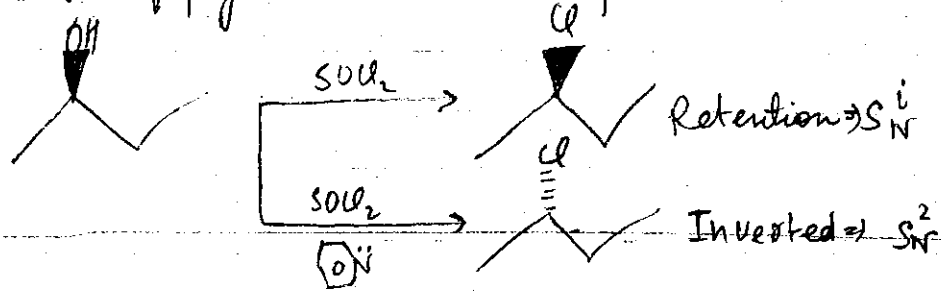


completed with S_N^i mechanism
4MCTS formed in this rxn.
Retention phenomenon observed
For formation of R-Cl this method is best method because gaseous by product are formed in this rxn.

* Darzen rxn in presence of Pyridine



Darzen rxn in presence of pyridine completed with S_N^2 mech.
In presence of pyridine inverted product is obtained.



④ Preperation Of Alkyl halide from alcohol

Net Rxn

$R-\ddot{O}-H$ + conc. H-X $\rightleftharpoons$ R-X + H_2O

(Poor leaving grp)

Mech

Step-I

conc. H-X $\rightleftharpoons$ $H^{\oplus}$ + $X^{\ominus}$

Step-II

$R-\ddot{O}H \xrightleftharpoons{H^{\oplus}} R-\overset{\oplus}{O}\overset{H}{\underset{H}{}}$ $\xrightleftharpoons[-H_2O]{\text{RDS (Bond breaking step)}}$ $R^{+} \xrightleftharpoons{X^{\ominus}} R-X + H_2O$

poor L.G ① Bond forming ② Fast step — Best L.G — [C^{+} intermediate]

Carbocation intermediate formed in this rxn
Formation of C^{+} → RDS of rxn
Rearrangement of C^{+} possible.
Reactivity of rxn ∝ Stability of C^{+}
Rxn follow S_N1 Path
Rate of rxn conc. HI > conc. HBr > conc. HCl > conc. HF → no rxn.

conc. HI, conc. HBr: strong acid ⇓ $[H^{+}]$ ↑ ⇓ R-O-R ↑

conc. HCl: weak acid ⇓ $[H^{+}]$ ↓ ⇓ R-O-R ↓

LUCAS Reagent

conc. HCl $\xrightarrow[\text{(anhy.)}]{ZnCl_2}$ H^{+} + $\ominus ZnCl_4$

H^{+} ⇓ (H^{+}) ↑ ⇓ ROR

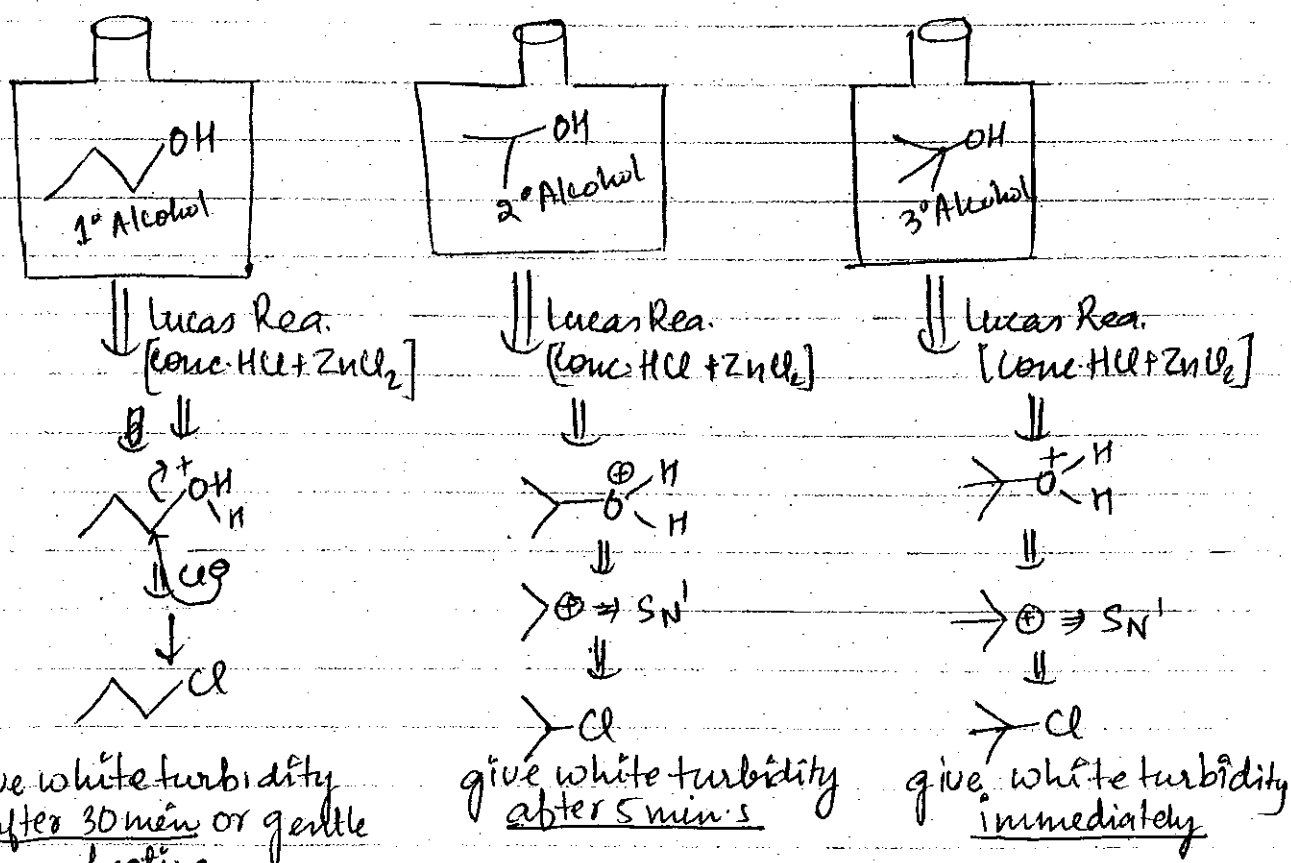
Lucas Reagent ⇒ [Conc. HCl + $ZnCl_2$ (anhyd.)]

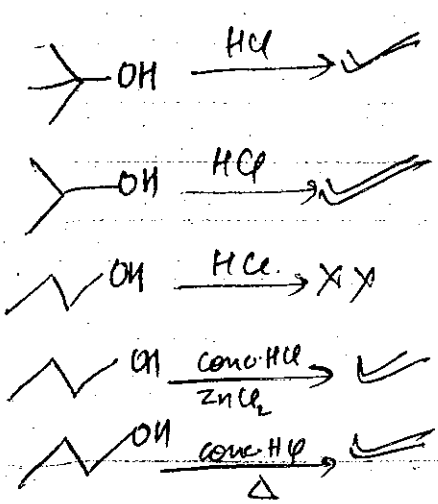
Conc. HCl → Acid; $ZnCl_2$ (anhyd.) → Lewis Acid

Rxn used in practical org. chem.

Lucas reagent used for detection of 1°, 2° & 3° Alcohol.

Lucas reagent soluble in alcohol & give R-Cl as a product & ● R-Cl give white turbidity in rxn medium.

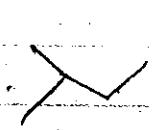


① 

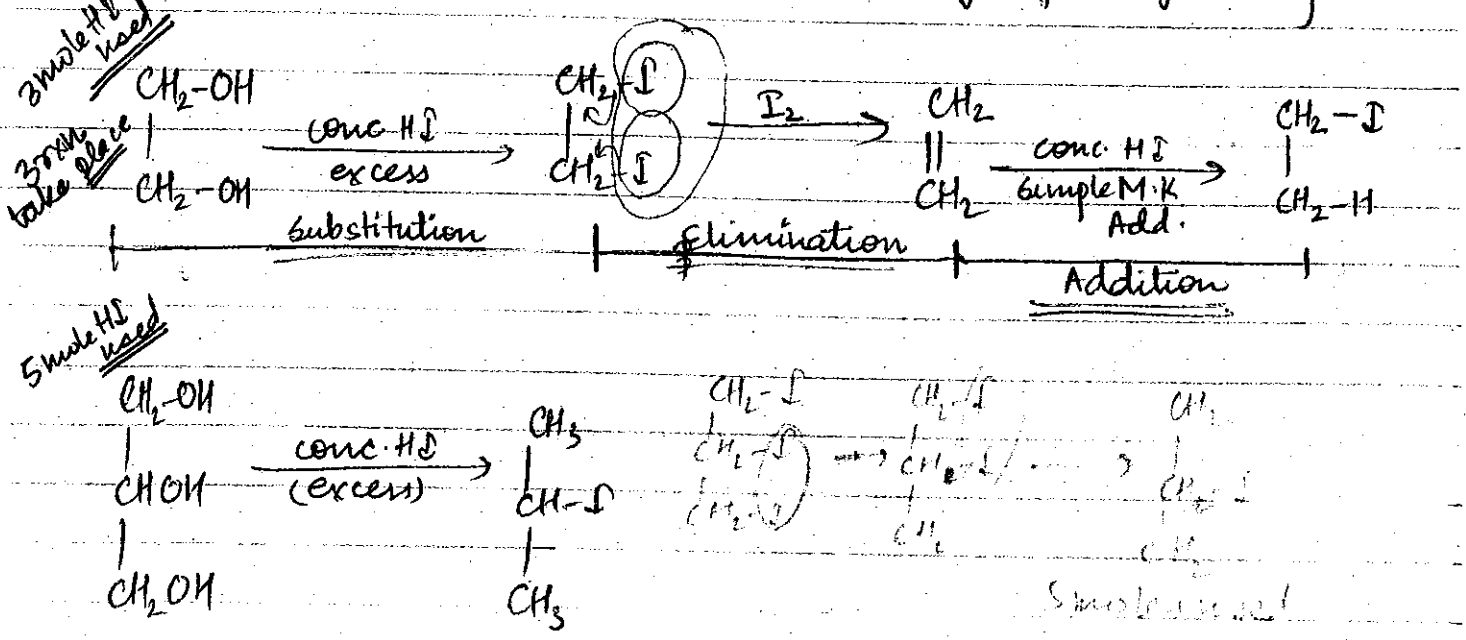
Following which one alcohol give white turbidity with Lucas Reagent ?

① $Ph-CH_2-OH$ ⇒ Immediate } Resonance stabilised

②  ⇒ Immediate }

③  ⇒ Not immediately. } C^+ का बनना RDS
Not C^+ on Rearrangement

Formation of alkyl halide from Polyhydroxy Group.



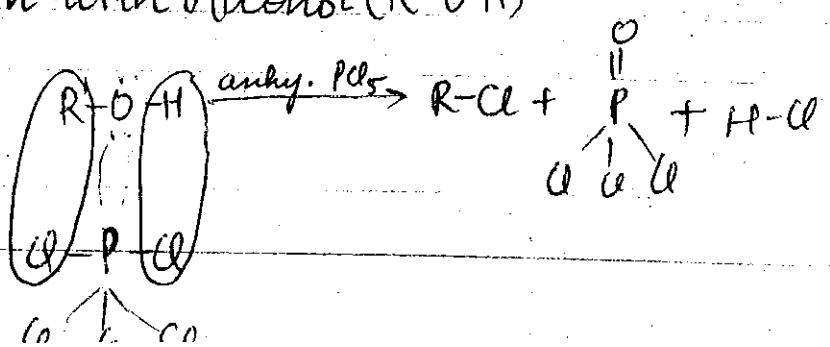
Rxn with Anhy. PCl_5

Anhy. PCl_5 ⟶ S_N2 Mech

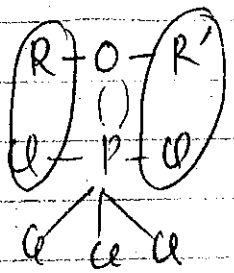
↳ $PCl_4^{\oplus}$ $PCl_6^{\ominus}$

Room temp (S_N1)
40° (S_Ni)

Ⓐ Rxn with Alcohol (R-O-H)

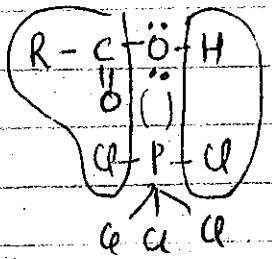


(B) Rxn with Ether → (R-O-R')



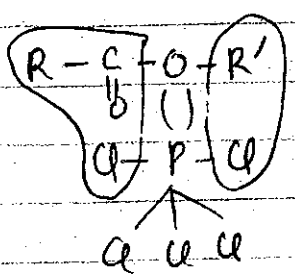
Anhy PCl_5, $R-Cl + R'-Cl + POCl_3$

(C) Rxn with Acid ($R-\overset{O}{\overset{\|}{C}}-OH$)



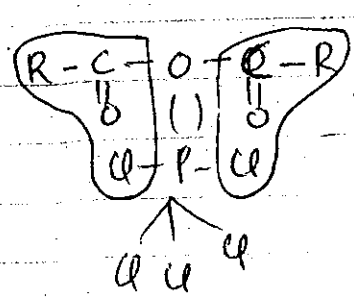
Anhy PCl_5 → $R-\overset{O}{\overset{\|}{C}}-Cl + POCl_3 + HCl$

(D) Rxn with Ester ($R-\overset{O}{\overset{\|}{C}}-O-R'$)



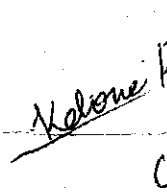
Anhy PCl_5 → $R-\overset{O}{\overset{\|}{C}}-Cl + R'-Cl + POCl_3$

(E) Rxn with Anhydride ($R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$)



Anhy PCl_5 → $2R-\overset{O}{\overset{\|}{C}}-Cl + POCl_3$

(F) Rxn with Aldehyde & Ketone



Anhy PCl_5 → $R-\underset{\underset{gem}{Cl\ \ Cl}}{C}-R' + POCl_3$

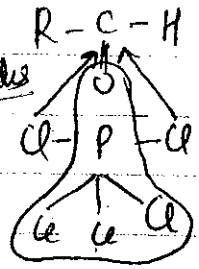
Mod 6

सूखे में S_N2

X_2 + Red P + HI
Strongest RA
(KMnO$_4$ को घटाएगा)

R-OH → 1 mol HI
R(OH)$_2$ → 3 mol HI
R(OH)$_3$ → 5 mol HI

(11) Aldehydes



$$R-CHO \xrightarrow{\text{Anhy. } PCl_5} R-CHCl_2 + POCl_3$$

(12) Rxn with Amides

$$R-CONH_2 \xrightarrow{\text{Anhy. } P_2O_5} R-C\equiv N$$

(Amide)

Q.1 $R-CONH_2 \xrightarrow{\text{Anhy. } P_2O_5} R-C(OH)_2-NH^+ \xrightarrow{H_2O/H_3O^+} R-COOH + NH_3$

95% H_2SO_4 ⇒ dilute ⇒ complete hydrolysis.

98% H_2SO_4 ⇒ partially hydrolysis

(13) Reaction With Anhy. PCl_3

Anhy. PCl_3 ⇒ S_N2 Mech.
(Red P + X_2)

$2P + 3X_2 \longrightarrow 2PX_3$ (same-same)

X = I, Br, Cl

$R-OH \xrightarrow{\text{anhy } PCl_3} R-Cl + H_3PO_3$

KEY POINT

R-O-H →
- $SOCl_2$, Darzen P. → R-Cl ⇒ S_Ni
- $SOCl_2$, Pyridine → R-Cl ⇒ S_N2
- conc. HX → R-X ⇒ S_N1
- conc. HCl, $ZnCl_2$, Lucas Re → R-Cl ⇒ S_N1 [2°, 3° ppt]
- anhy. PCl_5 → R-Cl ⇒ S_Ni
- anhy. PCl_3 → R-Cl ⇒ S_N2
- Red P + X_2 → R-X ⇒ S_N2

⑧ Ammonolysis Reaction (S_N)

S_N2 Mech

$R-X$ (excess) + NH_3 → $R-NH_2$ (1° Amine) + HX

S_N2 Mech

$R-NH_2$ + $R-X$ → $R-NH-R$ (2° Amine) + HX

S_N2 Mec

$R-NH-R$ + $R-X$ → $R-N(R)_2$ (R 3° Amine)

S_N2 Mech

$R-N(R)_2$ + $R-X$ → $R-N^{\oplus}(R)_3$ $X^{\ominus}$

Quaternary Ammonium salt

Williamson Ether Synthesis (S_N2)

$R-O^{\ominus}Na^{\oplus}$ + $R-X$ —PAS→ R-OR + NaX

Sodium Alkoxide. Alkyl halide. Ether

W.E.S is a kind of S_N2 rxn

$CH_3-O^{\ominus}Na^{\oplus}$ + CH_3-CH_2-X → $CH_3-CH_2-O-CH_3$ ⇒ S_N2 mech.

Sodium methoxide. 1° Alkyl halide. ether

337 NCERT

$CH_3-OH \overset{3.5}{\rightleftharpoons} Na-OH \rightleftharpoons CH_3-O^{\ominus}$ (3.5)

Rxn में equilibrium same EN of product anion

Acid-base rxn more stable की ओर जाती है।

unstable anion → Strong base.

$Na\cdot OH$ ↑↑

$CH_3-O^{\ominus}$ more behave as Base

(II) $CH_3-O^{\ominus}Na^{\oplus}$ + $H-CH_2-\underset{H}{\overset{CH_3}{C}}-X$ (2° Alkyl halide) ⟶ $CH_2=CH-CH_3$ (major) + $CH_3-CH(CH_3)-O-CH_3$ (minor)

E_2 mech

$CH_3-O^{\ominus}$ < Base, Nu$^{\ominus}$

(III) $CH_3-O^{\ominus}Na^{\oplus}$ + $H-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-X$ (3° Alkyl Halide) ⟶ $CH_2=C(CH_3)_2$

E_2 mech

(IV) $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O^{\ominus}Na^{\oplus}$ + $H-\underset{H}{CH_2}-X$ (1° Alkyl halide) ⟶ $CH_3-O-C(CH_3)_3$

S_N2 mech.

In W.E.S 2° & 3° alkyl halide give / favours Elimination Rxn & give Alkene as major product.

Ether Cleavage

① Ether Cleavage in presence of conc. HI

Step-I $Conc\ HI \rightleftharpoons H^+ + I^{\ominus}$

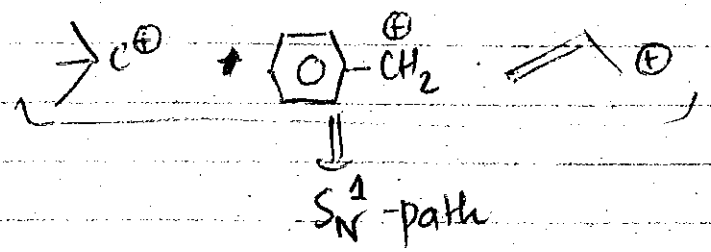
$R-\ddot{O}-R' \overset{H^{\oplus}}{\rightleftharpoons} R-\overset{\oplus}{O}(H)-R' \xrightarrow{I^{\ominus}} R'-I + R-OH$

(2p, 2p) Alkyl grp-I, Alkyl grp-II

KEY POINT ⇒ In case of conc. HI

1° Alkyl grp	⇒ S_N2 Rxn
2°	S_N2
3°	S_N1

Keypt : In ether cleavage when attack of iodide ion at alkyl gp then if following $C^{\oplus}$ is ~~followed~~ formed then rxn follow S_N^1 path.



(1) $CH_3-CH_2-O-CH_3 \xrightarrow{I^{\ominus},\ \text{conc. HI}} CH_3-I + CH_3-CH_2-OH$

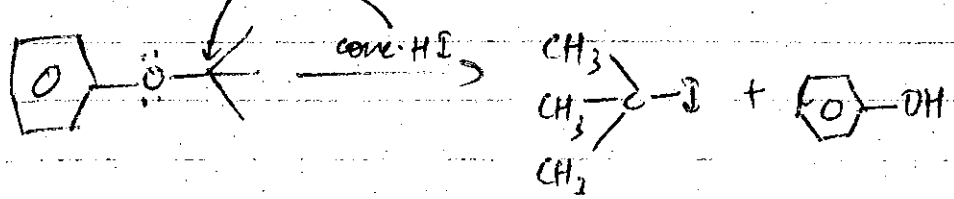
1° 1°

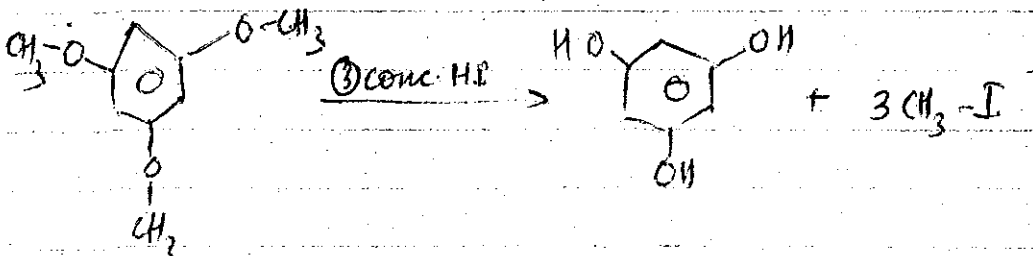
S_N^2 S_N^2

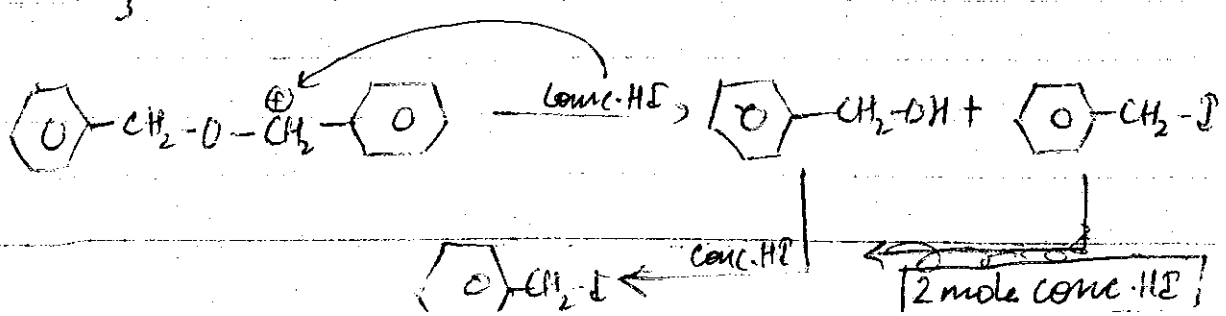
(2) $(CH_3)_3C-O-CH_3 \xrightarrow{I^{\ominus},\ \text{conc. HI}} (CH_3)_3C-I + CH_3OH$

3° 1°

S_N^1 S_N^2

(3) 

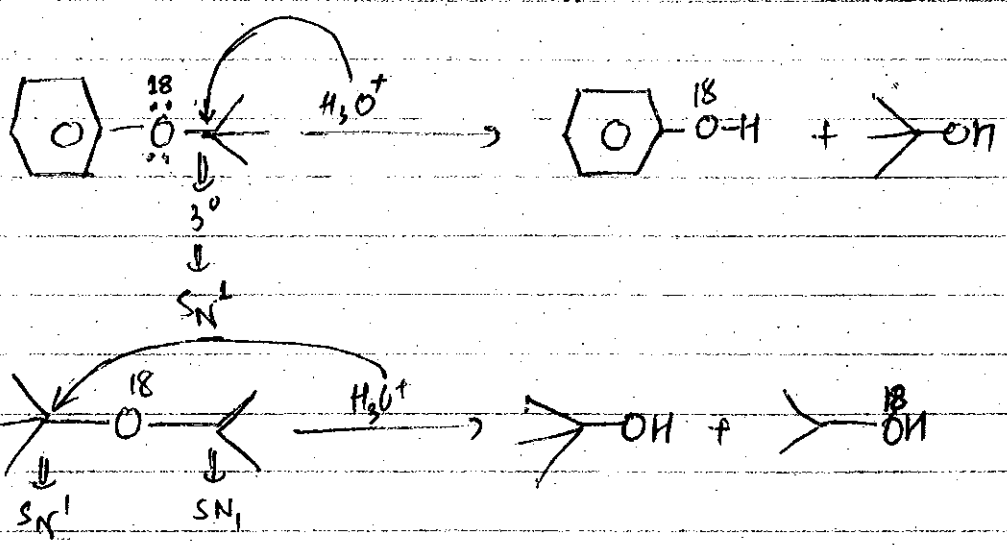
(4) 

(5) 

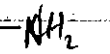
Ether cleavage in presence of H_3O^+ (dil H_2SO_4)

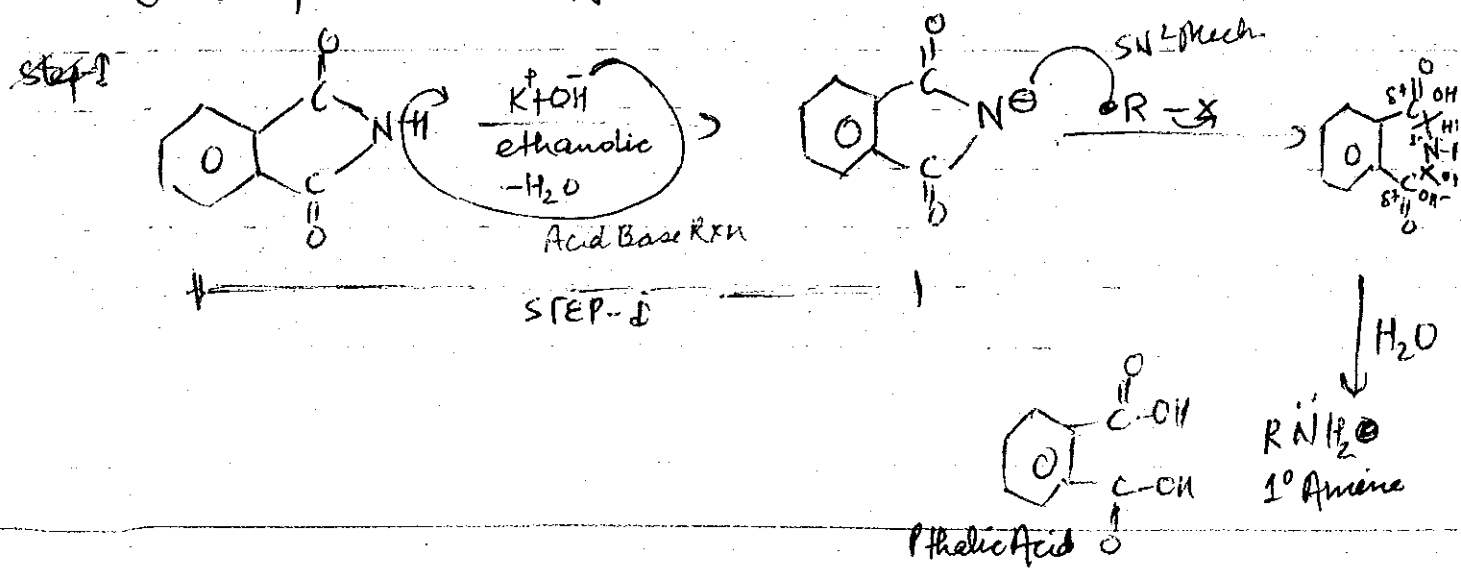
Hydrolysis of Ether

KEY POINT 1° Alkyl Group ⇒ S_N2
2° ⇒ S_N1
3° ⇒ S_N1



(11) Gabriel Phthalimide Rxn

→ Gabriel Phthalimide rxn used for preperation of 1° Amine
→ Aromatic Amine (  etc) 2° 3° amine cannot be formed by Gabriel Phthalimide rxn
→ Rxn completed with S_N2 mech.



Corey - House Synthesis

Net R+n

$$R-X \xrightarrow[\text{③ } R'-X]{\text{① Li, ② CuI}} R-R' \quad (\text{Alkane})$$

Mech

① $2R-X + 2e^- \longrightarrow 2R-Li + LiX$

$2Li^0 \longrightarrow 2Li^+$

② $2R-Li + CuI \longrightarrow R_2CuLi + LiI$

(R_2CuLi = Gillman's reagent) → OMC.

③ $R_2CuLi \xrightarrow{R^\ominus,\ SN^2} R-R'$

Symmetric & unsymmetrical both alkane can be formed by Corey house synthesis.
CH_4 cannot formed by this rxn.
Rxn completed with S_N2 Mech.

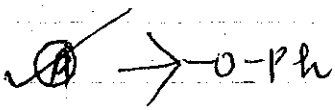
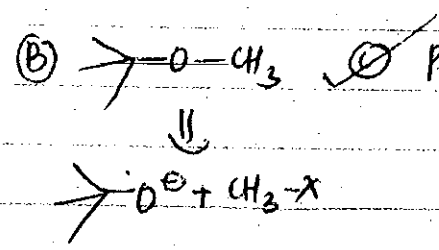
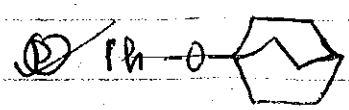
Eg $\left(CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}\right)_2 CuLi \xrightarrow{CH_3-X}$ ✓ S_N2

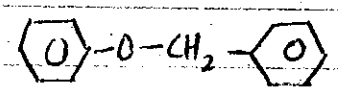
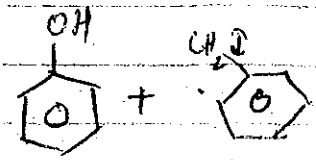
$(CH_3)_2CuLi \xrightarrow{\left(CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-X\right)}$ XXX S_N2

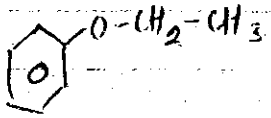
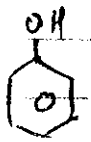
Elimination ✓ alkene

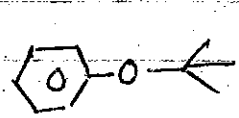
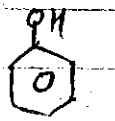
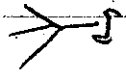
SHEET-16

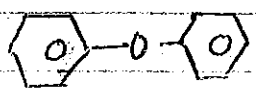
Q Which of the following ether can't form by williamson ether syn

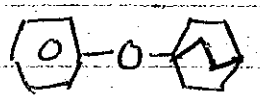
(A)  (B)  (C) Ph-O-Ph (D) 

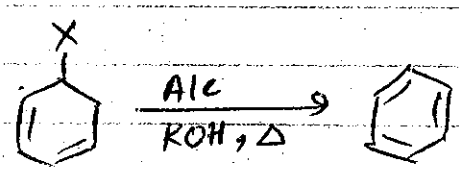
Ether Cleavage, (1)  conc HI → 

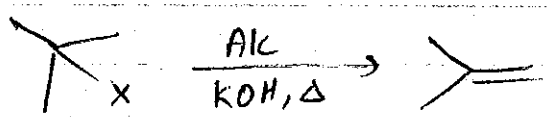
(2)  Conc. HBr →  + CH_3-CH_2-Br

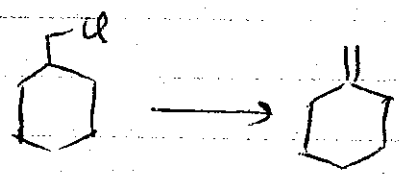
(3)  Conc. HI →  + 

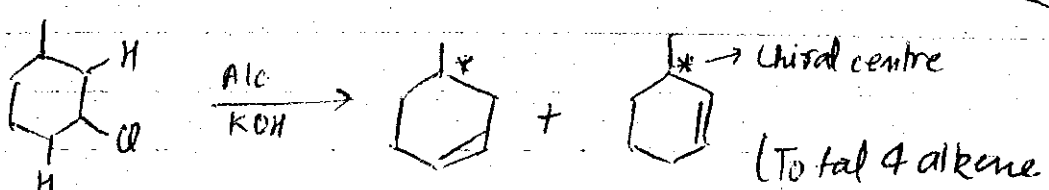
(4)  Conc HI → No cleavage

(5) 

E^2 elimination (1) 

(1') 

(3) 

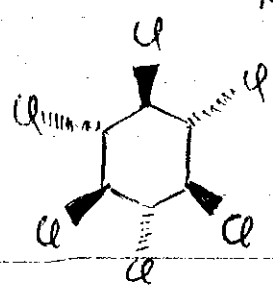
(4)  * → Chiral centre

(Total 4 alkene

(5) $CH_3-\underset{Cl}{CH}-CH_3 \xrightarrow[KOH,\Delta]{Alc.} CH_2=CH-CH_3$

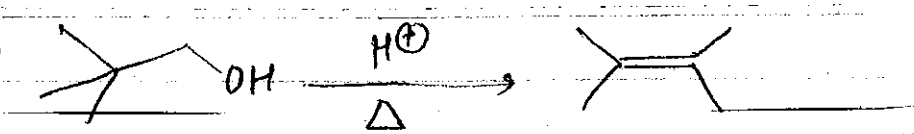
(6) $CD_3-\underset{Cl}{CD}-CD_3 \xrightarrow[KOH,\Delta]{Alc.} CD_2=CD-C$

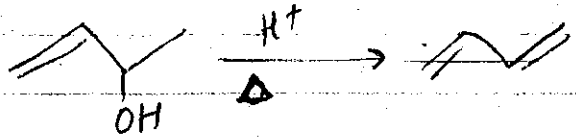
$\gamma_5 > \gamma_6$

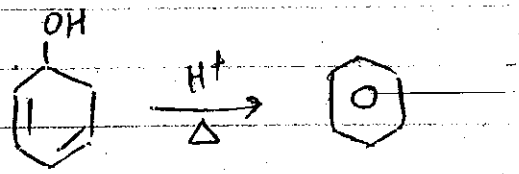
(7)  $\xrightarrow[KOH,\Delta]{Alc.}$ No E^2 elimination

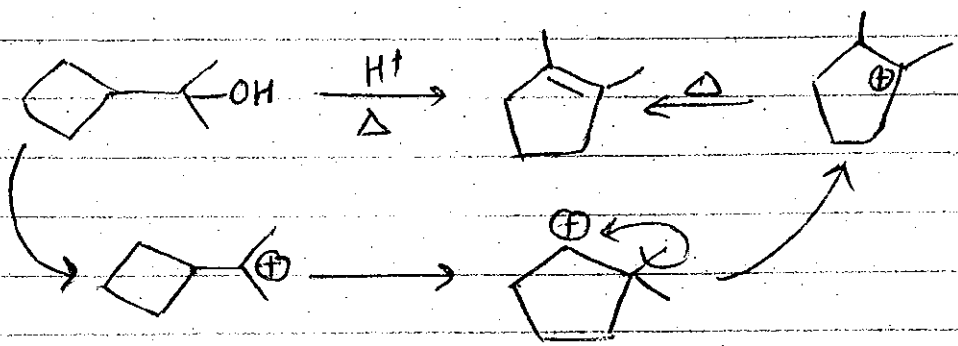
SHEET7

E^1 elimination

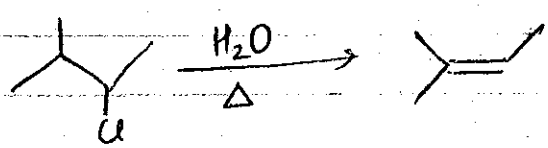
① 

② 

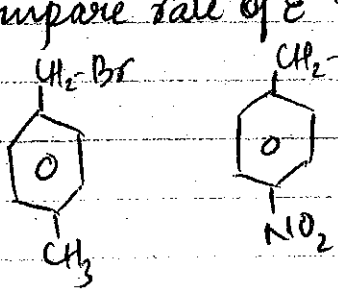
③ 

④ 

⑤ $Ph-CH_2-CH_2-OH \xrightarrow[\Delta]{H^+} Ph-CH=CH_2$

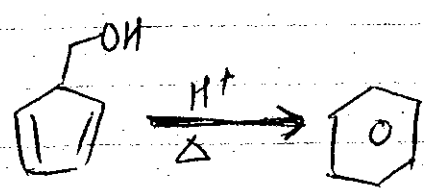
⑥ 

⑦ Compare rate of E^1 reaction



Rate of $E^1 \propto$ Stability of C^+

$a > c > b$

⑧ 

Reaction With Ambidentate Nucleo Electrophile

Nucleophile having more than one donor atom then it is a Ambidentate Nucleophile.

$\overset{\ominus}{C}\equiv\ddot{N}$ $\qquad$ $O^{\ominus}-\ddot{N}=O$

↳ Ambidentate $Nu^{\ominus}$

① $R-X$ $\xrightarrow[\text{II}]{Na^{+}CN^{-}/R-C\equiv N}$ $R-C\equiv N$ ⇒ S_N2 (major)

$\overset{\ominus}{C}\ddot{N}$

② $R-X$ $\xrightarrow[\text{II}]{Ag-C\equiv\ddot{N}}$ $R-N\equiv C$ ⇒ S_N2 (major)

covalent char.

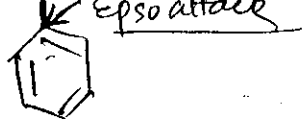
high ϕ

③ $R-X$ $\xrightarrow[\text{II}]{K^{+}\bar{O}-N=O}$ $R-O-N=O$ ⇒ S_N2 (major)

Ionic comp.

④ $R-X$ $\xrightarrow[\text{II}]{Ag-O-\ddot{N}=O}$ $R-NO_2$ ⇒ S_N2 (major)

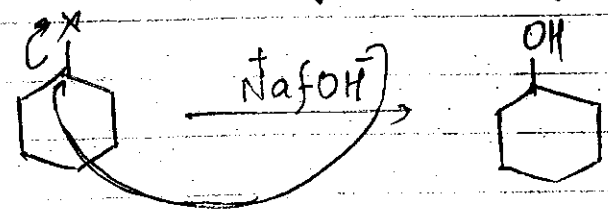
high ϕ



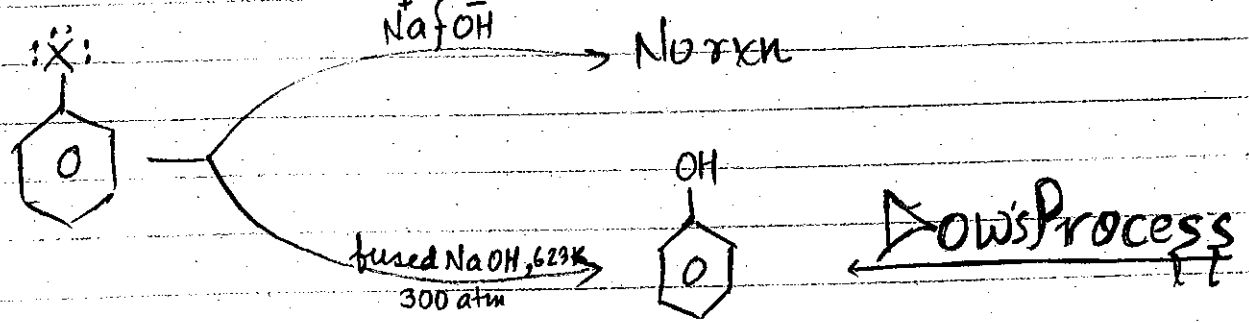
Indirect Substitution

Nucleophilic Substitution Aromatic Rxn (S_N^{Ar})

Hydrolysis Of Aryl halide

① 

⇒ S_N^2 Mech

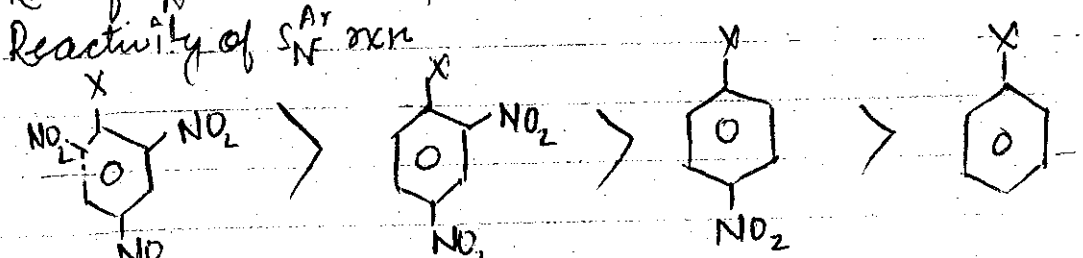


At room temp. aryl halide does not give S_N^1 & S_N^2 rxn due to partial double bond character but at drastic cond. (high temp & press.) Aryl halide having halide strong ewg at o- & p- position then it give S_N^{Ar} rxn.

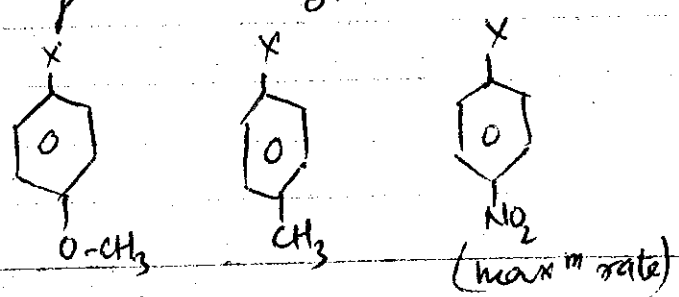
KEY POINT

Rate of S_N^{Ar} rxn ∝ EWG

Reactivity of S_N^{Ar} rxn



≃ gentle heating ≃ 368K ≃ 443K ≃ 623K



No rxn (max^m rate)

Nucleophilic Substitution through Addition followed by Elimination (S_N^{AE})

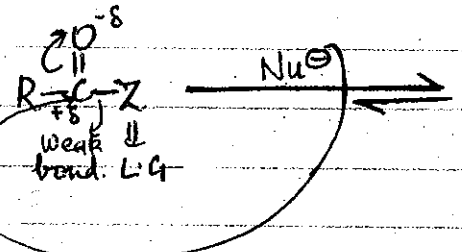
KEY POINT - 1

① $-\overset{O}{\overset{\|}{C}}-L.G$ — C having leaving grp hence it gives S_N^{AE} rxn

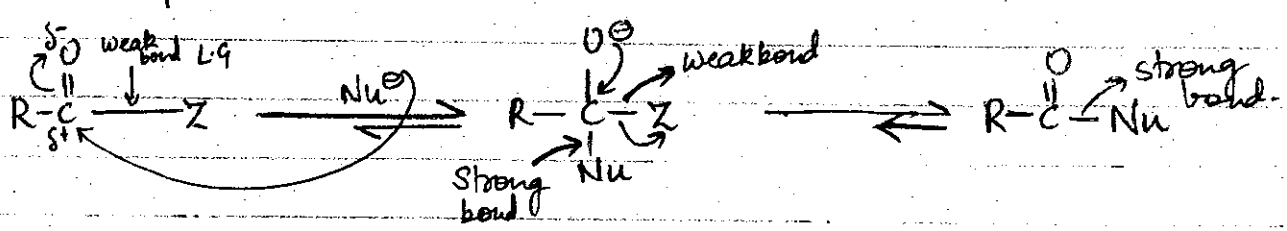
② Acid & Acid derivative give S_N^{AE} rxn due to presence of L.G. while carbonyl compound give NAR rxn (NO LG)

Motive ⇒ In S_N^{AE} rxn unstable acid derivative change into stable acid derivative.

Net rxn



Mech



Diff. Acid & Acid Derivative

(Next Page)

एक बार Acylation कराने में 42gm mass add होता है। 43-1 = 42gm

$CH_3-\overset{O}{\overset{\|}{C}}-$ (43)

$R-\ddot{O}\cdot$ (+H, -1) →

Concept

Acidhalide → more D.B char.

Anhydride

Ester

Amide

Acid → Max D.B char

UP

⇒ I-effect ⇓

⇒ +R-effect ↑

⇒ Partially D.B char. ↑

⇒ +δ Positive charge ⇓

⇒ Bond Strength ⇓

⇒ Bondlength ⇓

⇒ Rate of S_N^{AE} ⇓

DOWN

UP → बनाने → DOWN

UP → हटाने !! → DOWN

$R-\overset{O}{\overset{\|}{C}}-Cl$

$R=CH_3$ (Acyl) ⇒ Acylation Rxn

$R=H$ (formyl) ⇒ formylation Rxn

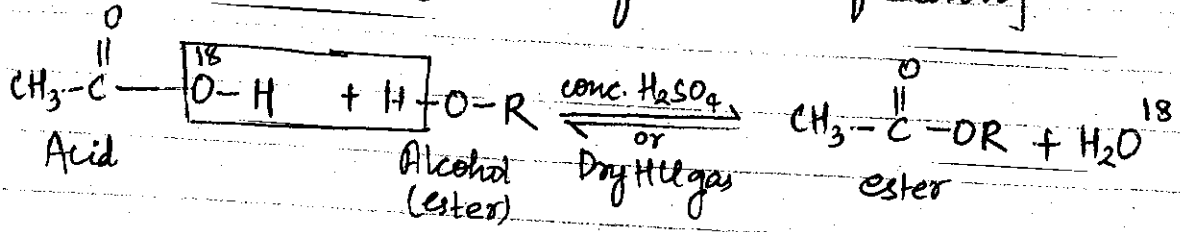
$R=$ Ⓞ {Benzoyl} = Benzoylation

$H-\ddot{O}H$	$> R-\overset{O}{\overset{\|}{C}}-OH$
$R-\ddot{O}H$	$> R-\overset{O}{\overset{\|}{C}}-OR$
$R-\ddot{N}H_2$	$> R-\overset{O}{\overset{\|}{C}}-NH-R$
Ⓞ$-\ddot{N}H_2$	$> R-\overset{O}{\overset{\|}{C}}-NH-$Ⓞ ⇒ Schotten-Baumen rxn
$CH_3-\overset{O}{\overset{\|}{C}}-O^{\ominus}Na^{\oplus}$	$> R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$
$\overset{-\delta}{R-Mgx}$ (1 mole)	$> R-\overset{O}{\overset{\|}{C}}-R$
CH_3-OH	$> R-\overset{O}{\overset{\|}{C}}-O-CH_3$
$Na-\ddot{I}$	> XXX
$Na-\ddot{B}r$	> XXX

P-379

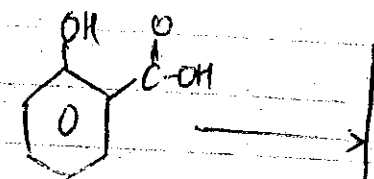
Esterification Rxn [Acid catalysed esterification]

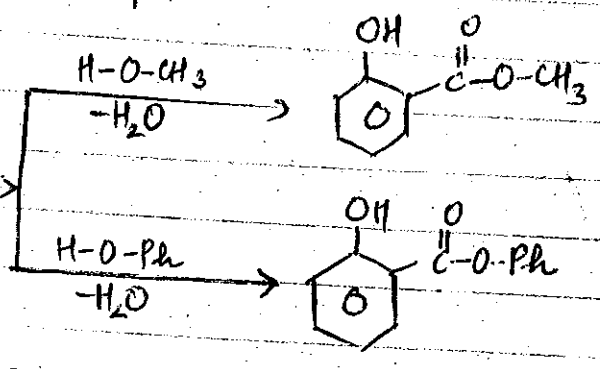
Net Rxn



Application Of Esterification

① Salicylic Acid

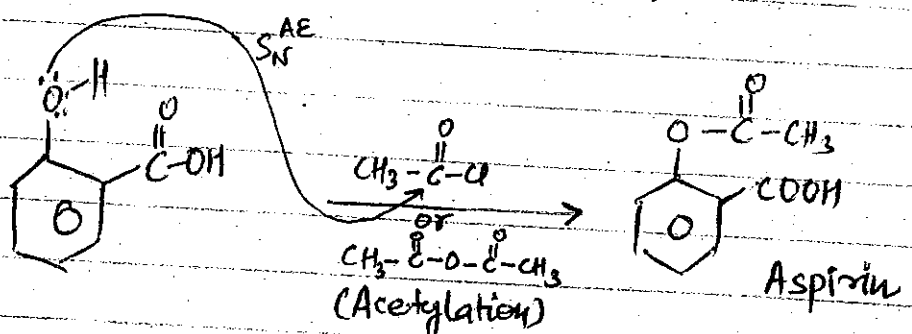




⇒ methyl salicylate
⇒ Oil of wintergreen
⇒ Use ⇒ joint pain

⇒ Phenyl Salicylate
⇒ Salol
⇒ Use ⇒ Astringent

② (Acetylation)

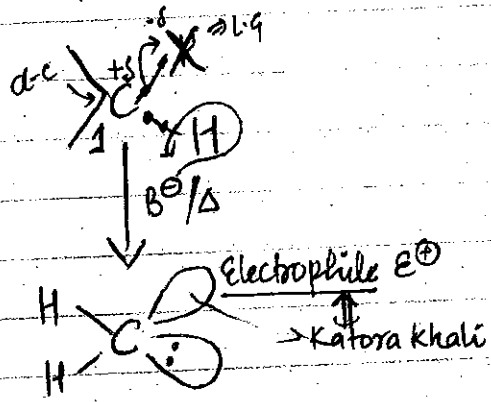


Aspirin

When acid react with alcohol in the presence of conc. H_2SO_4 or dry HCl gas then due to condensation rxn it form ester. This rxn is known as ESTERIFICATION.

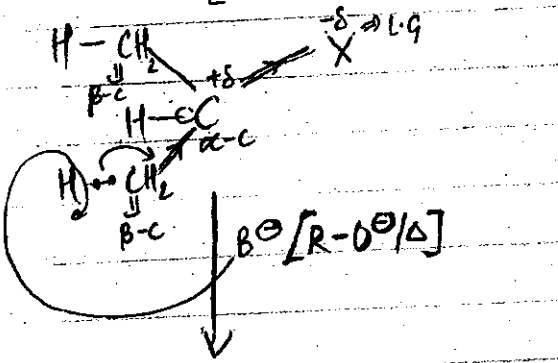
Elimination Reaction

α-Elimination
[1,1 - Elimination]



Carbene

β-Elimination
[1,2 - Elimination]



$CH_2 = CH - CH_3$ Alkene.

β-Elimination

E^2 - Elimination Rxn
eg. Dehydrohalogenation Rxn

E^1 Elimination Rxn
eg. Acidic dehydrat^n of Alcohol

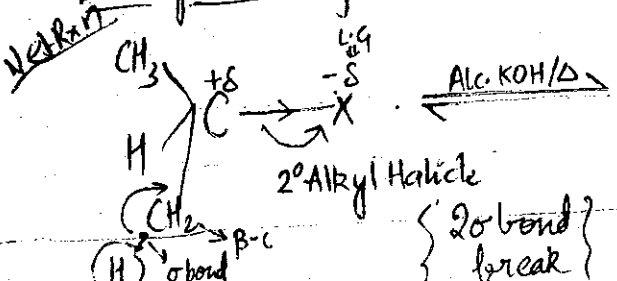
E^i - Elimination Rxn
(Intramolecular Elimination Rxn)

eg. Pyrolysis of Trialkyl Ammonium Ion
Pyrolysis of Ester

E^2 Elimination [Bimolecular Elimination Rxn]

Dehydrohalogenation Rxn

Mechanism



$CH_2 = CH - CH_3 + KX$ $\Delta H = (+)ve$

Mech

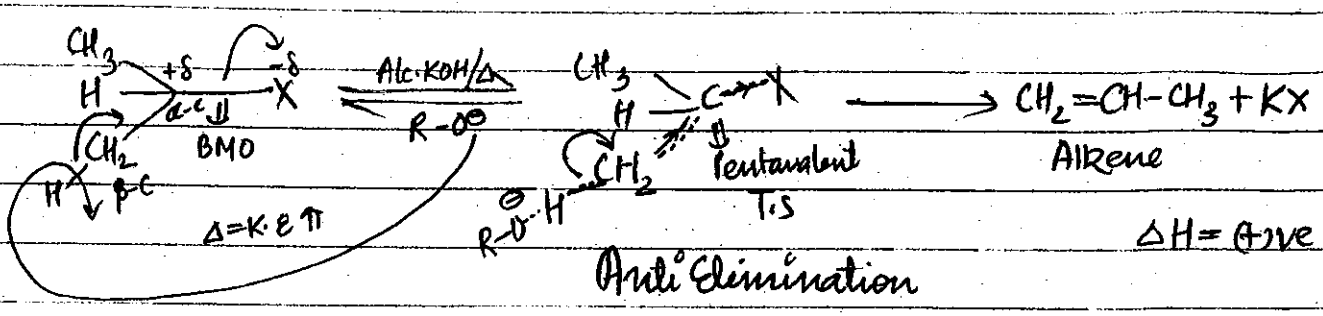
Alc. KOH ⇒ R-O(H) + K(+)(OH)(−) ⇌ R-O(−) K(+) + H_2O

3.5 3.5

Anion unstable rxn ⇌ वापस आ जाएगी | excess KOH डालेंगे Nu⊖ ↓ Base ↑ Rxn will occur

R-O⊖ K⊕ → Base

→ Nu⊖



Elimination rxn carried out at high temp (Δ)

anti elimination

rxn endothermic

molecularity of rxn is (2)

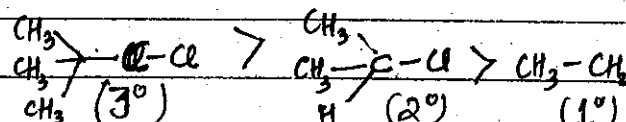
Order of rxn (2)

In E_2 rxn pentavalent T.S is formed.

In T.S of E_2 rxn partially double bond character develop.

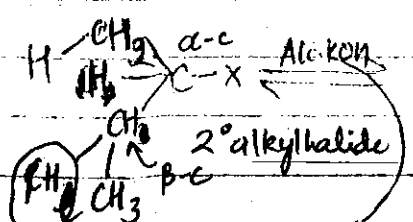
Reactivity of E_2 rxn ∝ Stability of alkene

Rate of E2 rxn :-



E2 rxn depends on ability of leaving group.

R-I > R-Br > R-Cl - R-F



Alc. KOH

(CH3)-CH=CH-CH3 + CH2=CH-CH2-CH3 + KX ΔH= -ve

G.S

major trans > cis

(major)

less stable alkene

(Minor)

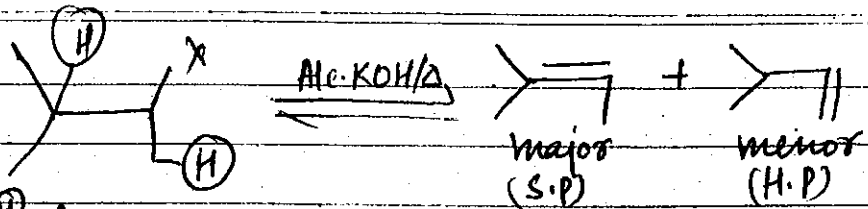
stable Alkene

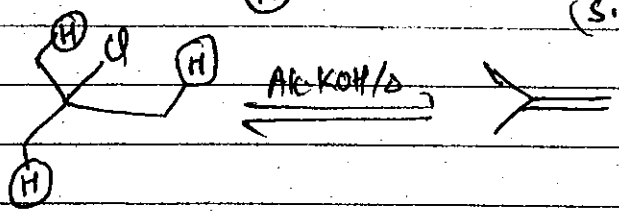
Saytzeff product

S.P

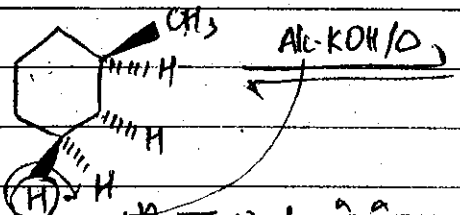
Hoffmann's Product

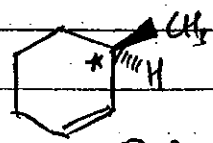
(H.P)

Q2 

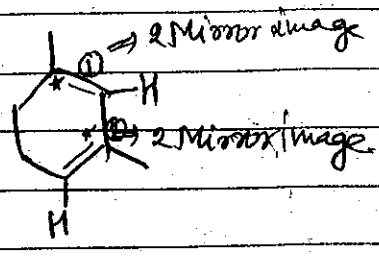
Q3 

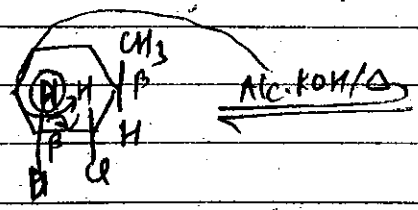
(same product by all H)

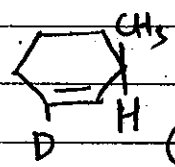
Q4 


② Product

anti Elimination H दूसरा wedge पे होगा और दूसरा Dash पे।



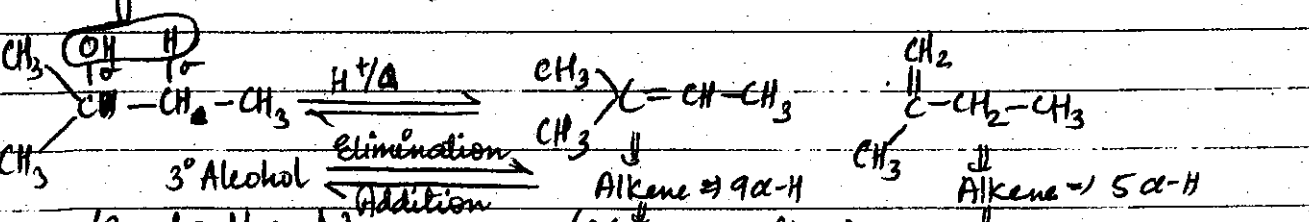
Q5 


② Product

E^1 Elimination Reaction [Unimolecular Elimination Rxn]

Acidic dehydration Of Alcohol

Mech Rxn



Dehydrating Agent
① conc. H_2SO_4 / Δ
② conc. H_3PO_4 / Δ
③ conc. $KHSO_4$ / Δ
④ Cu / 300°C ⇒ Dehydration of only 3° Alcohol.
1° & 2° alcohol ⇒ Oxidation
⑤ Al_2O_3 / Δ
⑥ P_2O_5 (Li_4O_2)

H+ खाएगा ~~E2~~ E1

OH निकल गया तो H निकालो (जहां पर Alkene stable हो)

Mech

Step-I $Conc\ H_2SO_4 \rightleftharpoons H^+ + O^{\ominus}-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$

(8 α-H)

(Carbocation Intermediate)

Step-II $CH_3-\overset{\overset{CH_3}{|}}{C}-CH_2-CH_3$ (:OH3 Poor leaving grp.) $\xrightleftharpoons{H^{\oplus}}$ $CH_3-\overset{\overset{CH_3}{|}}{C}-CH_2-CH_3$ (H–O(H)–H Best L.G.) $\xrightarrow[-H_2O]{RDS}$ $CH_3-\overset{\overset{CH_3}{|}}{C^{\oplus}}-CH-CH_3$

$CH_3-\overset{\overset{CH_3}{|}}{C^{\oplus}}-CH-CH_3 \rightleftharpoons$ $CH_3-C(CH_3)=CH-CH_3$ (H.P) + $CH_2=C(CH_3)-CH_2-CH_3$ (S.P)

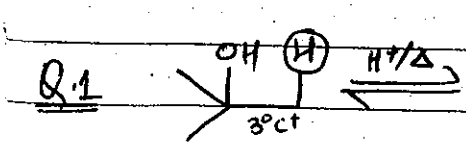
carried out at higher temp.
endothermic rxn
2 step rxn
C^{+} intermediate is formed in this reactⁿ
C^{+} formation ⇒ RDS of rxn
C^{+} rearrangement possible.
Reactivity of rxn ∝ Stability of C^{+}

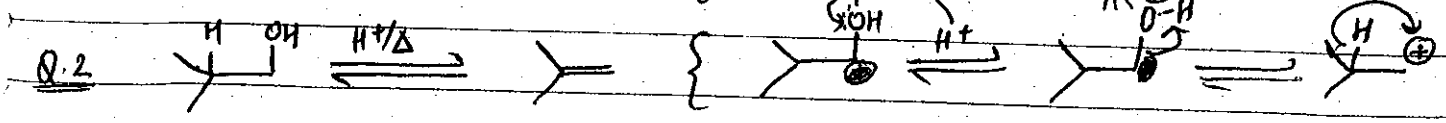
NOTE In dehydration rxn we cannot use conc. HX (HF, HBr...) as all these reagent favours substitution rxn (Good Nucleophile)

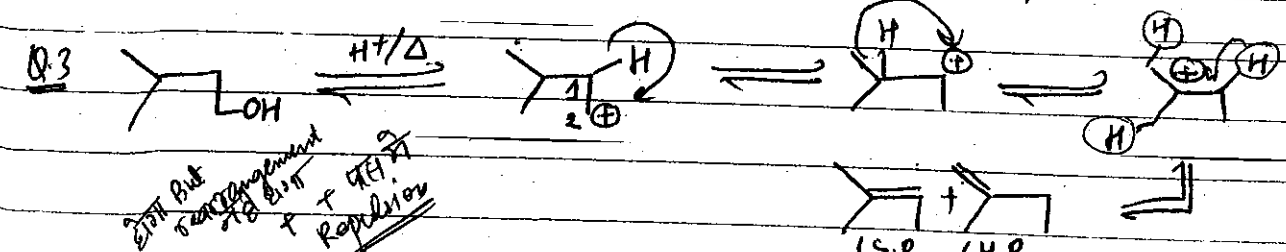
Rate of dehydration rxn ~~>OH~~ > >OH > ^OH

3° Alcohol 2° alcohol 1° Alcohol

Δ/PPS (H_2O, R-OH ···c+c) E_1 > 3°c+ > 2°c+ > 1°c+

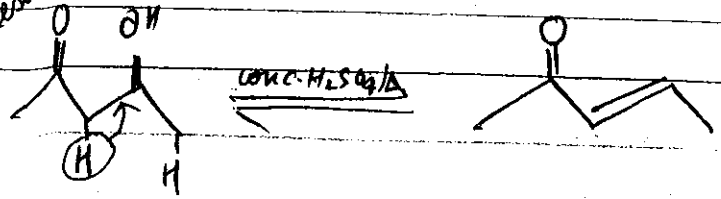
Q.1 

Q.2 

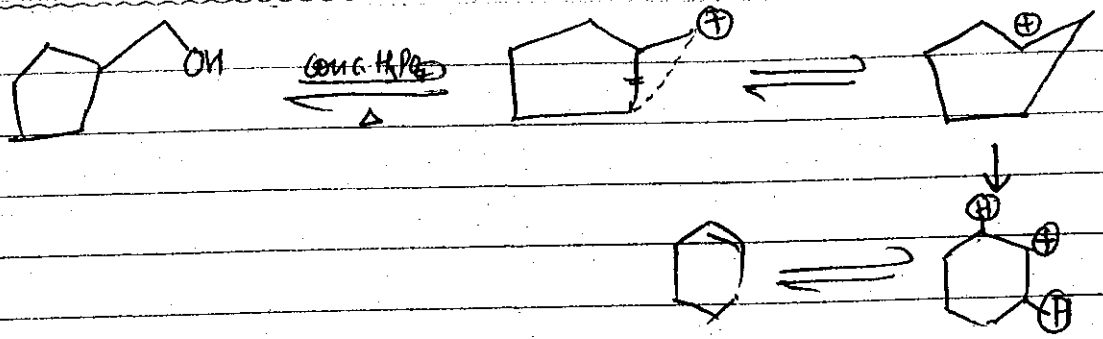
Q.3 

Zero. ESR But rearrangement ho sakta hai + + ve Repulsion

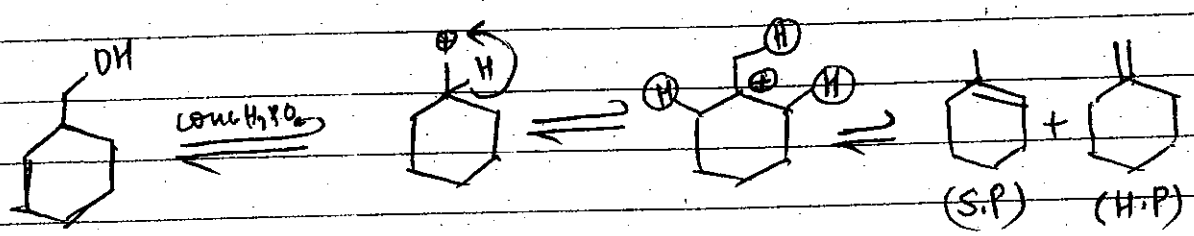
(S.P CH.P)

Q.9 

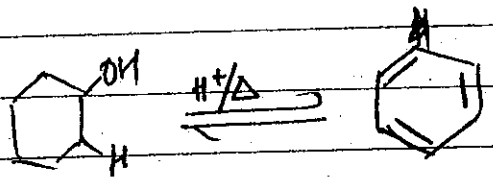
Q.5



Q.6



Q.7



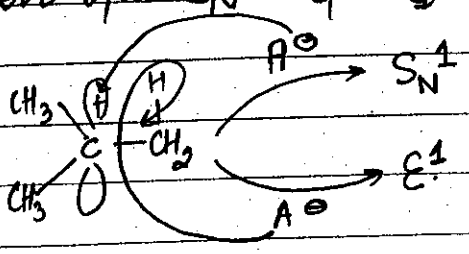
Saytzeff's Rule

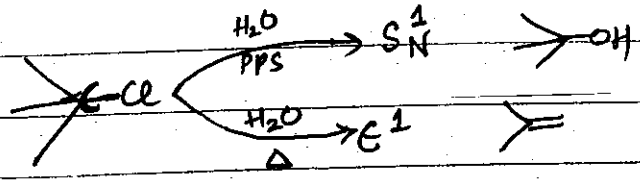
Acc. to Saytzeff, more alkyl substituted alkene is major product.

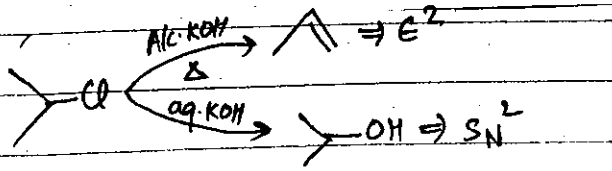
Hoffman's Rule

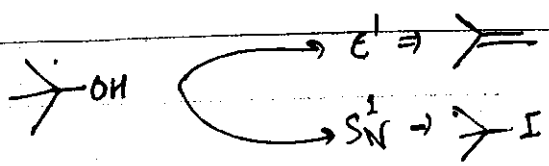
less alkyl substituted alkene will be major product

Comparison b/w S_N1 & E_1 & S_N2 & E_2

Key pt:- ① 

② 

③ 

④ 

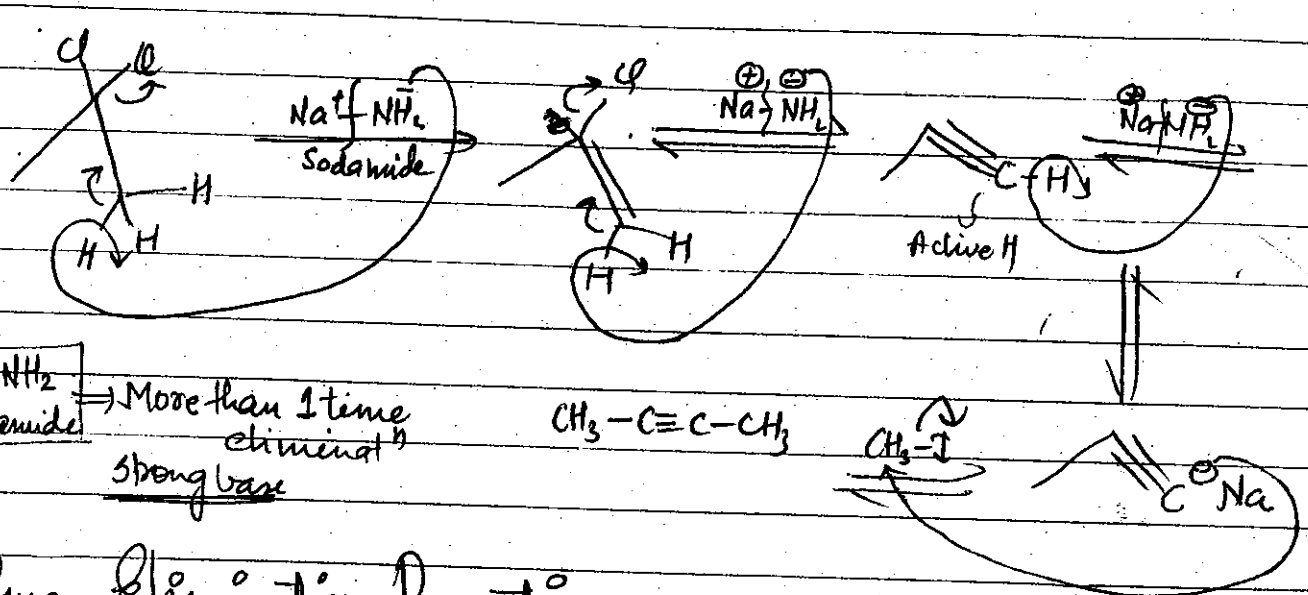
Br Br

पहले से H को खा जाए (E2)

$C_2H_5-OH \xrightarrow{conc.\ H_2SO_4}$ 170°C / 443K $\rightarrow CH_2=CH_2 \Rightarrow E^1$ { $CH_3-CH_2-\ddot{O}H \rightleftharpoons CH_3-CH_2-\overset{\oplus}{O}(H)H \rightleftharpoons CH_2-CH_2^{\oplus}(H)$; $CH_2=CH_2$ }

140°C / 413K $\rightarrow CH_3-CH_2-O-CH_2-CH_3$ (Williamson continuous ether syn.) S_N^2

Mech $2CH_3-CH_2-\ddot{O}H \xrightarrow{H^{\oplus}} CH_3-CH_2-\overset{\oplus}{O}(H)H \xrightarrow{CH_3CH_2\ddot{O}H} CH_3-CH_2-O-CH_2-CH_3 \Rightarrow S_N^2$



$NaNH_2$ Sodamide ⇒ More than 1 time elimination

Strong base

$CH_3-C\equiv C-CH_3$

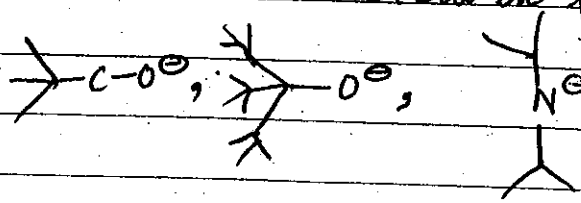
CH_3-I

3 Hoffman Elimination Reaction

It is an anti elimination

Kind of E^2 elimination

**Hoffman Eliminat^n rxn carried out in presence of sterically hindered base



If in E rxn if sterically hindered base not ⊕ then rxn carried out with poor L.G

$-F$, $-\overset{+}{N}R_3$, $-\overset{+}{S}R_2$ Poor L.G

anion like char. dev. in T.S.

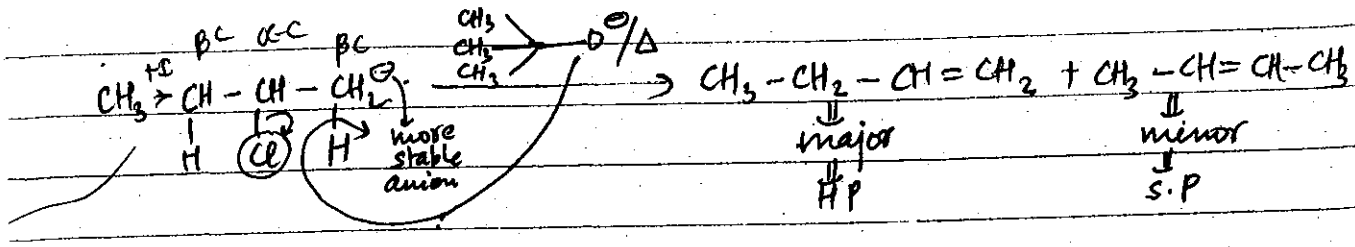
① $CH_3-\underset{H}{\underset{|}{CH}}-\underset{F}{\underset{|}{CH}}-\underset{H}{\underset{|}{CH_2}}^{\ominus} \xrightarrow{CH_3O^{\ominus}/\Delta} CH_3-CH_2-CH=CH_2 + CH_2-CH=CH-CH_3$

β-C, α-C, β-C; F: Poor L.G; H: more stable anion

major (HP) ; minor SP

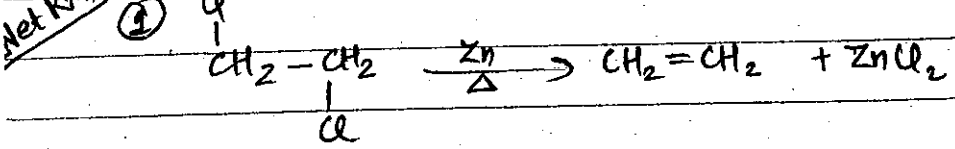
~~If Cl ⇒ then~~

If Cl with $CH_3O^{\ominus} \Rightarrow E^2$

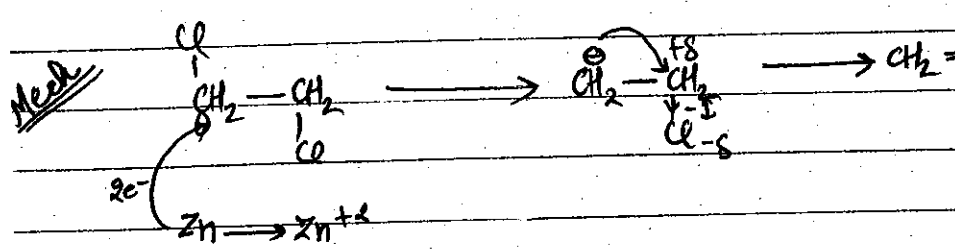


④ Elimination of Dihalogen

Net Rxn

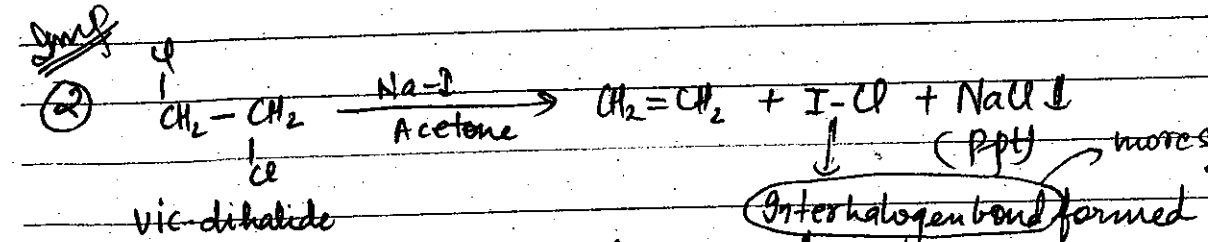


Mech



Rate of Rxn ⇒ R-I > R-Br > R-Cl > R-F

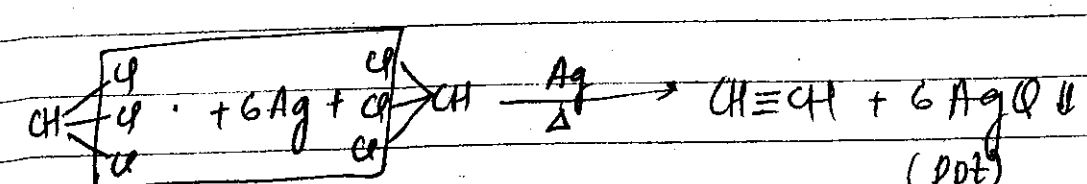
Synth

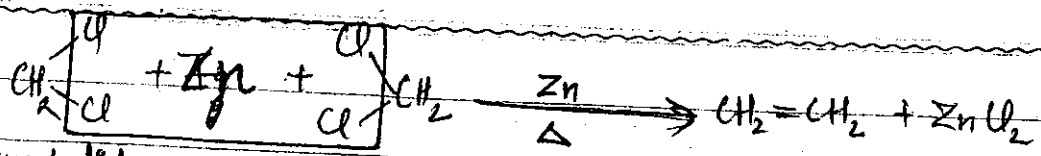


Rxn is anti elimination
Rxn is E^2 elimination & anti Elimination

③ Elimination of gem-trihalide & gem-Dihalide

①



(2) 

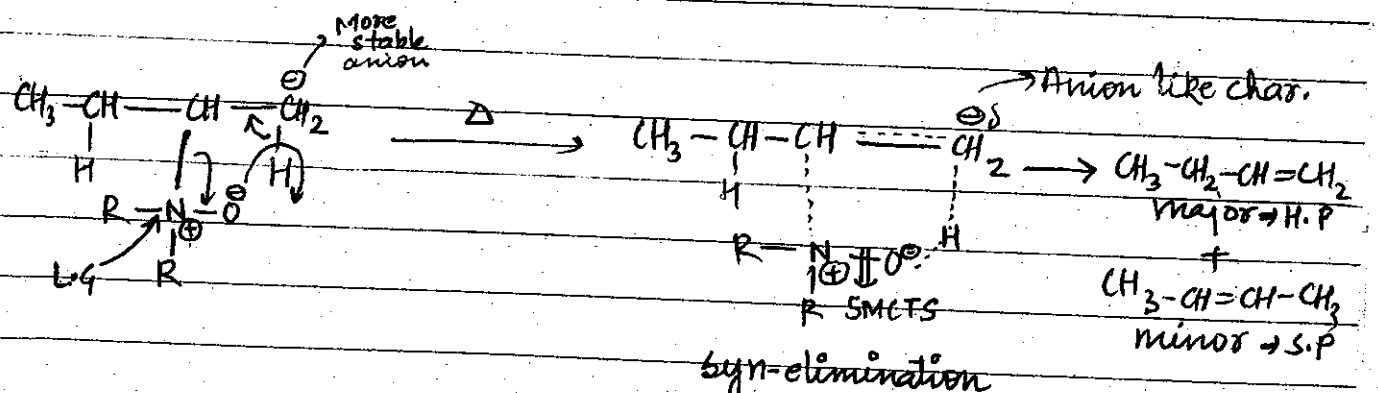
gem-halide.

(6) Ei Elimination Rxn [Intramolecular Elimination Rxn]

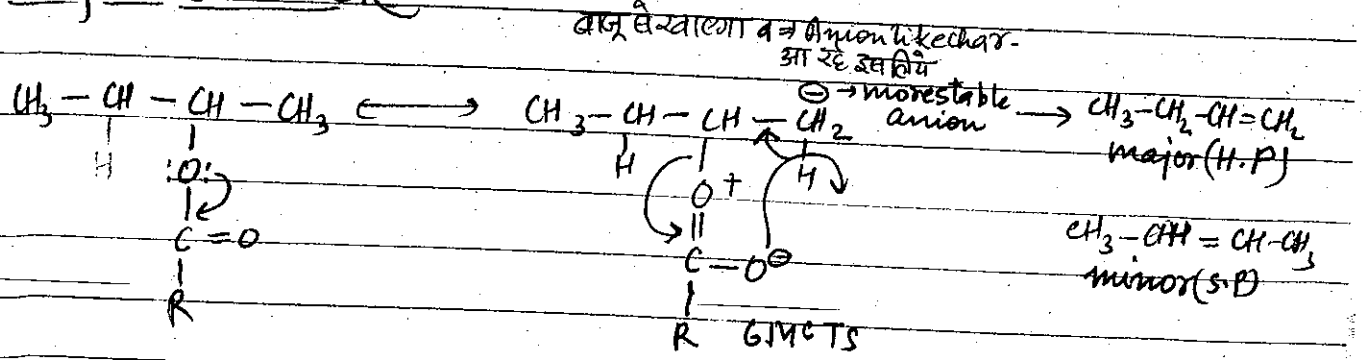
Rxn is carried out at higher temp.
Rxn completed with syn elimination

(A) PYROLYSIS OF TRIALKYL AMMONIUM ION ($R_3-\overset{\oplus}{N}-O^{\ominus}$)

5MCTS formed in this rxn
Anion like character dev. in T.S.



(B) PYROLYSIS OF ESTER



Oxidation Of Organic Chemistry

① Oxidation By Strong Oxidising Agent

A) $KMnO_4$ [H^+/$OH^\ominus$/Δ/Neutral]

Pink colour ⟶ colourless

B) $K_2Cr_2O_7$

Orange colour ⟶ green colour

⟹ same sant

1. $CH_3-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-OH \xrightarrow{KMnO_4} CH_3-\overset{\overset{O}{||}}{C}-H \xrightarrow{KMnO_4} CH_3-\overset{\overset{O}{||}}{C}-OH$

H 1°Alcohol

2. $CH_3-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH \xrightarrow{KMnO_4} CH_3-\underset{\underset{O}{||}}{C}-CH_3 \rightarrow$ No oxidat^n

H 2°Alcohol

3. $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH \xrightarrow{KMnO_4}$ No oxidat^n

CH_3 3°Alcohol

4. $H-\overset{\overset{O}{||}}{C}-H \xrightarrow{KMnO_4} H-\overset{\overset{O}{||}}{C}-OH \longrightarrow HO-\overset{\overset{O}{||}}{C}-OH$ $\quad CO_2\uparrow + H_2O$

Formic Acid

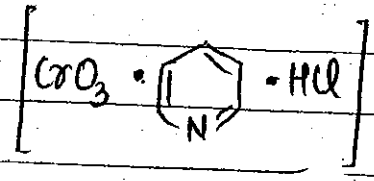
6. $R-\overset{\overset{O}{||}}{C}-H \xrightarrow{KMnO_4} R-\overset{\overset{O}{||}}{C}-OH$

6. $CH_3-\underset{\underset{O}{||}}{CH}\equiv\underset{\underset{O}{||}}{CH}-CH_3 \xrightarrow{KMnO_4} CH_3-\overset{\overset{O}{||}}{C}-H \xrightarrow{KMnO_4} CH_3-\overset{\overset{O}{||}}{C}-OH$

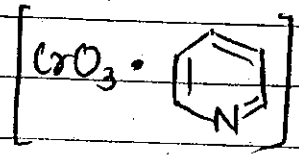
7. $CH_3-\underset{\underset{O}{||}}{C}\equiv\underset{\underset{O}{||}}{C}-CH_3 \xrightarrow{KMnO_4} CH_3-\overset{\overset{O}{||}}{C}-OH$ (Acid)

② Oxidation by Moderate Oxidising Agent

Ⓐ PCC (Pyridinium Chloro Chromate)



Ⓑ Collines Reagent



(C_5H_5N)

⇒ 1° Alcohol ⟶ Aldehyde
2° Alcohol ⟶ Ketone.

Ⓒ Zone's Reagent

[CrO_3, dil. H_2SO_4 in Acetone] 1° Alcohol ⟶ Aldehyde ⟶ Acid

Ⓓ Cu/300°C

① $CH_3-\underset{\underset{H}{|}}{\overset{H}{\overset{|}{C}}}-OH \xrightarrow{Cu/300^\circ C} R-\underset{H}{\overset{|}{C}}=O + H_2\uparrow$

1° Alcohol

(Dehydrogenation)
↓
Elimination

② $CH_3-\underset{CH_3}{\overset{H}{\overset{|}{C}}}-OH \xrightarrow{Cu/300^\circ C} CH_3-\underset{O}{\overset{||}{C}}-CH_3 + H_2\uparrow$

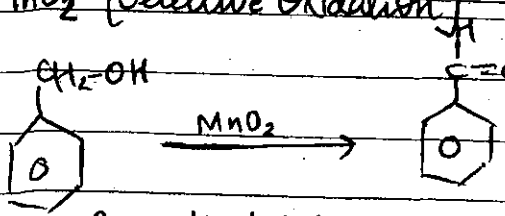
2° Alcohol

③ $CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{C}}}-OH \longrightarrow \underset{CH_3}{\overset{CH_3}{>}}C=C + H_2O$

3° Alcohol

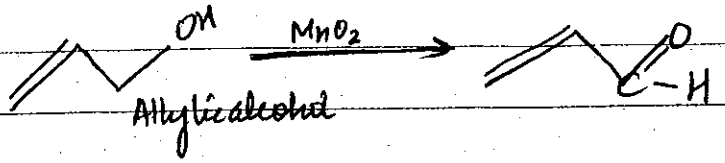
⇒ Dehydration Rxn.

Ⓔ MnO_2 {Selective Oxidation}



Benzylic alcohol

Complex will work यदि central metal से charge गायब हो जाए



3) Oxidation by Mild Oxidising Agent

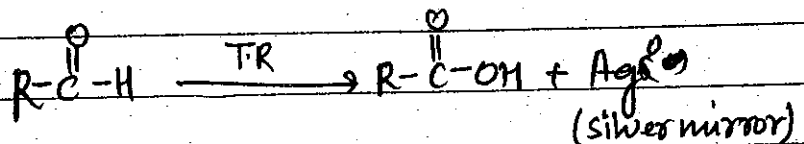
A) Tollen Reagent (T.R)

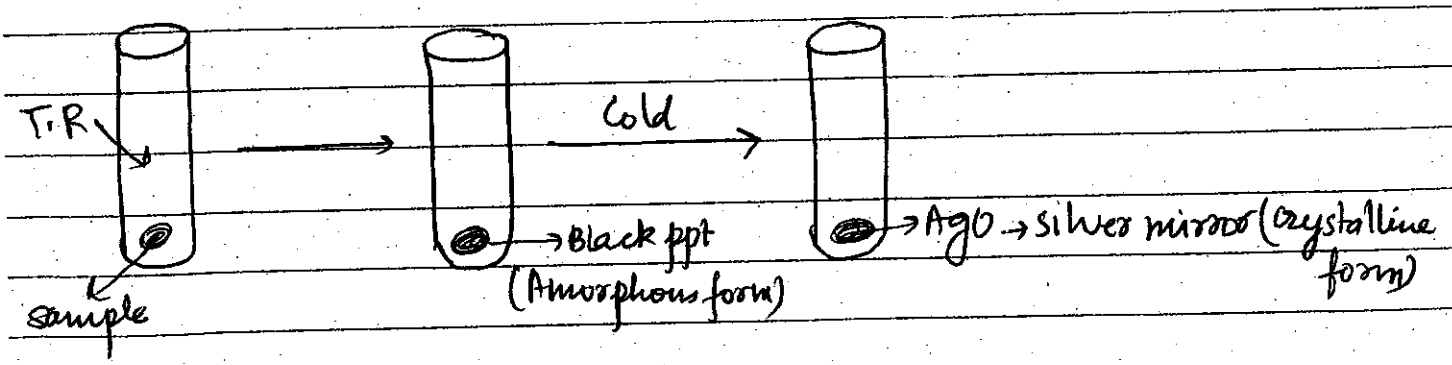
[Ammonical Silver Nitrate]

$[AgNO_3 + NH_4OH] \rightarrow$ T.R

$[Ag(NH_3)_2]OH \rightarrow$ T.R

[Diammine silver (I) hydroxide]



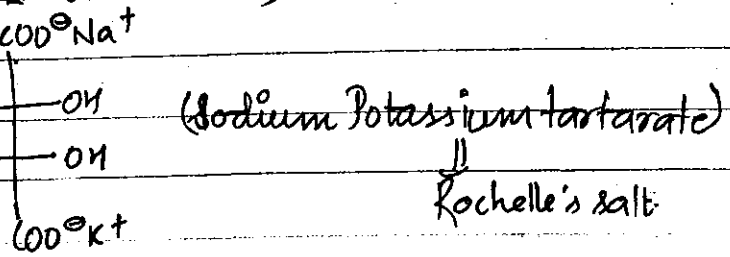


Tollen reagent oxidise all aliphatic & aromatic aldehyde & give silver mirror while Fehling & Benedict sol^n only oxidise aliphatic aldehyde (acc. to ECS)

(B) Fehling Sol^n

$F_A \Rightarrow CuSO_4 \cdot 5H_2O$ (Blue vitriol)

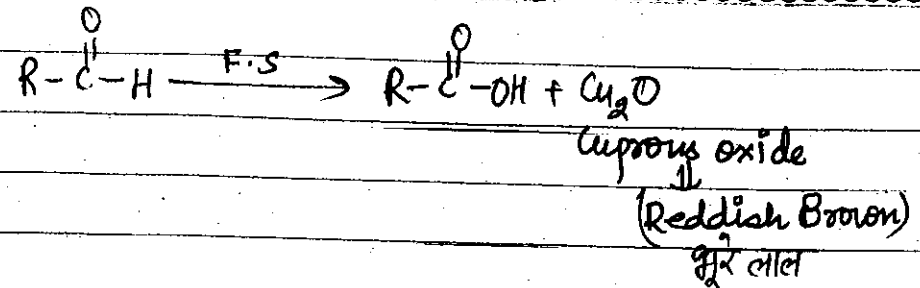
$F_B \Rightarrow NaOH$.



(Sodium Potassium tartarate)

||

Rochelle's salt



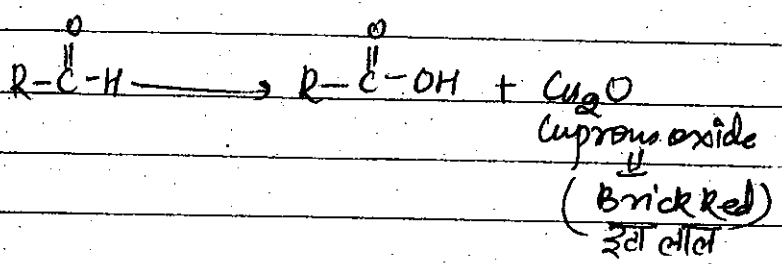
© Benedict Sol^{n}

$B_A \Rightarrow CuSO_4 \cdot 5H_2O$ (Blue vitriol)

$B_B \Rightarrow$ NaOH. CH_2-COO^-

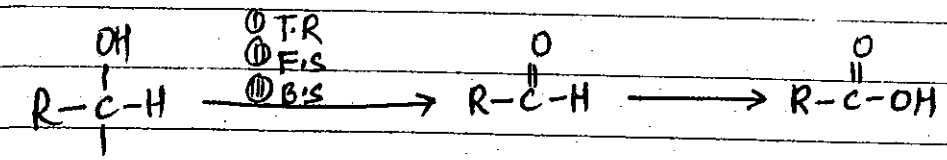
$HO-C-COO^-$

CH_2-COO^- (Citrate ion)



(d) Oxidation Of Hemiacetal

Hemiacetal give rxn with mild oxidising agent Tollen's Fehling & Benedict sol^{n} because all these reagent give rxn in basic med. & in basic med. hemiacetal change into aldehyde. & give rxn with mild oxidising agent



(e) Schiff Reagent

⇓

p-rosaline dye

⇓

Pink colour

⇓ SO_2

Colourless रंगहीन

$R-\overset{O}{\overset{\|}{C}}-R$ → No colour (No reappear)

$R-\overset{O}{\overset{\|}{C}}-H$ → Pink colour reappear

NiH_2 → सारे C=O को OH बना देता है।

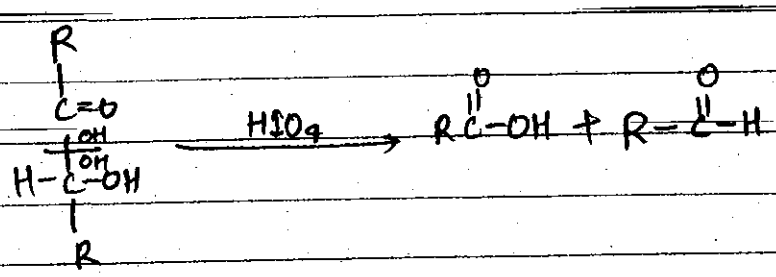
$LiAlH_4$ → संसार के सारे C=O को OH बना देता है।

SBH → Acid Halide & Aldehyde के C=O को OH बनाता है। Ketone

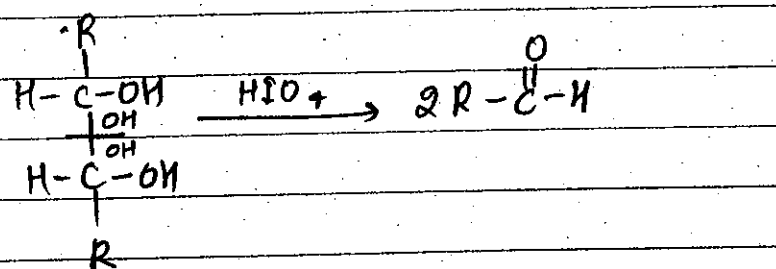
(Per Iodic Acid)

① Oxidation by HIO_4 (Periodic Acid)

(i)



(ii)



Reduction Of Organic Chemistry

	LAH [$LiAlH_4$]	SBH [$NaBH_4$]	Ni/H_2
① $R-\overset{O}{\overset{\|}{C}}-X \longrightarrow R-\overset{OH}{\overset{\|}{C}}H_2$	✓	✓	✓
② $R-\overset{O}{\overset{\|}{C}}-H \longrightarrow R-\overset{OH}{\overset{\|}{C}}H_2$	✓	✓	✓
③ $R-\overset{O}{\overset{\|}{C}}-R \longrightarrow R-\overset{OH}{\overset{\|}{C}}H-R$	✓	✓	✓
④ $R-\overset{O}{\overset{\|}{C}}-OR \longrightarrow R-\overset{OH}{\overset{\|}{C}}H_2 + R-OH$	✓	✗	✓
⑤ $R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R \longrightarrow 2\,R-\overset{OH}{\overset{\|}{C}}H_2$	✓	✗	✓
⑥ $R-\boxed{\overset{O}{\overset{\|}{C}}}-NH_2 \longrightarrow R-\boxed{CH_2}-NH_2$	✓	✗	✓
⑦ $R-\overset{O}{\overset{\|}{C}}-OH \longrightarrow R-\overset{OH}{\overset{\|}{C}}H_2$	✓	✗	✓

△

Red P, HI सारी Oxygen को $LiAlH_4$ → केवल Polar वाले को करेगा
निकाल देगा केवल C बचेगा Ni/H_2 → सबको करेगा
Oxygen का झंझट।

	LAH [$LiAlH_4$]	SBH [$NaBH_4$]	Ni/H_2
(8) $R-C\equiv N \longrightarrow RCH_2NH_2$	✓	✓	✓
(9) $R-N\equiv C \longrightarrow R-NHCH_3$	✓	X	✓
(16) $R-NO_2 \longrightarrow RNH_2$	✓	X	✓
	[$C_6H_5-NO_2 \rightarrow$ XXX लोचा है]		
(11) $CH_3-CH_2-X \longrightarrow CH_3-CH_3$	✓	X	✓
(12) $R-CH=CH-R \longrightarrow R-CH_2-CH_2-R$	X	X	✓
→ Non-Polar Bond को effect नहीं करता।			
(13) $R-C\equiv C-R \longrightarrow R-CH_2-CH_2-R$ ($LiAlH_4$)	X	X	✓

Strong Reducing Agent (Red P, HI)

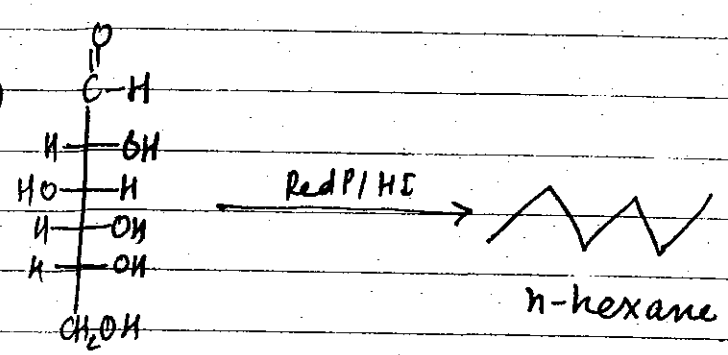
$R-CH_2-\overset{O}{\overset{\|}{C}}-H$

(1) $R-CH_2-\overset{O}{\overset{\|}{C}}-OH$ $\xrightarrow{Red\,P/HI}$ $R-CH_2-CH_3$

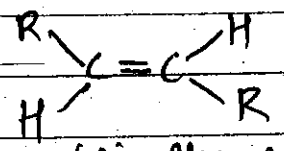
$R-\overset{O}{\overset{\|}{C}}-CH_3$

$R-CH_2-CH_2-OH$

(2)

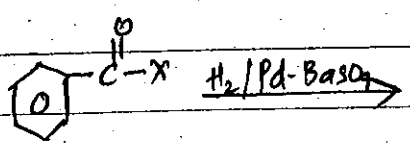


③ Partially Reduction by $H_2/Pd\text{-}BaSO_4/CaCO_3$
Lindlar catalyst

1. $R-C\equiv C-R \xrightarrow{H_2/Pd\,BaSO_4}$ 
Alkyne

(cis alkene)

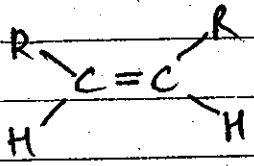
2 (i) $R-\overset{O}{\overset{\|}{C}}-X \xrightarrow{H_2/PdBaSO_4} R-\overset{O}{\overset{\|}{C}}-H$

(ii) 

} ⇒ ROSENMUND REDUCTION

3. $R-C\equiv N \xrightarrow{H_2/Pd\text{-}BaSO_4} R-CH=NH$
Imine

BIRCH REDUCTION

④ $R-C\equiv C-R \longrightarrow$ 

Alkyne. Trans-alkene

STEPHEN REACTION

$R-C\equiv N \xrightarrow[\text{(ii) } H_2O]{\text{(i) } SnCl_2+HCl\ (\text{Stephen reagent})} R-\overset{OH^-}{\underset{OH}{CH}}-\overset{H^+}{\underset{H^+}{NH_2}} \longrightarrow R-\overset{O}{\overset{\|}{C}}-H + NH_3$
Imine

MENDIUS REACTION

$R-C\equiv N \xrightarrow{Na+C_2H_5OH} RCH_2NH_2$

BUAVEAULT BEANC REACTION

$R-\overset{O}{\overset{\|}{C}}-\ddot{O}-R \xrightarrow{Na+C_2H_5OH} R-\overset{OH}{\underset{H}{CH_2}} + R-OH$

P-359

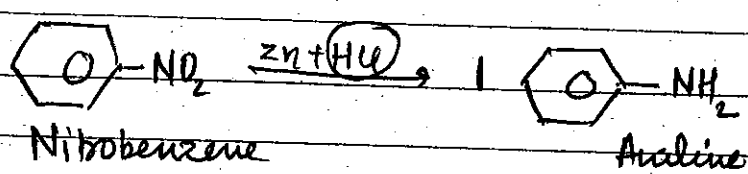
Reduction Of Alkyl halide

$R-CH_2-CH_2-X \xrightarrow[\text{(iii) } Na-C_2H_5OH]{\text{(i) } Fe+HCl \text{ (ii) } Sn+HCl} R-CH_2-CH_3$

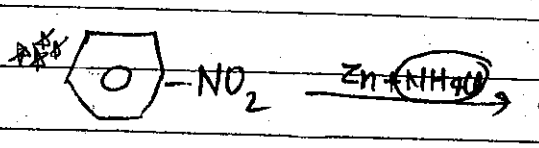
Reduction Of Nitro Compounds

① $R-NO_2 \xrightarrow[\text{(3) } Na+C_2H_5OH]{\text{(1) } Fe+HCl \text{ (2) } Sn+HCl} R-NH_2$

②

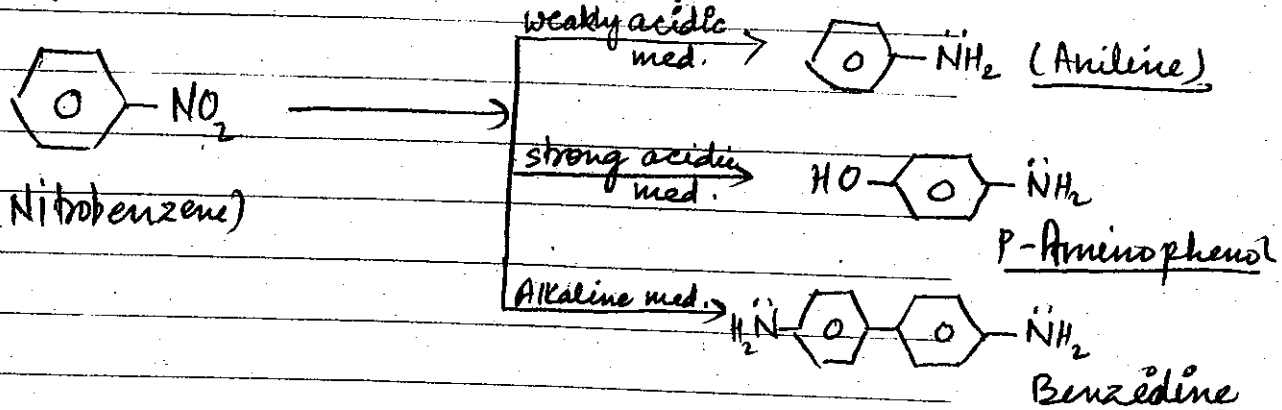


Nitrobenzene — Aniline (complete reduct^n)



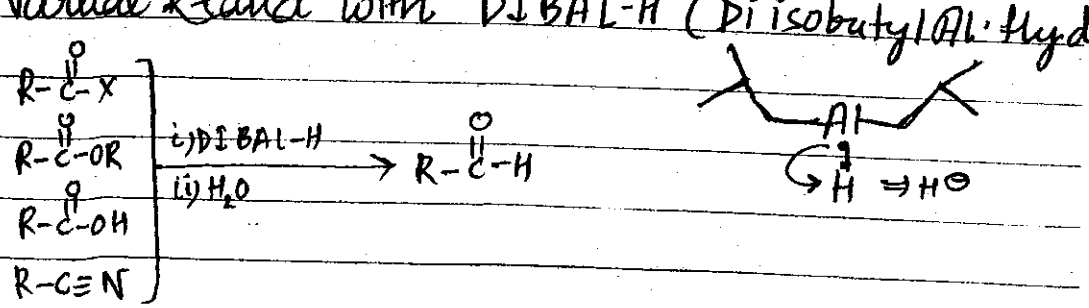
Partially Reduct^n

Electrolytic Reduct^n Of Nitro Compounds.



(Nitrobenzene) → Aniline; P-Aminophenol; Benzidine

Partial Reduct^n with DIBAL-H (Di isobutyl Al. Hydride)



(R) ① $R-\overset{O}{\overset{\|}{C}}-R \xrightarrow[HCl]{Zn-Hg} R-CH_2-R$ CLEMENSON REDUCTION

↳ Acidic Med.

② $R-\overset{O}{\overset{\|}{C}}-R \xrightarrow[\text{KOH/ethylene glycol, }\Delta]{NH_2-NH_2} R-CH_2-R$ WOLF KISHNER REDUCTION (WK)

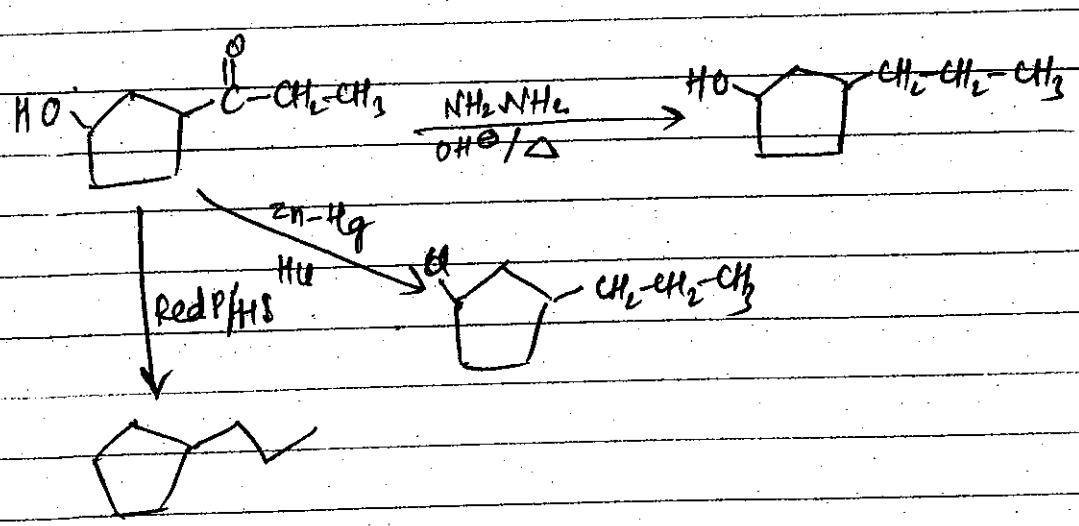
↳ Basic Med.

NH_2NH_2, $OH^{\ominus}/\Delta$

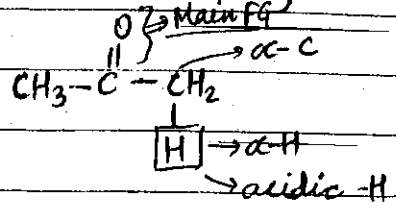
KEYPT :-

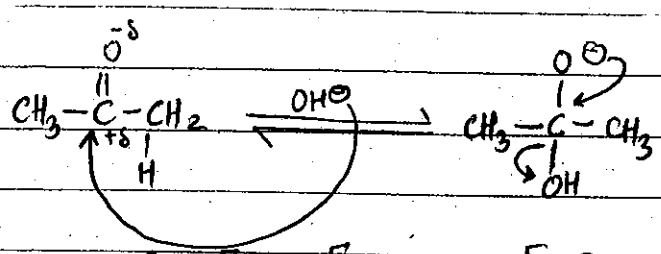
$-\overset{O}{\overset{\|}{C}}-$ ① Clemmenson Red. / ② Wolf Kishner Red. $\rightarrow -CH_2-$

Q1



Chemistry Of α-H



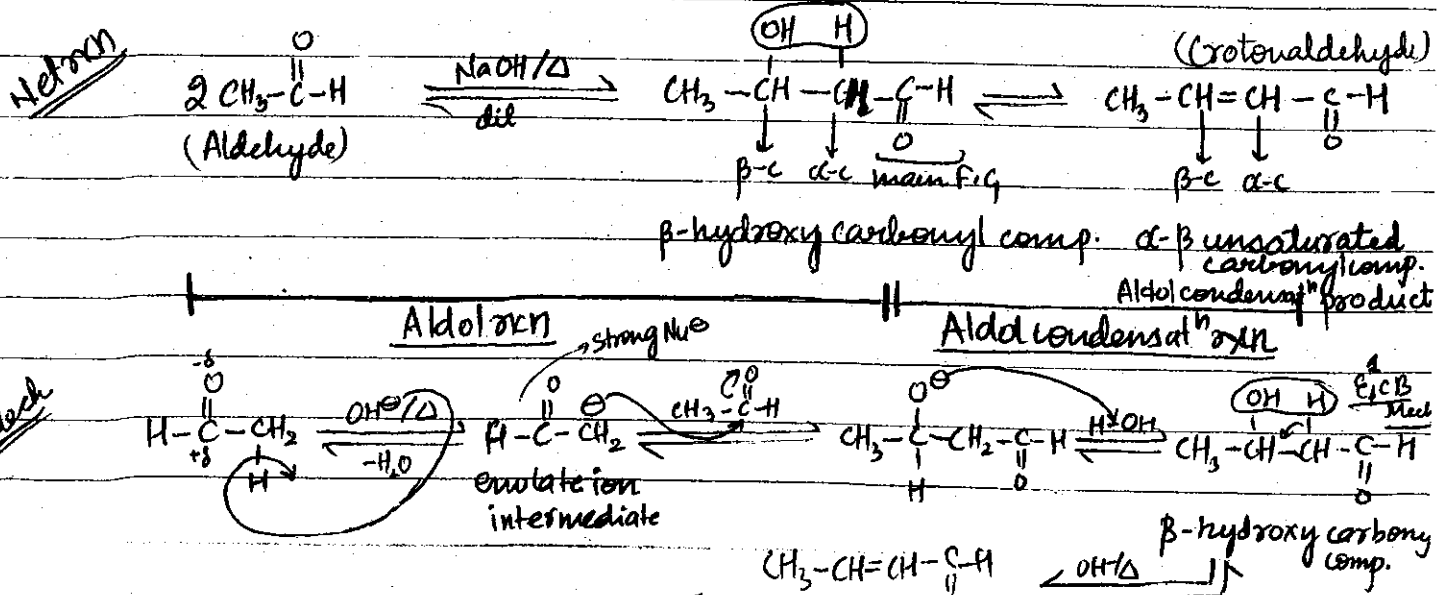


ALDOL CONDENSATION RXN

Aldehyde & Ketone having α-H give aldol condensation rxn.
Aldol con. rxn carried out at higher temp & reversible rxn controlled by Thermodynamics.
C-C bond formed in this rxn.
Aldol condensation rxn carried out in aq. alkaline med. (Dilute Alkali Med.)

i) NaOH/Δ
ii) $Ba(OH)_2$/Δ
⇒ Dil. Alkali Med.

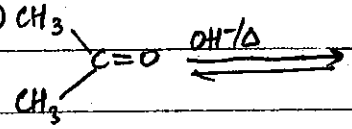
Formation of β-hydroxy carbonyl compound. is k/a Aldol rxn.
Formation of α-β unsaturated carbonyl comp. is k/a Aldol con. rxn
In aldol condensation rxn enolate ion is formed as a rxn intermediate

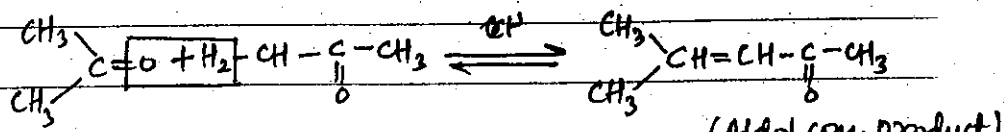


TYPE OF ALDOL

① Simple Aldol Condensat^{n} rxn.

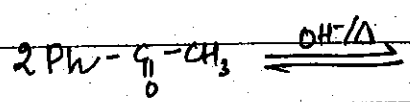
Whenever two same type of carbonyl compounds participate in aldol rxn.

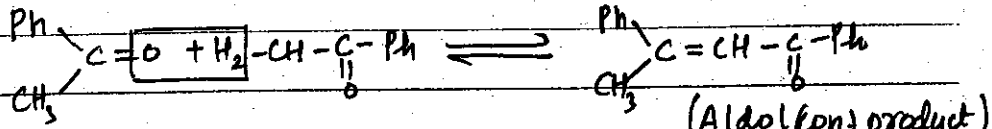
KEY POINT ① 



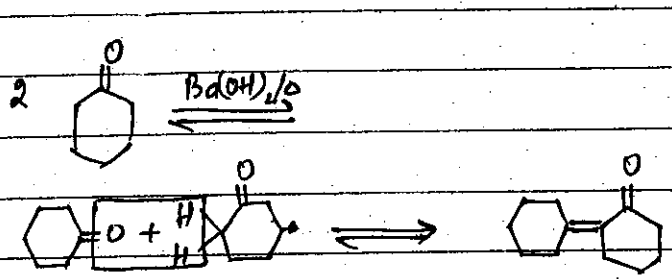
(Aldol con. product)

② Acetophenone



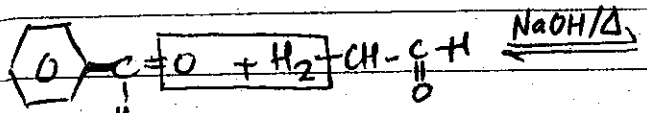


(Aldol (con) product)

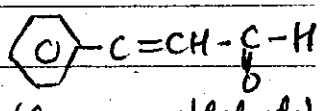
③ 

② Mixed/Cross Aldol Condensation Rxn

Whenever two diff. carbonyl compound participated in aldol con. Whenever one aliphatic aldehyde & other one aromatic aldehyde reacted in aldol condensat^{n} rxn then rxn is K/a CLAISEN SCHIMDT RXN.



Aromatic aldehyde — Aliphatic aldehyde

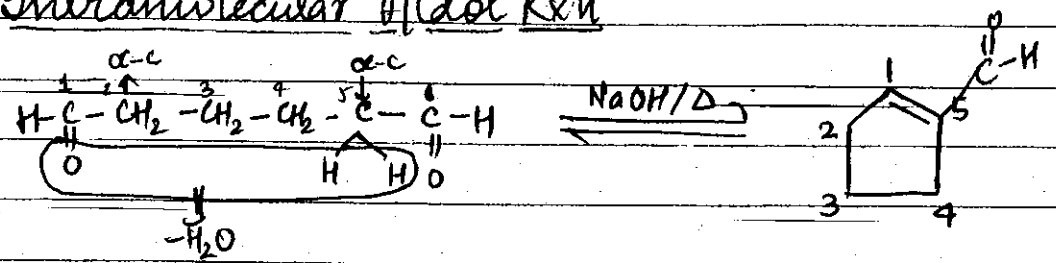


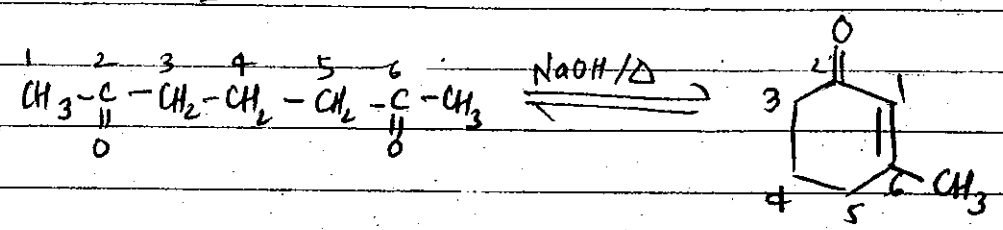
(Cinnamaldehyde)

Claisen Schimdt Rxn

C=O पर जहां +ve charge ज्यादा होगा वहां Attack ज्यादा होगा

Intramolecular Aldol Rxn





Following which one compound give aldol condensation rxn.

① $H-\overset{O}{\overset{\|}{C}}-H$ ✗✗✗

② $Ph-\overset{O}{\overset{\|}{C}}-H$ ✗✗✗

③ $Ph-\overset{O}{\overset{\|}{C}}-CH_3$ ✓

④ $Ph-\overset{O}{\overset{\|}{C}}-Ph$ ✗✗✗

⑤ $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H$ ✓

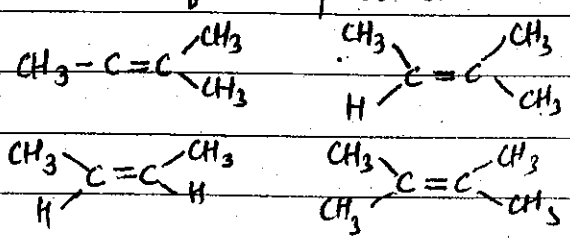
⑥ CH_3-NO_2 (Nitro Aldol) ✓

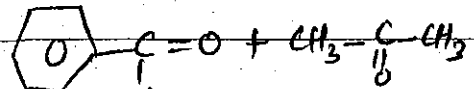
⑦ $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$ ✓

Q. $CH_3-\overset{O}{\overset{\|}{C}}-H + CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightleftharpoons{NaOH/\Delta}$ Total No of Aldol product

X Y

X X ⇒ 1
Y Y ⇒ 1
X Y ⇒ 1
Y X ⇒ 1
⇒ 4

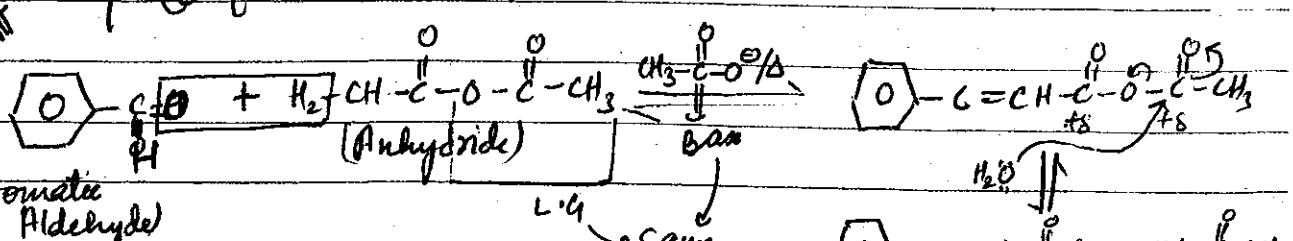


Q.  $\xrightleftharpoons{NaOH/\Delta}$ Total No. of Aldol product

X Y
Y Y
⇒ 2

PERKINS REACTION Anhydride का Aldol.

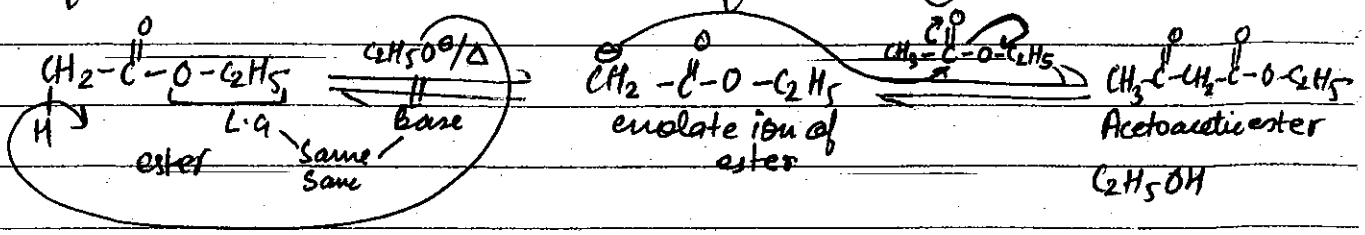
NaOH किया जा सकता है NaNH₂ का भी



Cinnamic acid

जैसा L.G वैसा Base लो।

③ CLAISEN ESTER CONDENSATION RXN

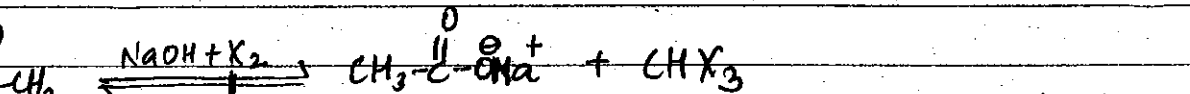


④ HALOFORM RXN (Iodoform test)
α-halogenation rxn.

① $CHCl_3$ → colourless liq. Use ⇒ Anesthetic comp. Do not give ppt with Ag. (C-Cl strong bond.)
Chloroform

② CHI_3 → Yellow crystalline solid Use ⇒ Antiseptic give yellow ppt with Ag
Iodoform

Net Rxn



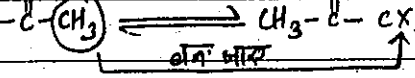
X=Cl (Chloroform)
X=Br (Bromoform)
X=I (Iodoform)

संलग्न के दो Comp. जिनमें $CH_3 \to CX_3$ में बदल जाता है।

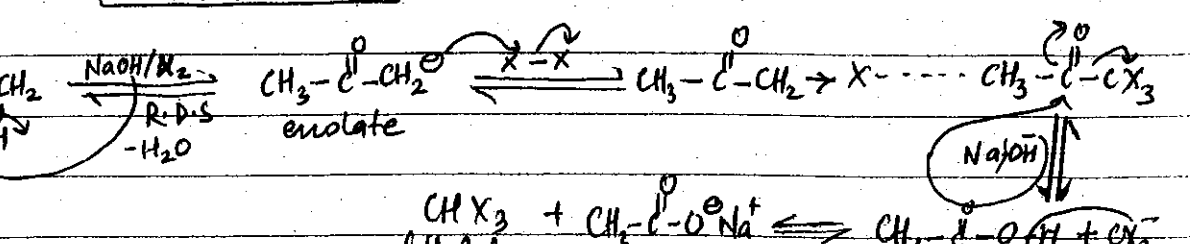
Cl_2, Br_2, I_2

Reagent ⇒ 1. X_2 + Alkaline Med. (NaOH, KOH --- etc)
2. $X_2 + NaOH$
3. ~~$NaOX$ (Sod. Hypohalite)~~
4. $OX^\ominus$
5. $X_2 + Na_2CO_3 + H_2O$
6. $CaOCl_2 + H_2O$ $[Ca(OH)_2 + Cl_2]$

example of Haloform Rxn

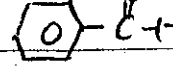
KEYPT :- 

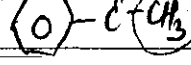
Mech



① $H-\overset{O}{\overset{\|}{C}}-H$ ××× No α-H, No Haloform

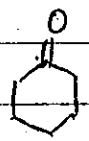
② $Ph-\overset{O}{\overset{\|}{C}}-Ph$ ××× Benzophenone, No α-H, No Haloform

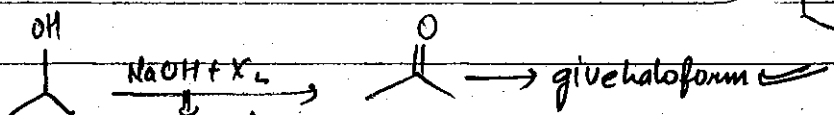
③  ××× No α-H, No haloform

④  → $-CX_3$ → give haloform ✓

⑤ $CH_3-\overset{O}{\overset{\|}{C}}-H$ → give haloform ✓

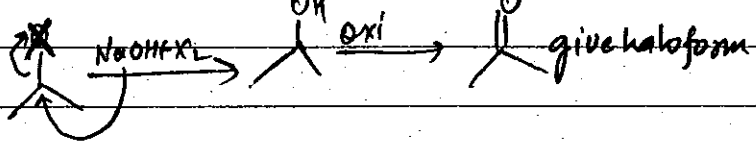
⑥ $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$ → No haloform ××

⑦  → No haloform ××

⑧  → give haloform ✓

2° Alcohol

⑨ $CH_3-CH_2-OH \xrightarrow{Oxi.} CH_3-\overset{O}{\overset{\|}{C}}-H$ give haloform

⑩  → give haloform

⑪ $CH_3-\overset{O}{\overset{\|}{C}}-OH$, $CH_3-\overset{O}{\overset{\|}{C}}-\underset{H}{N}H$ → give acid base rxn → No haloform rxn.

⑫ $CH_3-\overset{O}{\overset{\|}{C}}-O-C_2H_5 \xrightarrow{NaOH+X_2} CH_3-\overset{O}{\overset{\|}{C}}-OH + C_2H_5OH$

C_2H_5OH → $CH_3\overset{O}{\overset{\|}{C}}-H$ give haloform.

⑬ $CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{NaOH+X_2} 2CH_3-\overset{O}{\overset{\|}{C}}-OH$ ×× no haloform

Acid → No haloform

⑭ $Cl_3-\overset{O}{\overset{\|}{C}}-OH$ → give haloform rxn

HELL VOLHARD ZELINSKY RXN (HVZ Rxn)

α-halogenation of acid

Rxn used for preperation of a.a.

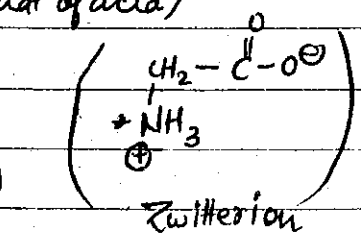
Net Rxn

$CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[(X=Cl,Br)]{Red\,P+X_2} CH_2(X)-\overset{O}{\overset{\|}{C}}-OH$ (α-halogenat^n of acid)

α-C, Main F.G

Use

$CH_2(X)-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{NH_3} CH_2(NH_2)-\overset{O}{\overset{\|}{C}}-OH$ (α A.A)



Zwitterion

CANNIZARO RXN (Without α-H)

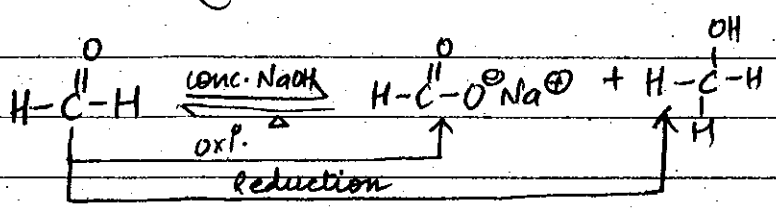
Carbonyl compound not having α-H give Cannizaro rxn.

Benzaldehyde, Formaldehyde

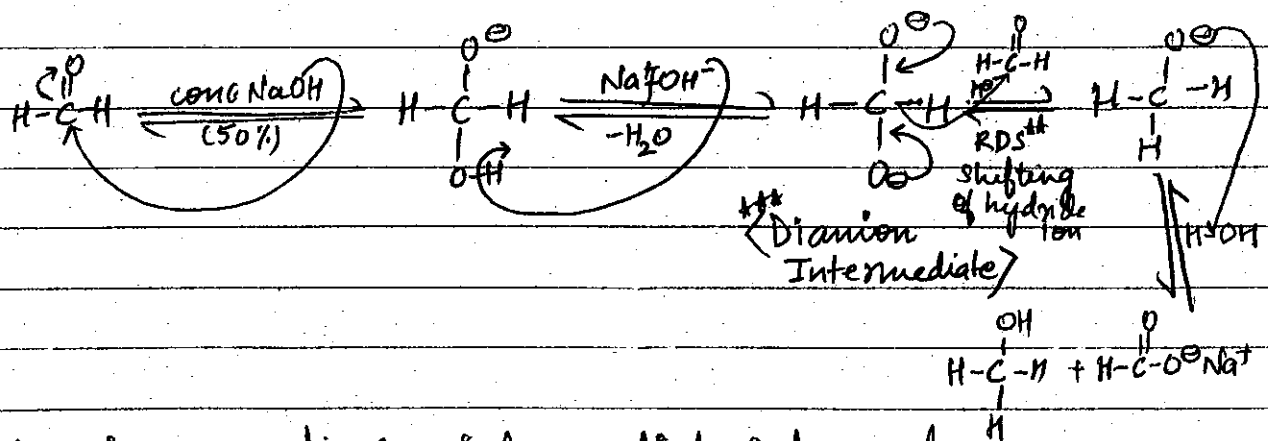
Carried out at higher temp & in conc. alkaline med.

conc. NaOH
Excess NaOH
50% NaOH
⇒ conc. Alkaline Med.

Disproportionation Rxn.



Mech

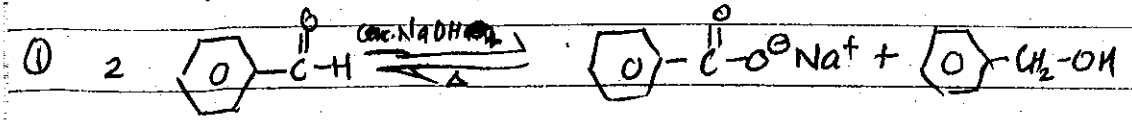


In Cannizaro rxn dianion intermediate is formed

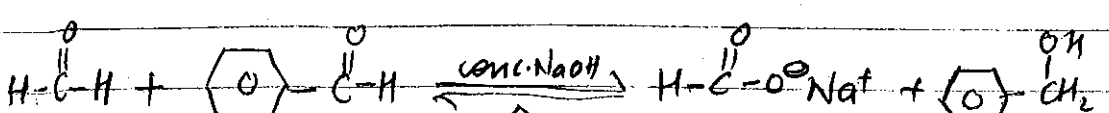
Shifting of hydride ion is RDS of rxn.

Type Of Cannizaro Rxn

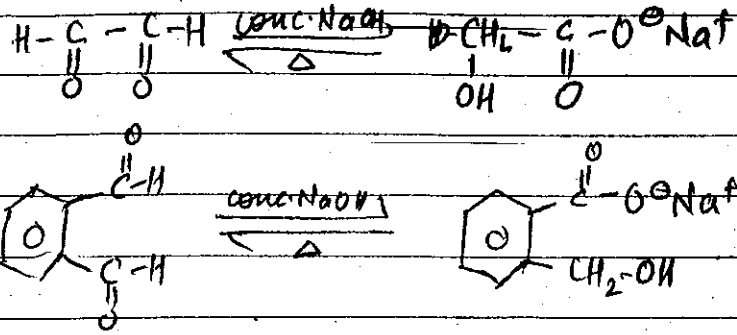
Simple Cannizaro Rxn



Mixed/Cross Cannizaro Rxn



Intramolecular Cannizaro Rxn



Some Special Rxn

① $CH_3-CH(CH_3)-CHO$ → give both aldol & Cannizaro

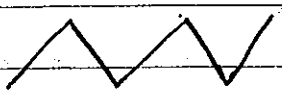
α-H है But फिर भी Cannizaro भी आएगा Alongwith aldol

② $(CH_3)_2C=O + CHCl_3 \longrightarrow (CH_3)_2C(OH)CCl_3$ Chloritone Use ⇒ Sedative hypnotics.

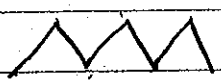
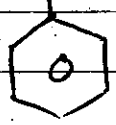
③ $6HCHO + 4NH_3 \longrightarrow (CH_2)_6N_4$ Urotropine Use ⇒ diuretics

④ $CHCl_3 + HNO_3 \longrightarrow CCl_3-NO_2$ Tear Gas.

Chemistry Of Aromatic Compounds

①  $\xrightarrow[Cr_2O_3/\Delta]{Al_2O_3/\Delta}$ 

All Correspondate Mote of oxide Aromatising Agent

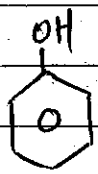
②  $\xrightarrow{\quad\quad}$ 

$CH_3-CH_2-CH_2-CH_3 \xrightarrow[\text{Branching}]{\text{Isomerising Agent}} \langle AlCl_3 + HCl \rangle$

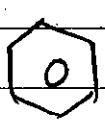
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

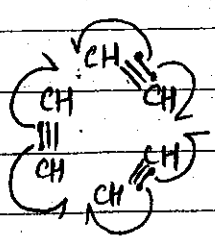
③  $\xrightarrow{Pd/\text{charcoal}}$ 

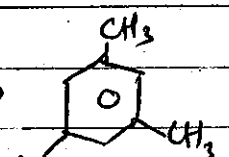
④  $\xrightarrow{Se/\Delta}$ 

⑤  $\xrightarrow{Zn\ Dust}$ 

Fenton Reagent ($Fe^{+2} + H_2O_2$)

⑥ $3\,CH\equiv CH \xrightarrow[\text{Fe tube}]{\text{Red hot}}$ 

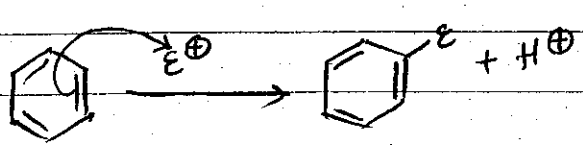


⑦ $CH_3-C\equiv CH \xrightarrow[\text{Fe tube}]{\text{Red hot}}$ 

(Mesitylene)

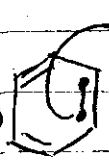
Aromatic compounds mainly give EsR.

EsR

Net Rxn 

$$\xrightarrow{E^{\oplus}} \text{E-Ar} + H^{\oplus}$$

Mech



$$\xrightarrow[\text{slowest step (NA)}]{E^{\oplus} + A^{\ominus}} \underset{\text{(C}^{+}\text{ intermediate)}}{\text{E-Ar-H}^{\oplus}} \xrightarrow[\text{fast}]{A^{\ominus}} \text{E-Ar} + A\text{-H} \quad \Delta H = -ve$$

(Aromatic)

① slowest step (NA)
② Bond forming step
③ RDS
④ Bond breaking step
σ-complex
Arrenium complex

Two step rxn
Exothermic rxn
** In ESR rxn generally first step is RDS of rxn but in case of Sulphonation & Iodination Second step is RDS of rxn.
In case of sulphonation & Iodination rxn give KIE.
Rate expression $r_{C_6H_6} = r_{C_6H_6} = r_{C_6T_6}$ (R.OR = same-same)
First step is RDS
eg. Chlorination Nitration F.C.R.

$r_{C_6H_6} > r_{C_6D_6} > r_{C_6T_6}$

Second step is RDS
eg. Sulphonation Iodination

KEY PT $CH_3 \rightarrow$ F.R $\rightarrow$ { Cl_2 hν / Br_2 hν / NBS / NCS / Br_2 Δ / Cl_2, Δ / SO_2Cl_2 ... etc }

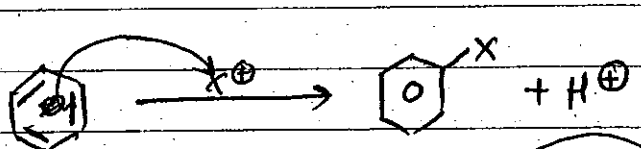
① Halogenation { $X^{\oplus}$ }
② Nitrogenation { NO_2^+ }
③ Sulphonation { SO_3 }
④ Friedel craft rxn
  ⓘ Alkylation { R^+ }
  ⓘⓘ Acylation { $R-\overset{\oplus}{C}=O$ }

All halogens are weakly deactivating group but o, p. directing groups.

Halogenation Rxn

$E^{\oplus} \Rightarrow X^{\oplus}$

Net Rxn



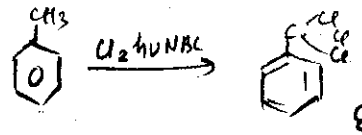
Formation of $E^{\oplus}$

① $:\ddot{X}-\ddot{X}: \xrightarrow[(Anhy)]{AlX_3} X^{\oplus} + AlX_4^{\ominus}$

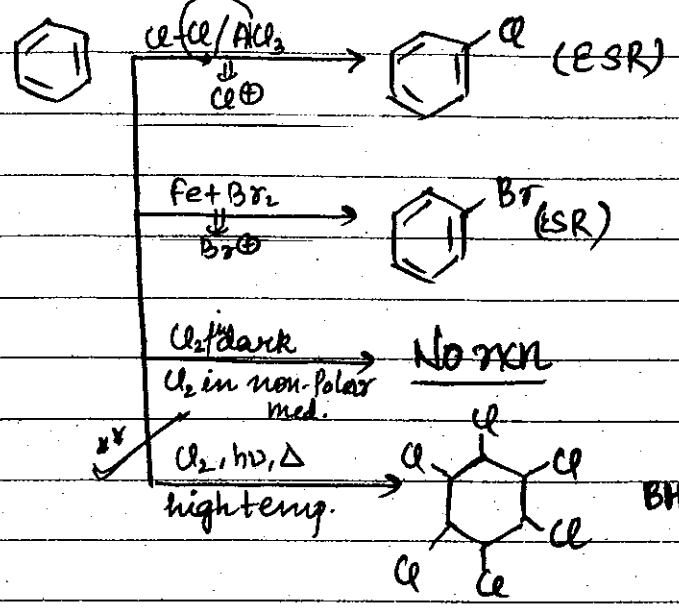
② $:\ddot{X}-\ddot{X}: \xrightarrow[(Anhy)]{FeX_3} X^{\oplus} + FeX_4^{\ominus}$

③ $3X_2 + 2Fe \longrightarrow 2FeX_3$ (same-same)

④ $X-OH \xrightarrow{H^+} X-\overset{\oplus}{O}(H)-H \xrightarrow{-H_2O} X^{\oplus}$

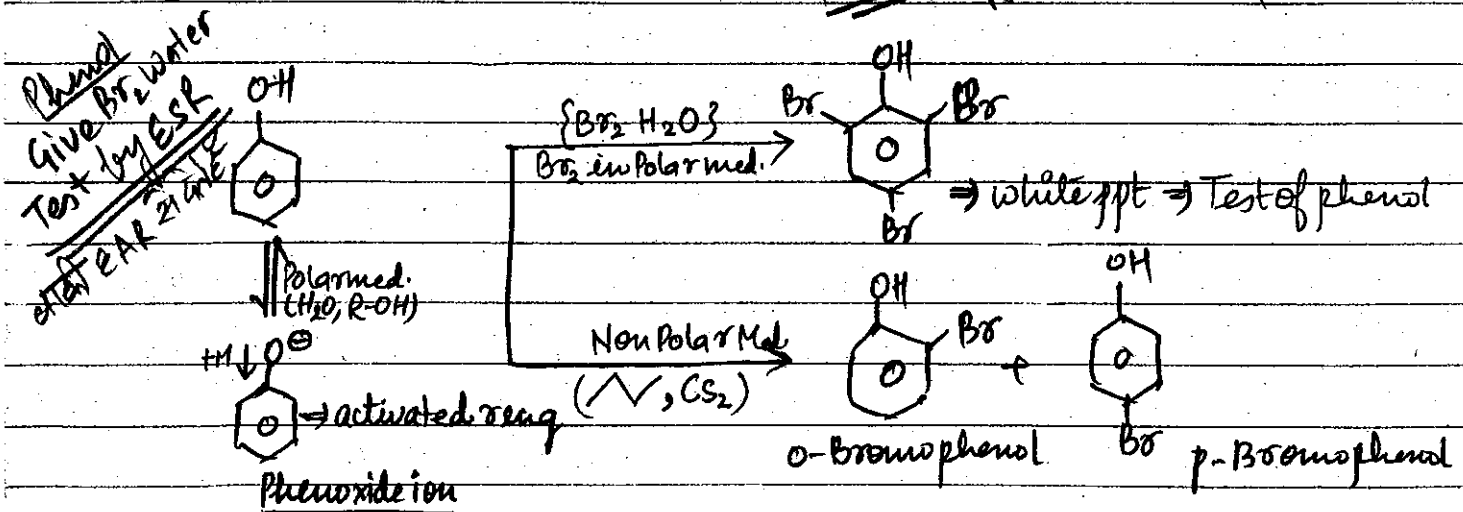


OH और +M OCH_3 होता है ESR में Rate OH में ज्यादा होता है। OCH_3 में।

① 

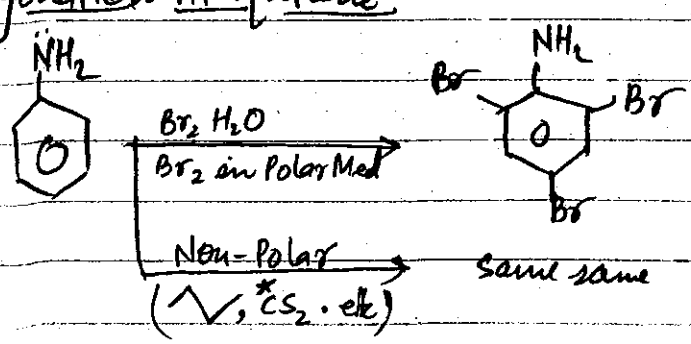
② Halogenation Of Phenol

Phenol में Polar में Tribromoproduct
Non-Polar में Monobromo product



Whenever halogenation rxn carried out at phenol in polar medium then due to acid base rxn phenol change into phenoxide ion. Bcz of it give tribromoproduct because ring is more activated & rxn also is a TEST OF PHENOL

③ Halogenation At Aniline

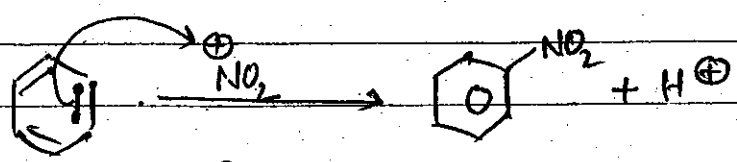


NH2 में Polar Non Polar same product +M NH2 very strong

Bcoz highly activated ring पर Direct Nitration नहीं होता है क्यों Oxidat^{n} हो जाता है। इसलिए पहले Sulphonat^{n} करते है तो Ring को Deactivate करते है।

Whenever halogenat^{n} carried out at aniline then aniline give tri bromoproduct en both med. because NH_2 group is very much activating group.

Nitration Rxn

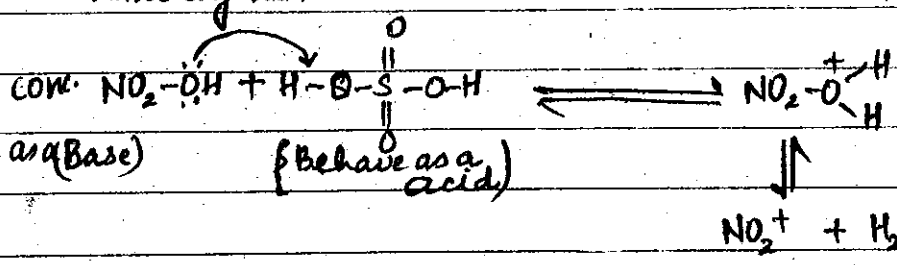


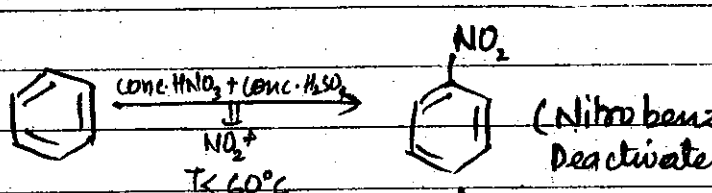
Formation of $e^{\oplus}$

① [conc. HNO_3 + conc. H_2SO_4)

⇓

Nitrating mix.





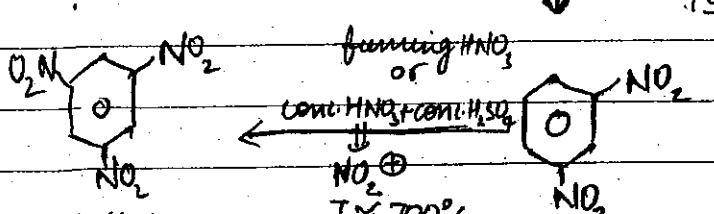
conc. HNO_3 + conc. H_2SO_4

⇓

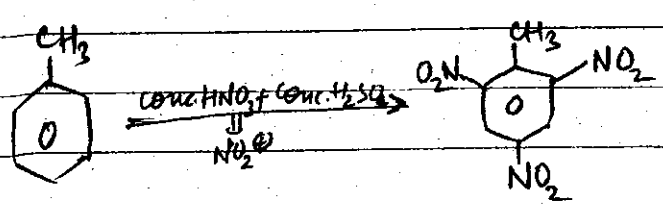
$NO_2^{\oplus}$

$T \simeq 90°C$

more than 1 time nitration because deactivated ring is present



②



Trinitro toluene

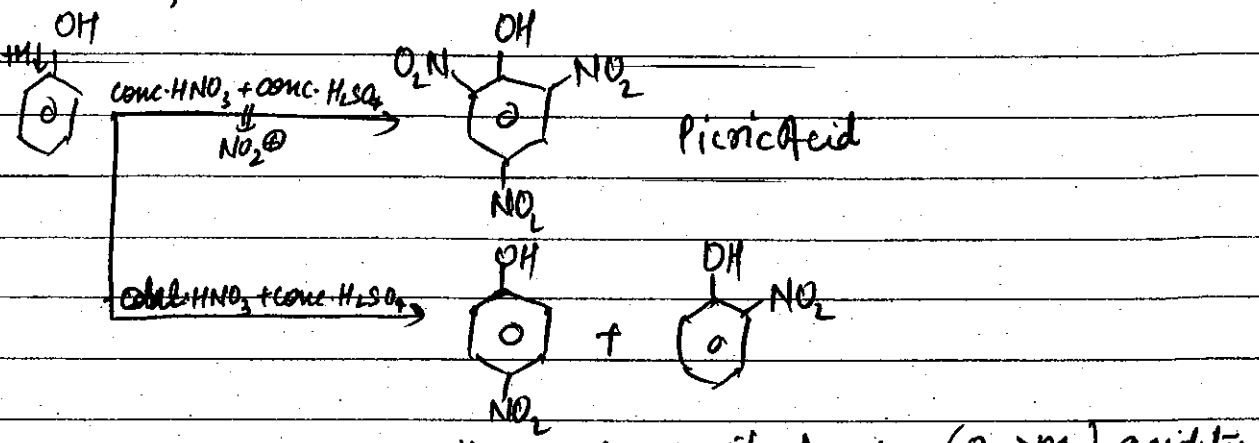
⇓

T.N.T

⇓

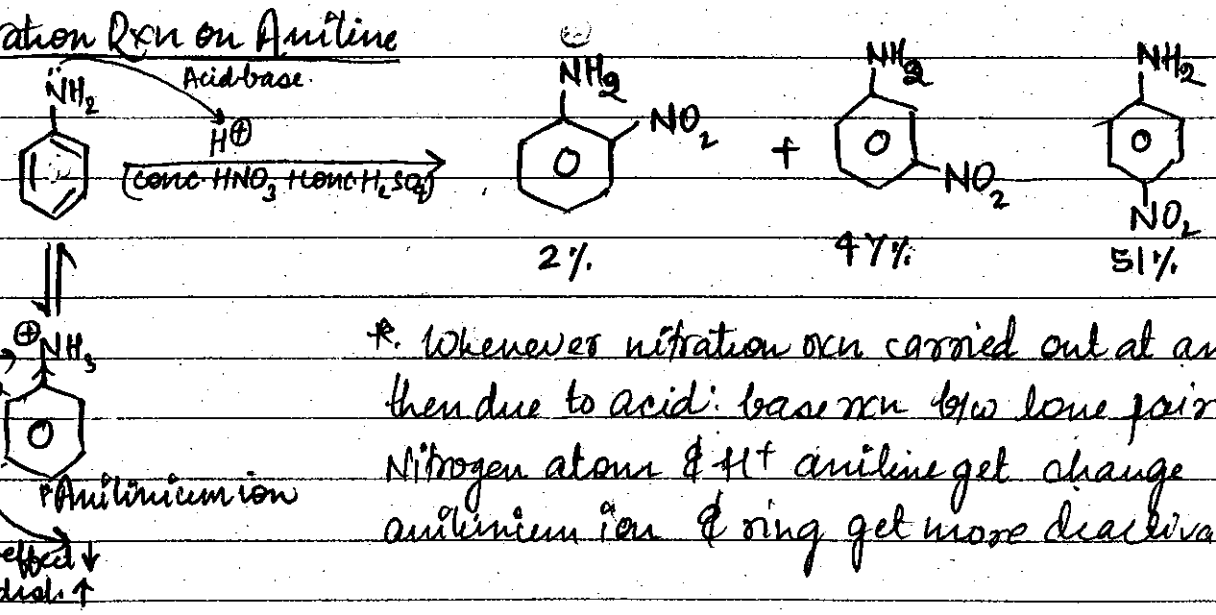
explosive

③ Nitration on phenol



o-nitrophenol p-nitrophenol (o- > m-) acidity

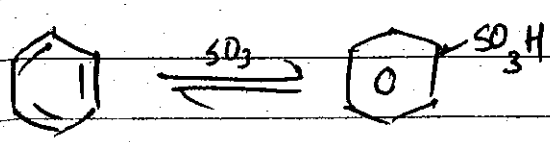
④ Nitration Rxn on Aniline



* Whenever nitration rxn carried out at aniline then due to acid-base rxn b/w lone pair of Nitrogen atom & H^+ aniline get change into anilinium ion & ring get more deactivated

Sulphonation Rxn

Net Rxn



(Benzene sulphonic Acid)

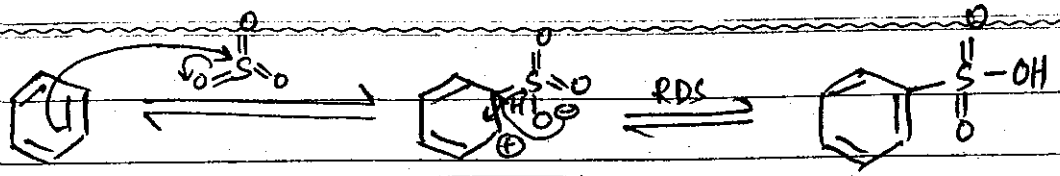
Formation of $E^{\oplus}$

① $H_2S_2O_7$ (Oleum) $\xrightarrow{\Delta}$ $SO_3 + H_2SO_4$

② conc. H_2SO_4

F. Radical से आगे
Friedel Craft

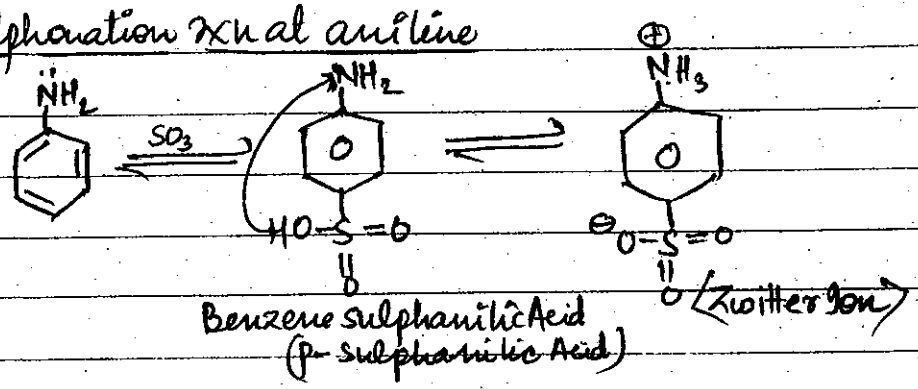
Mech



C⁺ intermediate

In case of sulphonation second step is RDS of rxn.
Rxn give KIE

Sulphonation rxn of aniline

① 

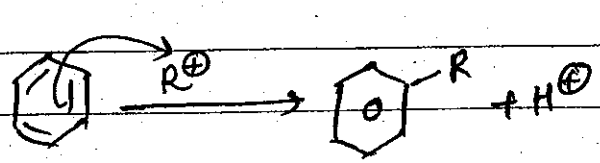
Benzene sulphanilic Acid
(p-sulphanilic Acid)

(Zwitter ion)

Friedel Craft Reaction

② Friedel craft alkylation rxn {R⁺}
e⊕ ⇒ R⊕

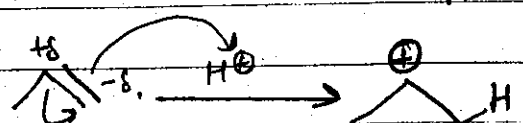
Net Rxn



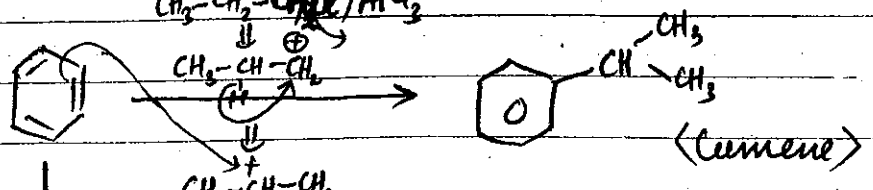
Formation of e⁺

① R-Cl $\xrightarrow{\text{anhy. } AlCl_3}$ $R^+ + AlCl_4^-$

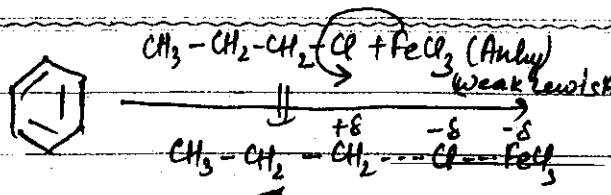
② R-OH $\xrightarrow{H^+}$ R-O(H)H $\longrightarrow$ $R^\oplus + H_2O$

③ 

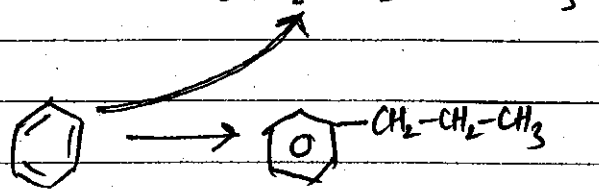
④ $CH_3-CH_2-Cl/AlCl_3$

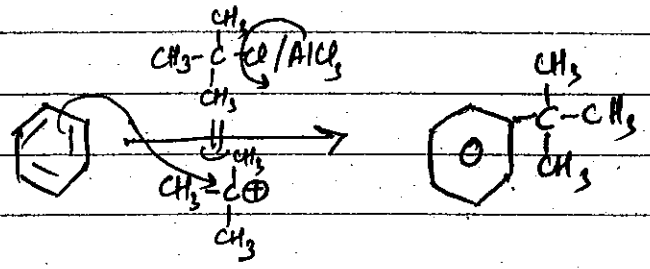


(Cumene)



{ Partially $C^{\oplus}$ form
No $C^{\oplus}$ rearrangement

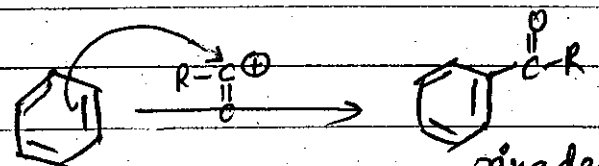




(b) Friedel Craft acylation Rxn

$E^{\oplus} \rightleftharpoons R-C\equiv O^{\oplus}$ (Acylinium ion)

Net Rxn



ring deactivate

Mech Formation of $E^{\oplus}$

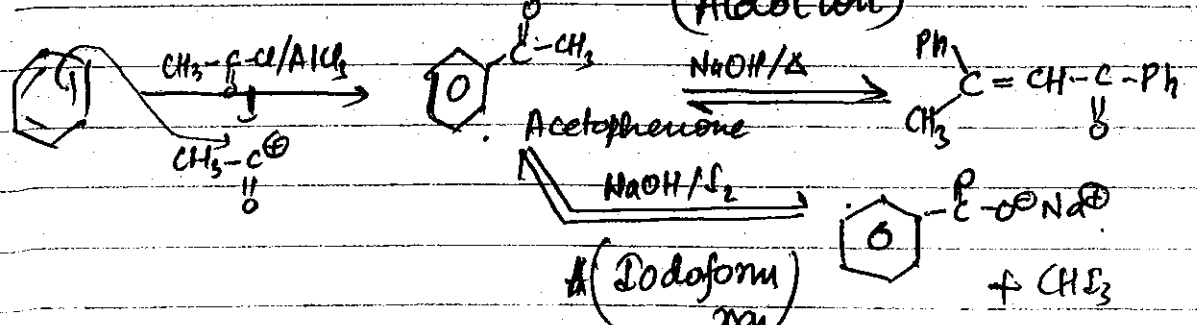
① $R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{AlCl_3\ (anhy)} R-C\equiv O^{\oplus}$

② $R-\overset{O}{\overset{\|}{C}}-\ddot{O}H \xrightarrow{H^{\oplus}} R-C\equiv O^{\oplus} + H_2O$

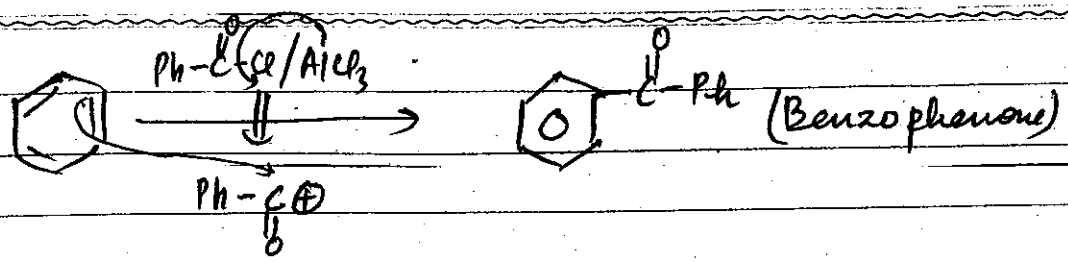
③ $R-\overset{:O:}{\overset{\|}{C}}-\ddot{O}: \xrightarrow{AlCl_3\ (anhy)} R-C\equiv O^{\oplus} \longrightarrow R-\overset{O}{\overset{\|}{C}}\oplus$

(Aldol low)

Q.1

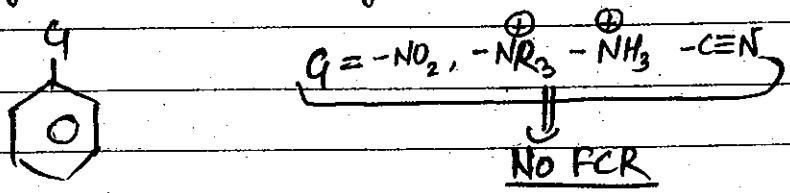


(Iodoform rxn)

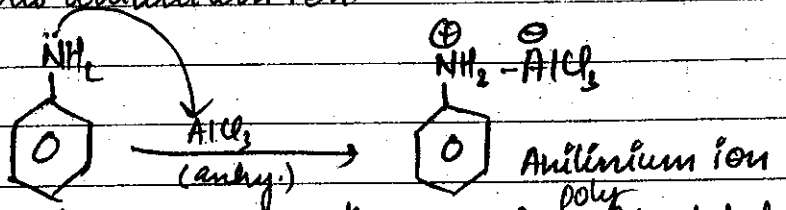


Disadvantage Of FCR

Highly deactivated ring do not give FCR rxn.



Aniline does not give FCR rxn. because due to acid base rxn aniline change into anilinium ion.

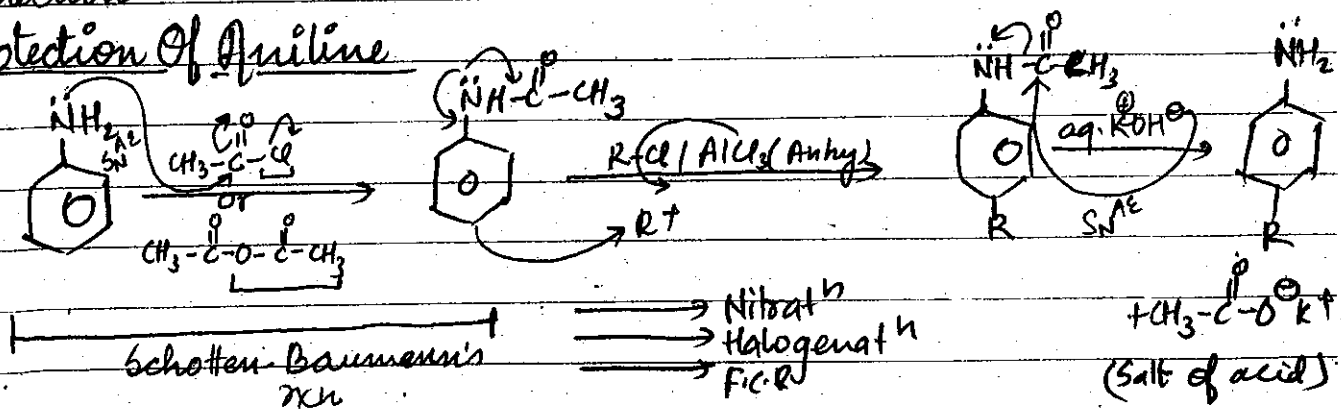


In Friedel craft alkylat^{n} rxn only polyalkylated product is formed

Nitrobenzene used as a solvent in FCR rxn.

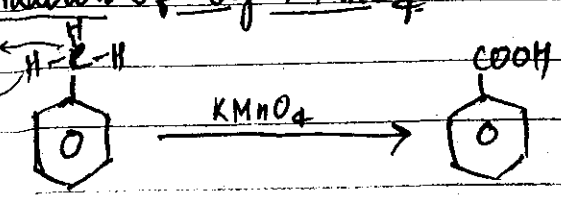
~~Protection~~

Protection Of Aniline



Oxidat^{n} Of Aromatic Compounds

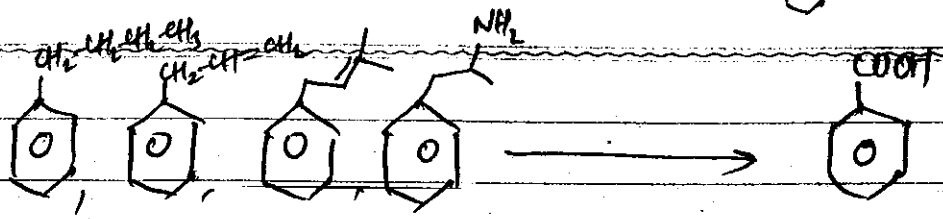
Oxidation Of by $KMnO_4$

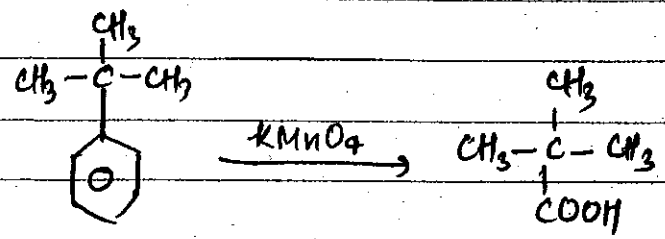


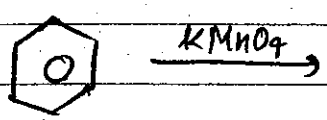
ek भी Benzylic H → benzoic acid

No " → COOH होगा ⬡ का

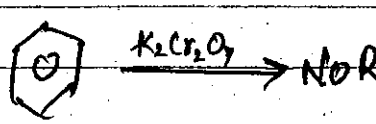
⬡ → No rxn

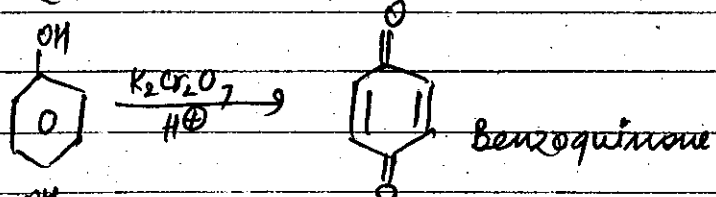


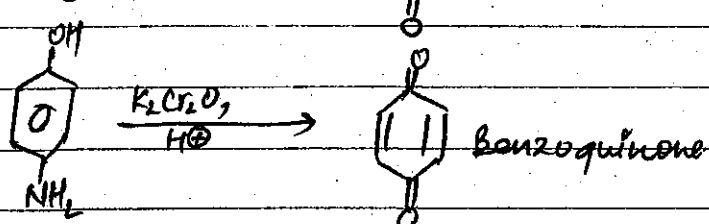
② 

③ 

Oxidation by $K_2Cr_2O_7$

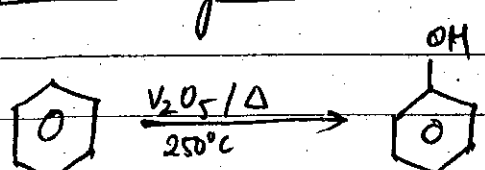
① 

② 

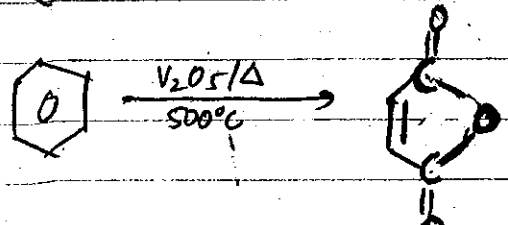
③ 

(p-amino phenol)

Oxidation by V_2O_5/Δ

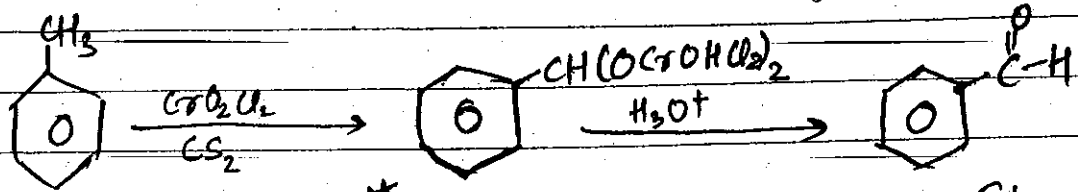


(Phenol)



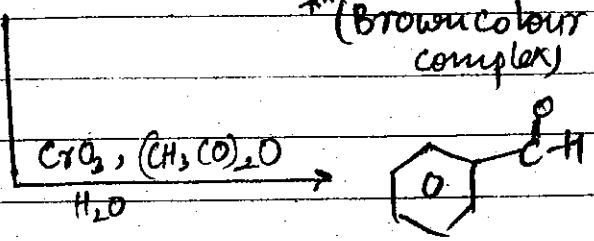
(Maleic anhydride)

Partial Oxidation Of Aromatic Compounds

① 

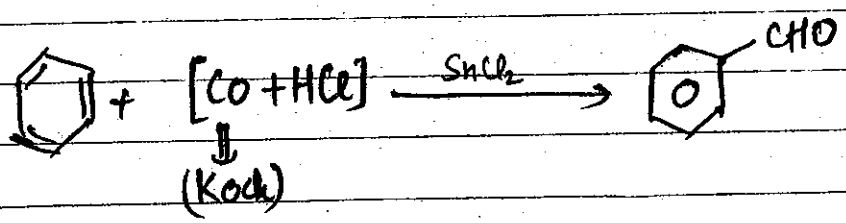
** (Brown colour complex)

Etard Rxn

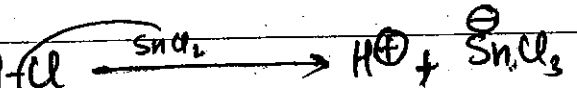


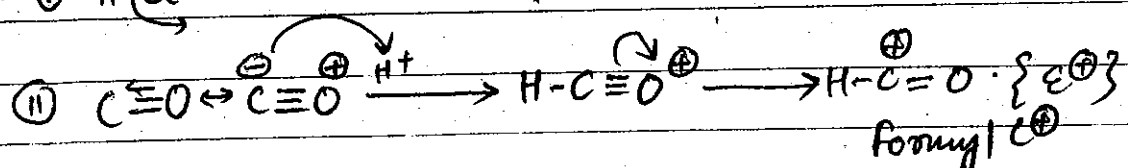
Formylation Rxn

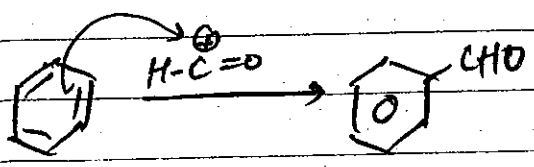
(I) Gatterman Koch Rxn

① 

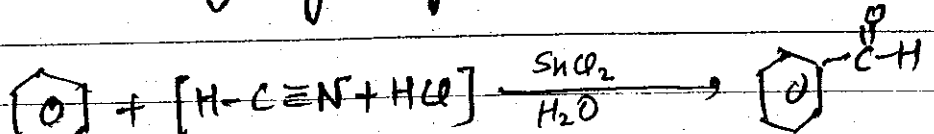
Mech

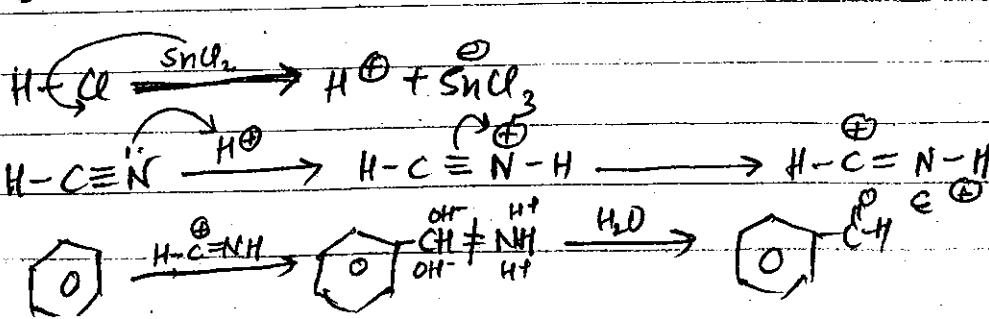
① 

② 

(III) 

II Gatterman Aldehyde Synthesis

Net Rxn 

Mech 

$NH_2 \rightarrow N_2$ बनता है 33 देंगे।

Test Of Amine

Diazotization Rxn

$-\ddot{N}H_2 \xrightarrow[(0°-5°C)]{(NaNO_2 + HCl)} -\overset{\oplus}{N}\equiv N \longrightarrow N_2\uparrow\uparrow$

(Poor L.G) (Best L.G)

Reagent → $NaNO_2 + HCl$
$HNO_2 + HCl$ ≠ same same (chalega)
HNO_2

Net Rxn

$R-NH_2 \xrightarrow[(0°-5°)]{NaNO_2+HCl} R-OH \underset{\text{(major)}}{} + N_2\uparrow + HCl.$

Mech

$R-\ddot{N}H_2 \xrightarrow[(0°-5°)]{NaNO_2+HCl} R-\overset{\oplus}{N}\equiv N\,\ddot{Cl}^{\ominus} \xrightarrow[R.D.S.]{N_2\uparrow} R^{+} \xrightarrow{H_2\ddot{O}:} R-OH + HCl + N_2\uparrow$

Best L.G (C⁺ intermediate)

$\boxed{NaNO_2 + HCl}$ $\overset{\oplus}{N}=O$ (Nitrosonium ion)
↳ Electrophile.

$H-\boxed{Cl + Na}-O-N=O \xrightarrow{-NaCl} H-\ddot{O}-N=O \xrightarrow{HCl} \overset{H_2\oplus}{O}-N=O$ (H)

$\downarrow -H_2O$

$\{e^{\oplus}\}\ \overset{\oplus}{N}=O$

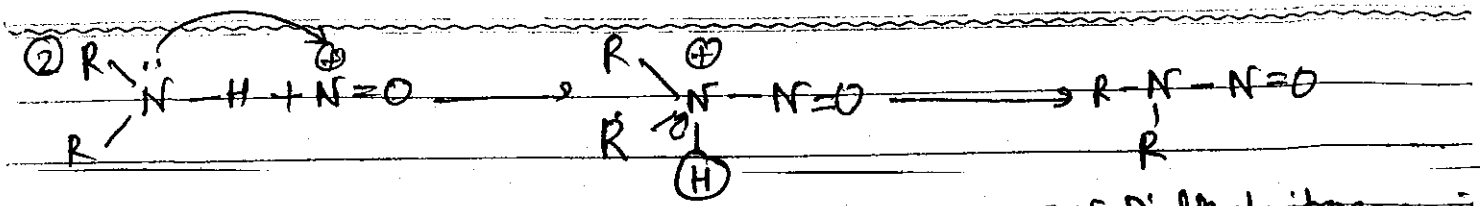
Rxn of 1°, 2° & 3° Amine with $NaNO_2 + HCl$

$\boxed{NaNO_2 + HCl} \Rightarrow \overset{\oplus}{N}=O$

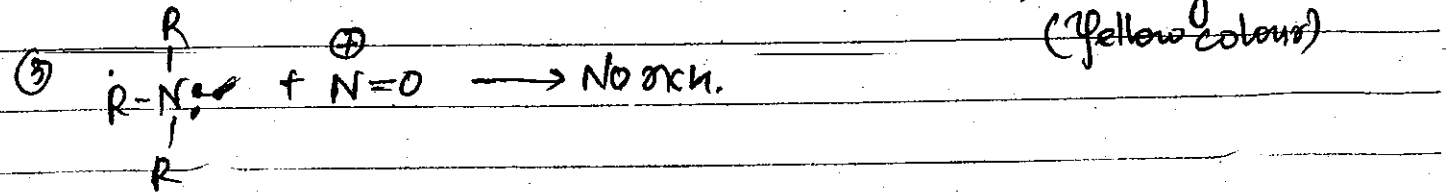
$R-\underset{H}{\overset{H}{N}} + O=\overset{\oplus}{N} \xrightarrow{-H_2O} R-\overset{\oplus}{N}=N \longrightarrow R-\underset{\text{Best L.G}}{\overset{\oplus}{N}\equiv N} \xrightarrow{N_2\uparrow} R^{+}$ (C⁺ inter.)

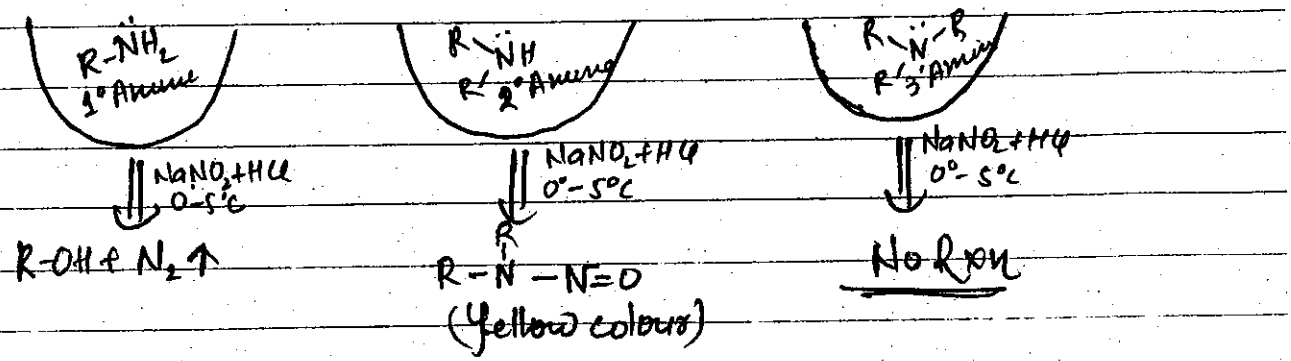
1° Amine

$R^{+} \xrightarrow{H_2O} N_2\uparrow\uparrow + HCl + R-OH$

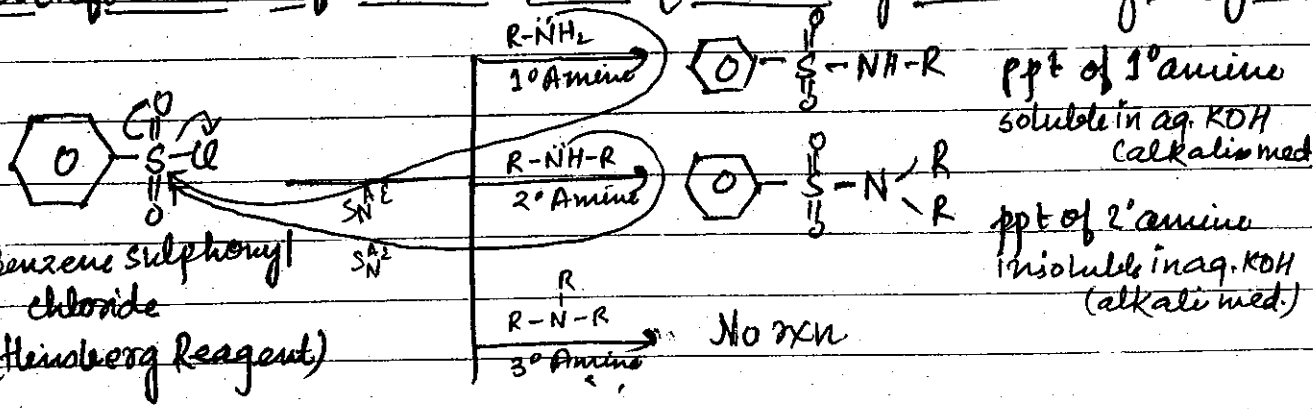


N, N-Dialkyl nitrosoamine
(Yellow colour)

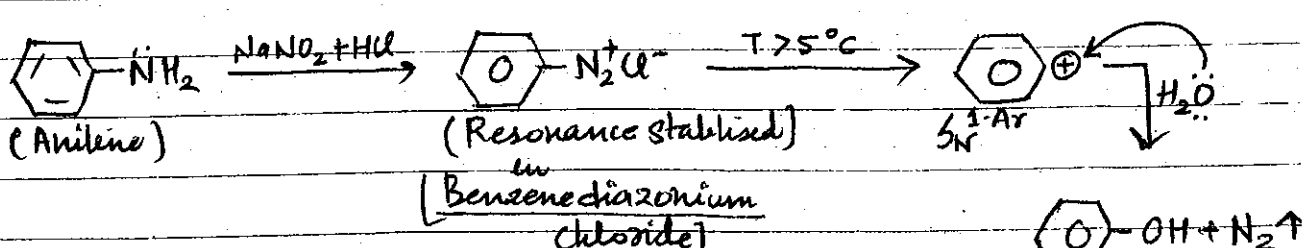




Identification Of 1°, 2° & 3° Amine by Hinsberg Reagent

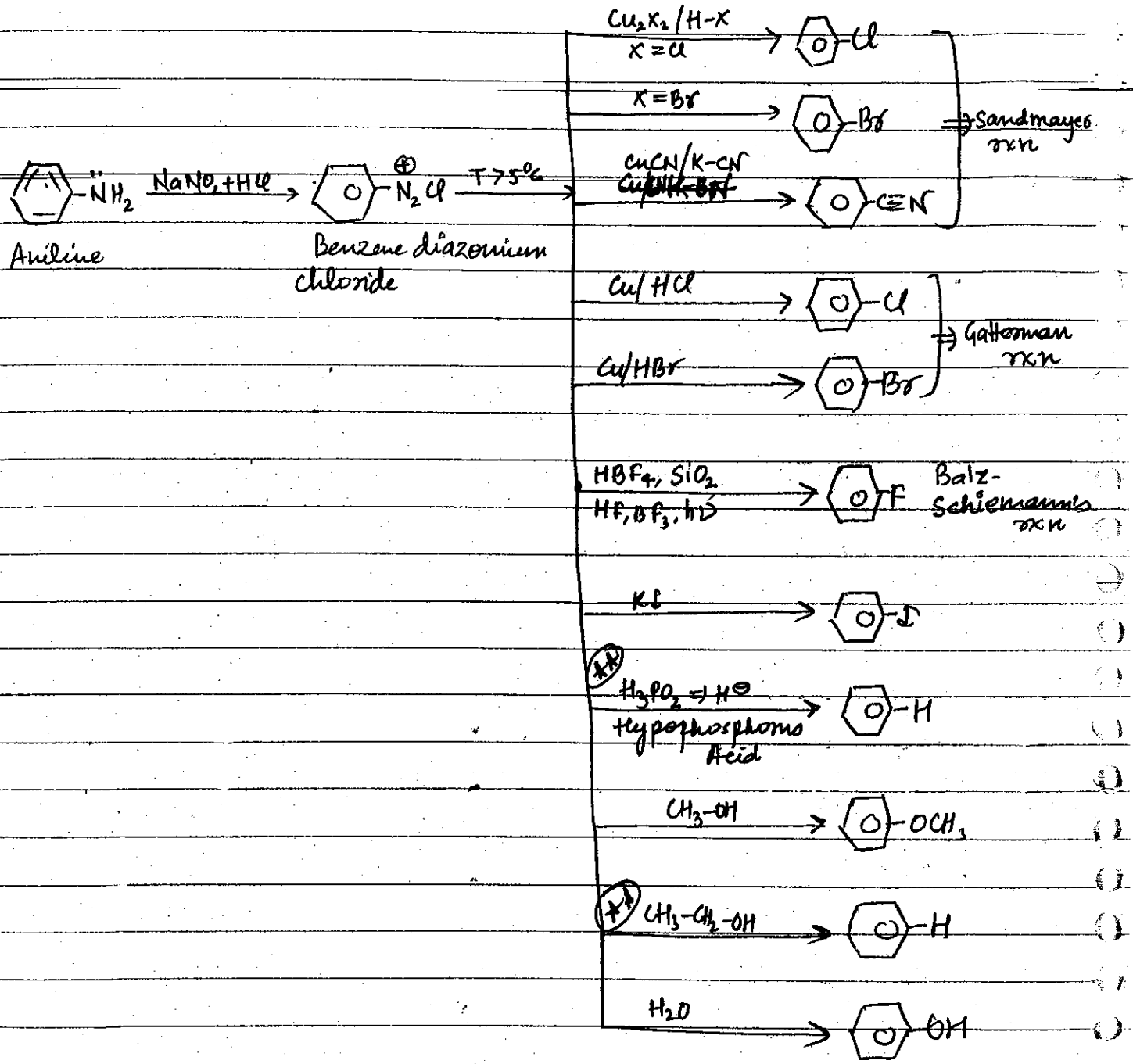


Chemistry Of Benzene Diazonium Salt

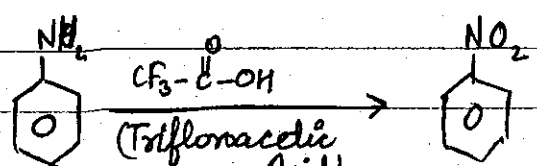


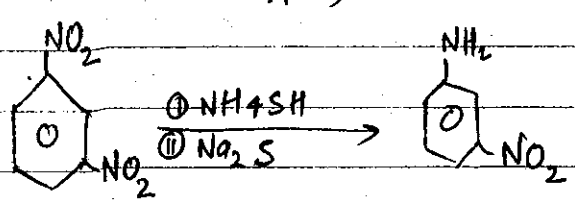
Rxn follow S_N^{1-Ar} path.

It is very rare mech. & only observe in benzene diazonium s-



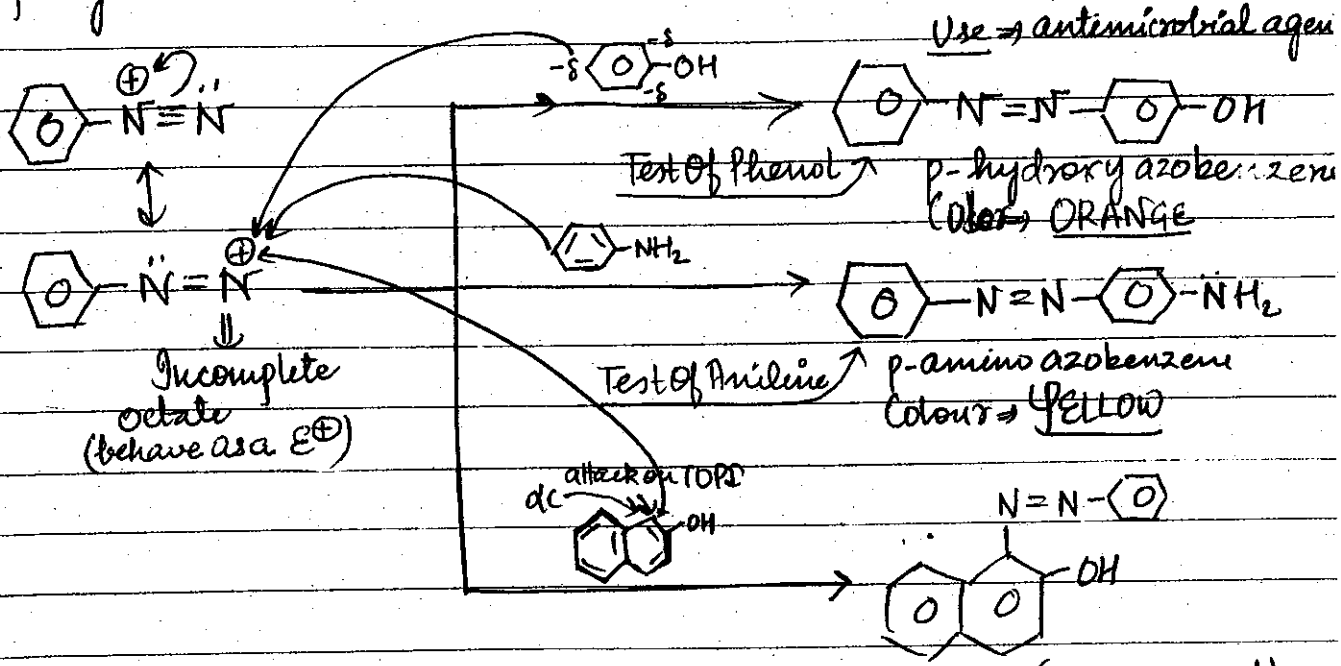
(1) $CH_3-NH_2 \xrightarrow[0^\circ-5^\circ C]{NaNO_2+HCl} CH_3-O-CH_3$

(2) 

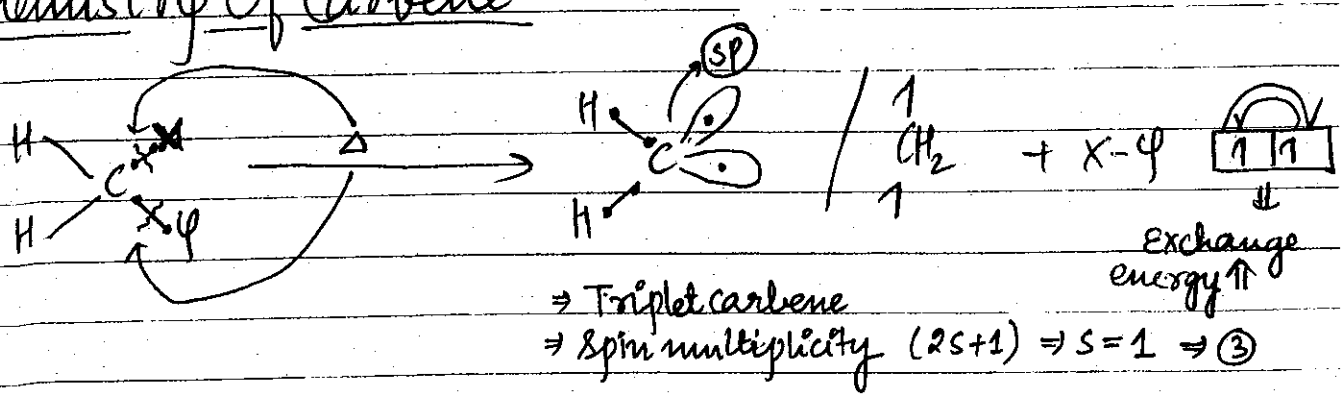
(3) 

Coupling Rxn

whenever benzene diazonium salt react with aromatic compound then it give dyes product. This rxn is k/a COUPLING RXN.
Benzene diazonium salt is a weak electrophile so it is coupled with highly activated ring.
Highly activated ring give coupling rxn. [Aniline, Phenol].
Coupling rxn is a ESR substitution

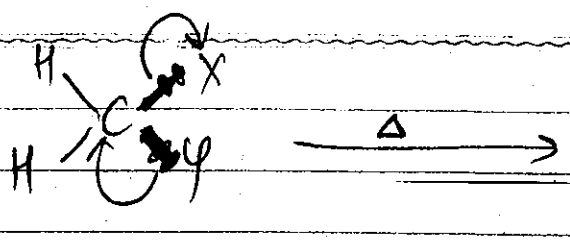


Chemistry Of Carbene



⇒ Triplet carbene
⇒ Spin multiplicity $(2S+1) \Rightarrow S=1 \Rightarrow 3$

Formed by homolytic cleavage
Incomplete octet
Behave as a electrophile
Hybridisat^{n} - sp

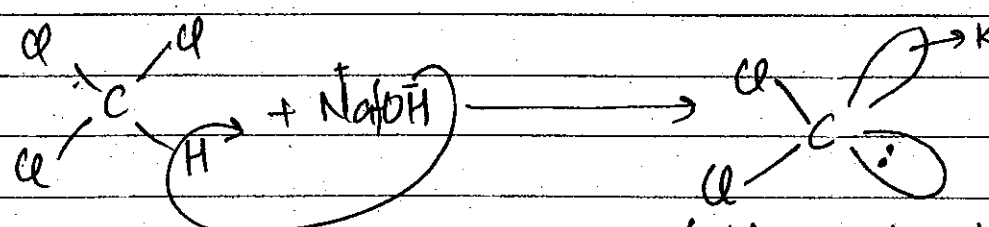
② 

singlet carbene (Engg Syllabus में है)

spin multiplicity $(2s+1) \Rightarrow s=0 \Rightarrow$ ①

Formed by heterolytic clevage.
Incomplete octet
behave as a electrophile.
sp^2 hybridisat^n
Generally triplet carbene is more stable than singlet carbene. Due to exchange energy (if back bonding not present) singlet may be more stable than triplet if back bonding is present.

~~CH_3OH~~ $\boxed{CHCl_3 + NaOH}$ ⇒ format^n of carbene in O.C



(Dichlorocarbene)

① Carbylamine Rxn / Isocyanide Test

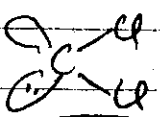
Net Rxn

$$R-\ddot{N}H_2 + CHCl_3 \xrightarrow{NaOH} R-N\equiv C$$

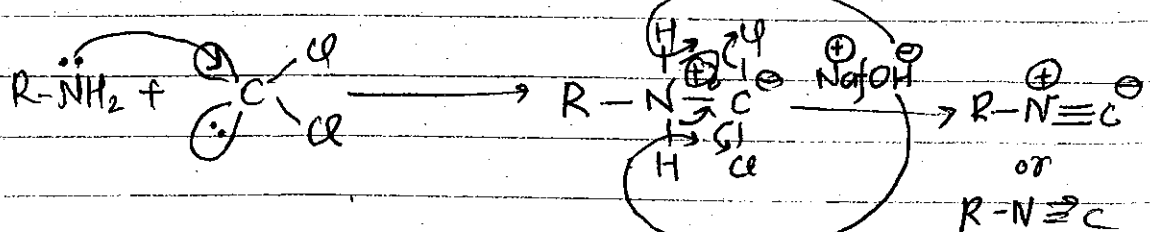
(Alkyl Isocyanide)

Mech

Step-I

~~$R-\ddot{N}H_2$~~ + $CHCl_3$ + NaOH ⟶ 

Step-II

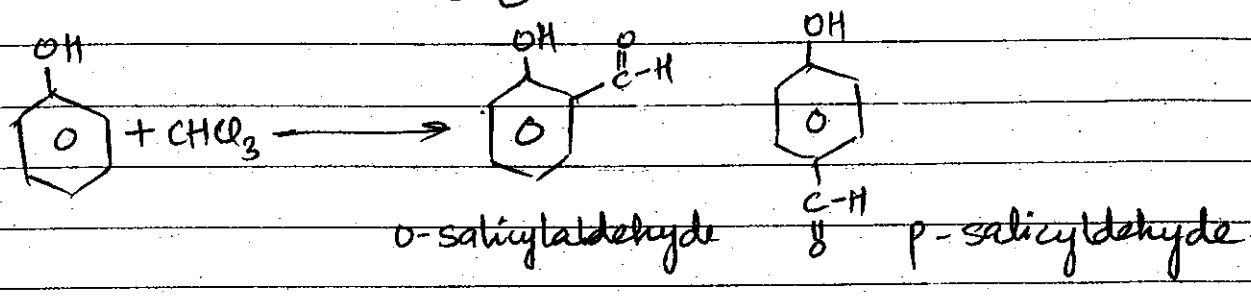


KEYPOINT 1° amine & aniline give carbylamine Rxn or Isocyanide test

2° amine, 3° amine & amide does not give isocyanide test

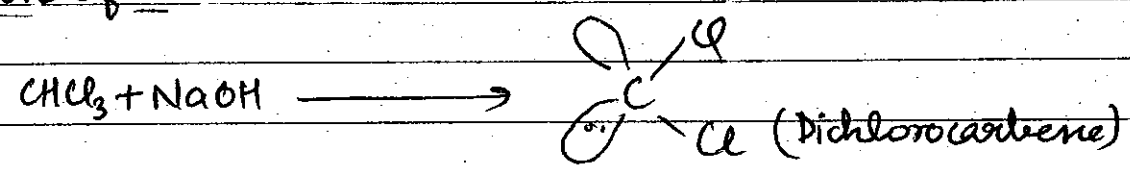
Reimer-Tiemann Rxn

Net Rxn

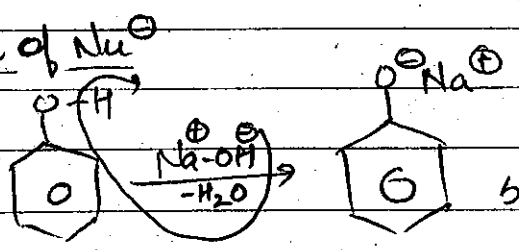


Mech

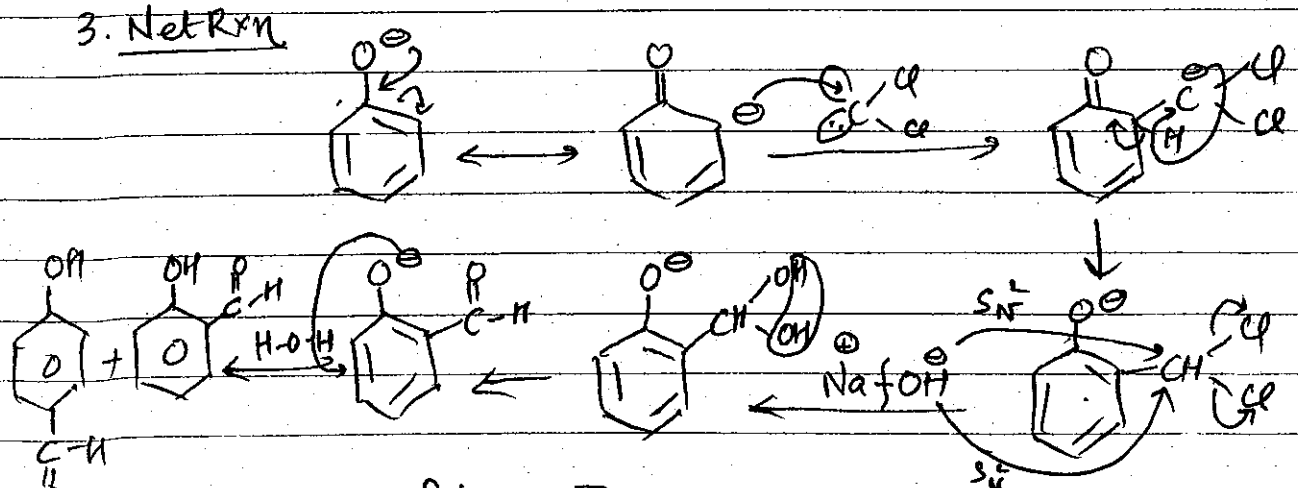
1. Formation of $E^{\oplus}$



2. Formation of $Nu^{\ominus}$

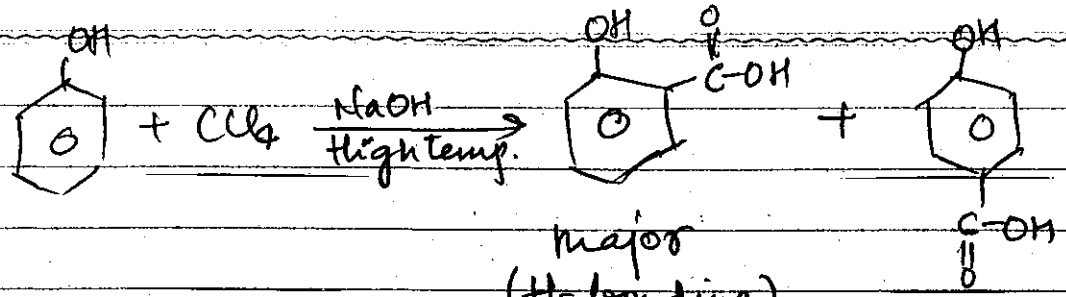


3. Net Rxn

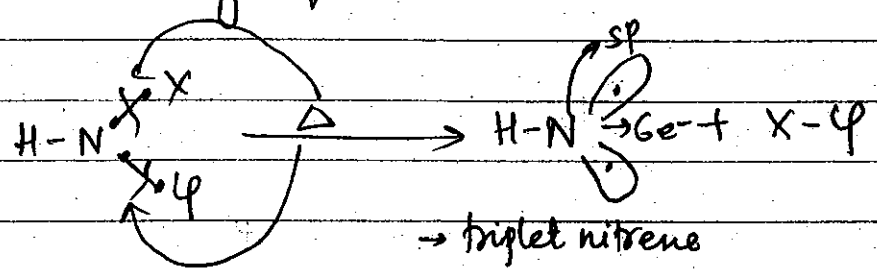


Reimmer-Tiemann

Whenever in ~~carbylamine~~ rxn if we use CCl_4 in place of $CHCl_3$ then rxn carried out at higher temp & give o- & p-salicylic acid as product

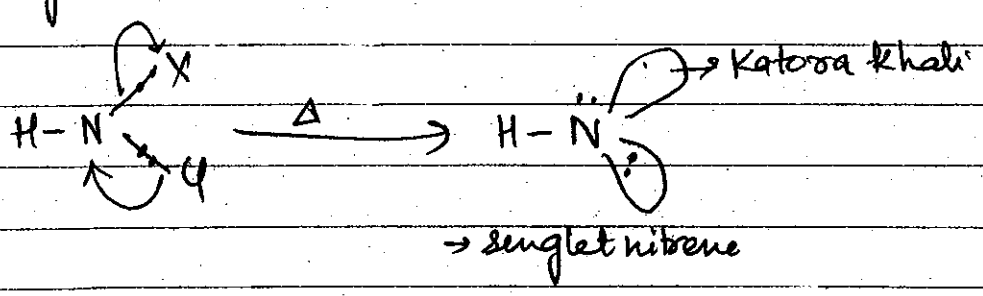
2. 

Chemistry Of Nitrene

① 

→ triplet nitrene

formed by homolytic cleavage
Incomplete octate
behave as a electrophile
Sp hybridised

② 

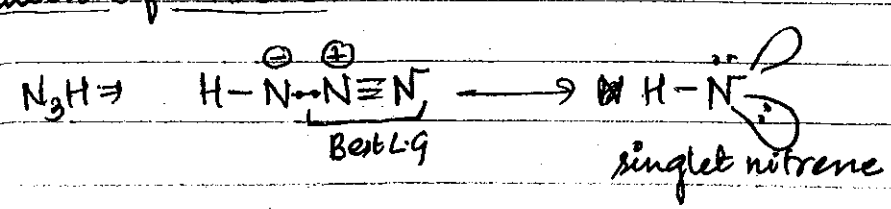
→ singlet nitrene

formed by heterolytic cleavage
Incomplete octate
behave as a $e^{\oplus}$
sp^2 hybridised.

N_3H ⇒ formation of nitrene of O.C.

Hydrazoic Acid

Formation Of Nitrene



Degradation Reaction Of Nitrene

① Curtius Rxn

$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[\text{Hydrolysis}]{Na-N_3}$

② Schmidt Rxn

$R-\overset{O}{\overset{\|}{C}}-OH + N_3H \xrightarrow[\text{Hydrolysis}]{}$

③ Hoffmann's Bromamide Rxn

$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\text{Hydrolysis}]{NaOH + X_2(Br)}$

④ Lossen's Rxn

$R-\overset{O}{\overset{\|}{C}}-\overset{L.G}{\underset{|}{N}}-H \xrightarrow[\text{Hydrolysis}]{NaOH}$

$\rightarrow R-NH_2$

Mech of Hoffmann's Bromamide Rxn

$R-\overset{O}{\overset{\|}{C}}-N\begin{matrix}H\\H\end{matrix} \xrightarrow[\underset{-H_2O}{\overset{\|}{NaOBr}}]{NaOH + Br_2} R-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{N}H \xrightarrow{Br-Br} R-\overset{O}{\overset{\|}{C}}-N-Br \xrightarrow{Na^+OH^-}$

$R-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{N}-\ddot{B}r: \longrightarrow R-\overset{O}{\overset{\|}{C}}-\ddot{N}: \longrightarrow$ Acyl Nitrene XXX (Wolf rearrangement)

$\longrightarrow \overset{O}{\overset{\|}{C}}\overset{OH}{\underset{OH}{\equiv}}N-R$ Alkyl isocyanate

$\xrightarrow{H^+} RNH_2 + HO-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{\text{Basic}} CO_3^{2-}$

Some Extra Reactions.

① Alkane

Sodalime decarboxylation Rxn

$$R-CH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\text{(ii) CaO}]{\text{(i) NaOH} \rightarrow \text{Sodalime}} R-CH_3 + Na_2CO_3$$

(3 : 1, Δ)

Mech

Step-1

$$R-CH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{NaOH} R-CH_2-\overset{O}{\overset{\|}{C}}-O^{\ominus} + H_2O$$

Step-2

$$R-CH_2-\overset{O}{\overset{\|}{C}}-O^{\ominus} \xrightarrow[RDS]{\Delta} R-CH_2^{\ominus} + C=O$$

($R-CH_2^{\ominus}$: Carbanion intermediate)

$$R-CH_2^{\ominus} \xrightarrow{NaOH} Na_2CO_3$$

Step-3

$$R-CH_2^{\ominus} \xrightarrow{H-OH} R-CH_3$$

Step down rxn (1 carbon less in product)

symmetrical & unsymmetrical both alkane can be formed by decarboxylation rxn

CH_4 can be formed by this rxn.

Carbanion intermediate formed

Formation of $C^{\ominus}$ is RDS.

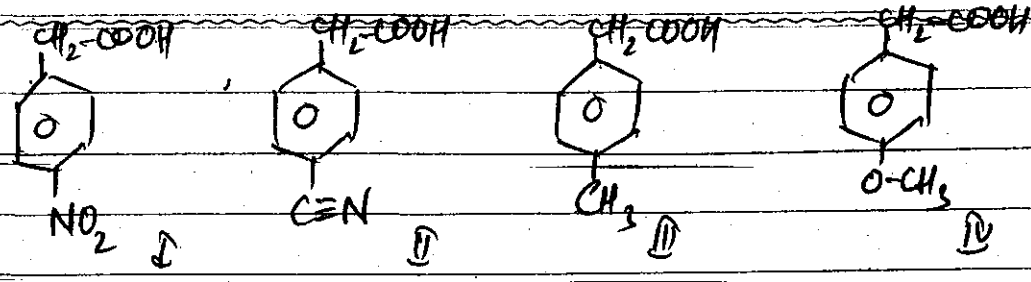
Rate of decarboxylation $\propto$ Stability of carbanion.

① $CH_3-\overset{\ominus}{C}H_2-\overset{O}{\overset{\|}{C}}-OH$ (A) $\quad CH_2=\overset{\ominus}{C}H-\overset{O}{\overset{\|}{C}}-OH$ (B) $\quad CH\equiv\overset{\ominus}{C}-\overset{O}{\overset{\|}{C}}-OH$ (C)

Rate $\Rightarrow$ $\boxed{C > B > A}$

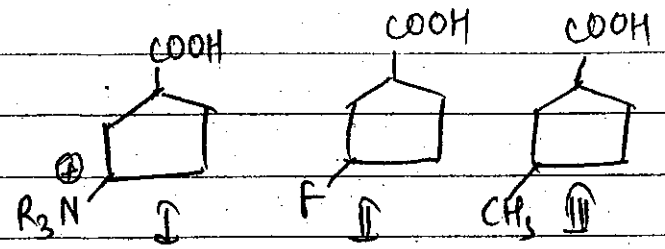
Alkyne ki oxn grignard ke sath J..

(2)



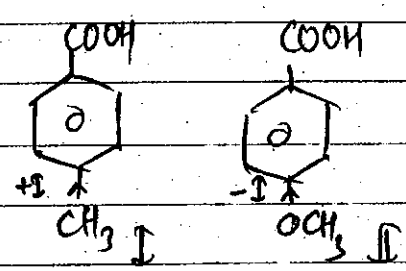
I > II > III > IV

(3)



I > II > III

(4)



II > I

Alkyne

Chemistry Of Terminal Alkyne

$CH_3-C\equiv C-H$ (Active-H)

$\xrightarrow[\text{Tollen's R}]{(NH_4OH + AgNO_3)}$ $CH_3-C\equiv C^{\ominus}Ag$ (White ppt)

Acid base rxn

$\xrightarrow[NH_4OH]{CuCl_2}$ $CH_3-C\equiv C^{\ominus}Cu$ (Red ppt

Alcohol & Phenol

Victer-Mayer Test (R.BC Test)

Red → colourless

Used for identification of 1°, 2° & 3° alcohol.

Comp (Given Alcohol)

↓ red P + I_2

Iodoalkane

↓ $AgNO_3$

Nitroalkane

HNO_2 ← ↓ $NaNO_2$ + HCl ($0°-5°$)

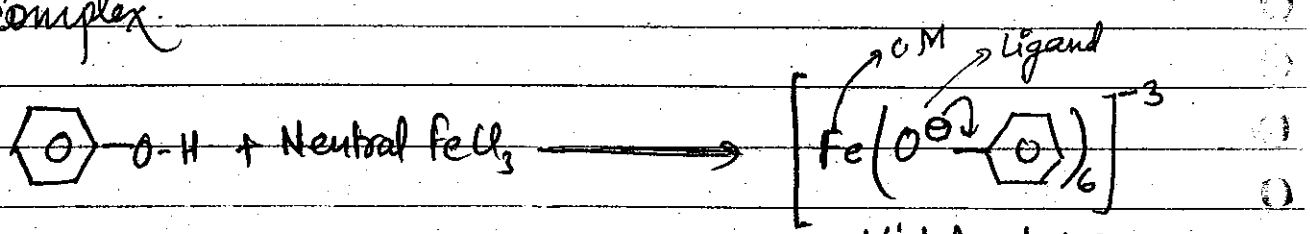
Comp (Nitrolic Acid & Pseudonitrole)

↓ Aq. KOH / NaOH

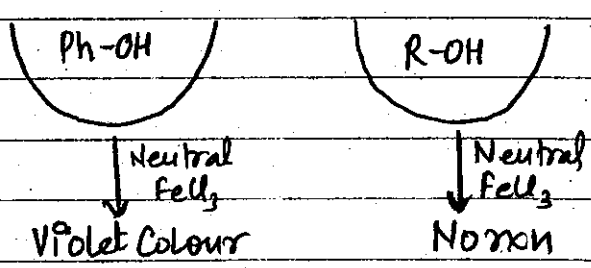
Red Colour (Blood Red)	Blue Colour	Colourless
1° Alcohol	2° Alcohol	3° Alcohol

② Rxn Of Phenol With Neutral $FeCl_3$

When phenol react with neutral $FeCl_3$ then it form VIOLET colour complex.



If -ve charge involve in reso. then all compound give rxn with neutral $FeCl_3$



Imp

③ Sodium Bicarbonate Test ($NaHCO_3$ test)

soluble hai Borat

⇒ Which one comp will give brisk effervescence with $NaHCO_3$

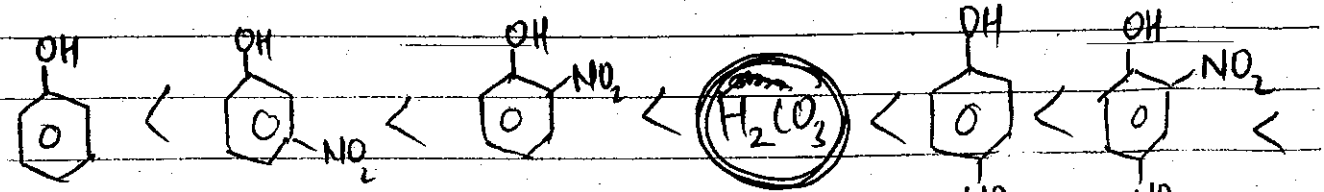
⇒ Which one comp evolve CO_2 with $NaHCO_3$

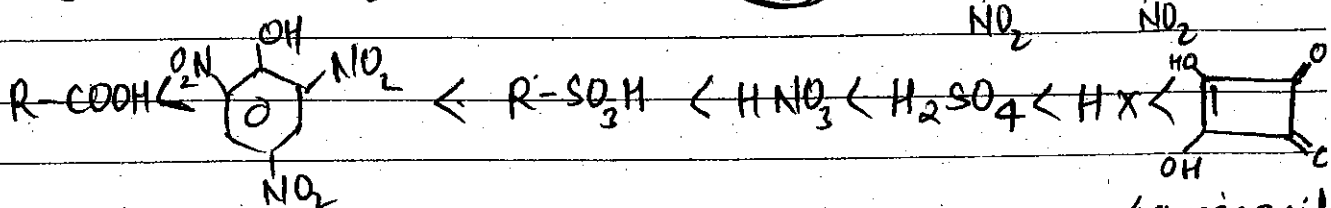
⇒ Which one comp soluble in $NaHCO_3$

} ⇒ same ques.

$NaHCO_3 \rightleftharpoons Na^+ + HCO_3^-$ { $\ominus O-\overset{O}{\overset{\|}{C}}-OH$ }

$H-A + HCO_3^- \rightleftharpoons A^- + H_2O + CO_2\uparrow$



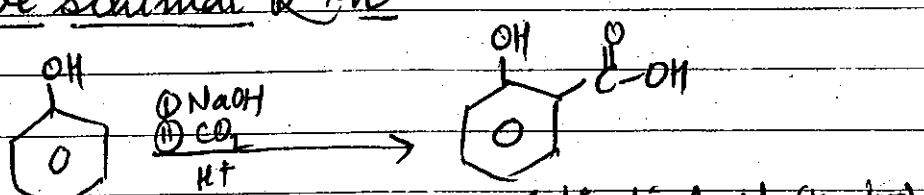


$< HClO_4$.

All carboxylic & sulphonic acid give CO_2 with $NaHCO_3$
Compound which are most acidic than o-nitrophenol give CO_2 with $NaHCO_3$

Comp. which are most acidic than H_2O soluble in NaOH (acid base)

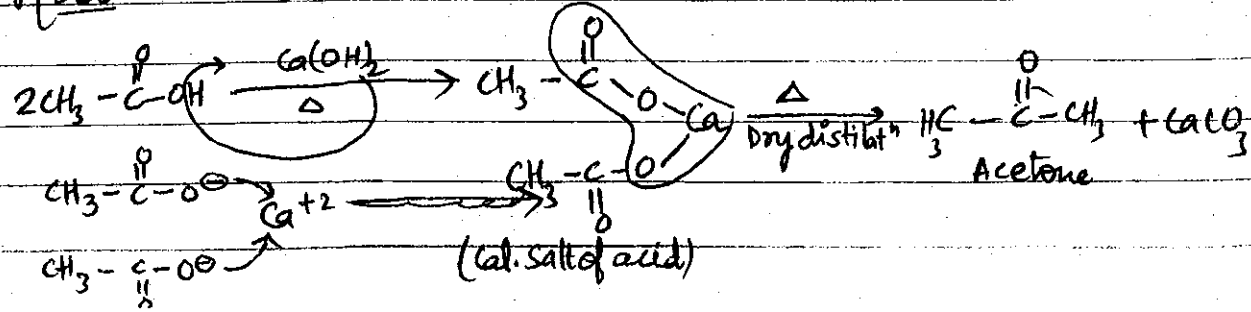
④ Kolbe Schmidt Rxn



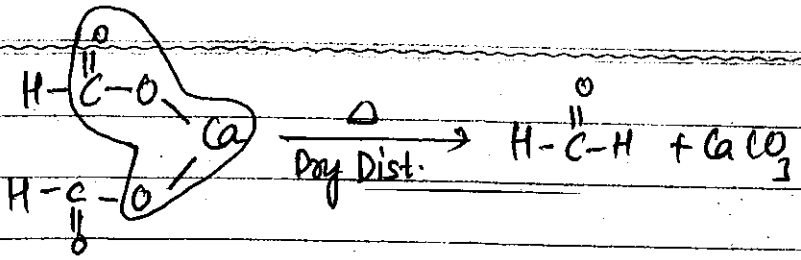
Salicylic Acid (major)

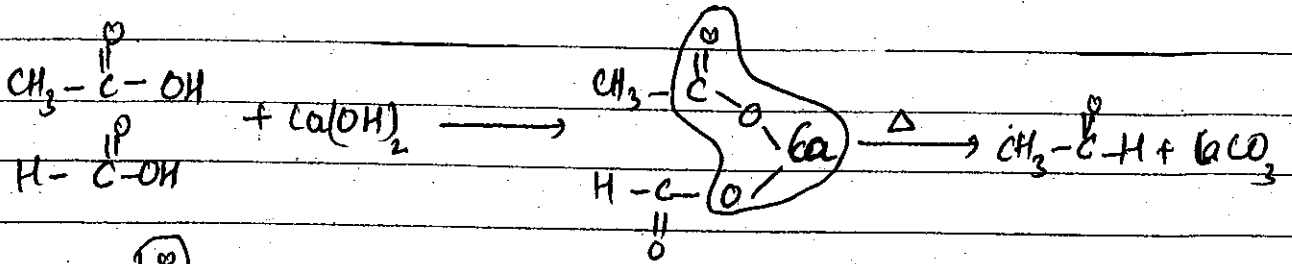
+ Carbonyl Comp.

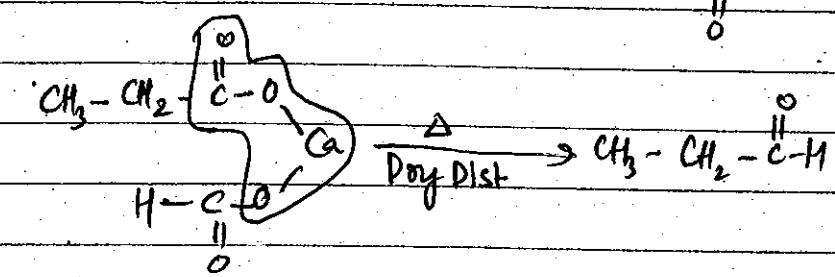
① Preperation Of Carbonyl Comp by dry distillat^n of Ca Salt of Acid



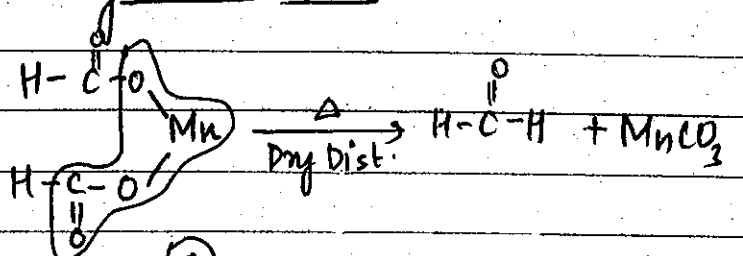
(Ca. salt of acid)

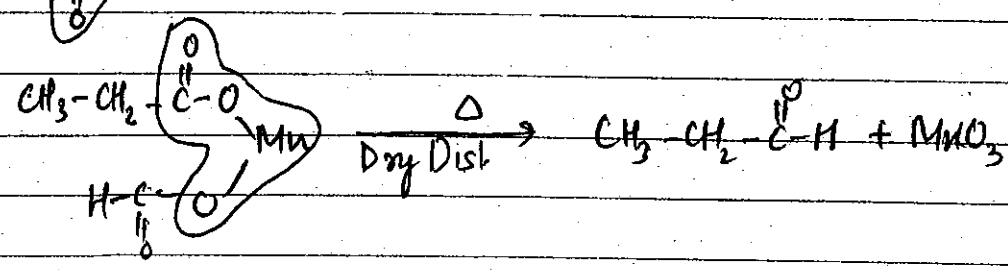
② 

③ 

④ 

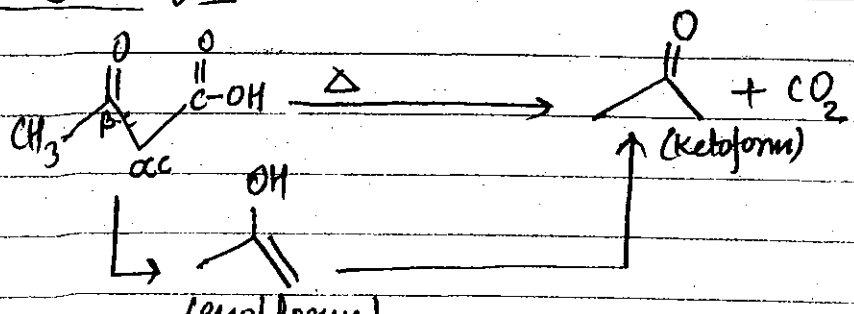
Heating With MnO

① 

② 

② Heating Effect

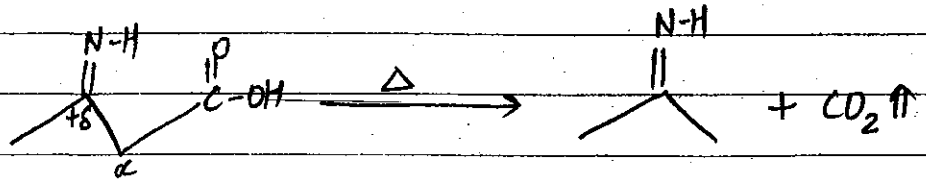
(A) β-Keto Acid

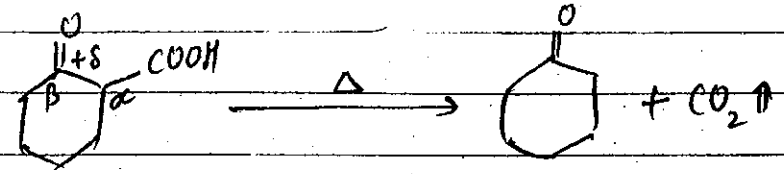


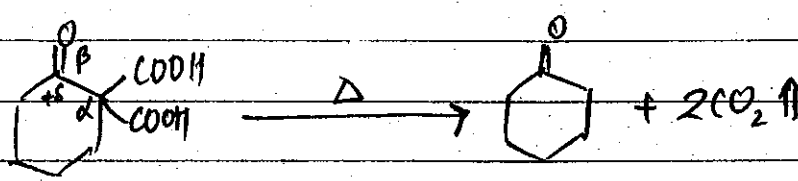
If Partially ⊕ve charge dev. at β-position in case of β-keto acid then

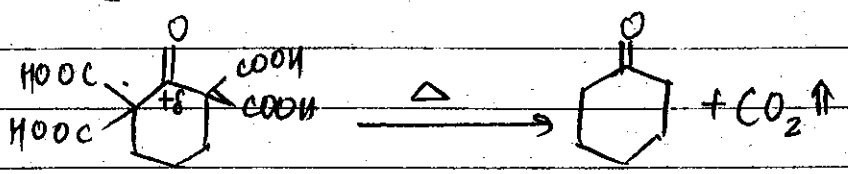
on heating it release CO_2.

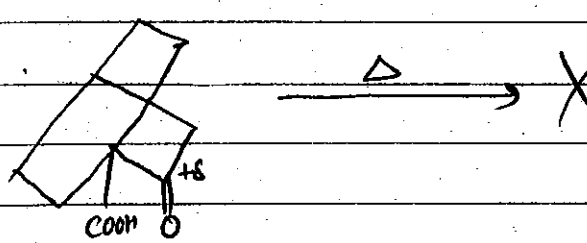
enol form formed in this rxn, 6MCTS formed in this rxn

⑤ 

③ 

④ 

⑤ 

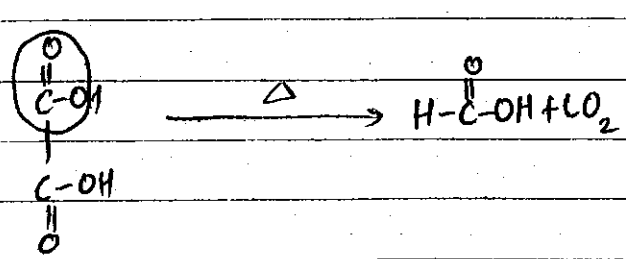
⑥ 

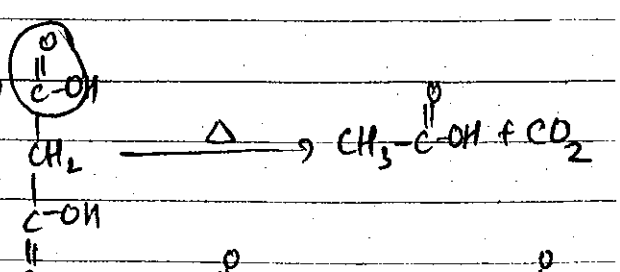
⟶ XXX <Bredt's Rule Violated>

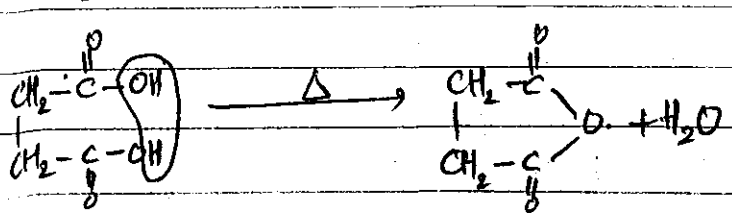
Dicarboxylic Acid Of Organic Chemistry

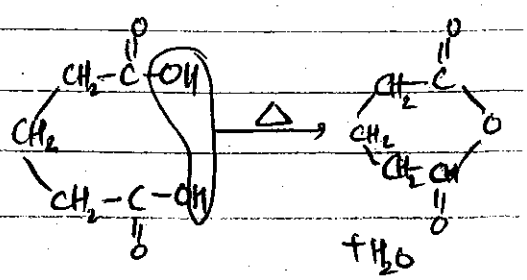
OM SH AP

CO_2 H_2O $CO_2\uparrow + H_2O$

① 

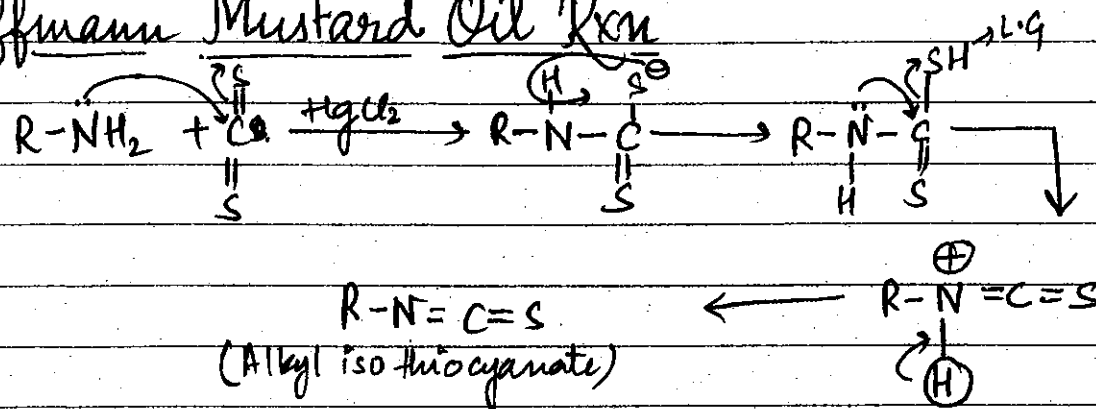
② 

③ 

④ 

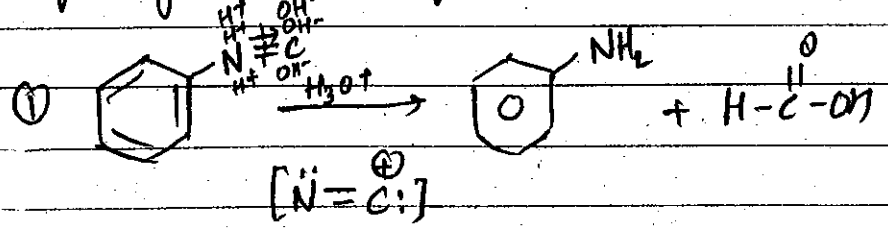
Amine

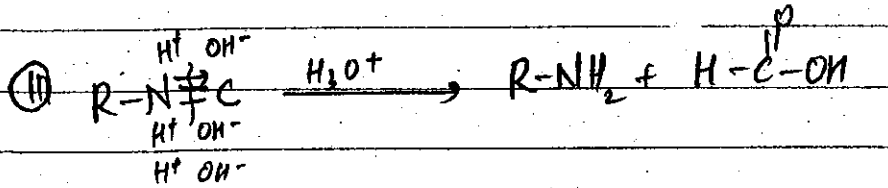
Hoffmann Mustard Oil Rxn



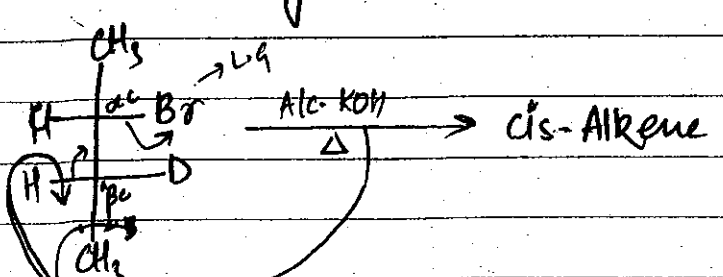
rxn used for detection of 1° Amine

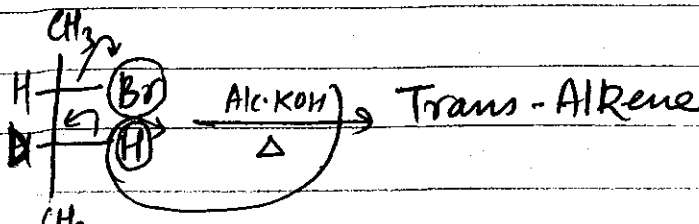
Hydrolysis Of Isocyanide





Stereochemistry Of E2 Rxn





① $R-\overset{O}{\overset{\|}{C}}-OH + SOCl_2 \longrightarrow R-\overset{O}{\overset{\|}{C}}-Cl$

② $R-\overset{O}{\overset{\|}{C}}-\overset{H}{\underset{H}{N}} \xrightarrow[\Delta]{P_2O_5} R-C\equiv N$

374-375 NCERT

③ $R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{NH_3} (A) \xrightarrow{\Delta} R-\overset{O}{\overset{\|}{C}}-NH_2$

$R-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}-\overset{\oplus}{NH_4} \xrightarrow{-H_2O}$

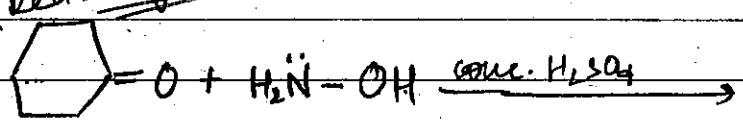
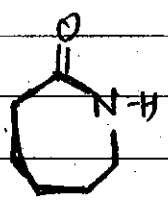
P-331 NCERT

④ $CH_3-\underset{OH}{CH}-CH_3 \xrightarrow[440K]{85\%\ H_3PO_4} CH_3-CH=CH_2 + H_2O$

$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH \xrightarrow[358\ K]{20\%\ H_3PO_4} CH_3\diagdown C=CH_2 \diagup CH_3 + H_2O$

Bihar-2019

Backmann's Rearrangement

⑤  + $H_2\ddot{N}-OH \xrightarrow{Conc.\ H_2SO_4}$ 

Caprolactum

In Sheet

$R-C\equiv N \xrightarrow[H_3O^+]{R-Mg-X} R\diagdown C=N^{\ominus} \diagup R$

$\downarrow H-OH$

$R\diagdown \overset{OH^-}{\underset{OH^-}{C}}=\overset{H^+}{\underset{OH^+}{NH}} \diagup R \longrightarrow R\diagdown C=O \diagup R$

Imine

Syn Addition KEPT Halide (Neat Alkyl Halide)
Remove cyclic halonium ion
Tendency for attacking on alkene

SNAr
SN1 E1

Applicat^n of Esterificat^n (conc. COOH)

$CH_3-\overset{O}{\overset{\|}{C}}-C_6H_5$ Haloform ग्रा॰

Sodium bisulphite test से ग्रा॰ ($NaHSO_3$)

D.S SIR

① Pyrolysis Of Alkane

Alkane $\xrightarrow[\text{Absence of } O_2]{\Delta}$ i) Alkane + Alkene

(less no. of C atom) (less/same no. of C)

ii) Alkene + H_2

~~iii)~~ Alkane + Alkane

Free Radical Elimination Mech.

i) $CH_4 \xrightarrow[-O_2]{500^\circ C} C + 2H_2$

ii) $CH_2(\cdot)-CH_2(\cdot) \xrightarrow[-O_2]{\Delta} CH_2=CH_2 + H_2$

iii) $CH_2(\cdot)-CH_2-CH_3(\cdot) \xrightarrow[-O_2]{\Delta} C-C=C + H_2$

$CH_2=CH_2 + CH_4$

iv) $C-C-C-C \xrightarrow[-O_2]{\Delta} C-C-C=C + H_2$

$C-C=C-C + H_2$

$C-C=C + CH_4$

$C=C + C_2H_6$

~~QQ~~

Biomolecules

Energy
Oxidat^n

Carbohydrate

optically active polyhydroxy aldehyde / ketone
↓ aldose ↓ ketose

Glucose (Aldehexose) Fructose (Ketohexose)

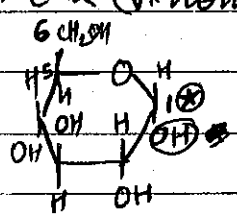
$-CHO \quad +OH$

$-\overset{\overset{O}{\|}}{C} \quad +OH$

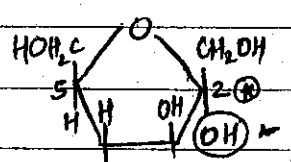
Anomers

→ Glucose → C-1 (Anomeric "C")
→ Fructose → C-2 (Anomeric "C")

⑥ No. C always outside



α-Glucose



α-fructose

H keside wale C ⑤ No C

Epimers

configurat^n change other than anomeric position.

C-2 Mannose
C-3 Allose
C-4 Galatose

Polyhydroxy ketone show test with Tollen's & Fehling

Reducing Sugar:

Reducing properties of carbohydrate depend on -OH group on anomeric C. In reducing suger -OH group on anomeric C not involves in bond formation or free

eg. All monosaccharide

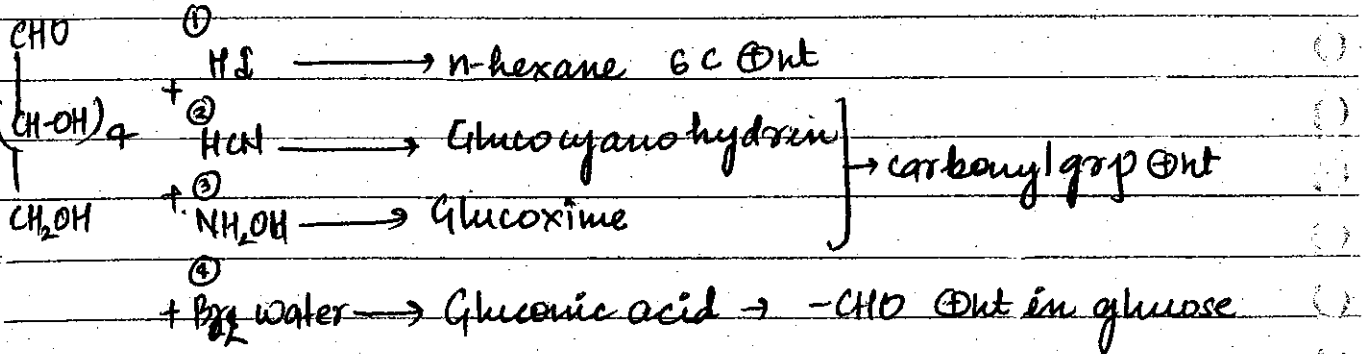
* Due to enolisat^{n} (tautomerisat^{n}) fructose ~~show~~ react with Tollen or Fehling

Maltose & lactose

Non-Reducing Suger -OH group on anomeric C involve in bond formation

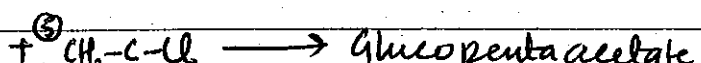
eg. All polysacchrides & sucrose.

React^{n} of Glucose



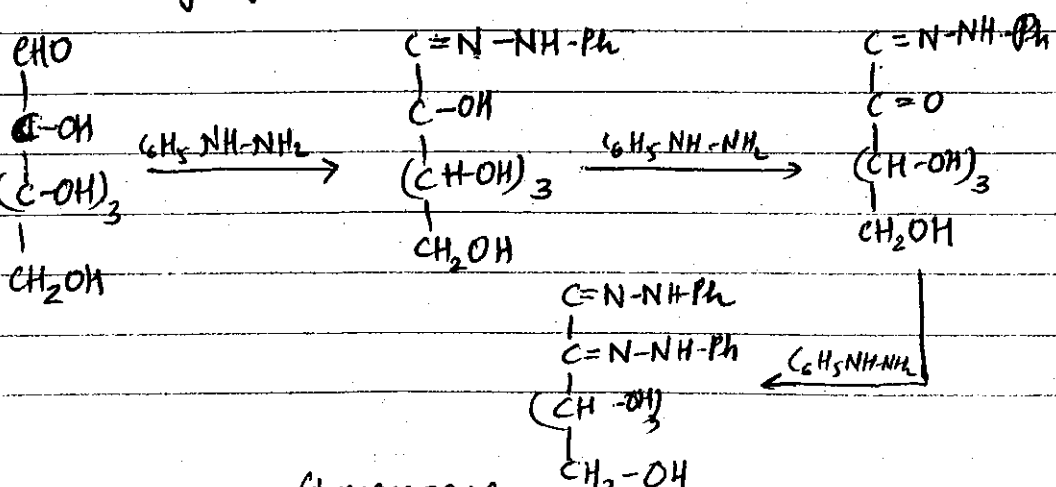
* Rxn with Br_2 water differentiate Glucose & fructose molecule

Fructose + Br_2 water → No rxn



⇒ React^{n} with phenylhydrazine

3mole req.



Glucosazone

* L-Glucose → Mirror image of D-Glucose

Imp **

Glucose Mannose & Fructose form same type of osazone due to same configuration on C_3 to C_6

Reacⁿ with periodic acid (HIO_4)

i) $C(OH)-C(OH) \longrightarrow C(OH) + C(OH) \xrightarrow{-2H_2O} 2HCHO$

Break C-C bond add 1-1 OH on each.

ii) $C(OH)-C(=O)H \longrightarrow C(OH) + HCOOH$

$C(OH) \rightarrow HCHO$

$CHO \longrightarrow HCOOH$

$H-C-OH \longrightarrow HCOOH$

$HO-C-H \longrightarrow HCOOH$

$H-C-OH \longrightarrow HCOOH$

$H-C-OH \longrightarrow HCOOH$

$CH_2OH \longrightarrow HCHO$

$Glucose + HIO_4 \longrightarrow 5HCOOH + HCHO$

Cellulose + $CH_3-C(=O)-Cl$ ⟶ ester formed (जितने जितने OH होंगे) OH को बनाएगा → $OCOCH_3$ (OAc)

Mutarotation

Change in specific rotation is known as Mutarotation

All reducing sugar show mutarotaⁿ but absent in Non-Reducing sugar (SUCROSE)

α-Glucose ⇌ Mix ⇌ β-Glucose

⊕110° ⊕52° ⊕19°

Inversion :-

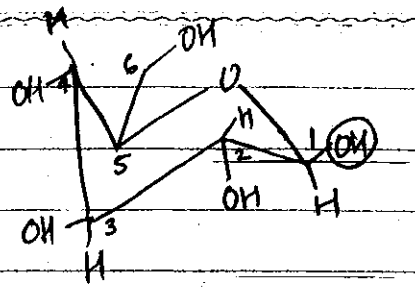
Sucrose ⟶ Glucose + Fructose

⊕66° ⊕52° ⊖92°

dextro

$\downarrow -20°$

* Dextro → Laevo



(1) Ketohexose

~~(2) Aldohexose~~

(3) α-furanose

~~(4) β-pyranose~~

Protein

Polymer of α-Amino Acid.

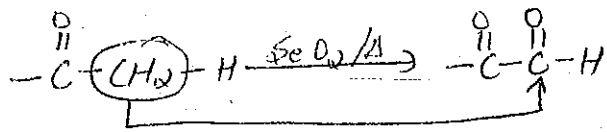
α-L a.a. only involve in formatⁿ of protein chain

except Glycine all are optically active

Alcohol ← Dichromate, Victor Mayer, Lucas

Aldehyde ← Tollen, Benedict, Schiff, Fehling

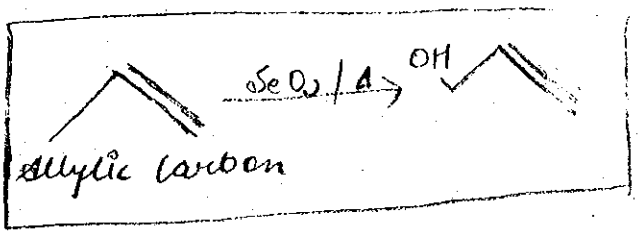
OXIDATION BY SeO_2/Δ :- SKC SIR



$-\overset{\overset{O}{\|}}{C}-$ के बगल वाले Carbon को $-\overset{\overset{O}{\|}}{C}-$ बना देता है।

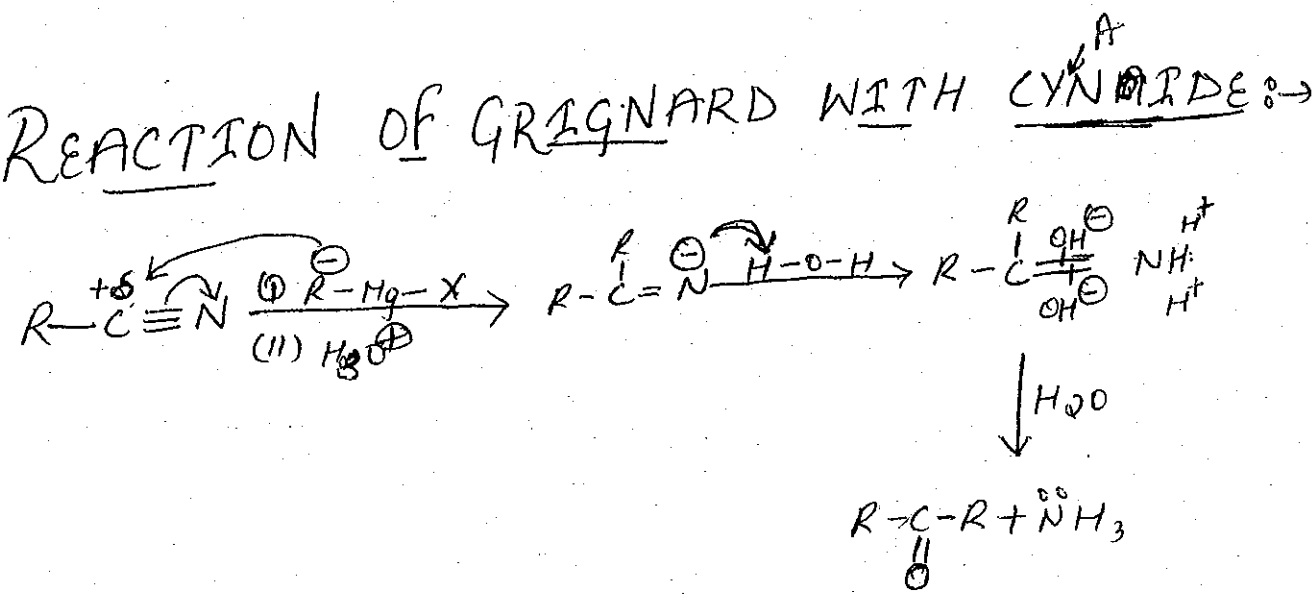
(1) $H-CH_2-\overset{\overset{O}{\|}}{C}-H \xrightarrow{SeO_2/\Delta} H-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-H$

[glyoxal]



2) $H-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_3 \xrightarrow{SeO_2/\Delta} H-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-CH_2-CH_3 + H-CH_2-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-CH_3$

REACTION OF GRIGNARD WITH CYANIDE :→



POPOFF'S RULE :→

(1) $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3 \xrightarrow[(II)\ High\ temp.\ (III)\ High\ Pressure]{(I)\ KMnO_4/H^+} H-\overset{\overset{O}{\|}}{C}-OH + CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OH$

small alkyl group → change into acid

big alkyl group

(2) $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$ $\xrightarrow[\text{(ii) High temp.}\\\text{(iii) High pressure}]{\text{(i) } KMnO_4/H^+}$ $CH_3-\overset{O}{\overset{\|}{C}}-OH + CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH$

(3) $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_3$ $\xrightarrow[\text{(ii) High temp.}\\\text{(iii) High pressure}]{\text{(i) } KMnO_4/H^+}$ $CH_3-\overset{O}{\overset{\|}{C}}-OH +$ $CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OH$

BAEYER VILLEGER OXIDATION :-

(1) $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ $\xrightarrow[\text{[Peroxy acid]}]{CH_3-\overset{O}{\overset{\|}{C}}-O-O-H}$ $CH_3-\overset{O}{\overset{\|}{C}}-O-CH_3$ $\xrightarrow{[O]}$

[Migratory Aptitude → $-H > 3^\circ$ Alkyl group $> 2^\circ$ Alkyl group $> -C_6H_5 > -CH_3$]

(2) $CH_3-\overset{O}{\overset{\|}{C}}-H$ $\xrightarrow[[O]]{CH_3-\overset{O}{\overset{\|}{C}}-O-O-H}$ $CH_3-\overset{O}{\overset{\|}{C}}-O-H$

(3) $CH_3-\overset{O}{\overset{\|}{C}}-C_6H_5$ $\xrightarrow[\text{(i) [MCPBA]}]{C_6H_5-\overset{O}{\overset{\|}{C}}-O-O-H}$ $CH_3-\overset{O}{\overset{\|}{C}}-O-C_6H_5$

$\Rightarrow$

(4) $CH_2-CH-CH_3$ $\xrightarrow{\text{(i) } R-Mg-X}$ $CH_2-CH-CH_3$ $\xrightarrow{H^+}$ $R-CH_2-CH-CH_3$ (OH)

REACTION OF GRIGNARD REAGENT WITH CO_2 :-

$R-\overset{-\delta}{Mg}-X + C(=O)=O \longrightarrow R-C(=O)-O^{\ominus}\,{}^{\oplus}Mg-X \xrightarrow{H_2O} R-\overset{O}{\overset{\|}{C}}-OH + Mg(OH)X$

CHEMISTRY OF CARBIDES:-

1) $Al_4C_3 + 12\,H_2O \longrightarrow CH_4 + Al(OH)_3$
(Aluminium carbide)

2) $CaC_2 + H_2O \longrightarrow CH{\equiv}CH + Ca(OH)_2$
(Calcium carbide) (Acetylene)

3) $Mg_2C_3 + H_2O \longrightarrow CH_3{-}C{\equiv}CH + Mg(OH)_2$
(Magnesium carbide) (Propylene)

OXIDATION OF ALKANE :-

$$C_nH_{2n+2} + \frac{3n+1}{2}O_2 \longrightarrow nCO_2 + (n+1)H_2O$$

1) $CH_4 + O_2 \xrightarrow[523^\circ C]{Cu} CH_3{-}OH$

2) $CH_4 + O_2 \xrightarrow[\Delta]{MoO_3} H{-}\overset{O}{\overset{\|}{C}}{-}H + H_2O$

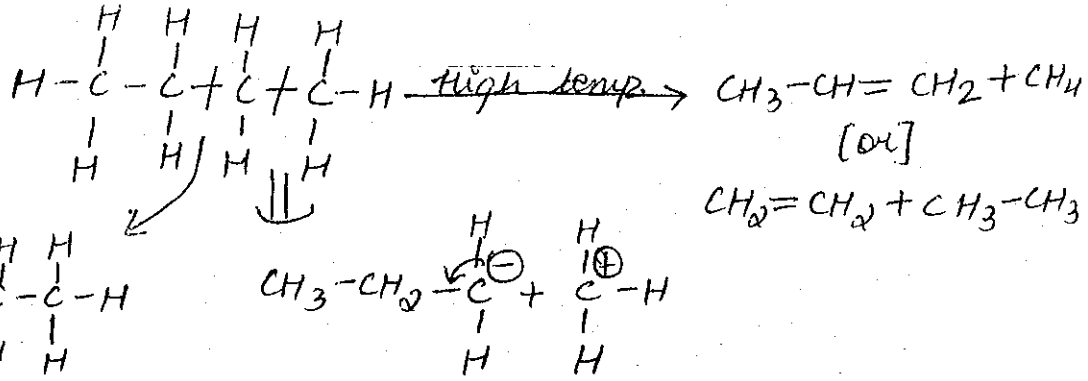
3) $CH_3{-}CH_3 + 3O_2 \xrightarrow[\Delta]{(CH_3COO)_2Mn} CH_3{-}\overset{O}{\overset{\|}{C}}{-}OH + H_2O$

4) $CH_3{-}\overset{CH_3}{\overset{|}{C}}{-}\underset{3^\circ H}{(H)} \xrightarrow[\text{(Pink colour)}]{KMnO_4/\Delta} CH_3{-}\overset{CH_3}{\overset{|}{C}}{-}OH$
(Colourless)

5) $\underset{2^\circ H}{(H)} \xrightarrow[\Delta]{KMnO_4}$ No Reaction

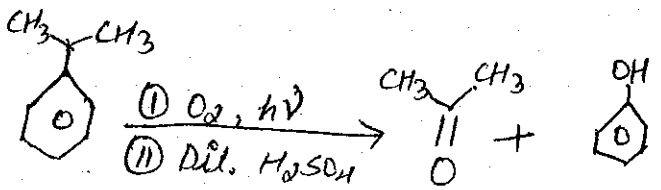
PYROLYSIS OF ALKANE ⟶ (Cracking)

→ reaction completed with free radical Elimination

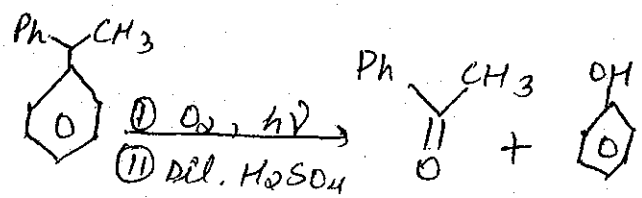


PHENOLE FROM CUMENE :-⟶

(1)

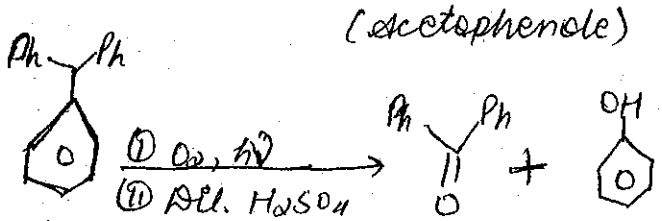


(2)

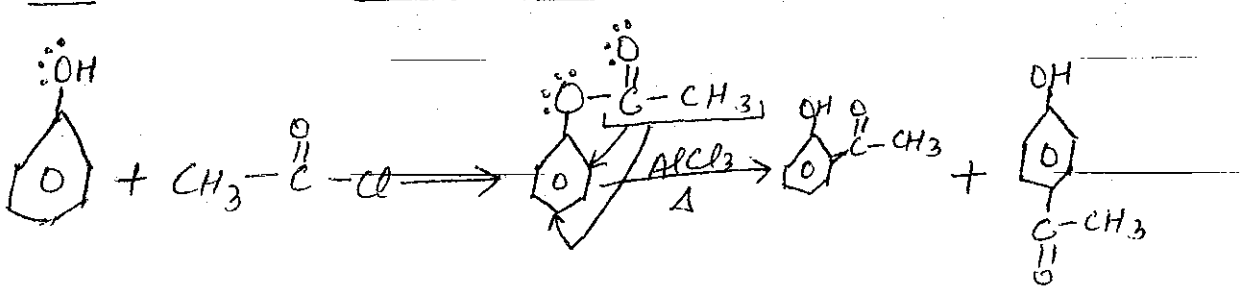


(acetophenole)

(3)



FRIES REARRANGEMENT :-



HYDROCARBON

REACTION CHART FOR ALKANES

GMP

(1) $R-C\equiv CH$ or $R-CH=CH_2$ —H_2, Ni, 200–300°C, Sabatier senderens rxⁿ→

(2) $R-X$ —Red P/HI or $LiAlH_4$→

(3) $R-Mg-X$ —HOH or ROH or NH_3 or RNH_2→

(4) RX —Na/ dry ether, Wurtz reaction→

(5) RX —Zn, Frankland's reaction→

(6) $R-\underset{\underset{O}{\|}}{C}-Cl$ or ROH or $R-\underset{\underset{O}{\|}}{C}-R$ or RCHO —Red P/HI→

(7) $R-\underset{\underset{O}{\|}}{C}-R$ —Zn–Hg/Conc. HCl, Clemmensen reduction→

(8) $R-\underset{\underset{R}{|}}{C}=O$ or $(RCH_2CH_2)_3B$ —H_2N-NH_2, Wolf Kishner reduction→ —H_2O→

(9) RCOONa —NaOH + CaO, Δ→

(10) RCOONa —Kolbe's electrolytic synthesis→

(11) Al_4C_3 —H_2O→

$R-CH=CH_2$ / B_2H_6

R–H or R–R or C_nH_{2n+2}

GR

(1) —X_2, hv or UV light or 400°C→ RX

(2) —Nitration→ $R-N\overset{O}{\underset{O}{<}}$

(3) —Sulphonation $H_2S_2O_7$→ Alkyl Sulphonic acid

(4) —SO_2Cl_2, Reed reaction, hv→ $RSO_2Cl \rightarrow R-Cl$

(5) —$AlCl_3$ / HCl, Isomerisation→ Branched alkanes

(6) —Pyrolysis, 500–700°C→ Alkenes + CH_4 or C_2H_6

(7) —(Cr) or (Mo) or Al_2O_3, 500°C→ Aromatic compound

(8) —CH_2N_2, step up rxⁿ→ Higher alkane

(9) —O_2, Δ→ $CO_2 + H_2O$

Combustion

REACTION CHART FOR ALKENES

GMP

(1) $R-CH_2-CH_2-OH \xrightarrow[\Delta/-H_2O]{\text{conc. } H_2SO_4}$

(2) $R-CH_2-CH_2-X \xrightarrow[-HX]{\text{alc. KOH}}$

(3) $R-CH_2-CH\langle^{X}_{X} \xrightarrow[\text{for higher alkene}\ -X_2]{Zn\ dust/\Delta}$

(4) $\begin{matrix} R-CH-CH_2 \\ | \quad | \\ X \quad X \end{matrix} \xrightarrow[\Delta]{Zn\ dust}$

(5) $R-C\equiv CH \xrightarrow[CaCO_3]{H_2/Pd}$

(6) $\begin{matrix} RCH-COOK \\ | \\ RCH-COOK \end{matrix} \xrightarrow{\text{Kolbe's electrolytic synthesis}}$

(7) $(C_2H_5)_4N^+OH \xrightarrow{\Delta}$

(8) $R-\underset{\underset{O}{\|}}{CO}-CH_2-CH_2-R \xrightarrow{\text{Pyrolysis}}$

(9) $R-H \xrightarrow{\text{Pyrolysis}}$

(10) $CH_2=CHCl \xrightarrow[(ii)Me-I]{(i)Mg}$

(11) $R-CH=O \xrightarrow[\text{wittig reaction}]{CH_2=PPh_3}$

$R-CH=CH_2$ or C_nH_{2n}

GR

(1) $\xrightarrow[200-300°C]{H_2, Ni} R-CH_2-CH_3$

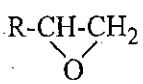
(2) $\xrightarrow{X_2} R-CHX-CH_2X$

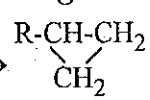
(3) $\xrightarrow{HX} R-CHX-CH_3$

(4) $\xrightarrow{HBr, Peroxide} R-CH_2-CH_2Br$

(5) $\xrightarrow{HOCl} R-CH(OH)-CH_2Cl$

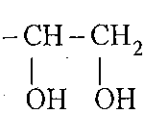
(6) $\xrightarrow[+H_2O]{dil.H_2SO_4} R-CH_2(OH)-CH_3$

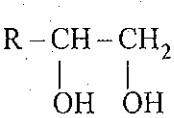
(7) $\xrightarrow[Ag\,300°C]{1/2O_2}$ 

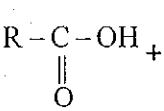
(8) $\xrightarrow{+CH_2N_2}$ 

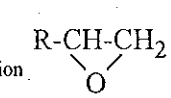
(9) $\xrightarrow{BH_3} (RCH_2CH_2)_3B$

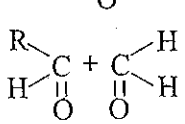
(10) $\xrightarrow[\Delta]{O_2} CO_2 + H_2O$

(11) $\xrightarrow{OsO_4}$ 

(12) $\xrightarrow[1\%\,alkaline\,KMnO_4]{Bayer\ reagent}$ 

(13) $\xrightarrow{strong\ oxidant}$  $+ CO_2 + H_2O$

(14) $\xrightarrow[Pr\,iles-chalev's\,reaction]{Per\ acid}$ 

(15) $\xrightarrow[ozonolysis]{O_3/Zn, H_2O}$ 

(16) $\xrightarrow[500°C]{Cl_2}$ Substitution product

REACTION CHART FOR ALKYNES

GMP

(1) $CH_2Br–CH_2Br \xrightarrow{alc.KOH,\ NaNH_2}$

(2) $CH_3–CHBr_2 \xrightarrow{alc.KOH,\ NaNH_2}$

(3) $CHCl_3 \xrightarrow[\Delta]{Ag\ powder}$

(4) $CHBr_2–CHBr_2 \xrightarrow[\Delta]{Zn\ dust}$

(5) $\begin{matrix}CHBr\\ \|\\ CHBr\end{matrix} \xrightarrow{Zn}$

(6) $CH_2=CH–Cl \xrightarrow{alc.KOH,\ NaNH_2}$

(7) $\begin{matrix}HC-COONa\\ \|\\ HC-COONa\end{matrix} \xrightarrow{Kolbe's\ electrolytic\ synthesis}$

(8) $CaC_2 \xrightarrow{H_2O}$

(9) $2C + H_2 \xrightarrow[Berthelot's\ process]{electric\ arc,\ 1200°C}$

(10) $CH_3–C\equiv CH \xrightarrow{(i)Na\ (ii)R–X} CH_3–C\equiv CR$

(11) $CH_3–C\equiv CH \xrightarrow{(i)CH_3MgI\ (ii)R–X} CH_3–C\equiv CR$

C_2H_2

GR

(1) $\xrightarrow[Ni]{H_2} C_2H_4,\ C_2H_6$

(2) $\xrightarrow{X_2} C_2H_2X_4$

(3) $\xrightarrow[Peroxide]{HBr} CH_2BrCH_2Br$

(4) $\xrightarrow[No\ peroxide]{HBr} CH_3–CHBr_2$

(5) $\xrightarrow{HOCl} Cl_2CH–COOH$

(6) $\xrightarrow{HCN,\ Ba(CN)_2} CH_2=CHCN$

(7) $\xrightarrow{CH_3COOH,\ Hg^{+2}} CH_3CH(OCOCH_3)_2$

(8) $\xrightarrow[(Kucherov's\ reaction)]{Hg^{+2},\ 80°C,\ dil.\ H_2SO_4} CH_3CHO$

(9) $\xrightarrow{Conc.\ H_2SO_4} CH_3CH(HSO_4)_2$

(10) $\xrightarrow[HgSO_4]{C_2H_5OH/H_2O} CH_3CHO$

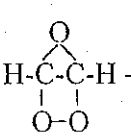
(11) $\xrightarrow{NaNH_2} NaC\equiv CNa$

(12) $\xrightarrow[(Tollen's\ Reagent)]{AgNO_3+NH_4OH} AgC\equiv CAg$ white ppt.

(13) $\xrightarrow{Cu_2Cl_2+NH_4OH} CuC\equiv CCu$ red ppt.

(14) $\xrightarrow{Combustion\ O_2} CO_2 + H_2O$

(15) $\xrightarrow{Bayer\ Reagent} \begin{matrix}CHO\\ |\\ CHO\end{matrix} \longrightarrow HCOOH$

(16) $\xrightarrow[Ozonolysis]{O_3}$  $\xrightarrow{+H_2O} HCOOH$

(17) $\xrightarrow[(Red\ hot\ iron\ tube)]{Trimerisation}$ benzene

(18) $\xrightarrow[[Ni(CN)_2]]{Tetramerisation} C_8H_8$ or 1,3,5,7-cyclo octa tetraene

(19) $\xrightarrow[[Cu(NH_3)_2]^+\ or\ Cu_2Cl_2.NH_4Cl]{Dimerisation}$ butenyne