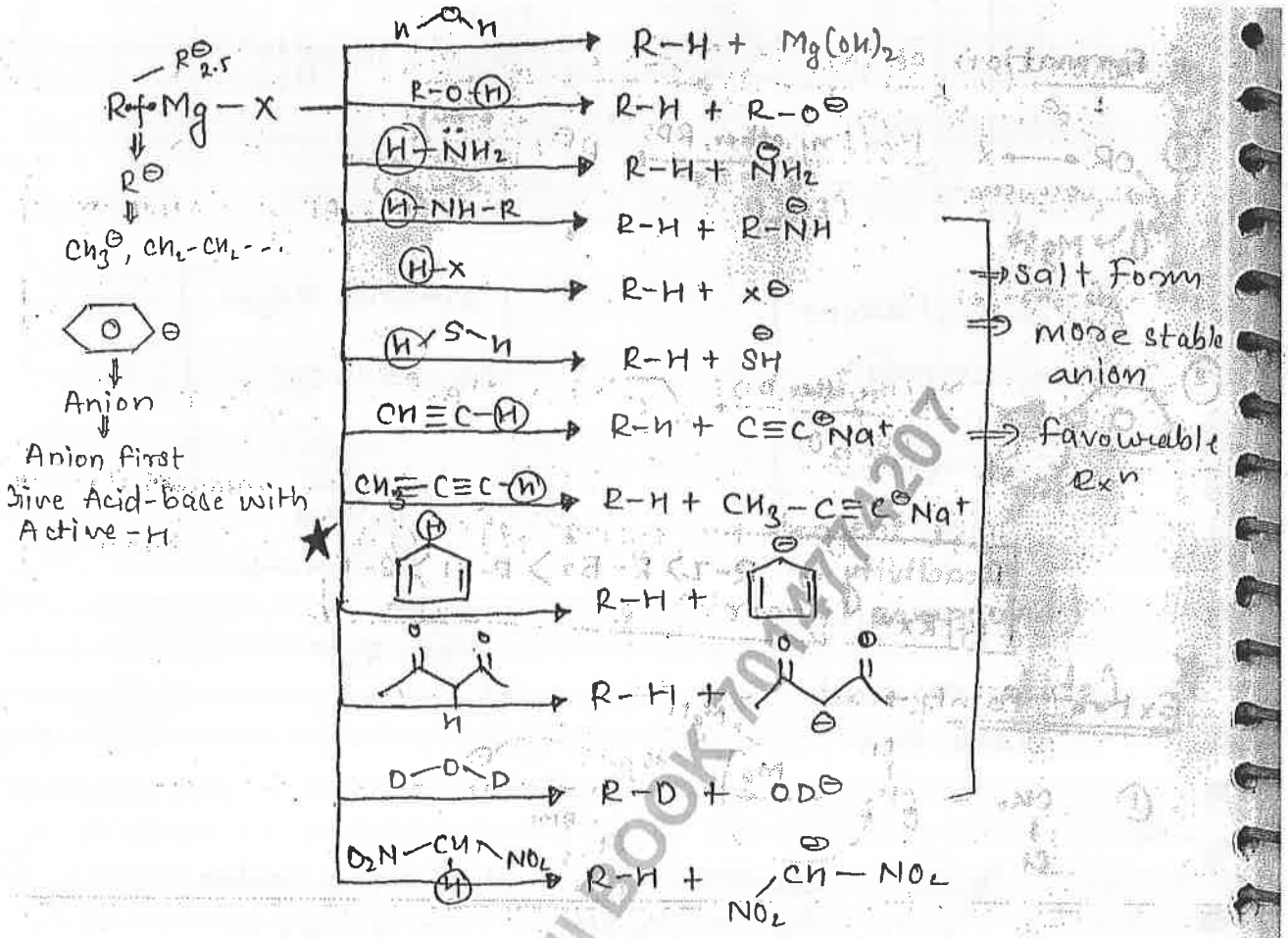


Some extra Acid Base Rxn :

1) $CH_3-CH_2-\overset{-\delta}{O}-\overset{+\delta}{H} \xrightarrow[e^-]{-Na \to Na^+} CH_3-CH_2-O^{\ominus}Na^+ + \frac{1}{2}H_2\uparrow$ (gur-gur)

$Na + H^{\ominus}$ (metal hydride) $\Rightarrow$ + $H_2\uparrow$ (gur-gur)

$Na + NH_2^{\ominus} \Rightarrow NH_2^{\ominus}$ $\rightarrow CH_3-CH_2-O^{\ominus}Na^+ + NH_3\uparrow$

2) $CH_3-C\equiv C-H \xrightarrow[e^-]{Na \to Na^+} CH_3-C\equiv C^{\ominus}Na^+ + \frac{1}{2}H_2\uparrow$

$Na + H \Rightarrow H^{\ominus}$ $\Rightarrow$ + $H_2\uparrow$

$Na-NH_2^{\ominus} \Rightarrow NH_2^{\ominus}$ $\rightarrow CH_3-C\equiv C^{\ominus}Na^+ + NH_3\uparrow$

(3) $CH_3-C\equiv C-H \xrightarrow{Na^+OH^-} CH_3-C\equiv C^{\ominus}Na^+$ ⇒ Backward XXX

less Stable Anion

(4) $CH\equiv CH \xrightleftharpoons{NaOH}$ XX Backward

Terminal Alkyne

$CH_3-C\equiv C-(H)$

or

$C\equiv C-(H)$

(i) Na

(ii) Na–H

(iii) $NaNH_2$

give All Acid Base Rxn

Internal Alkyne

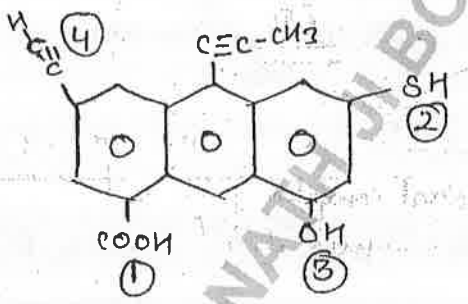
$CH_3-C\equiv C-CH_3$

(i) Na

(ii) Na–H

No Rxn

Q.



How many moles of R–Mg X consumed = ?

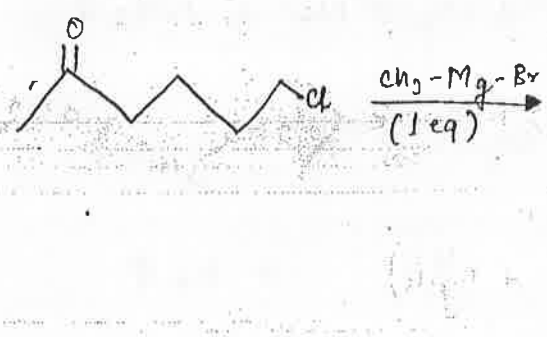
(4)

$R-Mg-X \xrightarrow[\text{(Chloramine)}]{NH_2-Cl} R-NH_2 + R-H$

(major) (minor)

$(NH_2-L.G)$

Q

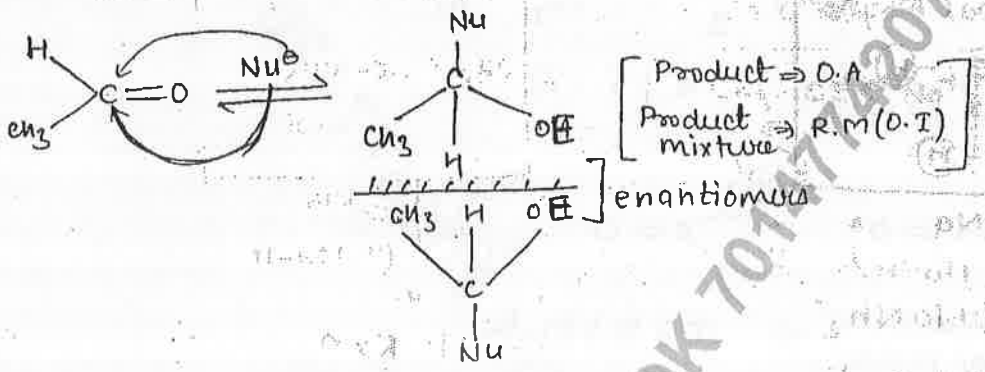


NAR [Nucleophilic addition Reaction]

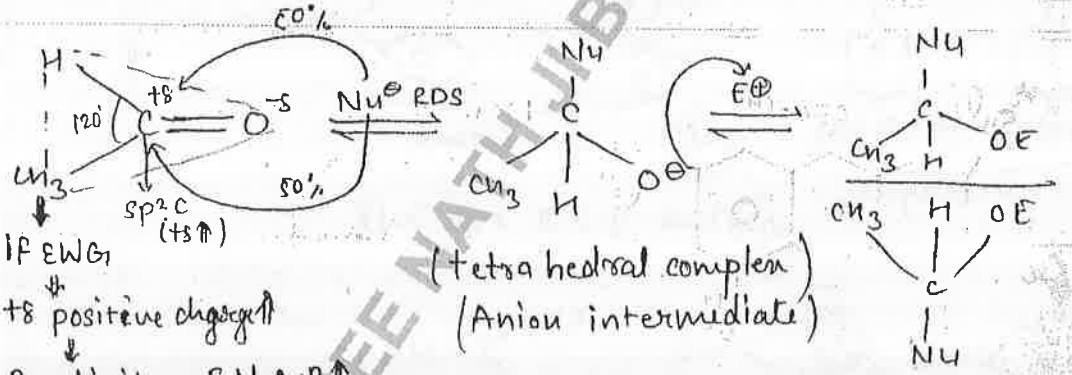
Nucleophilic addition Rxn is characteristic rxn of carbonyl compound.

* NAR give nucleophilic addition because there is no L.G

NET RXN:-



Mech



If EWG ⇓ ts positive charge↑ ⇓ Reactivity of N.A.R↑

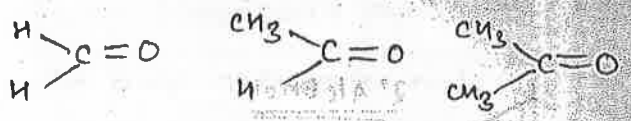
* Reactivity of NAR ∝ +δ positive charge At sp^2 C-Atom (δ^+_{ts} ↑)

* NAR ∝ $\frac{1}{\text{Steric hindrance}}$

* Reactivity NAR ⇒ Aldehyde > Ketone

(Both Aliphatic & Aromatic Aldehyde)

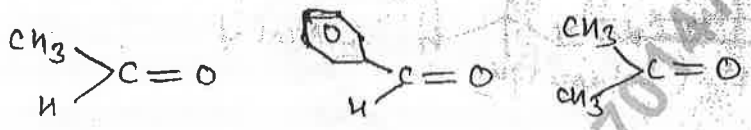
Q. Find out the correct order of reactivity of NAR for following compound.

1. 

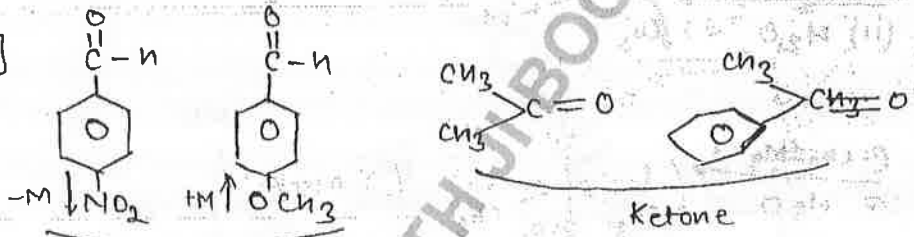
Reactivity of NAR ⇒ I > II > III

2. 

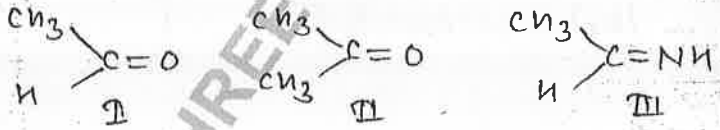
Reactivity of NAR ⇒ II > I > III

3] 

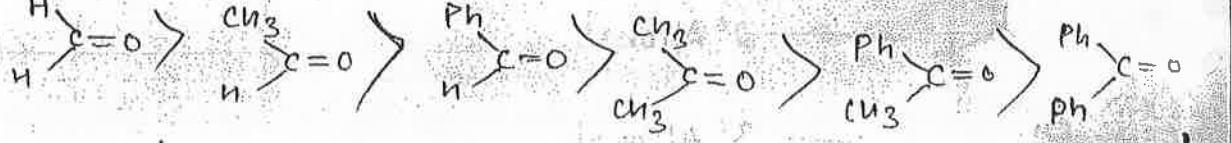
Reactivity of N.A.R ⇒ I > II > III

4] 

NAR ⇒ I > II > III > IV

5] 

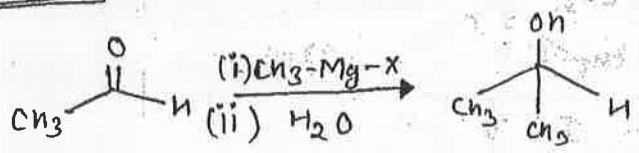
NAR ⇒ I > II > III



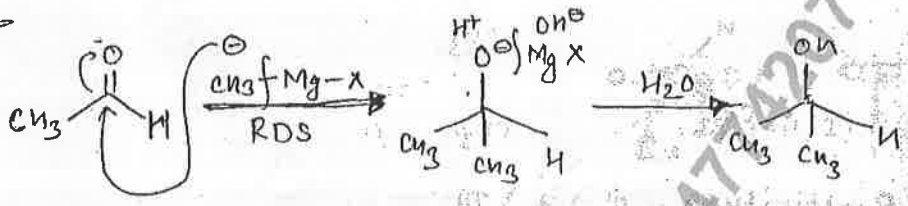
Addition of Anionic Nucleophile

① Addition of R-Mg-X →

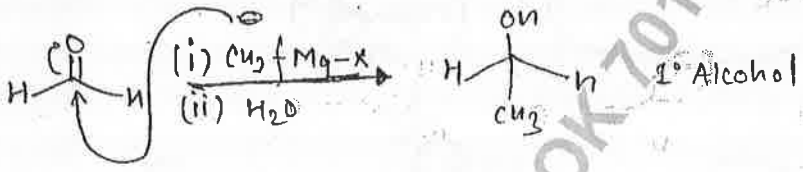
NET Rxn:-

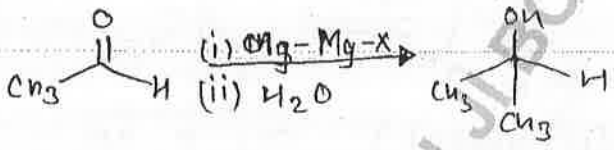


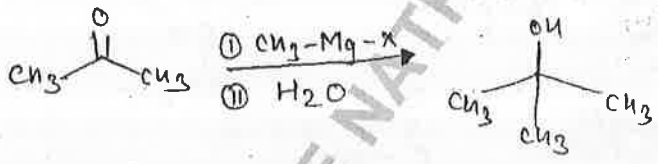
Mech

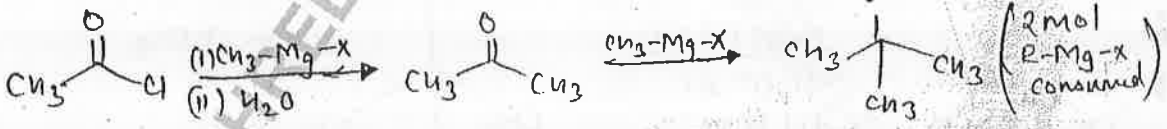


Eg

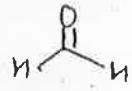
① 

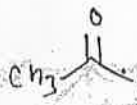
② 

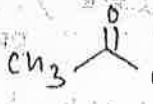
③ 

④ 

KEYPOINT :

①  ⟶ 1° Alcohol

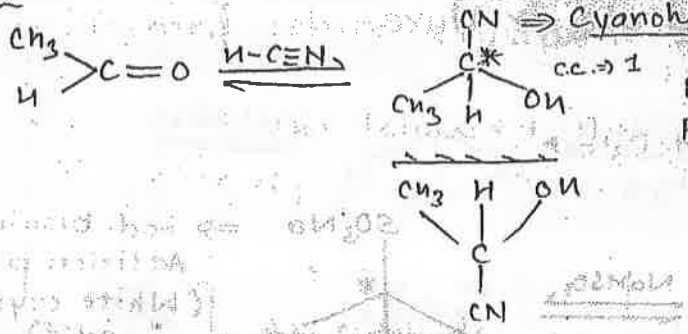
②  ⟶ 2° Alcohol

③  ⟶ 3° Alcohol

* $R^{\ominus}$ & $H^{\ominus}$ is a strong $Nu^{\ominus}$ & there is no L.G thats why rxn is irreversible

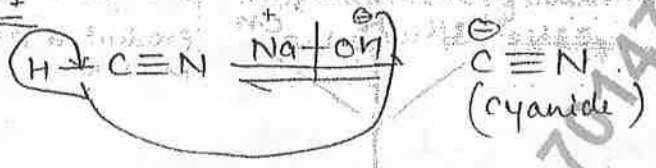
⑪ Addition of $HC\equiv N$ → (Hydrogen cyanide) :-

NET Rxn

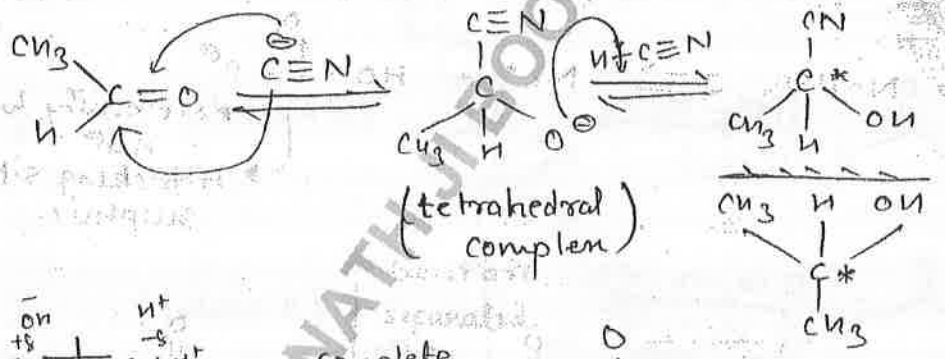


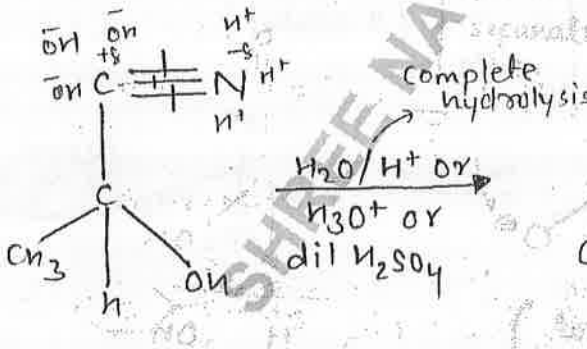
Mech

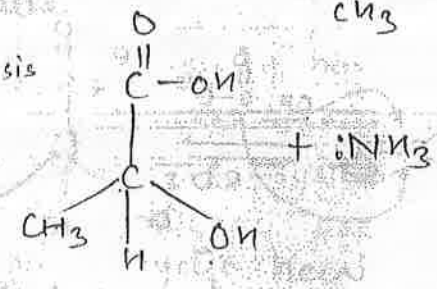
Step-I



Step-II





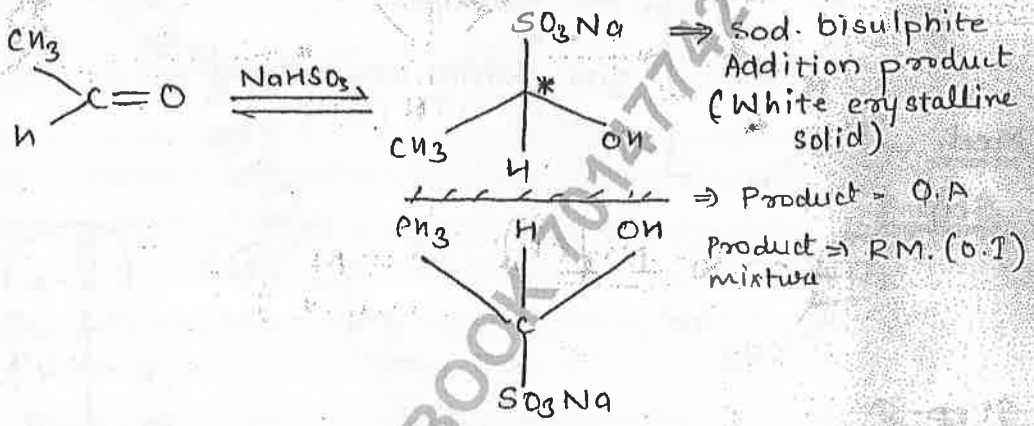


* formation of cyano-hydrine is NAR
* During addition HCN at carbonyl compound by NAR then due to generation of chiral center all aldehyde [except formal aldehyde] & all unsymm. ketone give Recimic mixture.

~~Addition of~~

* Addition of $NaHSO_3$ →

NET Rxn

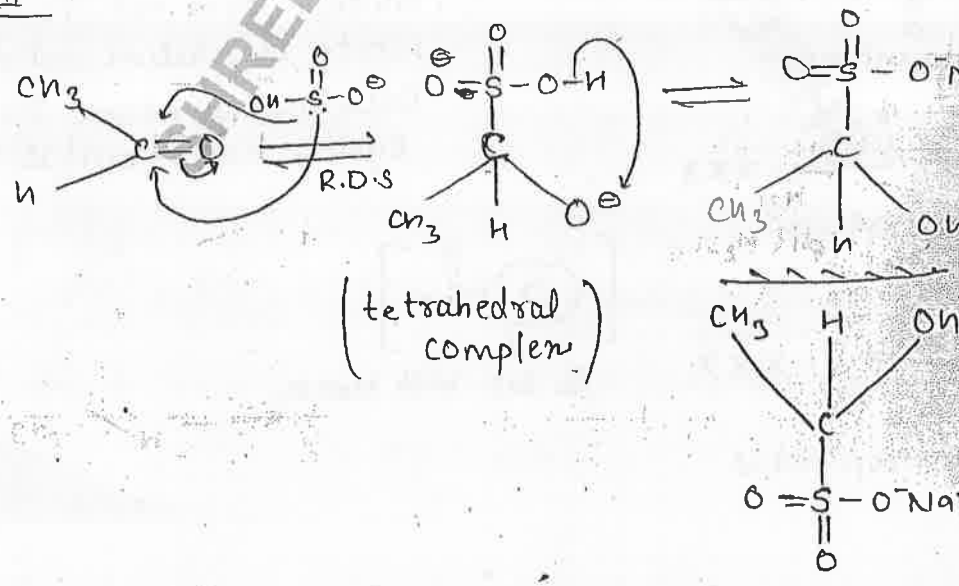


Mech

Step-I → $NaHSO_3 \rightleftharpoons Na^+ + HO-\overset{\overset{O}{\|}}{\underset{\cdot\cdot}{S}}-O^{\ominus}$

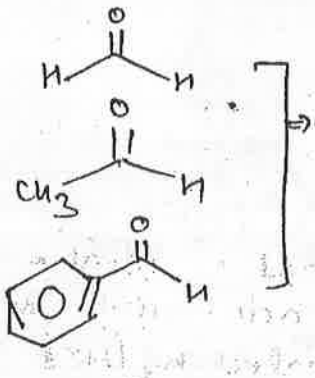
→ sterically hind. nu⊖
→ Attacking site sulphur.

Step-II →

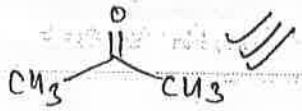


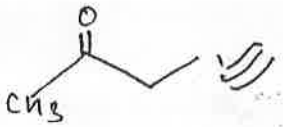
* Rxn used in POC
* All aldehyde [Aliphatic, & Aromatic] formed white crystaline solid with $NaHSO_3$.
* In case of ketone ohly methyl ketone [unhindered] ketone formed white crystaline solid with $NaHSO_3$

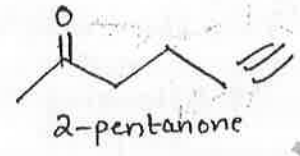
Q. Which one of the following give withe crystaline solid with $NaHSO_3$.

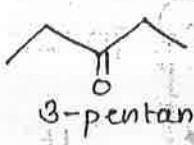
(1) 

→ All Aldehyde ⇓ give white crystallined solid with $NaHSO_3$

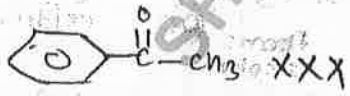
(2) 

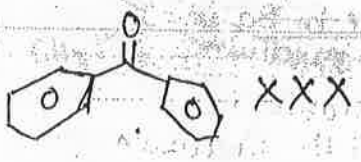
(3) 

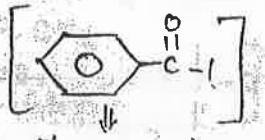
(4) 
2-pentanone

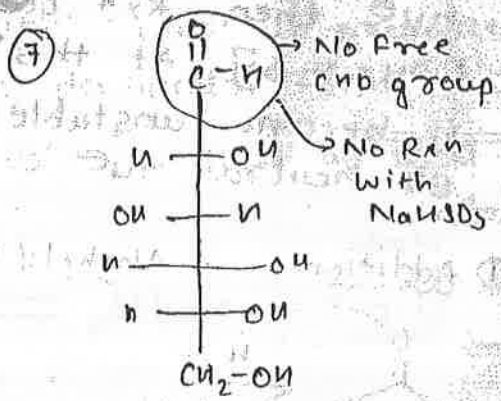

3-pentanone

Both are separated by $NaHSO_3$

(5) 
Acetophenone

(6) 
Benzophenone

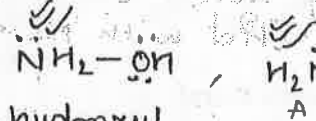

⇓ No Rxn with $NaHSO_3$

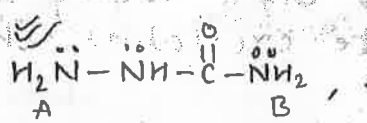
(7) 

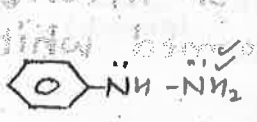
Despite having aldheyde Glucose does not form white crystaline solid becoz Glucose present in cyclic hemi-acetal form.

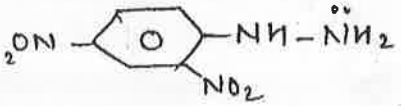
Addition of weak/Nutral $Nu^{\ominus}$:-

Neutral nu$^{\ominus}$ ⇒ R-OH, H_2O, NH_3, $R-NH_2$, $R-\ddot{N}H-R$, NH_2-NH_2 hydrazine


hydroxyl amine

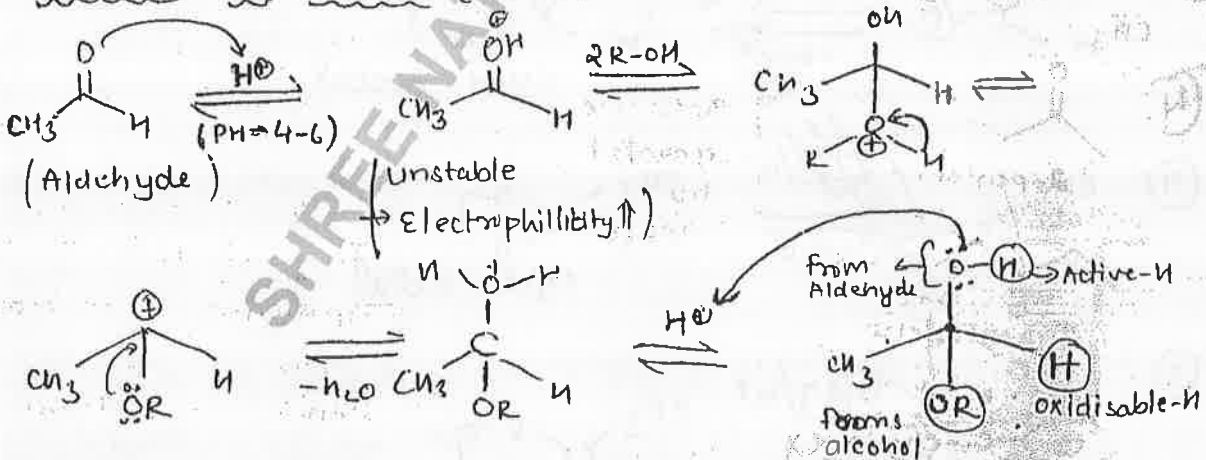

Semicarbzide [IIT-2017]

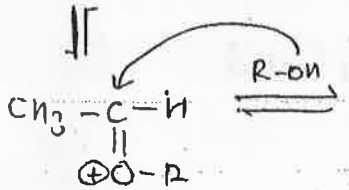

phenyl hydrazine

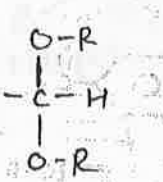

2,4,-DNP

* Whenever NAR carried with neutral or weak nu$^{\ominus}$ then Rxn occur in slightly acidic medium [PH = 4-6]. At this PH [O] protonated by [H^+] & become unstable and give rxn with weak or neutral nu$^{\ominus}$

① Addition of Alcohol: (R-OH):-

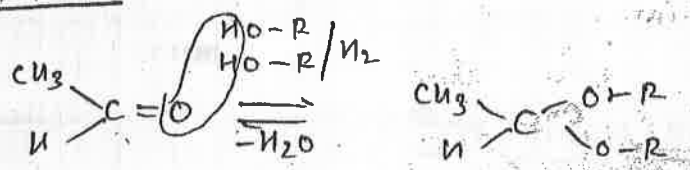




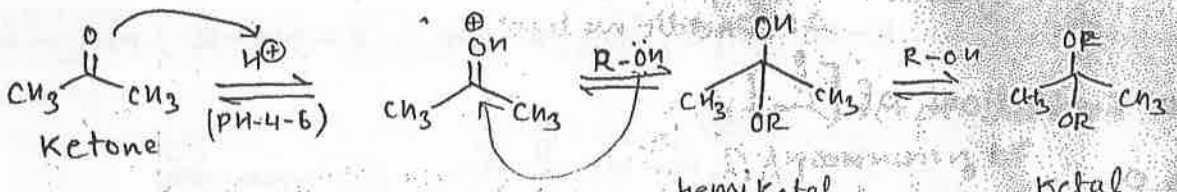

Acetal (Diether)

Acetal
⇒ Stable in Basic medium
⇒ Unstable in Acidic medium

KEY POINT

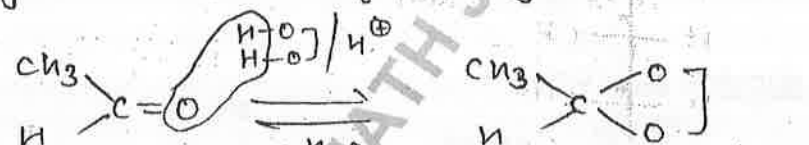


(11)

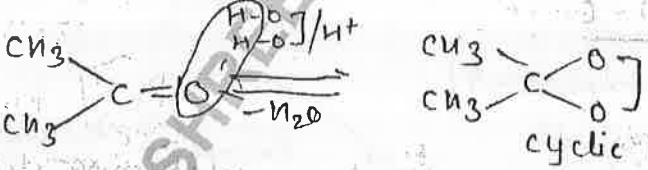


* Whenever aldehyde react with alcohol in presence of slightly acidic med. then Hemiacetal form.
* Hemiacetal is highly unstable in acid as well as basic medium but in basic medium Hemiacetal give all Rxn of aldehyde.

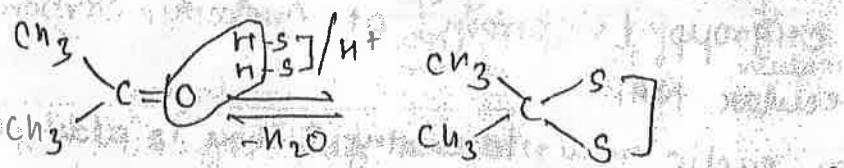
(2)



(4)



(5)

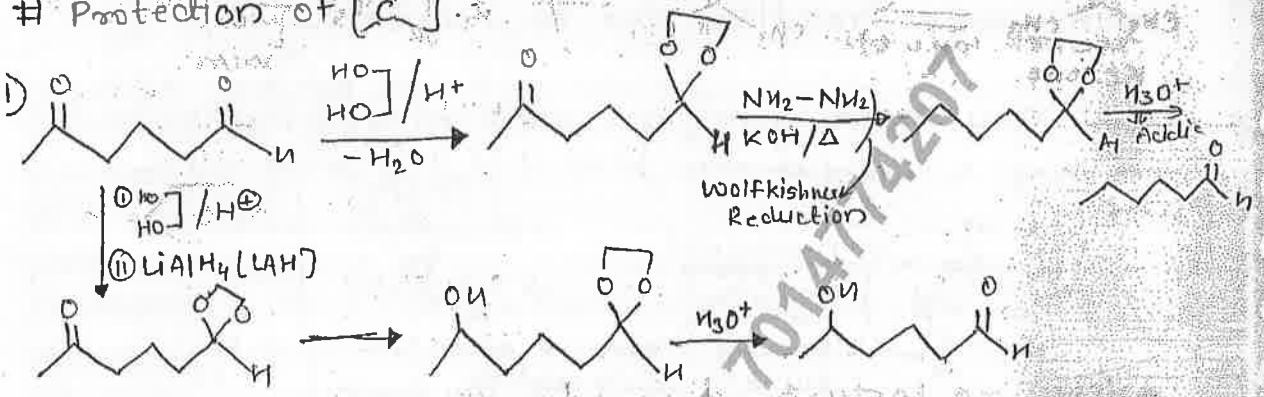


Acetal form stable in Basic Medium & unstable in Acidic medium.

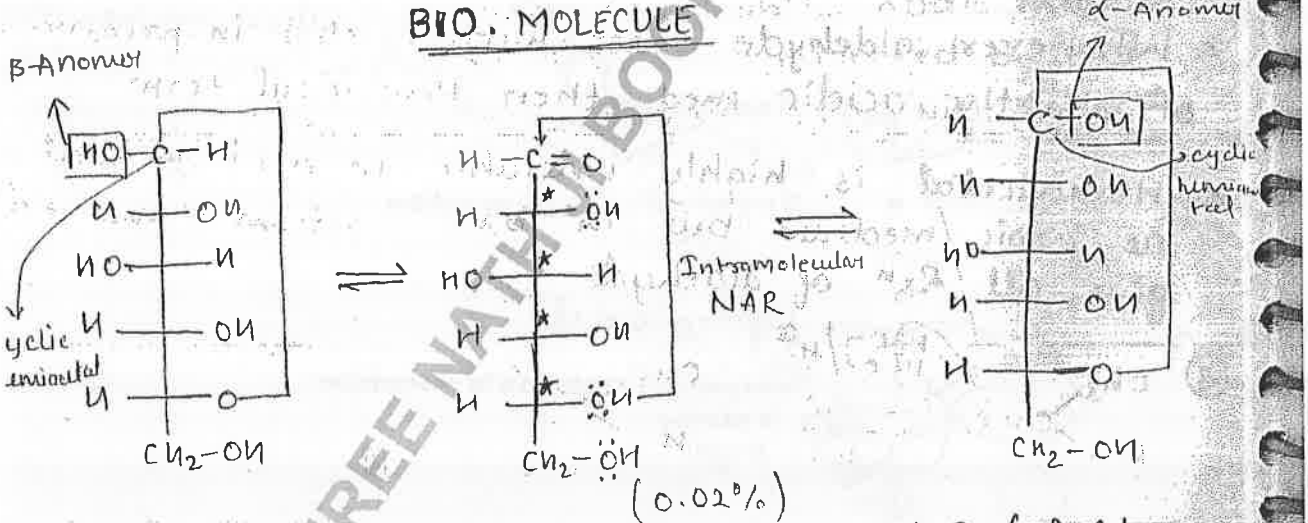
KEY POINT:-

cyclic Acetal highly unstable in Acidic medium.

Protection of [C=O]:-



BIO. MOLECULE



β-(D-(+)-Glucopyranose 64%

D(+)-Glucose (0.02%)

α-D-(+)-Glucopyranose (34%)

* In aq. condⁿ glucose Form cyclic hemiacetal ring due to addⁿ of OH group [5th carbon] at Anomeric carbon by intramolecular NAR

* Glucose form cyclic hemiacetal ring & there is no aldehyde gp.

* At anomeric carbon :-

if OH group is Right side ⟶ α-Anomer

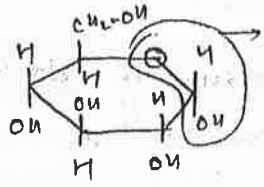
if OH " is Left side ⟶ β-Anomer

* In open chain stru. of Glucose ⟶ 4 C.C.
* In cyclic stru. of Glucose ⟶ 5 C.C.
* All monosaccharide & all disaccharide except sucrose are reducing sugars & give phenonmenon of muta ~~rotio~~ rotation due to hemiacetal grp.
* If any sugar give rxn with mild O. Agent like tollence, fehling & benedict soln rxn. then it is a Reducing Sugar

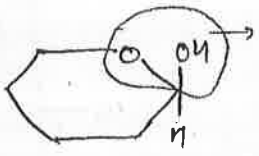
Amylase	Amylopectin
→ linear poly	→ Branched poly
→ H_2O soluble	→ H_2O insoluble
→ 80-20% of total starch	→ 80-82% of total starch

all polysaccharide are non-reducing sugar like starch, cellulose

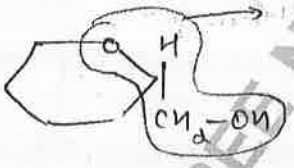
(1)



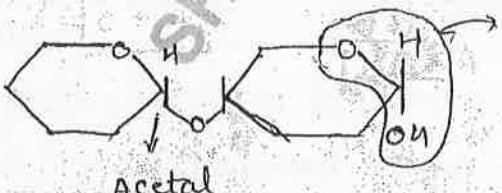
(2)



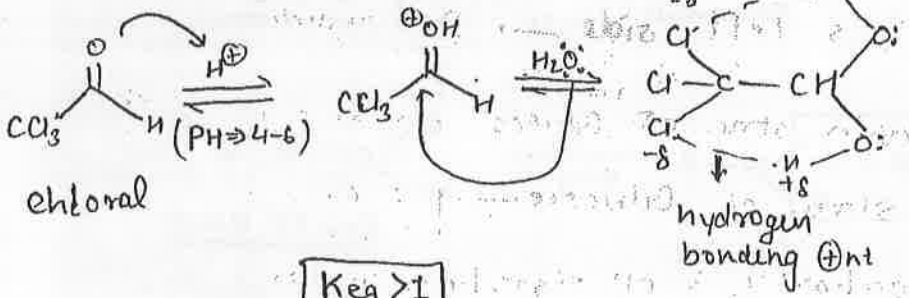
(3)



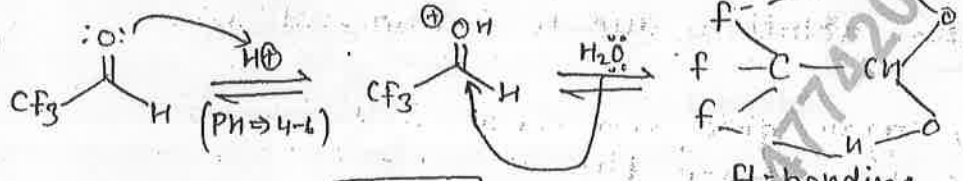
(4)



(2) Addition of H_2O :-

(1) 

Keq > 1

(2) 

Keq > 1

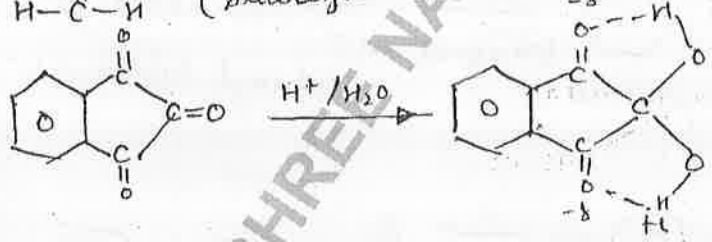
k following compounds have Keq > 1 during addition of H_2O

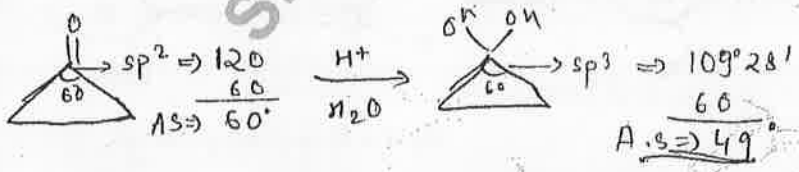
Keq > 1

(1) CCl_3-CHO

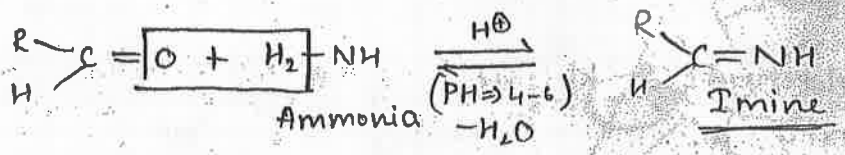
(2) CF_3-CHO

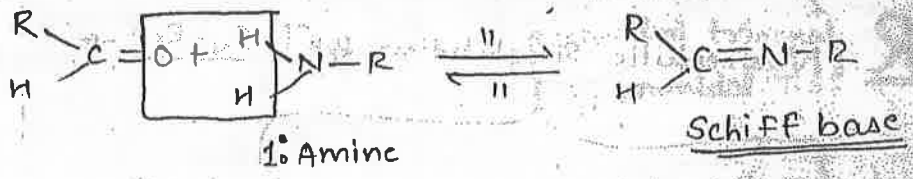
(3) $H-\overset{O}{\overset{\|}{C}}-H$ (Stabbized due continues addition of H_2O)

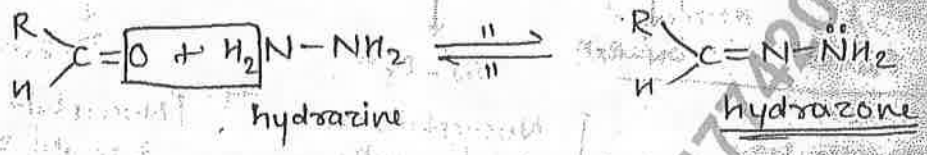
(4) 

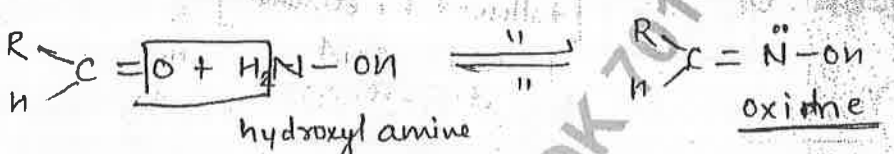
(5) 

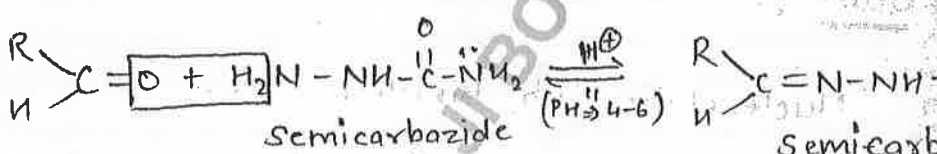
Addition of NH_3 & NH_3 derivatives :-

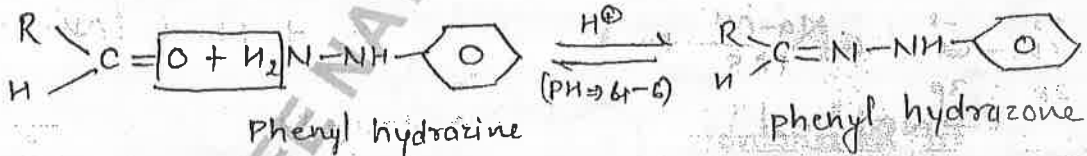
① 

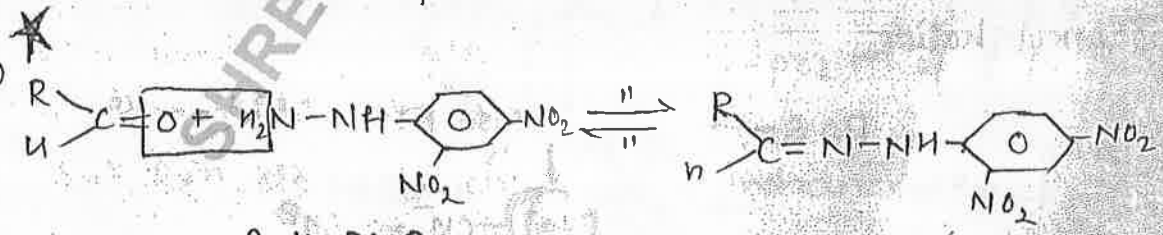
② 

③ 

④ 

⑤ 

⑥ 

⑦ 

(Yellow, organe or Red solid)

★ 2,4 DNP is a qualitative analysis for aldehyde & ketone.

* 2,4 DNP aldehyde & ketone k C=O ko pehchane ka kam karta h..

NSR [Nucleophilic Substitution Rxn] S_N-Rxn →

- Direct Sub
  - S_N^2-Rxn (molecularity)
  - S_N^1-Rxn
  - S_N^i-Rxn
  - eg (i) R-X, (ii) R-OH, (iii) R-OR
- Indirect sub
  - S_N^{AE}-Rxn — Nucleophilic sub^s through addn followed by elimination — eg. Acid & Acid derivatives
  - S_N^{Ar}-Rxn — Nucleophilic sub^l Aromatic Rxn — Hydrolysis of Aryl halide

Direct Sub^s :-

① S_N^2-Rxn (Nucleophilic Sub^s Bimolecular Rxn)

NET Rxn

$CH_3-\overset{2p}{\underset{+\delta}{CH_2}}-\overset{3p}{\underset{-\delta}{Cl}}$ (Weak bond) $\xrightarrow[PAS]{Na-OH}$ $HO-\overset{2p}{CH_2}-CH_3$ (strong bond) + NaCl (ΔH = -ve)

1° Alkyl halide

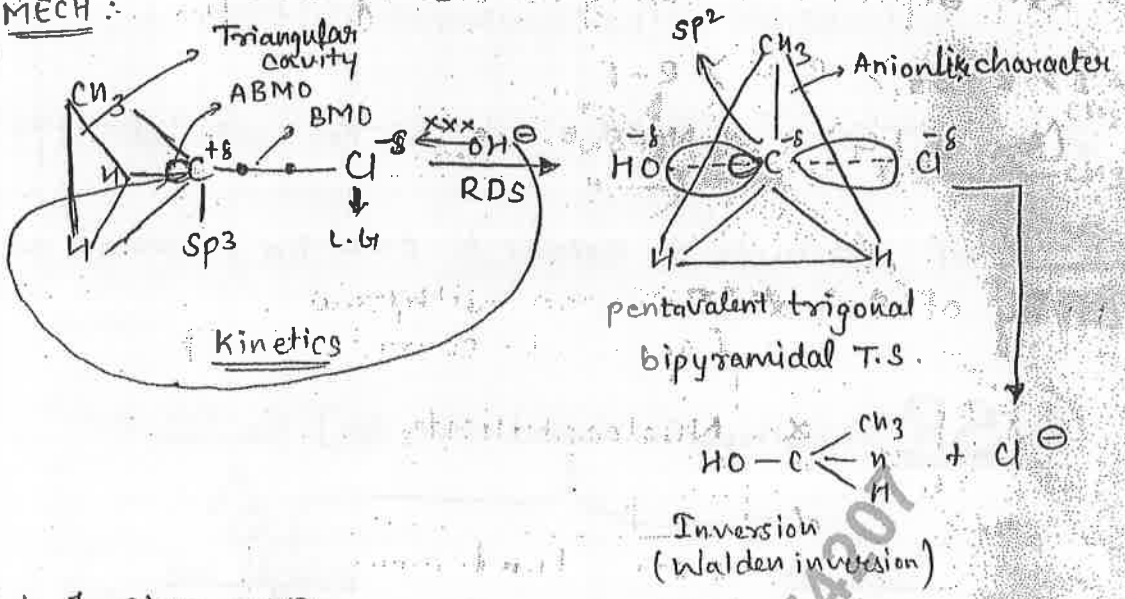
PAS → Acetone, DMSO, DMF, DMA ... etc

$Na^{\oplus}-OH^- \rightleftharpoons OH^{\ominus}$

* Small Substrate
* Anion present
* PAS

Dasstic → SN'

MECH :-



$$HO-C(CH_3)(H)(H) + Cl^{\ominus}$$

Inversion (Walden inversion)

* 1- step rxn.
* Rate expression ~~are~~ $(r) \Rightarrow [CH_3CH_2-Cl]^1 [OH^-]^1$
* Order of Rxn ⇒ 2
* Molecularity of Rxn ⇒ 2
* SN^2 Rxn carried out in PAS
* In S_N^2 Rxn pentavalent trigonal bipyramid T.S formed
* Anion like character developed in T.S.
* R-X bond breaking of Rxn is R.D.S step.
* In S_N^2 Rxn "inversion" phenonmenon obs.
* Whenever $Nu^{\ominus}$ attak at Anti-posith of L.G then inversion phenommenon occur.
* S_N^2 Rxn depends on steric hindrance.
* Reactivity of S_N^2 Rxn →

$$CH_3-Cl > CH_3-CH_2-Cl > \underset{CH_3}{\overset{H}{\overset{CH_3}{>}}}C-H > \underset{CH_3}{\overset{CH_3}{\overset{CH_3}{>}}}C-Cl$$

1° Alkyl halid — 2° — 3° Alkyl halid

No S_N^2 Rxn

* S_N2 Rxn depends on ablity of Leaving Group

* R-I > R-Br > R-Cl > R-F
  (Acc. to LG) — No S_N2-Rxn.

KEY POINT

Reactivity of S_N2 $\propto$ Eelectron Withdrawing Group [EWG]
[Anion like character in PTS]

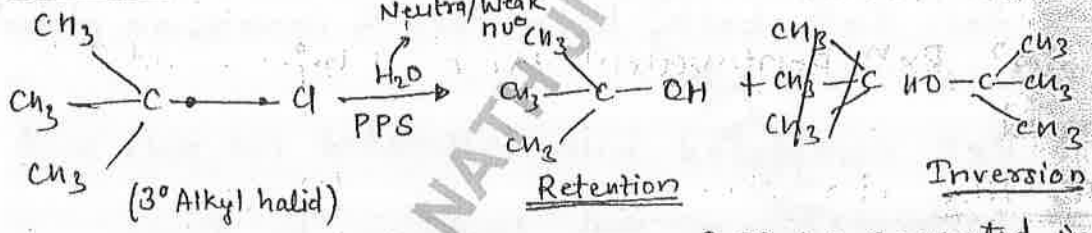
$\propto$ Nucleophilicity

$\propto \frac{1}{\text{steric hinderance}}$

Anti-bonding main attack ⟶ SN^2
phele attack ho jai ⟶ E_2

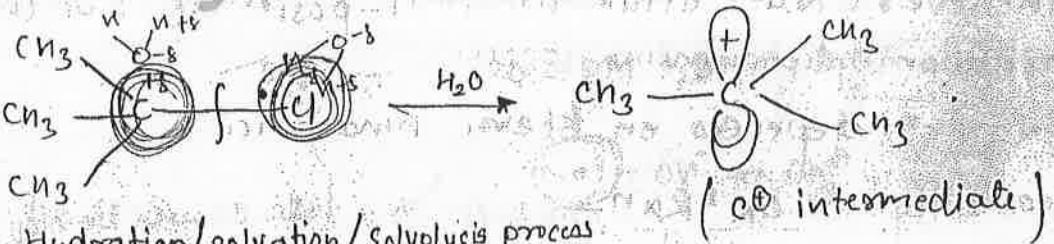
S_N1 [Nucleophilic Sub. Unimolecular Rxn]

NET RXN



{ IF C.C. Generated in product than product is R.M. (Not 100% Recimisation) }

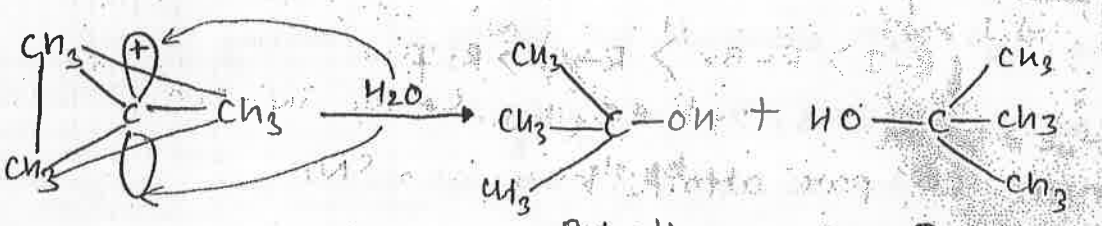
STEP-1



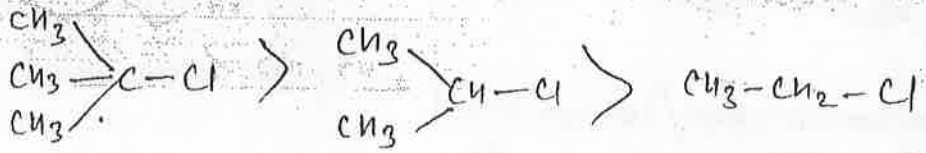
Hydration/solvation/Solvolysis process

[Intimated ion Pair Mech]

STEP-II



* Two step rxn
* Rate expression (γ) = $K\left[\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\!\!>\!C-Cl\right]^1$
* Order of Rxn = 1
* Molecularity of Rxn = 1
* Rxn carried out in pps.
* $C^{\oplus}$ intermediate formed in these Rxn
* formation of carborcation is R.D.S
* **Reactivity of Rxn $\propto$ stability of $C^{\oplus}$**
* $C^{\oplus}$ Rearrangement possible in SN_1.
* In S_N1 Rxn both Retention & inversion phenomena occur.
* S_N1 Rxn completed with intimated ion pair mech.
* In intimated ion pair mech. tendency to form inverted product more than Retented product i.e 100% of Recimiation not occur.
* S_N1 Rxn is more exothermic than S_N2 Rxn
* Reactivity of S_N1 Rxn



3° Alkyl halide 2° Alkyl halide 1° Alkyl halide

* Reactivity of S_N1 - Rxn (Acc. to L.G)

$$R-I > R-Br > R-Cl > R-F$$

↳ No S_N1 - Rxn

Anion C⊕ pare attack kare ⟶ S_N1

Anion bagal se H kha ye ⟶ E_1

* Conclusion of S_N1 & S_N2

1° Alkyl halide ⟶ S_N2 - mech.

2° Alkyl halide → PPS (H_2O) → S_N1 - Mech.
2° Alkyl halide → PAS (DMSO) → S_N2 - mech

3° Alkyl halide ⇒ S_N1 - Mech

* Determinatn of S_N1 & S_N2

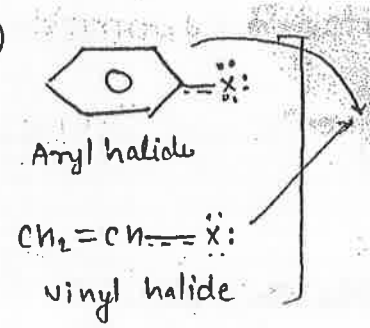
S_N2	S_N1
* Anion present	* Anion absent
* PAS	* PPS
* Thota (small) Substrate (1°, 2° Alkyl halide)	* large substrate

* Explain ~~Aryl halide~~ & vinyl halide

Except

* ~~Explain~~ Aryl halide & vinyl halide does not give S_N1 & S_N2 rxn. While allylic & benzylic position is Favourable condn for S_N1 & S_N2 Rxn.

(1)



In C–X bond ⇒ Due to Reso ⇒ Poor L.G

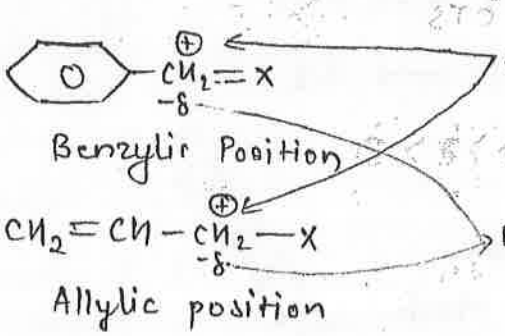
⇓

Partially D.B. character Developed

⇓

No S_N1 & S_N2 – Rxn

(2)



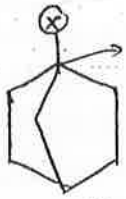
Stable carbocation formed ⇒ give S_N1 ~~& S_N2 – Rxn~~

BC_2 stable ⇒ give S_N2 – Rxn (T.S. Form)

give Both S_N1 & S_N2

(3) R–F ⇒ Poor L.G ⇒ No S_N1 & S_N2 Rxn.

(4)

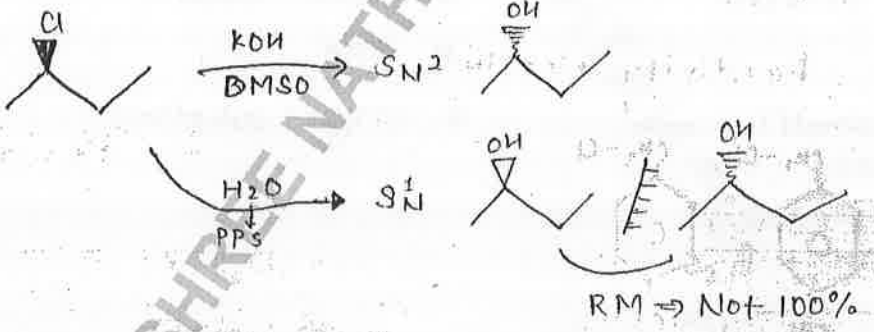


3° Alkyl halide ⇒ No S_N1 & S_N2 Rxn

Bredts Rule violated

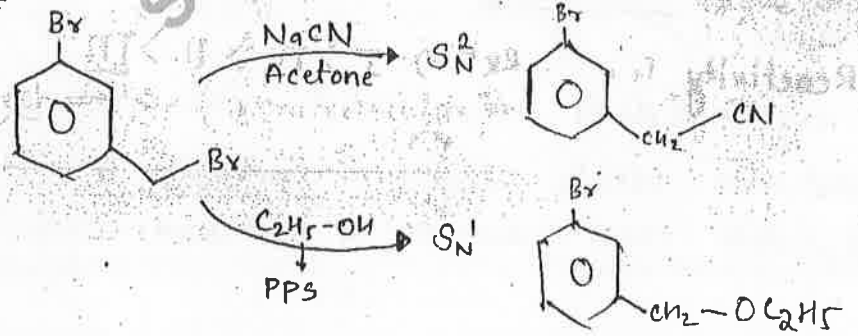
Bridge cyclo comp.

Q.1



RM ⇒ Not 100%

Q.2

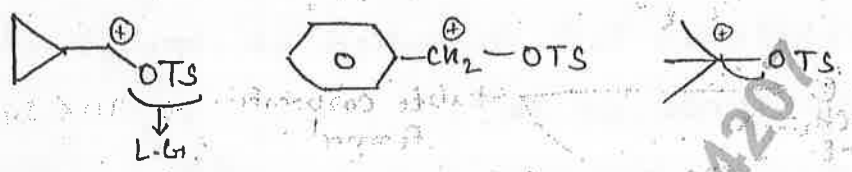


(IIT 2013)

Q.3 CH_3-CH_2-X $\quad$ $H-\overset{O}{\overset{\|}{C}}-CH_2-X$

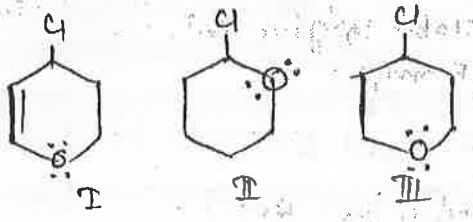
Rate of $S_N2-Rx^n \Rightarrow$ II > I

Q.4



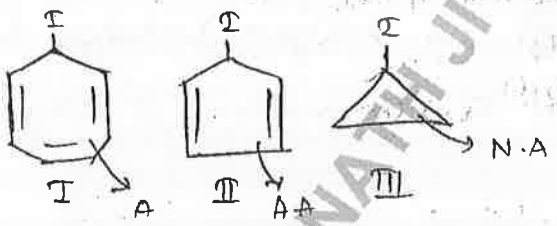
Reactivity ~~Ratio~~ of $S_N1-Rx^n \Rightarrow$ I > II > III

Q.5



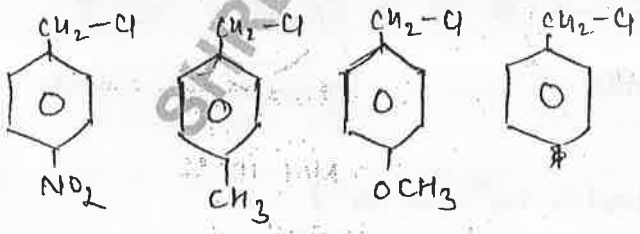
Reactivity of $S_N1-Rx^n \Rightarrow$ I > II > III

Q.6



Reactivity of $S_N1-Rx^n \Rightarrow$ I > III > II

Q.7



Reactivity for $S_N2\ Rx^n \Rightarrow$ I > IV > II > III

* Various Reaction Based on S_N1 & S_N2 :-

① Finkelstein Rx^n ⇒

$$R-Cl \xrightleftharpoons[\text{Acetone (Dry}]{Na-I} R-I + NaCl \downarrow$$

(PPt)

* finkelstein Rx^n also known as halogen exchange method
* In finkelstein Rx^n formation of PPt of NaCl is driving force of Rx^n.
* Rx^n follow S_N2 path.

② Swart Rx^n ⇒

$$R-Cl \xrightarrow[DMf]{Ag-F} R-F + AgCl \downarrow$$

(White ppt)

Eg ⇒ AgF, COF_2, H_2F_2 ---

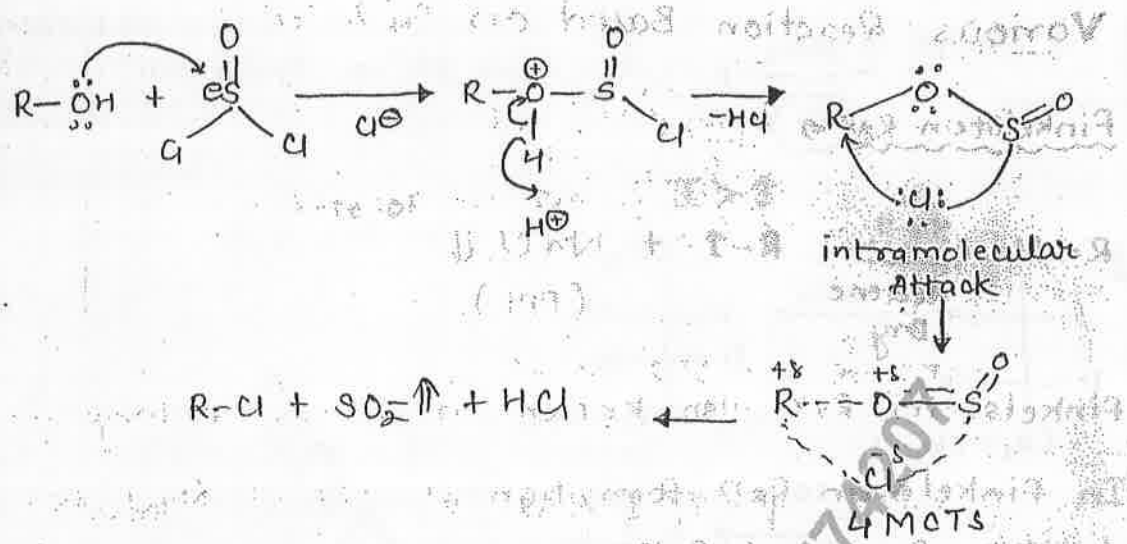
* Swart Rx^n also known as halogen exchange Rx^n.
* Swart Rx^n also used for formation of Alkyl flowride

③ ** Darzen Rx^n ⟶

$$R-OH + SO_2Cl_2 \longrightarrow R-Cl + \underbrace{SO_2 \uparrow + HCl \uparrow}_{\text{gascous biproduct.}}$$

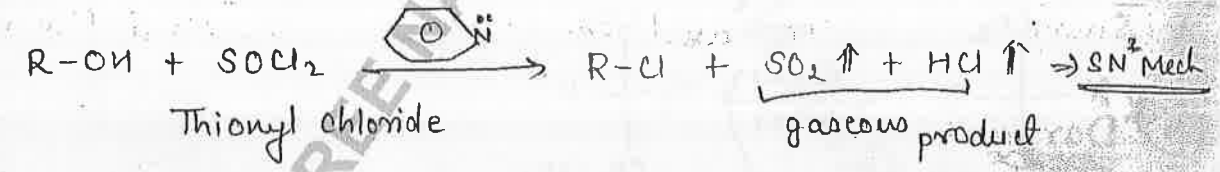
Thionyl chloride

Mech ⇒ S_Ni (intramolecular $nu^{\ominus}$ Sub Rx^n)



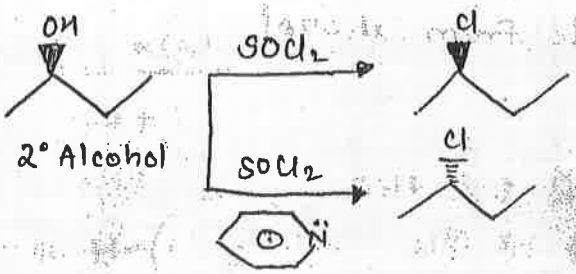
* Rxn completed with S_Ni Mech.
* 4 MCTS formed in these Rxn.
* for formation of R–Cl this is best method becoz gaseous by product formed in Rxn medium.
* Retention phenomenon observed in this rxn.
* ~~Darzens~~

Darzen Rxn in Presence of Pyridine.



* Whenever Darzen Rxn carried out in presence of Pyridine then Rxn completed with S_N2 Mech.
* In presence of pyridine inversion phenomenon observed.

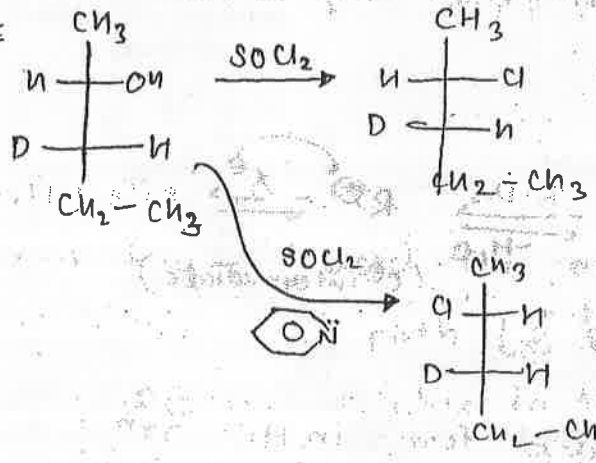
Q.1



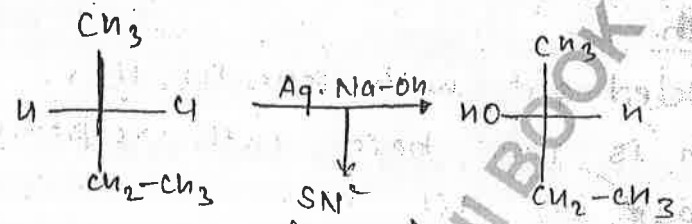
⇒ S_N' ⇒ Retention.

→ SN^2 → Inversion.

Q.2

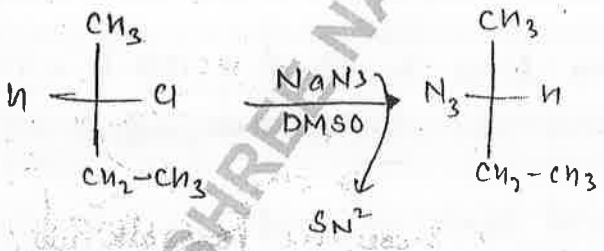


Q.3



2° Alkyl halide (Major)

Q.4



④ formation of Alkyl halide from alcohol.

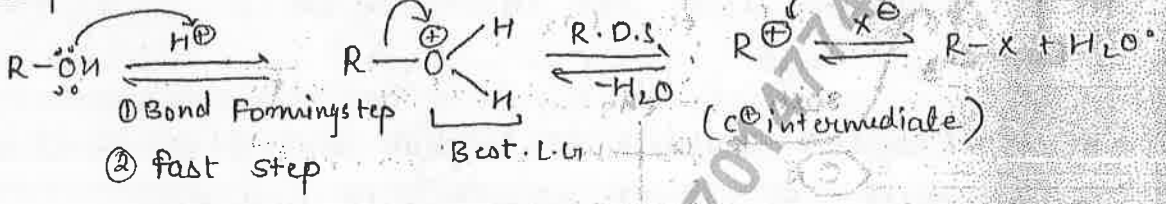
Net Rxn

$$R-OH + \text{conc. } HX \rightleftharpoons R-X + H_2O$$

Mech

Step-I ⇒ conc HX $\rightleftharpoons$ $H^{\oplus} + X^{\ominus}$ ⇒ good nu$^{\ominus}$

Step-II →



* Carbocation intermediate form in this rxn.
* Rxn follow S_N1 path.
* Whenever rxn carried out with conc. HI, HBr, then Rate of rxn is fast becoz both are strong Acid, whikl in case on HCl rate of rxn is slow becoz HCl is a weak acid (marical)
* Reactivity of Rxn ⇒

conc HI > conc HBr > conc HCl > conc. HF

→ Rate of Rxn is fast
↳ Becoz both are strong Acid

↳ R.OR is slow
↳ Becoz HCl is weak acid.

LUCAS REAGENT

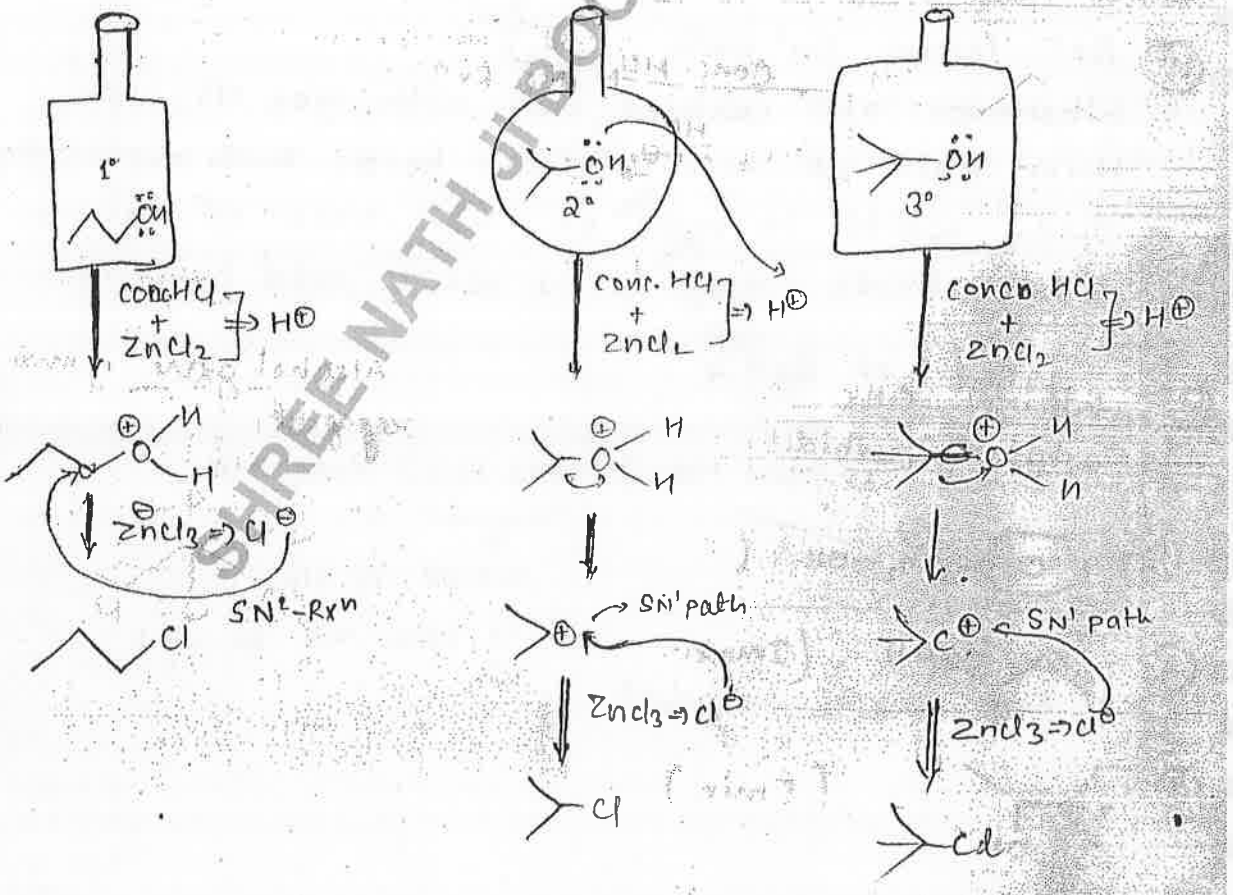
[conc. HCl + $ZnCl_2$ (Anhyde)]

conc H–Cl $\xrightarrow{Zn\text{-}Cl_2}$ (L.A) $H^{\oplus}\uparrow + ZnCl_3^{\ominus}$

$\Downarrow$

$[H^+]\uparrow \Rightarrow R\text{-}O\text{-}R\uparrow$

* Rxn used in POC
* Lucas Reagent used for identification of 1°, 2°, 3°-Alcohol
* Rxn follow S_N1 path [2° & 3° Alcohol]
* Lucas Reagent soluble in Alcohol and give R–Cl as a product & R–Cl give White turbitlity.



given white turbidity after 30 min on gentle heating

Give white turbidity after 5 min

Give white tur. immediately

Q. CH_3-CH_2-OH → NaCl → X

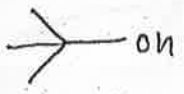
NaCl + HCl → (Δ) →

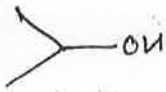
NaI → X

NaI + H_2SO_4 → X → H_2SO_4 is an O.A. It will oxidised $I^{\ominus}$ to I_2. reaction wrong occur

NaI + H_3PO_4 →

Q.1 Rxn of Diff. Alcohol with conc. HCl.

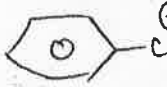
(I)  conc HCl

(II)  conc HCl; conc HCl + $ZnCl_2$; conc. HCl (Δ)

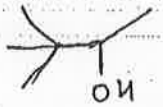
(III)  conc. HCl → No Rxn

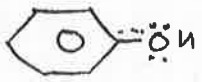
conc. HCl + $ZnCl_2$ → ; $ZnCl_2$; conc. HCl (Δ) → } चलेगा

Q.2 Which one of the following Alcohol give immediate white turbidity with Lucas regagent.

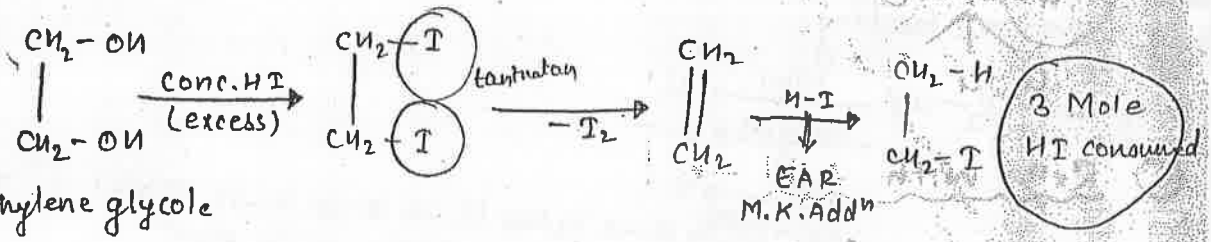
(1)  (Immediate)

(2)  (Immediate)

(3)  (5 min)

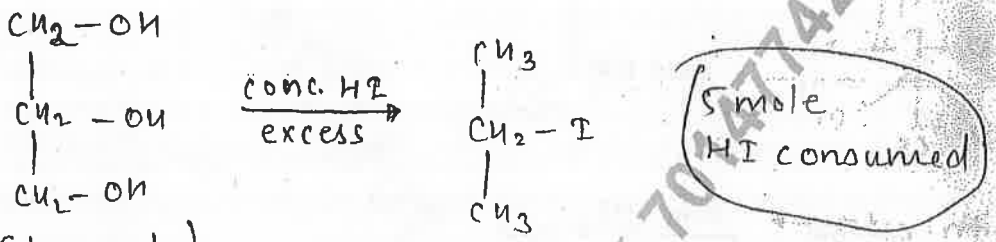
(IV)  (No Rxn)

⑤ formation of alkyl Iodide halide from polyhydroxy compound:-

① 

Ethylene glycole

Sub | Elimination Rxn | Addn Rxn

② 

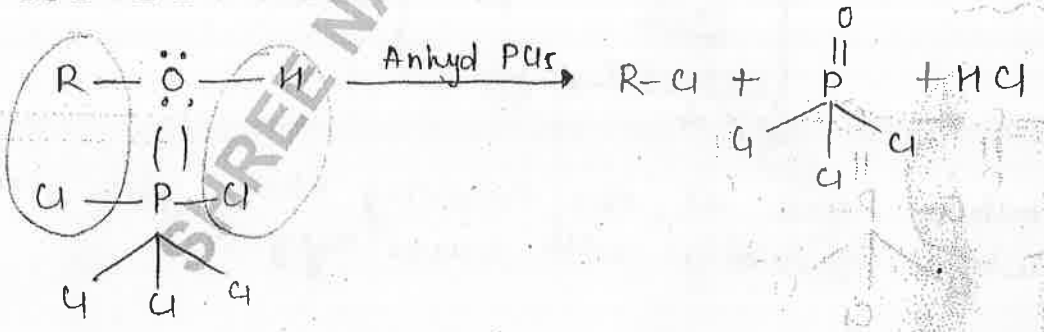
(Glycerol)

⑥ Rxn with Anhydrous PCl_5 :

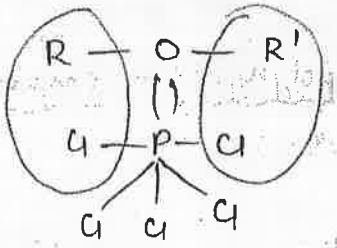
Ⓐ ~~Rxn with~~ Anhyd. $PCl_5 \longrightarrow \overset{\oplus}{PCl_4} + \overset{\ominus}{PCl_6}$

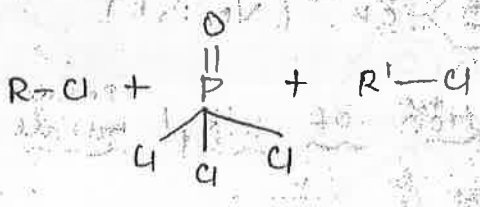
↳ दूसरा → S_N2 – Mech.

Ⓐ Rxn with Alcohol :

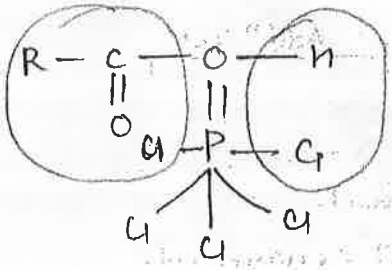


(B) Rxn with ether →

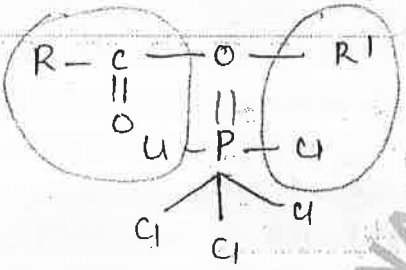


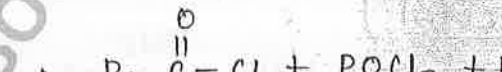


(C) Rxn with Acid →

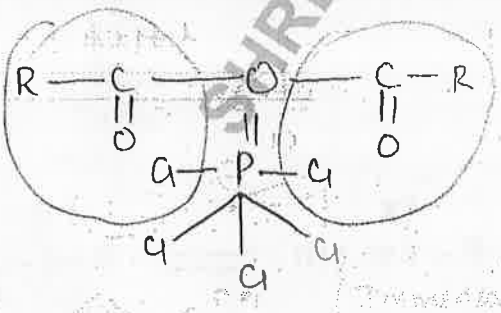


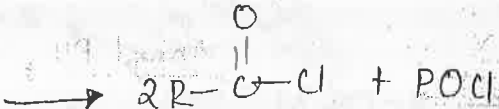
(D) Rxn with ester →



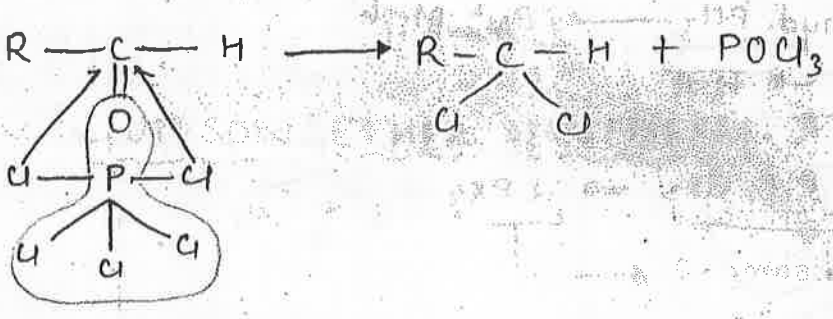


(E) Rxn with anhydride →

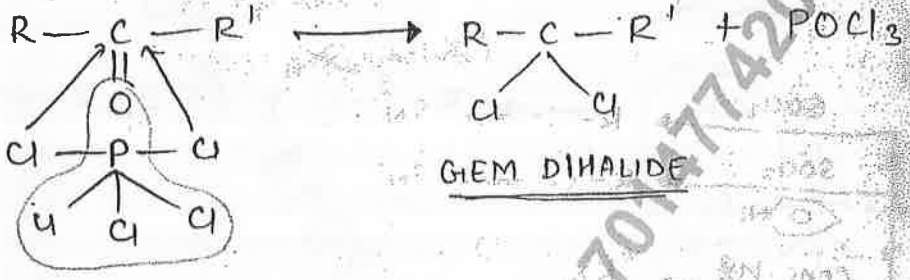




(F) Rxn with Aldehyde →

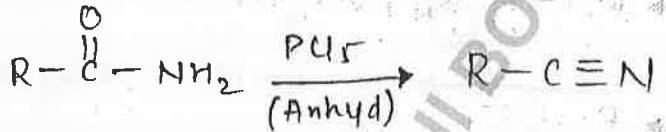


(G) Rxn with ketone →

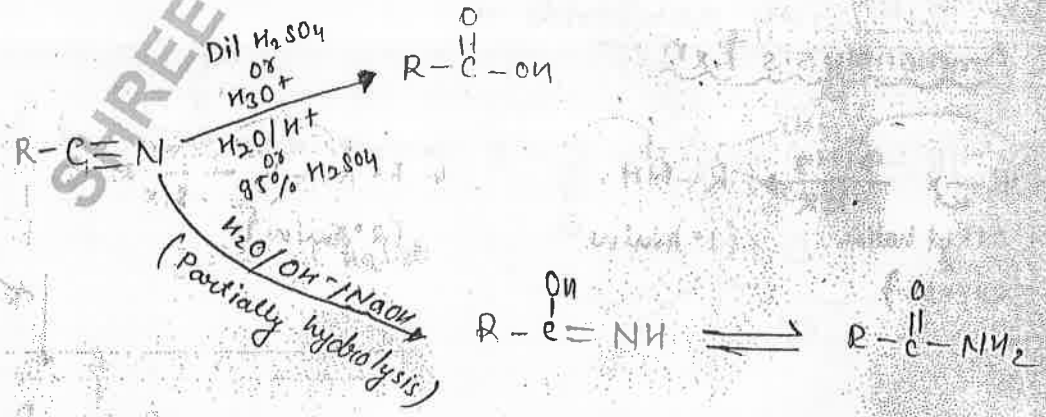


GEM DIHALIDE

(H) Rxn with Amide →



①



⑦ Rxn with Anhyd. PCl_3 :-

Anhyd. PCl_3 ⟶ S_N^2 Mech
↳ सूखा

$2\ Red\ P + 3X_2 \Rightarrow 2\ PX_3$
↳ same -2

Net Rxn

$R-OH \xrightarrow{Anhydri\ PCl_3} R-Cl + H_3PO_3$

KEY POINT

$R-OH$ →
- $SOCl_2$ → $R-Cl \Rightarrow S_N^i$
- $SOCl_2$ + Pyridine → $R-Cl \Rightarrow S_N^2$
- Conc. HX → RX
- Conc HCl + $ZnCl_2$ → $R-Cl \Rightarrow S_N^i$ (2° & 3°)
- Anhyd PCl_5 → $R-Cl$ ⎫
- Anhyd PCl_3 → $R-Cl$ ⎬ S_N^2
- $2Red + 3Cl_2$ → $R-Cl$ ⎭

⑧ Ammonolysis Rxn :-

1) $R-X \xrightarrow[-HX]{\ddot{N}H_3} R-\ddot{N}H_2 \xrightarrow[-HX]{R-X} R-\ddot{N}H-R \xrightarrow[-HX]{R-X} R-\ddot{N}(R)-R$

1° Alkyl halide (excess) — (1° Amine) — (2° Amine) — (3° Amine)

$\xrightarrow{R-X}$

$R-\overset{R}{\underset{R}{N^+}}-R$ Quaternary ammonium salt

~~# Am~~

(ii) $R-X \xrightarrow[\text{excess}]{\ddot{N}H_3} R-\ddot{N}H_2$ (major)

(1° Amine)

WILLIUMSON ETHER SYNTHESIS ☆☆

* It is a S_N^2 Rxn.

NET Rxn

$$R-O^{\ominus}Na^{\oplus} + R-X \longrightarrow R-O-R' + NaX \Rightarrow S_N^2 \text{ Mech.}$$

Sod. Alkoxide (1° Alkyl halide)

~~(2° & 3° Alkyl halide)~~

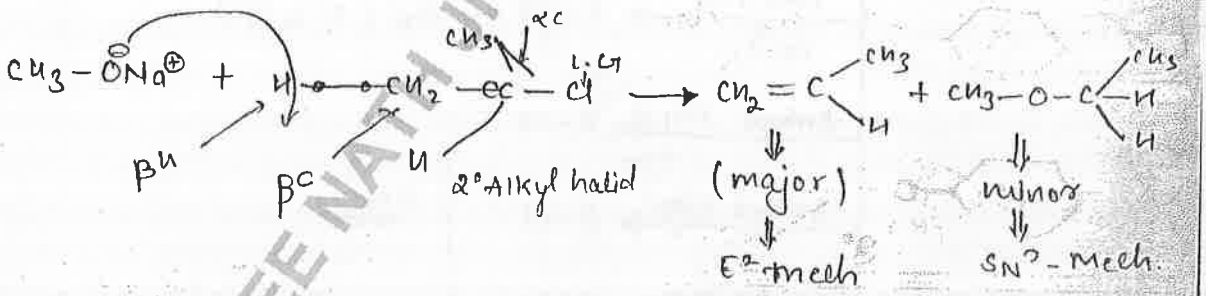
Eg

(i) $CH_3-O^{\ominus}Na^{\oplus}$ +  $\Rightarrow S_N^2$ Mech.

Sod. metnoxide

1° Alkyl halide

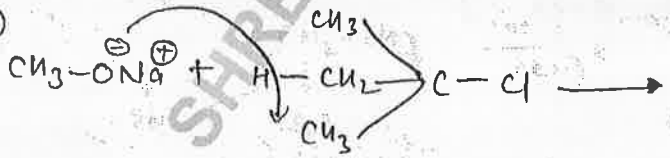
CH_3-ONa^{+} → Base ✓✓ / → Nu

(ii) $CH_3-O^{\ominus}Na^{\oplus}$ + 

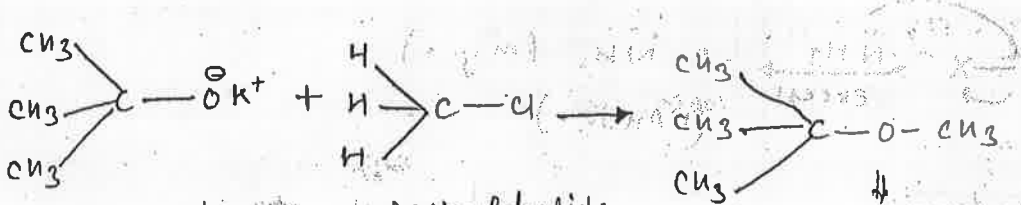
β^H β^C H 2° Alkyl halid

(major) → E^2 mech

minor → S_N^2 - Mech.

(iii) CH_3-ONa +  $\Rightarrow E^2$ Mech.

3° Alkyl halide

(iv) 

Pot. t-butoxide 1° Alkylchloride S_N2 Mech.

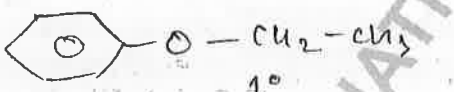
* In williamson ether synthesis Rxn 1° Alkyl halide form ether by S_N2-Mech.
* In WESR 2° & 3° Alkyl halide form alkene as a major product. & favours to elimination Rxn.

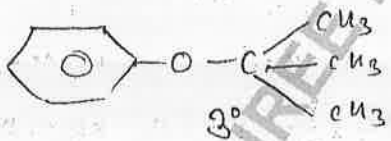
Q. Which of the following ether can not perpared by WESR.

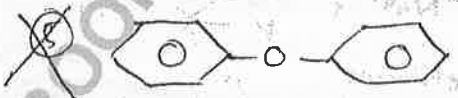
(1) Ether main one side 1° Alkyl group होना चाहिए।

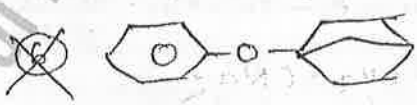
(1) $CH_3-O-CH_2-CH_3$ (1°)

(2) 

(3) 

(4) 

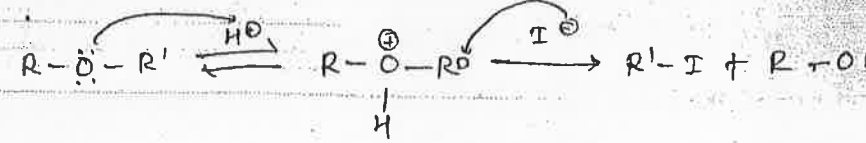
(5) 

(6) 

(10) Ether cleavage :-

(A) Rxn with conc. HI :-

Step-I ⇒ conc HI $\rightleftharpoons$ $H^+ + I^\ominus$

Step-II ⇒ 

① Key Point → for conc. HI

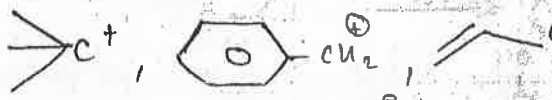
① 1° Alkyl group ⇒ S_N2 - Mech.

2° " " ⇒ S_N2

3° " " ⇒ S_N1

KEY POINT

In ether cleavage during attack of iodide ion at alkyl group if following c⊕ form in the rxn medium then Rxn follow S_N1 path.



⊕ ⇒ S_N1 - Mech.

① $CH_3-CH_2-\ddot{O}-CH_3$ $\xrightarrow{I^\ominus,\ \text{conc. HI}}$ $CH_3-I + CH_3-CH_2-OH$

(CH_2: 1°, S_N2; CH_3: 1°, S_N2)

② $(CH_3)_2CH-O-CH_2-CH_3$ $\xrightarrow{I^\ominus,\ \text{conc. HI (excess)}}$ $CH_3-CH_2-I + (CH_3)_2CH-OH$

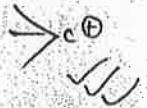
(CH: 2°, S_N2; CH_2: 1°, S_N2)

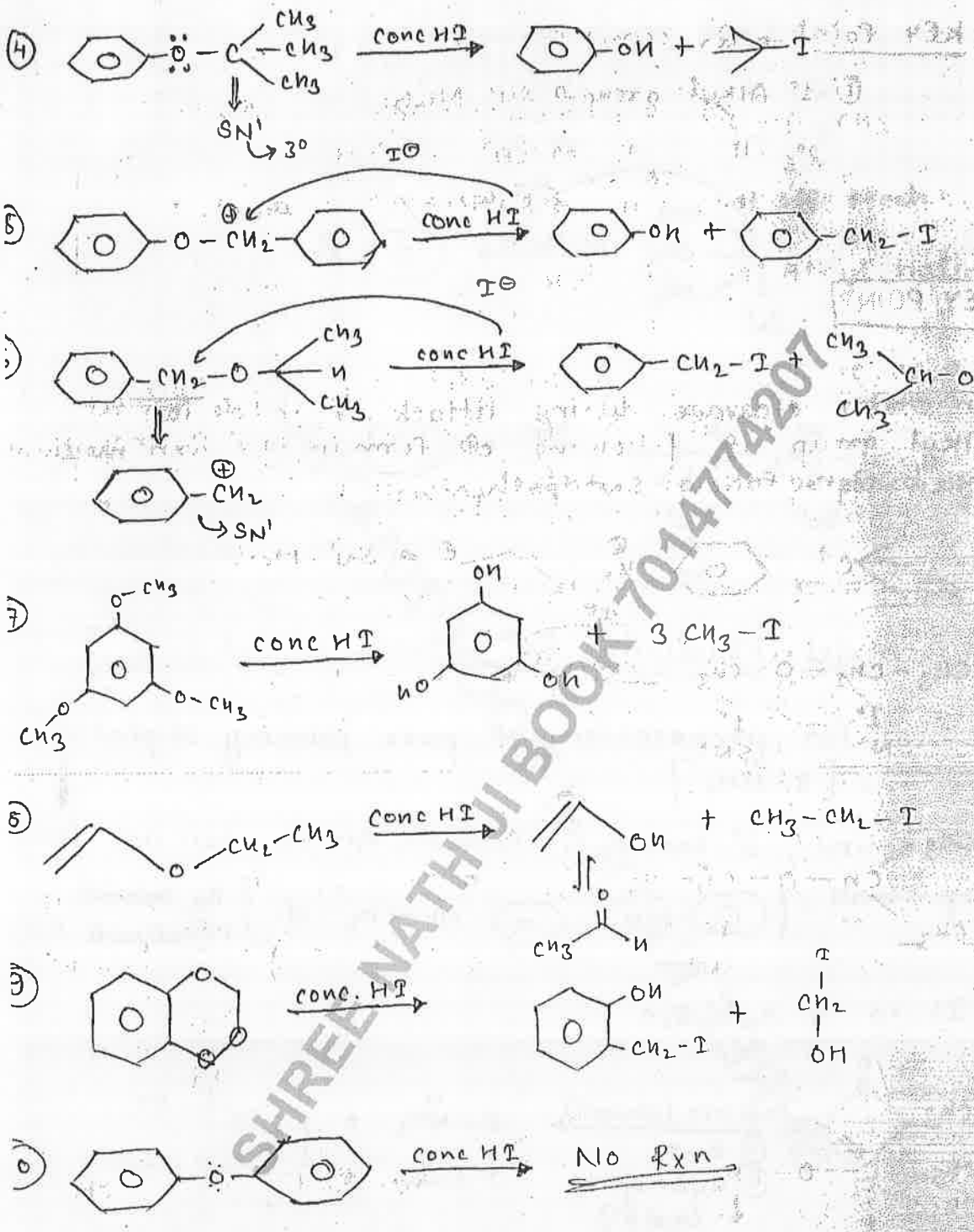
2 mole HI consumed

$(CH_3)_2CH-OH \xrightarrow{\text{conc HI}} (CH_3)_2CH-I$

③ $(CH_3)_3C-O-CH_2-CH_3$ $\xrightarrow{I^\ominus,\ \text{conc HI (excess)}}$ $>C-I + CH_3-CH_2-OH$

(C: S_N1; CH_2: S_N2)





(B) Rxn with dilute H_2SO_4 / H_3O^+ :-

Step-I :- $H_3O^+ \rightleftharpoons H^+ + H_2O$

Step-II :- $R-\overset{\overset{18}{\cdot\cdot}}{\underset{\cdot\cdot}{O}}-R' \xrightleftharpoons{H^+} R-\overset{\oplus}{\underset{H}{O}}-R' \xrightarrow{H_2\overset{18}{\ddot{O}}:} R'-OH + R-\overset{18}{O}H$

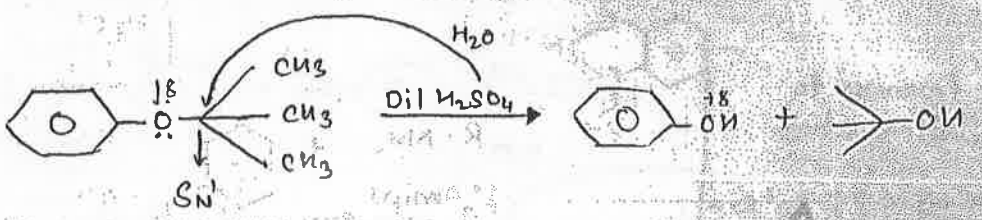
KEY POINT :- for dil H_2SO_4 / H_3O^+ →

1° Alkyl group ⇒ S_N2

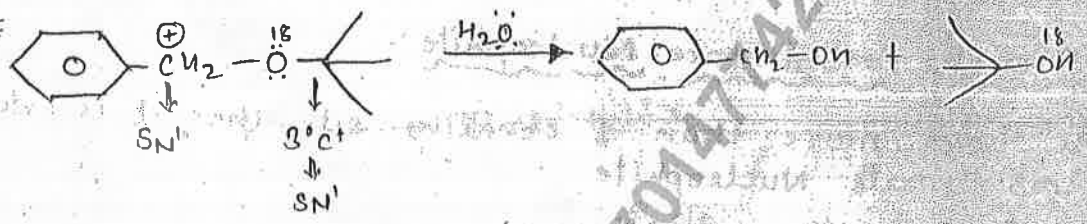
2° " " ⇒ S_N1

3° " " ⇒ S_N1

Q.1

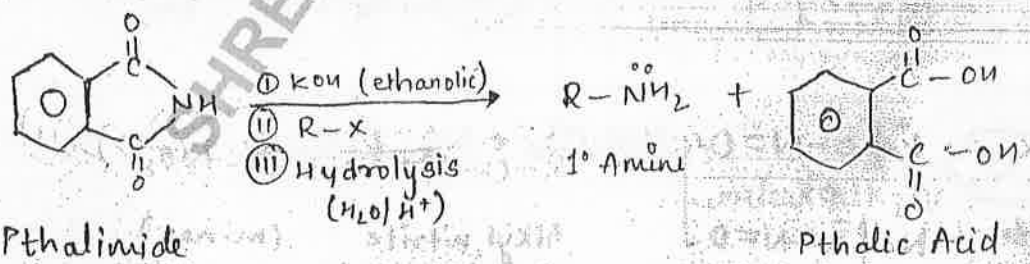


Q.2



11] Gabriel Pthalimide Rxn

* Used for preparation of pure primary aliphatic Amine [$R-\ddot{N}H_2$]
* 2° Amine, 3°-Amine & Aromatic Amine can not formed ~~by Gab~~ [$\ddot{N}H_2$, $-NH-CH_3$ -- etc] By Gabriel Pthalimide Rxn.
* It is a S_N2 - Rxn



Pthalimide

Pthalic Acid

④ $R-X + Ag-O-\overset{\ddot{O}}{N}=O \longrightarrow R-NO_2 + R-O-N=O$

2° Alkyl halide — covalent character high of — Silver nitrate — (major) — (minor) ⇒ S_N1 mech

⑬ Correh house Rxn

Net Rxn

$R-X \xrightarrow[\text{(ii) } CuI]{\text{(i) } Li} R-R'$ (iii) $R'-X$

MECH

STEP-①

$R^{\ominus} \quad X^{\ominus}$

$R \bullet\!\!-\!\!\bullet X \longrightarrow R-Li + LiX$

$2e^- \curvearrowright 2Li \longrightarrow 2Li^+$

$R^{\ominus}$ चुंबक

(ii) $2R^{\ominus}-Li^{\oplus} + CuI \longrightarrow R_2CuLi + LiI$

Gillman Reagent

(iii) $R_2CuLi \xrightarrow{R-X} R-R' \Rightarrow S_N2$-Mech.

(Alkyl halide)

(2° & 3° ✗ → Elimination)

Q

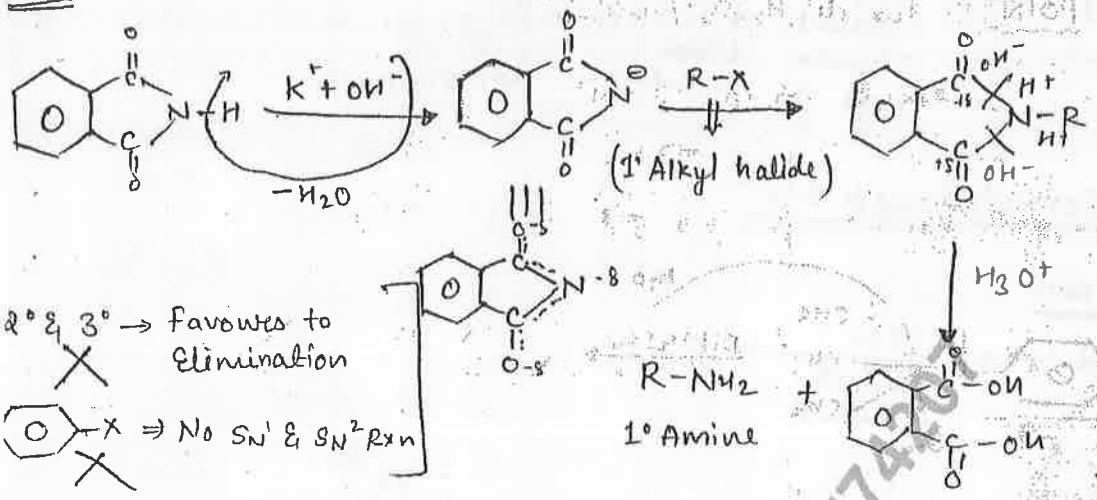
① $(CH_3)_2CuLi \xrightarrow{CH_3-CH_2-X} CH_3-CH_2-CH_3$

unsymmetrical

(ii) $(CH_3)_2CuLi \xrightarrow{CH_3-X} CH_3-CH_3$

Symmetrical Alkane

IECH



2° & 3° → Favours to Elimination

⇒ No S_N1 & S_N2 Rxn

$R-NH_2$ +

1° Amine

Rxn with Ambidentate Nucleophile :-

Nu⁻ have more than 1 donating site then it is called Ambidentate Nucleophile.

Eg. $\overset{\ominus}{C}\equiv\ddot{N}$, $\overset{\ominus}{O}-\ddot{N}=O$

SN_2

$R-X$ + $Na^{\oplus}\ \overset{\ominus}{C}\equiv\ddot{N}$ or $K^{\oplus}\ \overset{\ominus}{C}\equiv N$ → $R-C\equiv N$ + $R-N\overset{\cdot\cdot}{=}C$ ⇒ S_N2 Mech

1° Alkyl halide

(major)

ionic comp

SN_1

$R-X$ + $Ag-C\equiv\ddot{N}$ → $R-N\overset{\cdot\cdot}{=}C$ + $R-C\equiv N$ ⇒ S_N1 Mech

Alkyl halide

covalent character

$Ag^{\oplus}$ ⇒ high Φ.

(major) (minor)

$R-X$ + $K^{+}\ \overset{-}{O}-N=O$ or $Na^{+}\ \overset{-}{O}-N=O$ → $R-O-N=O$ + $R-NO_2$

Alkyl halide

Pot. nitrite.

Alkyl nitrite (major) (minor)

* Both Sym & Unsym. Alkane can be formed by this Rxn.
* CH_4 can not formed by this rxn.
* Rxn completed with S_N2-Mech.

(14) Rxn with Ag_2O →

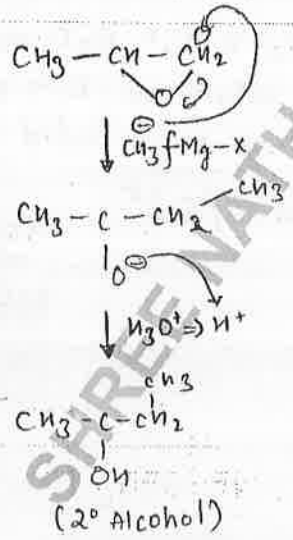
Ag_2O —(Ag/Moist)→ AgOH
Ag_2O —(Dry)→ Ag_2O

(1) $R-X \xrightarrow[moist]{Ag_2O} R-OH$

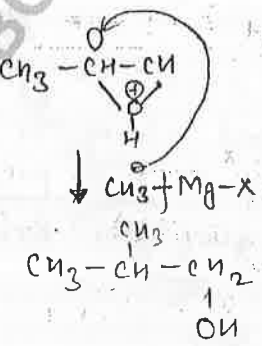
(2) $R-X \xrightarrow[Dry]{Ag_2O} R-O-R$

(15) Ring Opening :-

In this case Nu⁻ attack that side having less steric hindrance



(2° Alcohol)



(1° Alcohol)

Nu⊖ attack that side where form maximum stable cation.

INDIRECT SUBSTITUTION

Substitution → Aliphatic Alkyl halide / Aromatic halide

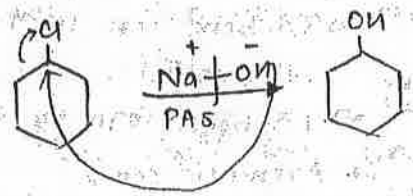
(1) 30%

S_N^{Ar} - Mech

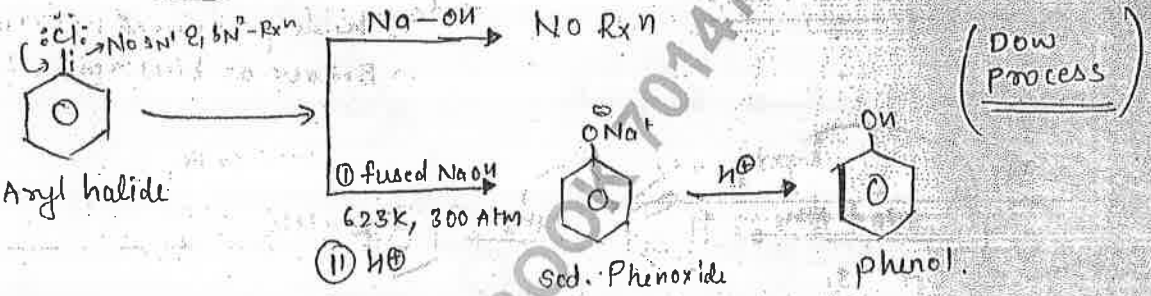
S_N^{AE} - MECH.

1] S_N^{Ar}. [Nucleophilic substitution Aromatic Rxn]

* Hydrolysis of Aryl halide:-

(I) 

⇒ S_N^2 - Mech.

(II) 

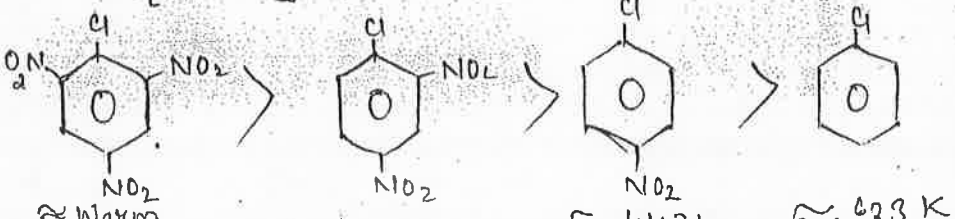
* Aryl halide does not give S_N^1 & S_N^2 Rxn. due to partially to doubled bond character but whenever Rxn carried out at higher temp or high pressure or Aryl halid having strong EWG then it give S_N^{Ar} Rxn [S_N^{2-Ar} / S_N^{AE}

303, 304, NCERT

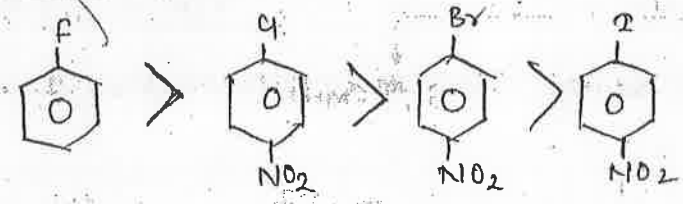
Keypoint

Reactivity of S_N^{Ar} ∝ EWG.

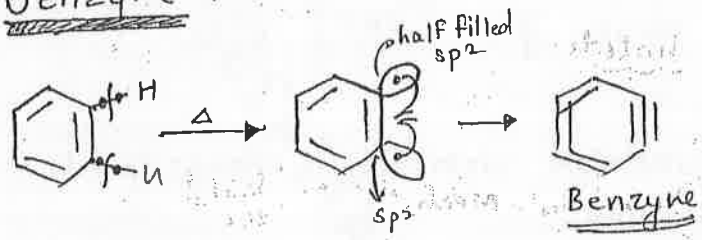
Reactivity of S_N^{Ar} [S_N^{2-Ar}]



Reactivity of S_NAr ⇒

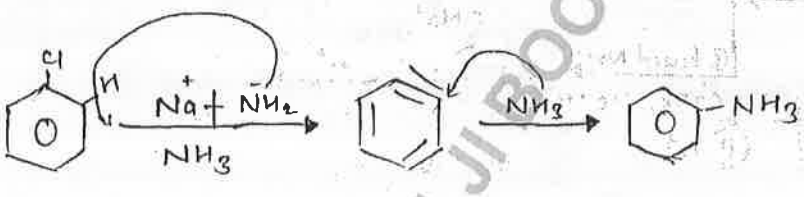


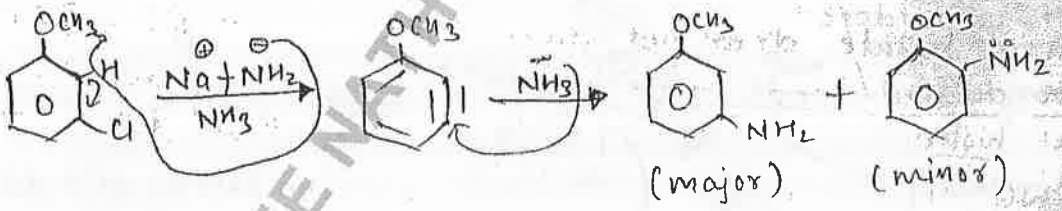
Benzyne →



→ All C-Atoms are ⇒ sp^2 hyb
→ Total no. of π bond = 4
⇒ 3 π-bond form by Pure P-orbital
⇒ 1 π-bond form by sp^2 hyb.
⇒ Aromatic comp.
⇒ highly strained molecule
⇒ Behave as Electrophile ($E^{\oplus}$)

Q.

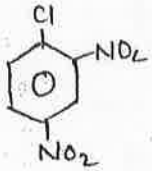
(I) 

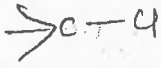
(II) 

(major) (minor)

Q Reactivity order of for sub Rxn:.

(I) 

(II) 

(III) 

(IV) 

Reactivity order ⇒ III > IV > II > I

S_N^{AE} Rxn

* Nucleophilic substitution through addition followed by Elimination Rxn.

$R-\overset{\overset{O}{\|}}{C}-L.G$ ⇒ ① [c=o] having leaving group that is why given S_N^{AE} Rxn.

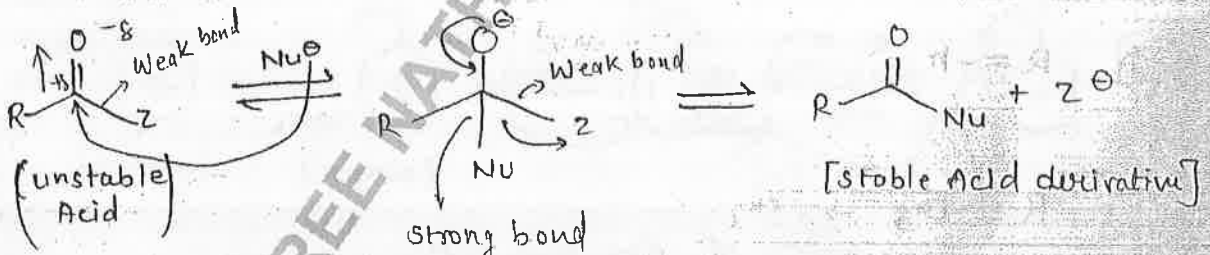
② Acid & Acid derivaties having L.G & give S_N^{AE} Rxn. while carbonyl comp. give [NAR] becoz their is no L.G.

AIM . In S_N^{AE} Rxn unstable derivaties changed into stable acid derivaties.

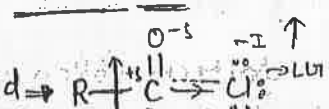
NET RXN

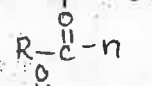
{unstable Acid. derivatie] [stable Acid deri.]

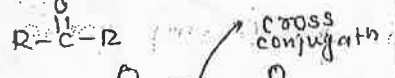
MECH

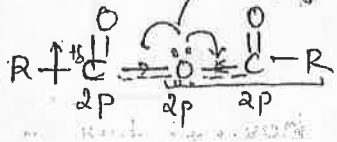


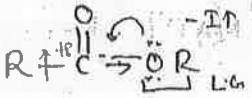
Concept of S_NAE :-

1) Acid halid ⇒ 

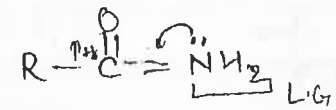
Aldehyde ⇒ 

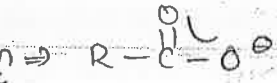
Ketone ⇒ 

2) Anhydride ⇒ 

3) Ester ⇒ 

4) Acid ⇒ 

5) Amide ⇒ 

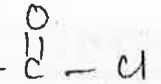
6) Acetate ion ⇒ 

UP
- → -I - effect ↓
- → +M -effect ⇓
- → Partially +ve positive charge 
- → Partially D.B character ⇑
- → Bond length ⇓
- → Bond strength ⇑
- → Reactivity of S_NAE ⇓

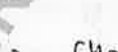
UP ↓ बनाते down

UP ↑ हटे ×××× down

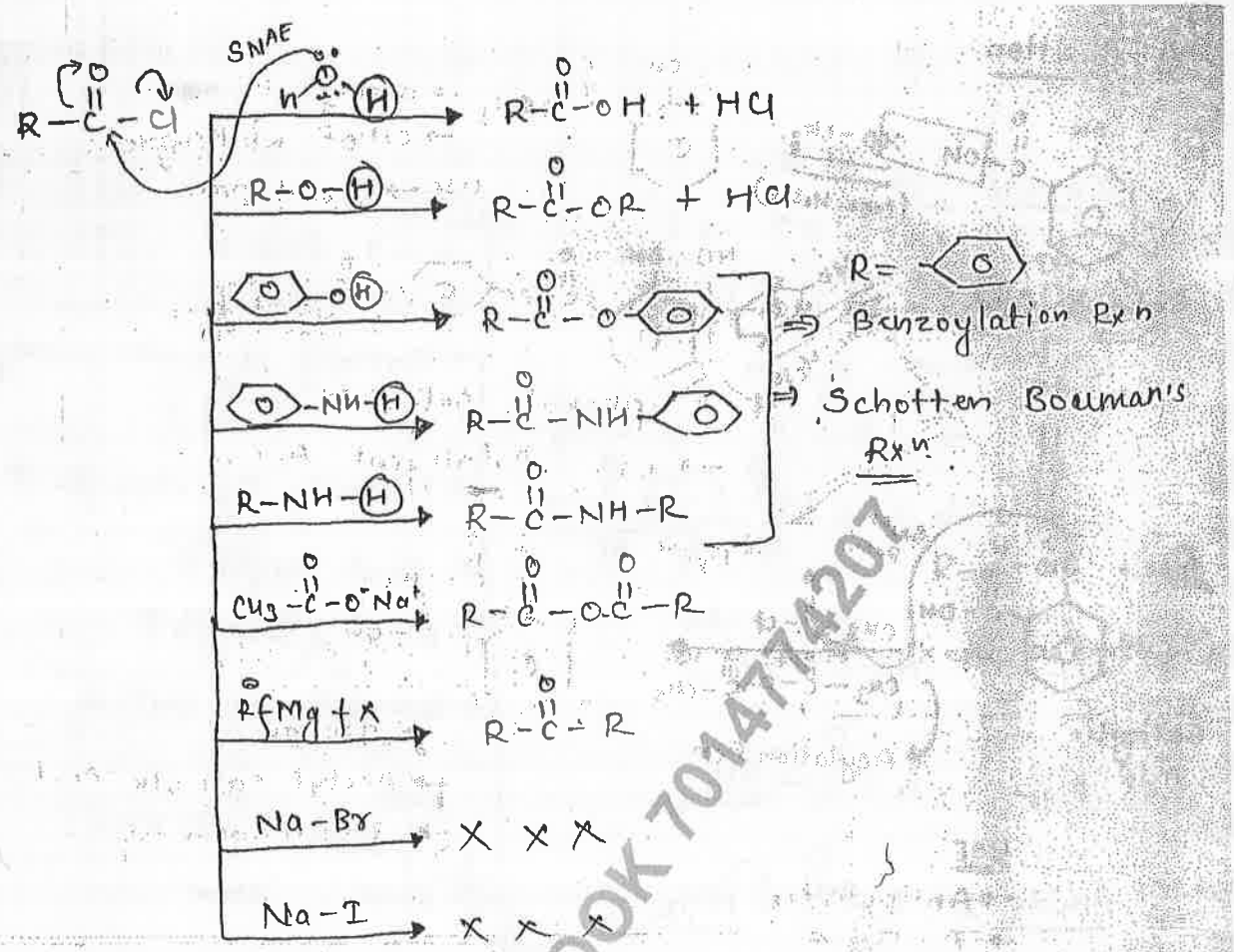
down



① R = -H →  (Formyl)
Formylation

② R = $-CH_3$ →  (Acyl)
Acylation Rxn

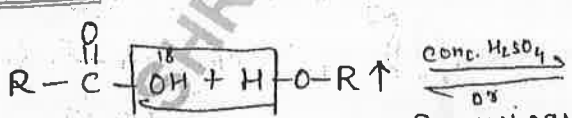
③ R =  →  (Benzoyal)
Benzoylation



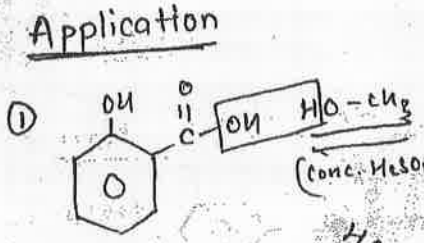
Esterification:-

* Whenever acid reacts with alcohol in presence of conc. H_2SO_4 or Dry HCl gas then it form estr this rxn is known as Esterification.
* Generally Rxn follow ⇒ S_N^{AE} Mech.

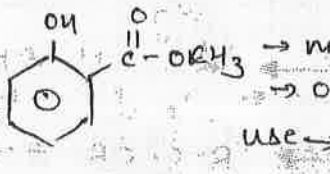
NET Rxn



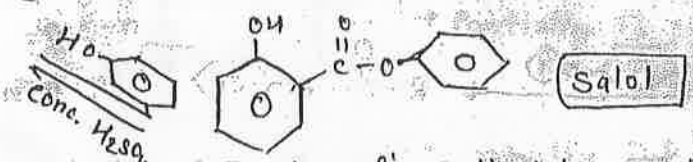
Application

① 

Salicylic Acid



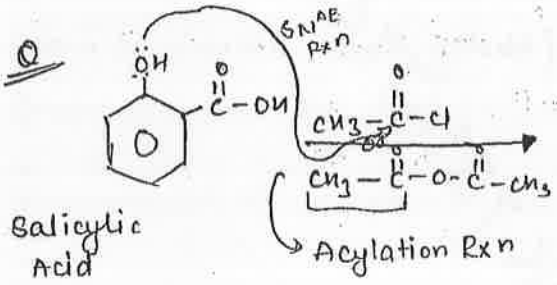
→ methyl salicylate
→ oil of wintergreen
use → Joint pain



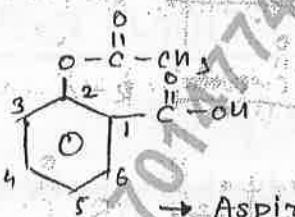
phenylic salicylate

NAR → Ether cleavage

→ use :- Astringent / Antiseptic

② 

Salicylic Acid



→ Aspirin
→ Acetyl salicylic Acid
→ 2-Ethanoyl oxy.

USE

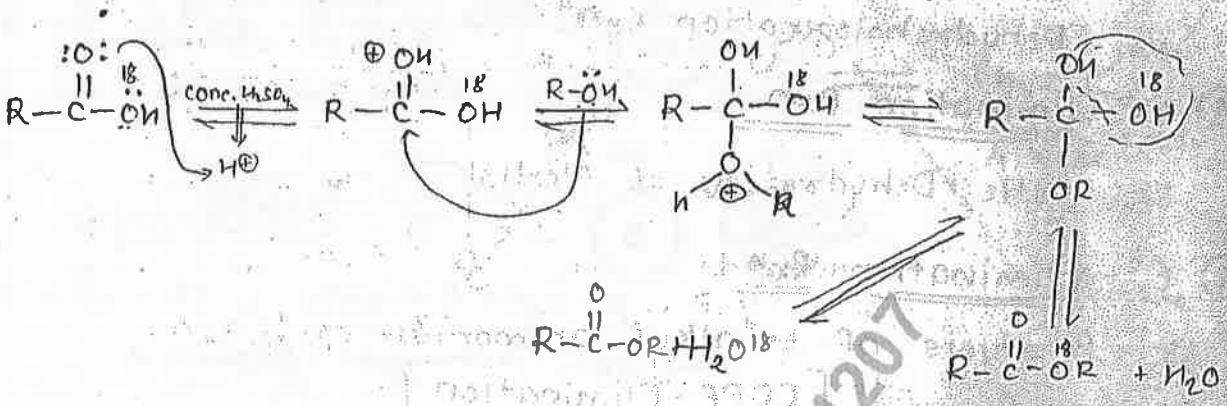
→ Antipyretic
→ Analgesic
→ Anti inflammatory → O-Acetoxy benzene carboxylic
→ Anti coagulation Action

Reactivity of Esterification $\propto \frac{1}{\text{Steric hindrance}}$

① $CH_3-\ddot{O}H > CH_3-CH_2-OH > CH_3-\underset{CH_3}{CH}-OH$

② $H-\overset{O}{\overset{\|}{C}}-OH > CH_3-\overset{O}{\overset{\|}{C}}-OH > CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH > CH_3-\underset{CH_3}{CH}-\overset{O}{\overset{\|}{C}}-OH$

Mech of Esterification

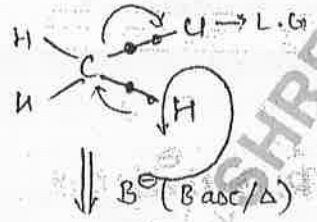


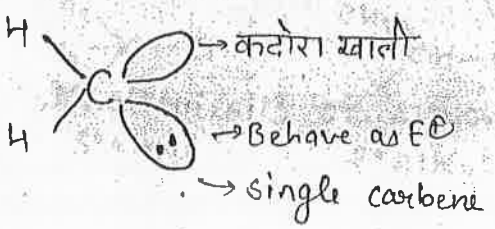
ELEMINATION Rxn (AWay form alkene as product)

- X_2 ⇒ Dehalogenation
- HX ⇒ De hydrohalogenation
- H_2 ⇒ De hydrogenation
- CO_2 ⇒ De carboxylation.
- H_2O ⇒ Dehydration

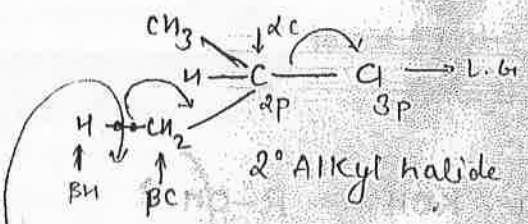
Elimination Rxn

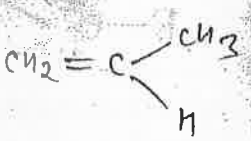
α - Elimination (1,1 - Elimination)





β - Elimination (1,2 - Elimination)





* β-ELIMINATION :-

① E_2^2 elimination Rxn.

Ex. Dehydrohalogenation Rxn.

② E_1^1 Elimination Rxn

Ex. Acetic Dehydration of Alcohol.

③ E_i^i - Elimination Rxn

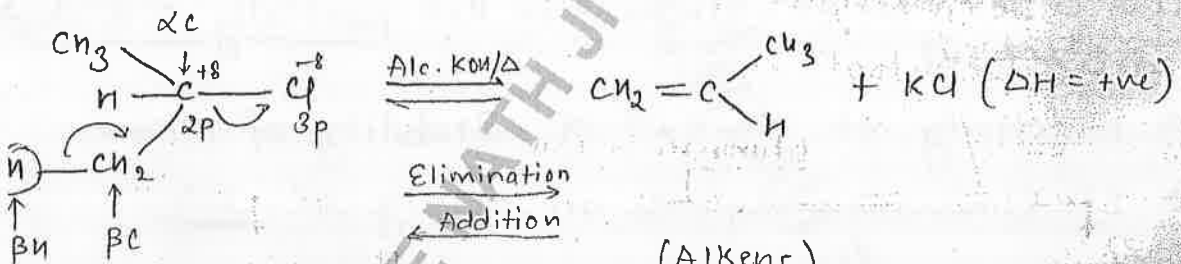
Ex Pyrolysis of trialkyl ammonium oxide ion.

[COPE - Elimination]

E^2 - Elimination Rxn : (Bimolecular elimination Rxn)

Ex. Dehydrohalogenation Rxn.

NET Rxn



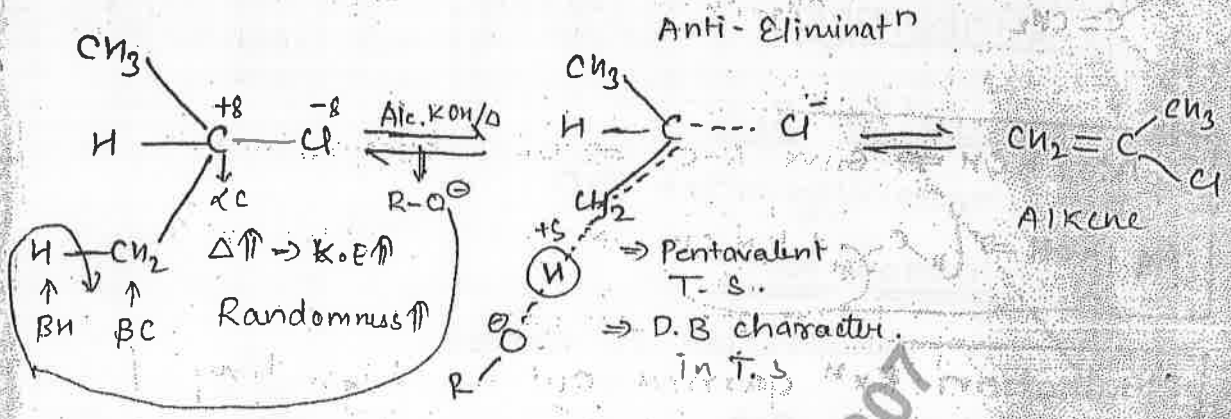
→ 2° Alkyl halid
→ 2 σ-bond break
→ DU ⇒ 0

(Alkene)
→ 1 π-bond form
→ DU. ⇒ 1

→ Alc. KOH ⇒ R–OH ⇑ + K⁺ ⁻OH (3.5) ⇌ $R-O^{\ominus}$ ($-H_2O$)

give $R-O^{\ominus}$ → Base
→ $Nu^{\ominus}$ → favours to Elimination Rxn

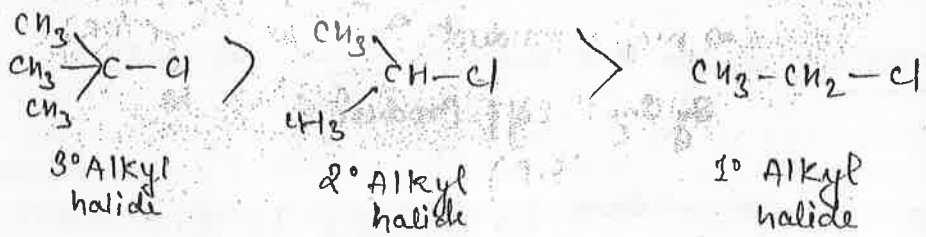
NET MECH-1

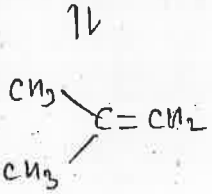


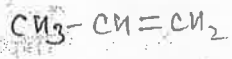
* Rxn carried out at higher temp.
* Endothermic Rxn
* Rxn completeled with Anti-elimination.
* Order of Rxn = 2
  Molecularity of Rxn = 2
* Pentavel Transition state formed in this Rxn
* In PTS of E2-Elimination Rxn partially D.B chara. developed
* Reactivity of E2-Rxn ∝ Stability of alkene.
* E2-Elimination depends on ability of L.G.
* Rate of E2-Rxn.

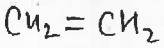
  R-I > R-Br > R-Cl > R-F

* Reactivity of E_β^2-Rxn.

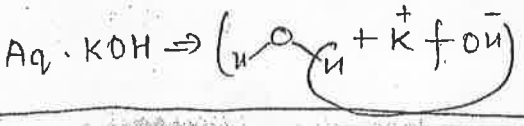








Alc. KOH ⇒ Give $R-O^{\ominus}$ ⇒ Give Elimination Rxn

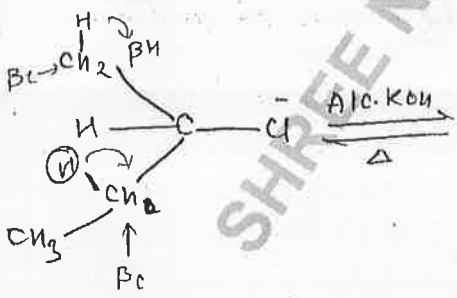
Aq. KOH ⇒  ⇌ OH^- ⇒ Favours to Sub Rxn

Elimination Rxn carried out at high temp.

Substitution " " " " low temp

$R-O^{\ominus}$ $CH_3-CH_2-O^{\ominus}$   $Na-NH_2^{\ominus}$	Δ ⇒ mostly favours to Elimination Rxn

Q.1



Alc. KOH, Δ

$CH_3-CH=CH-CH_3$ + $CH_2=CH-CH_2-CH_3$

Give G.I → cis, Trans

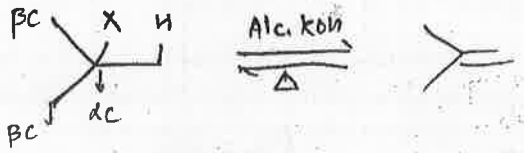
Trans ⇒ more stable Alkene (6-H) ⇒ major product

By Zeff Product (S.P)

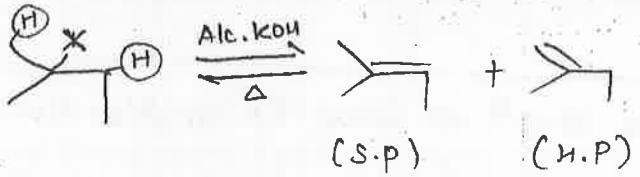
minor product (2-Hrn)

Hoffmann's Product (H.P)

Q.2

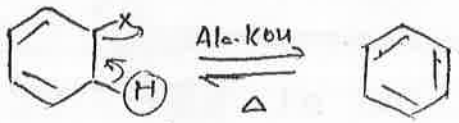


Q.3

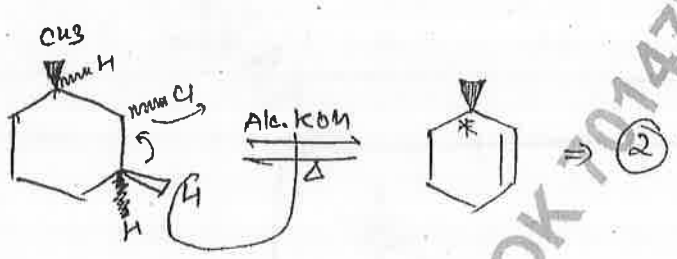


(S.P) (M.P)

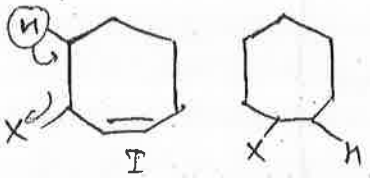
Q.4



Q.5

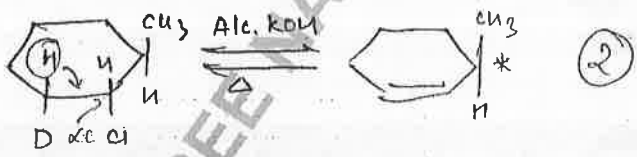


Q.6

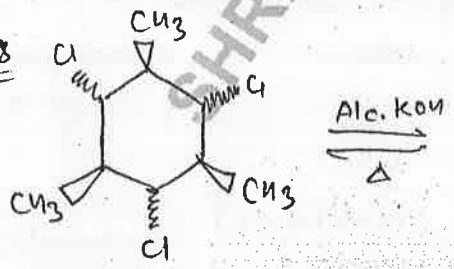


Rate of E2-Rxn ⇒ I > II

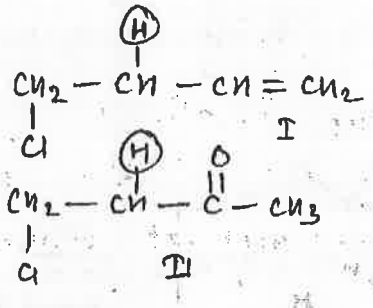
Q.7



Q.8



No. Rxn.

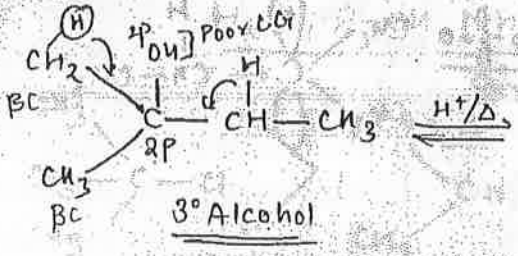
9] 

Rate of E^2 => II > I

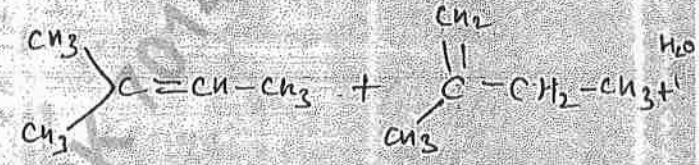
E^1 (unimolecular elimination Rxn)

Eg. Acidic ~~red~~ dehydration of Alcohol.

NET Rxn



3° Alcohol



=> 9 α-H

=> major product (S.P.)

=> 5 α-H

=> less stable Alkene

=> minor product (H.P.)

Dehydrating agent

(i) conc. H_2SO_4/Δ

(ii) Conc. H_3PO_4/Δ

(iii) Conc. $KHSO_4/\Delta$

(iv) $Cu/300°C$ → Oxidation => 1° & 2° Alcohol; only dehydration => 3° Alcohol

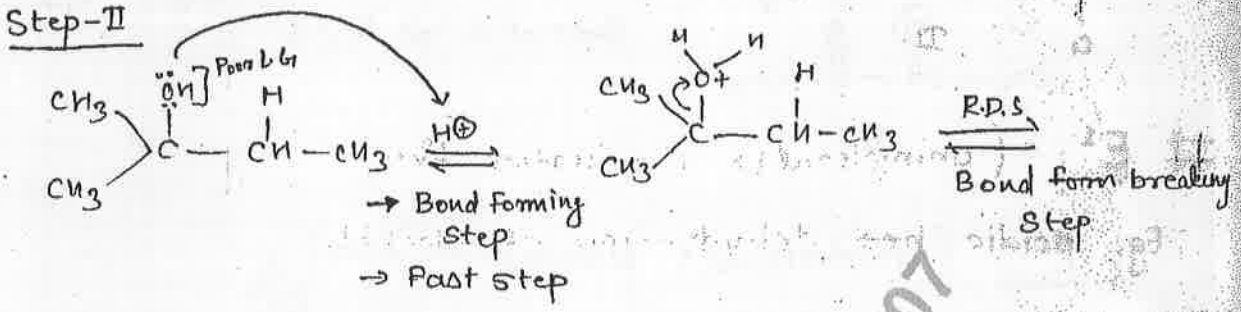
(v) Al_2O_3/Δ

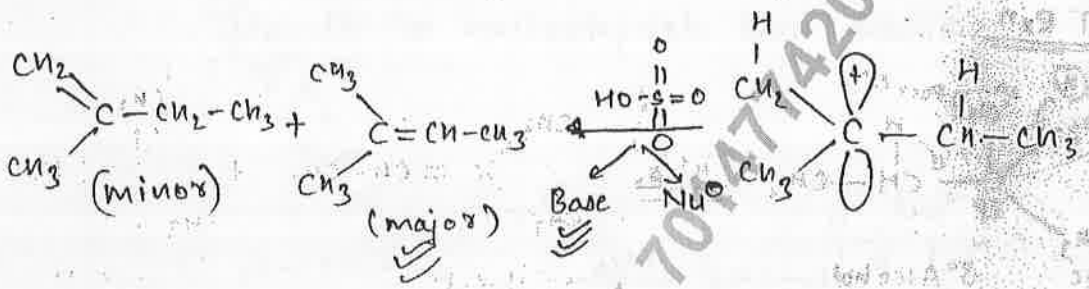
(vi) P_2O_5 (P_4O_{10})$/\Delta$

Mech.

Step-I Conc. $H_2SO_4 \rightleftharpoons H^+ + HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O^{\ominus}$

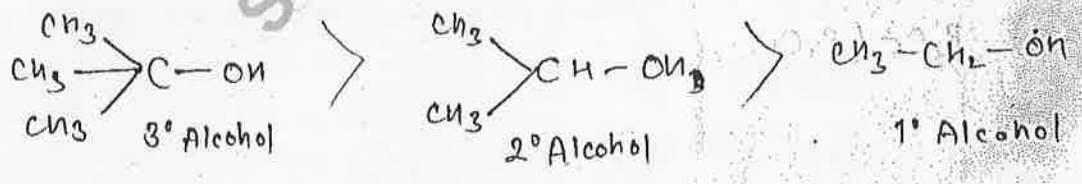
Step-II





* Rxn carried out at higher temp.
* 2-step rxn.
* Molecularity ⇒ 1
* order ⇒ 1
* Carbocation intermediate formed in this rxn
* Formation of $C^{\oplus}$ is R.D.S of rxn.
* Carbocation rearrangement possible.
* Reactivity of Rxn $\propto$ stability of carbocation.

Rate of Dehydration:-

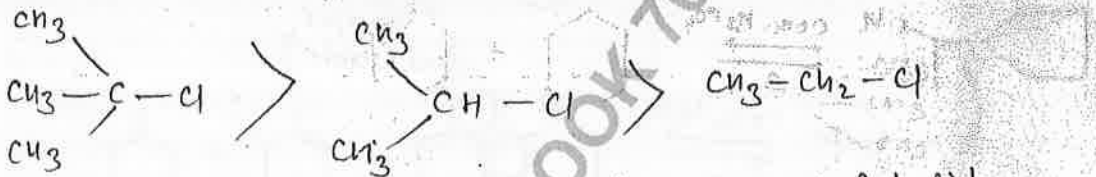


NOTE :- 1

* In Acidic dehydration of Alcohol we can not use conc. HX [HI, HBr] Because all these reagents favours to the substitution Rxn.

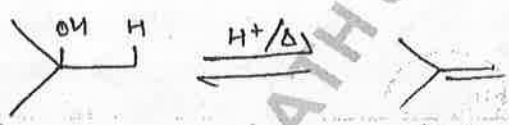
* In Acidic dehydration of Alcohol we can not use dil H_2SO_4 because in this case due to addition at alkene rxn favours to backward direction.

NOTE-2 → H_2O, R-OH, NH_3/Δ, high temp ⇒ E'-mech.



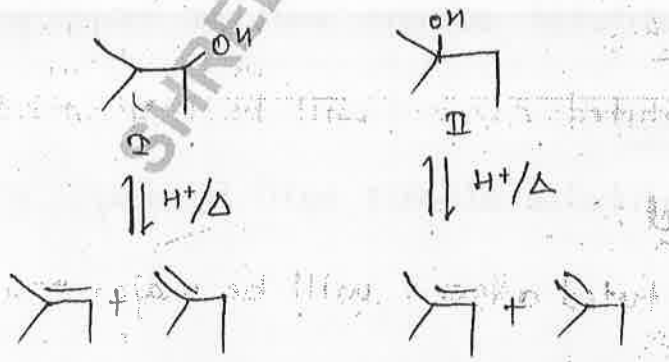
3° Alkyl halid 2° Alkyl halid 1° Alkyl halid.

Q.1



3° Alcohol (Alkene)

Q.2

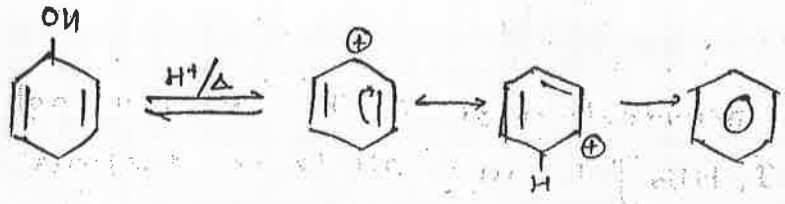


(S.P). (H.P) (S.P) (H.P)

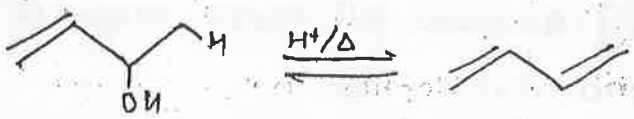
Rated of dehydration = II > I

Rate does not depend upon rearrangement of ⊕

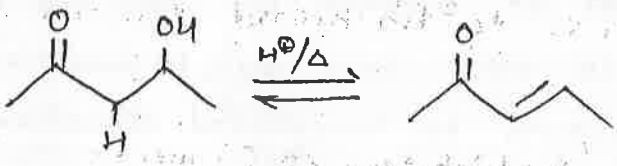
Q.3



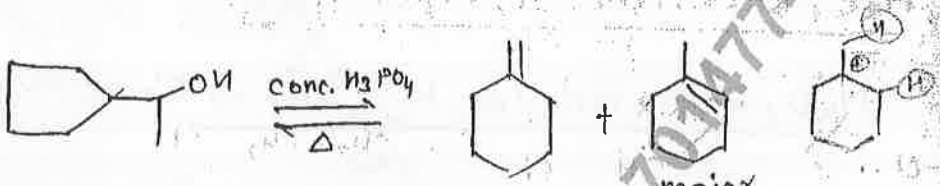
Q.4



Exam
Q.5



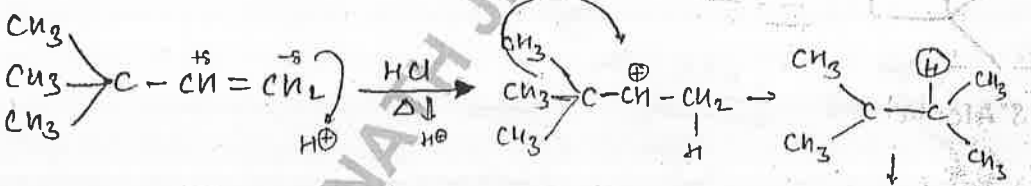
Q.6



major
(stable)

Q.7

(B)



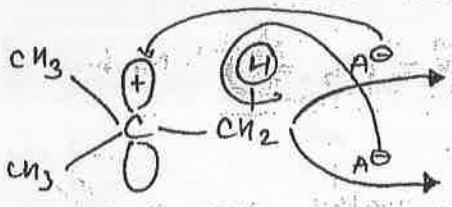
Sayt's zeft product :-

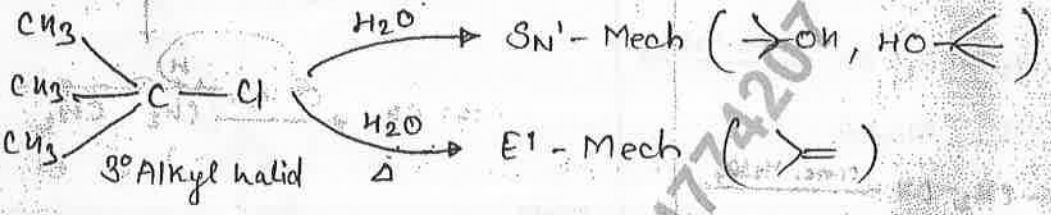
More alkyl substituted alkene will be major product

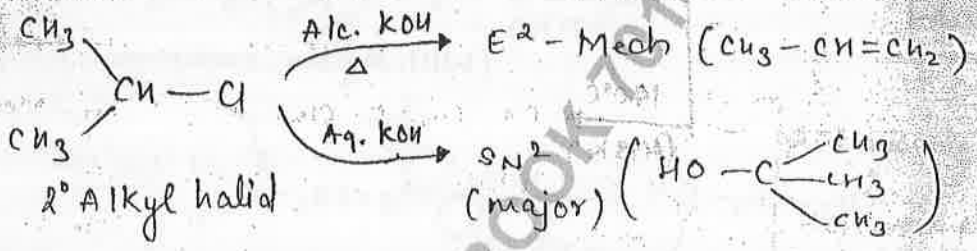
Hoff man's product :-

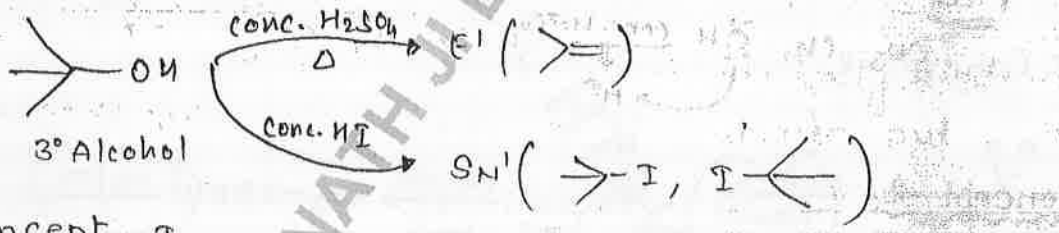
less alkyl substituted alkene will be major product

Comparison b/w $S_N1 . E1$ & $S_N2 . E2$ ★★

① 

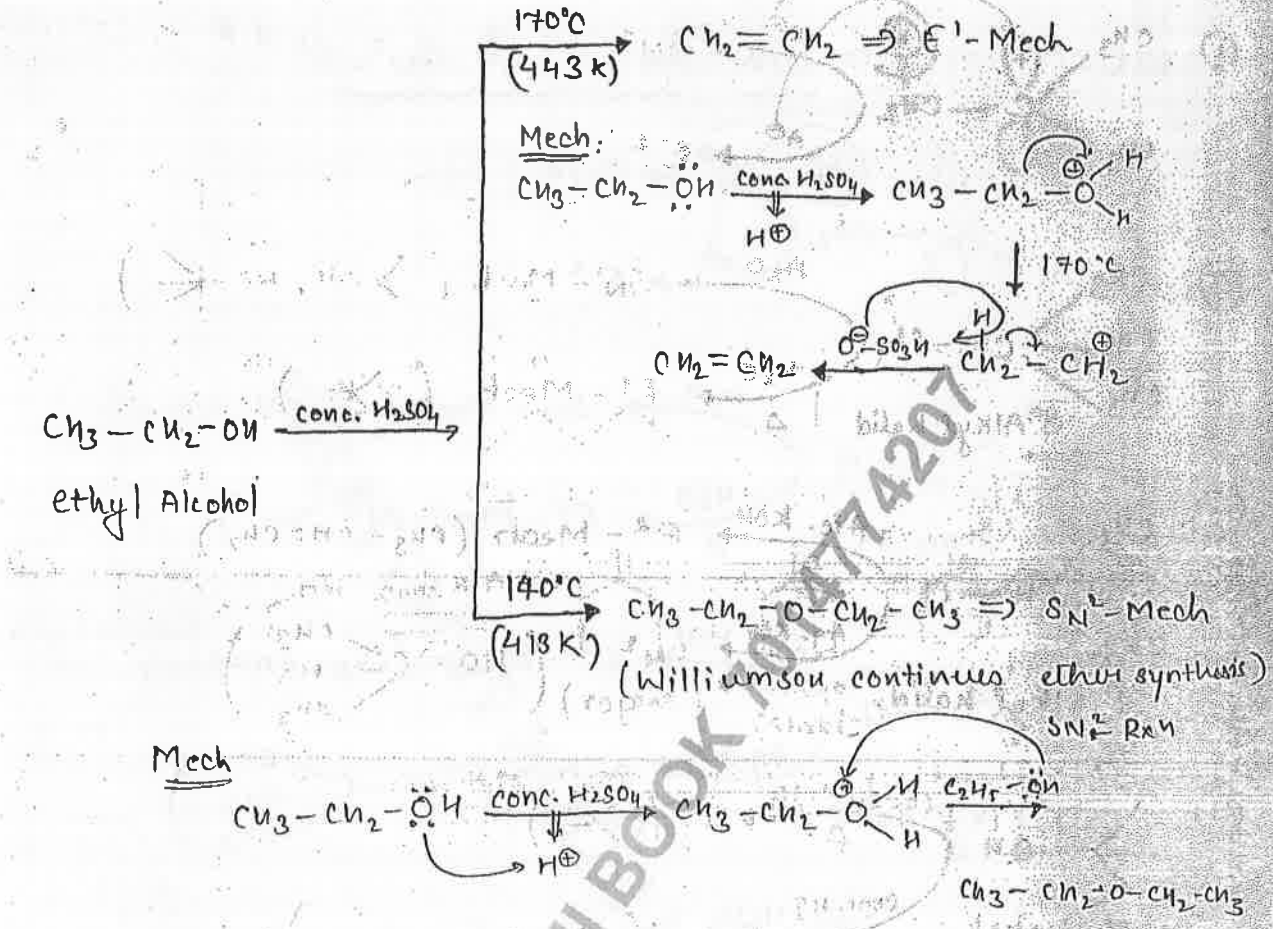
② 

③ 

④ 

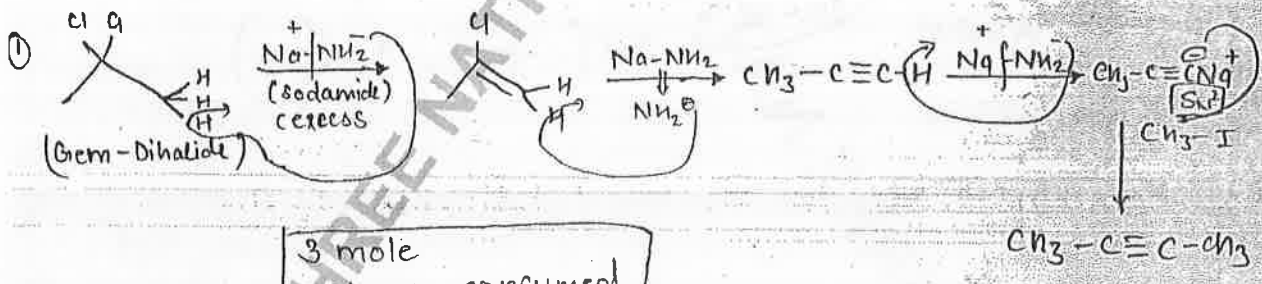
Concept - I.

Concept-1 :

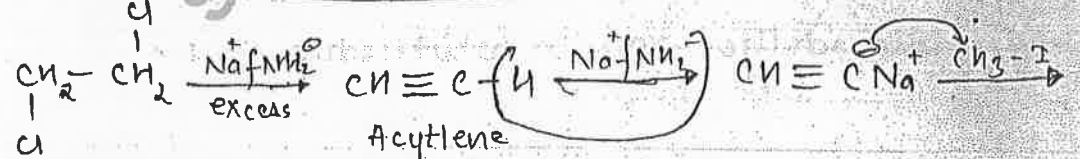


Mech

Concept-2 :

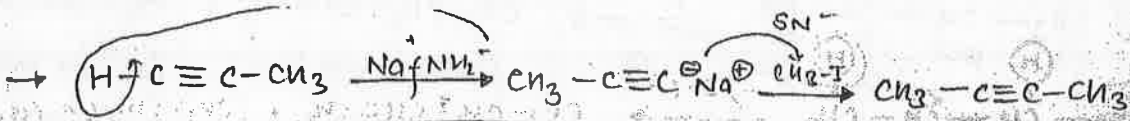
① 

3 mole $NaNH_2$ consumed

② 

Vic-dihalide

2 mole $NaNH_2$ consumed



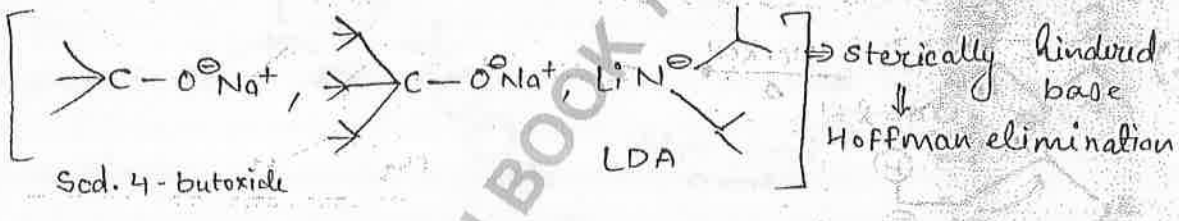
2-Butyne

Total 4 mole $NaNH_2$ consumed

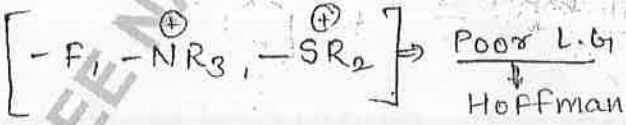
More than one time Elimination ⇒ Strong base $NaNH_2$

Hoffman Elimination Rxn :-

* It is a E^2 & Anti-elimination
* Hoffman elimination rxn carried in presence of sterically hindered base.

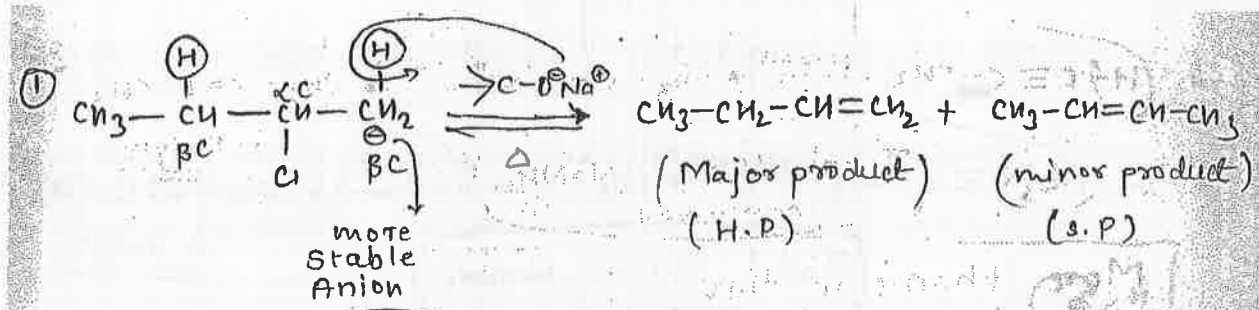


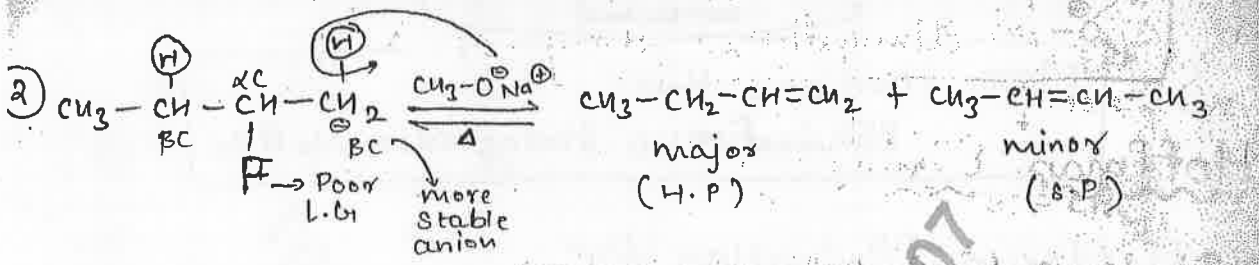
* In hoffman elimination rxn if sterically hindered base not present then rxn is carried out with poor L.G.



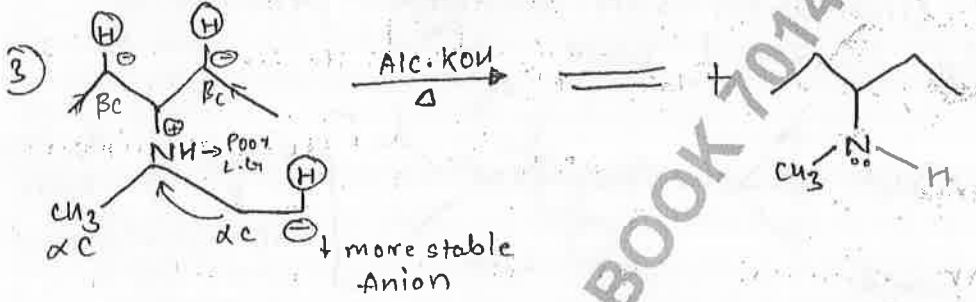
* In Hoffman elimination rxn anion like character developed in T.S.

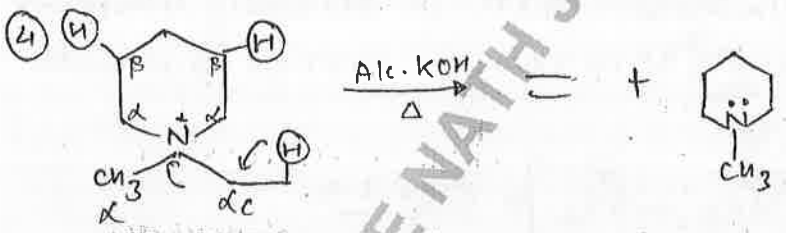
F, $-\overset{\oplus}{N}R_3$, $-\overset{\oplus}{S}R_2$ – L.G hoto H-nikal ne ke bat Anion ki stability check karege





(II) $\underset{\Delta}{\overset{\text{Alc. KOH}}{\rightleftharpoons}}$ $CH_3-CH_2-CH=CH_2 + CH_3-CH=CH-CH_3$





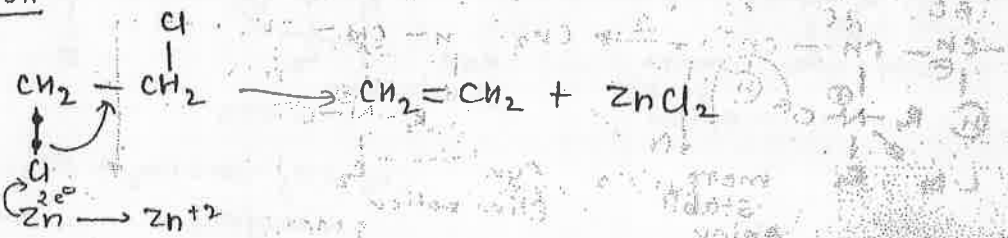
#ELIMINATION OF DIHALOGEN: ★

* It is E_2 & Anti-elimination Rxn.

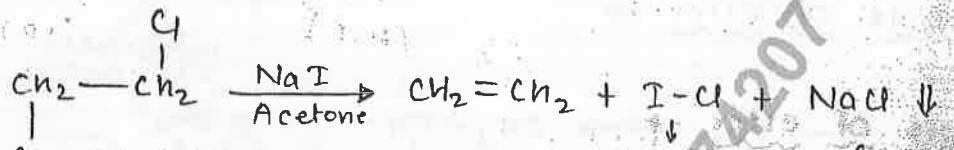
(1) $CH_2(Cl)-CH_2(Cl) \xrightarrow[\Delta]{Zn} CH_2=CH_2 + ZnCl_2$

Vic-Dihalide

MECH



Reactivity of Rxn :- R–I > R–Br > R–Cl > R–F

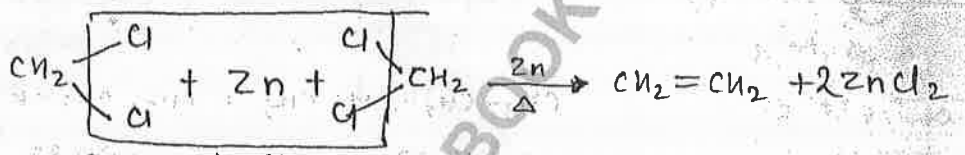
(ii) 

vic-Dihalide

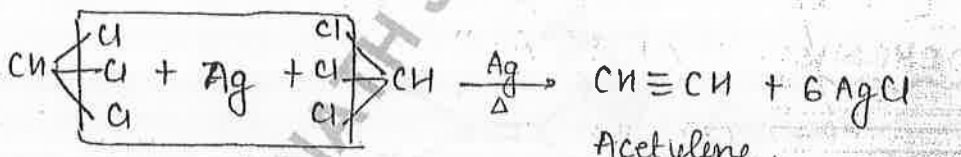
intershalogen bond

(PPt)

ELIMINATION OF GEM DI & TRIHALIDE

(i) 

GEM Dihalide

(ii) 

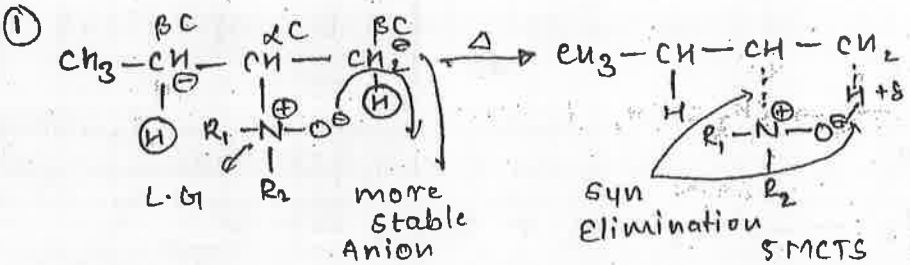
GEM-Trihalide

Acetylene.

E^i - (intramolecular no elimination Rxn)

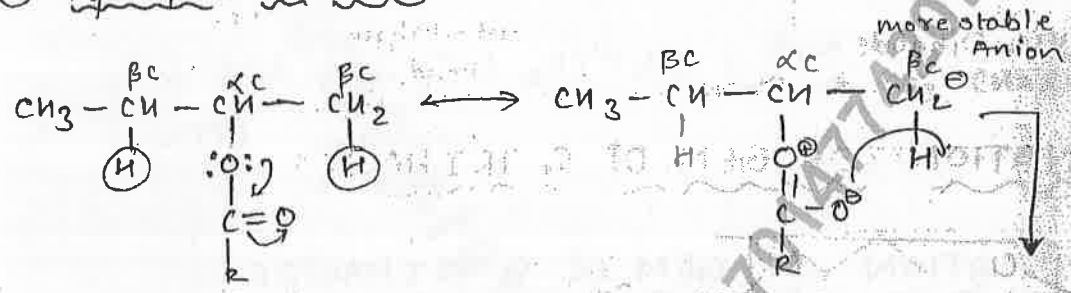
* Rxn carried out at higher temp.
* Rxn completed with syn elimination.
*
* (A) Pyrolysis of tri-alkyl Ammionium oxide anion [COP elimination]
* Rxn completed with syn elimination.
* 5-MCTS form in this rxn.
* Anion like character developed in TS.

(1)



$CH_3-CH_2-CH=CH_2$ + $CH_3-CH=CH-CH_3$
(major) (H.P) (minor) (S.P)

(B) Pyrolysis of ester →

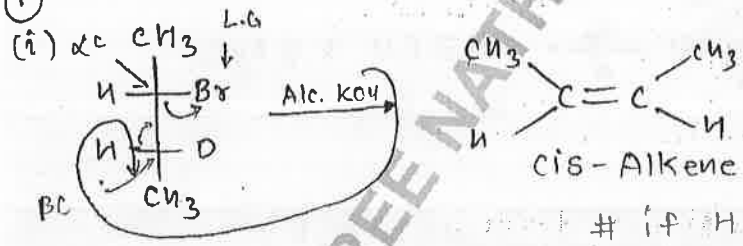


$CH_3-CH_2-CH=CH_2$ + $CH_3-CH=CH-CH_3$
major (H.P) minor (S.P)

STERIOCHEMISTRY OF E2 Rxn :-

(1)

(i)

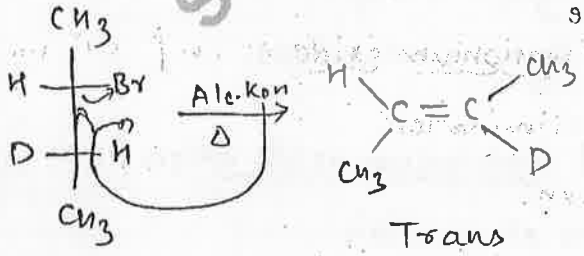


cis-Alkene

if H & L.G eliminated From opp. side → Cis-Alkene

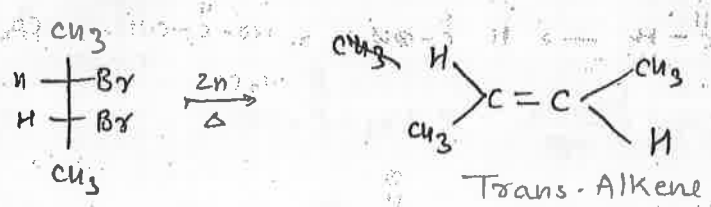
if H & L.G eliminated From same side → Trans-Alkene

(ii)

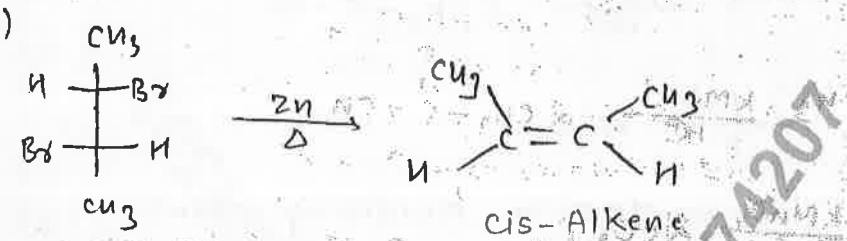


Trans

(2)

(i) 

Trans-Alkene

(ii) 

cis-Alkene

OXIDATION OF OC

(A) Oxidation by strong oxidising agent:-

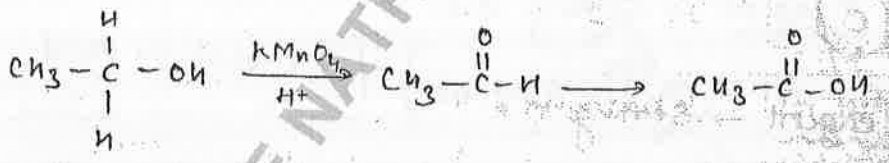
① $KMnO_4$ [$H^+/NaOH/H^+, \Delta$/hot]

Pink colour ⟶ colourless

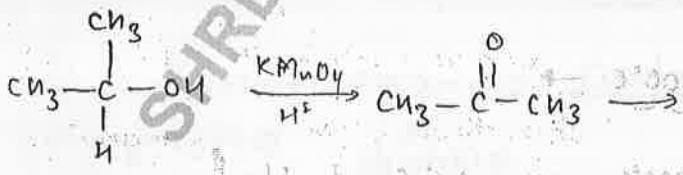
② $K_2Cr_2O_7$ [$H^+/NaOH, \Delta$/hot]

Orgaue colour ⟶ green colour

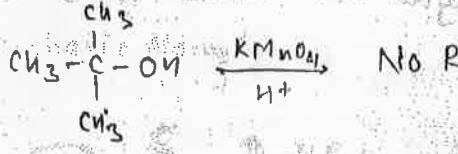
$KMnO_4$
$K_2Cr_2O_7$
CrO_3/H_3O^+
H_2CrO_4
→ Strong OA.

① 

1° Alcohol

② 

2° Alcohol

③ 

3° Alcohol.

(4) $H-CH_2-OH \xrightarrow[H^+]{KMnO_4} H-CHO \longrightarrow H-COOH \longrightarrow HO-CO-OH \longrightarrow CO_2 + H_2O$

Methanol — H_2CO_3

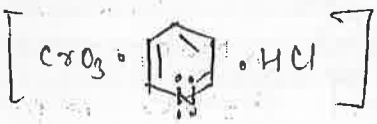
(5) $CH_3-CH=CH-CH_3 \xrightarrow[HO^\ominus]{KMnO_4} 2\,CH_3-COOH$

(6) $CH_3-C\equiv C-CH_3 \xrightarrow[H^+]{KMnO_4} 2\,CH_3-COOH$

(7) $CH_2=CH_2 \xrightarrow[H^+]{KMnO_4} 2CO_2\uparrow$

(B) Oxidation by moderate Oxidising agent.

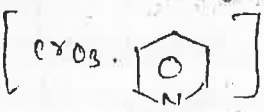
(A) PCC (Pyridine chloro chromate) → Best method for Aldehyde synthesis



1° Alcohol → Aldehyde

2° Alcohol → Ketone.

(B) Collins Reagent :-



(C) Jone's Reagent → Strong O.A

(CrO_3, dil H_2SO_4 in Acetone) (1° Alcohol → Acid; 2° " → Ketone)

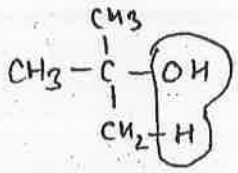
(2) Oxidation by Cu/300°C →

(1) $CH_3-CH_2-OH \xrightarrow{Cu/300^\circ C} CH_3-CHO + H_2\uparrow$

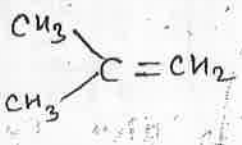
1° Alcohol — Aldehyde — Dehydrogenation

(11) $CH_3-CH(CH_3)-OH \xrightarrow{Cu/300^\circ C} CH_3-CO-CH_3 + H_2\uparrow$

Ketone

(iii) 

3° Alcohol

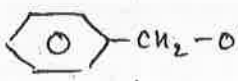
$\xrightarrow{Cu/300°C}$ 

+ H_2O (Dehydration)

NCERT

Cu / 300°C → Elimination ✓✓
→ oxidation ✓✓
→ Dehydration ✓✓
→ Dehydrogenation ✓✓

(3) Oxidation by MnO_2 → (Selective oxidation)
↳ Brown colour → colourless.

(i) 

$\xrightarrow{MnO_2}$ 

Benzyl Alcohol

(ii) $CH_2 = CH - CH_2 - OH \xrightarrow{MnO_2} CH_2 = CH - \overset{O}{\overset{\|}{C}} - H$
Allylic Alcohol

(C) Oxidation by Mild Oxidising agent :-

(A) Tollen's Reagent (T.R) → (Ammonical silver nitrate).

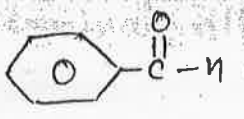
⇒ $AgNO_3 + NH_4OH \rightarrow$ T.R ✓

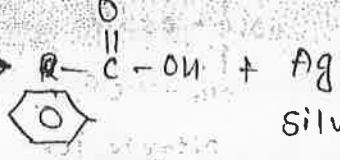
T.R → oxidation
→ Acid-base Rxn.

⇒ $[Ag(\overset{\text{Ligand}}{\overset{\curvearrowleft}{NH_3}})_2]OH$ ⇒ Basic medium

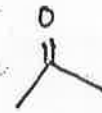
CIM. Diammine silver (I) hydroxide

(i) $R - \overset{O}{\overset{\|}{C}} - H \xrightarrow{T.R} R - \overset{O}{\overset{\|}{C}} - OH + AgO$
Aliphatic Aldehyde — silver mirror.

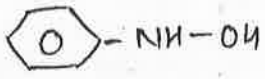
(2) 

$\xrightarrow{T.R}$ 

+ AgO
Silver Mirror.

(B) 

(α-hydroxyl keto)



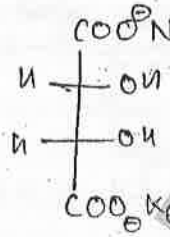
⇒ give Rxn with Tollen's T.R & Silver mirror

* All Alliphatic & aromatic give rxn with T.R & Form silver mirror.
* Formic acid give rxn T.R & form Silver mirror.

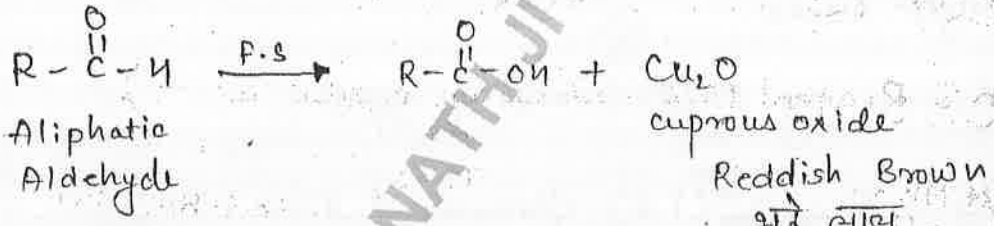
(B) Fehling Soln (F.S) :-

$f_A \Rightarrow CuSO_4 . 5H_2O$ (Blue vitriole)

$f_B \Rightarrow NaOH$ → Basic medium



Sod. Pot. tartarate (Rochelle salt)



Aliphatic Aldehyde

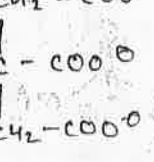
Cu_2O cuprous oxide Reddish Brown भूरे लाल

* F.S only oxidised to Aliphatic aldehyde.

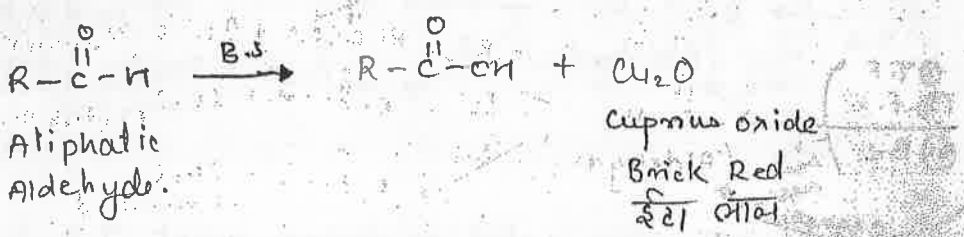
(C) Benedict soln (B.S) →

$B_A \rightarrow CuSO_4 . 5H_2O$ (Blue vitriole)

$B_B \Rightarrow NaOH$ → Basic Medium



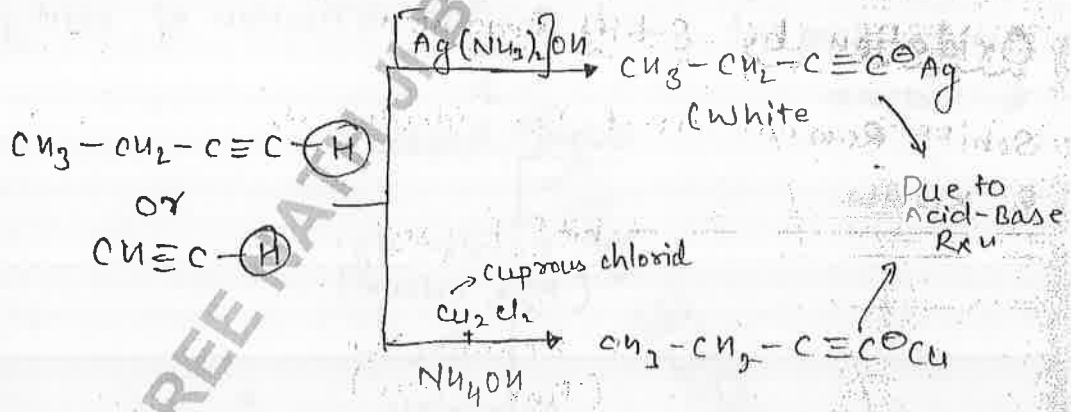
Citrate ion



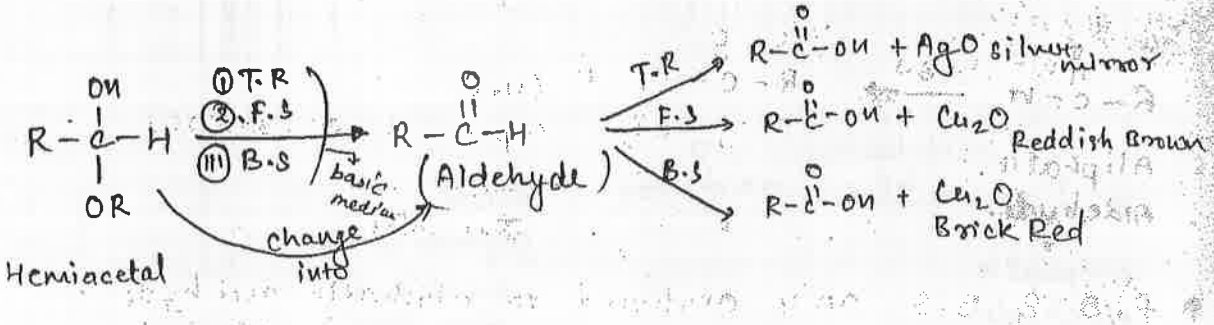
* f.s & B.S only oxidisied to aliphatic aldehyde i.e f.s & B.S use for identification of aliphatic & aromatic aldehyde

* All monosaccharide & disaccharide except sucrose give rxn with mild O.A T-R, F.S & T.S. becoz all these reagent give rxn in basic medium. & in the basic medium Hemiketal change in aldehyde & all reducing sugar have hemiacetal group.

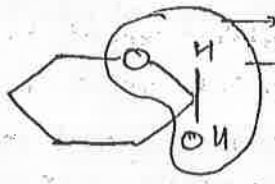
(E) Rxn with terminal Alkyne :→



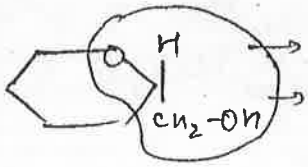
* All terminal alkyne and acetylene give acid base rxn with T.R & form white ppt. while internal alkyne does not react with T.R. i.e Tollen's Reagent used for identification of internal & terminal alkyne



* Hemiacetal give rxn with mild oxidising agent T.R, F.S, B.S due to basic medium.

(I) 

→ Hemiacetal
→ Reducing Sugar
(give Rxn with T.R, F.S, B.S)

(II) 

→ No Hemiacetal
→ No Reducing Sugar.

⑥ Oxidation by Schiff Reagent:

* Schiff Reagent used For identification of aldehyde & ketone.

Schiff Reggent
↓
P-Rosaline dye
(Pink colour)
↓ SO_2
Colourless

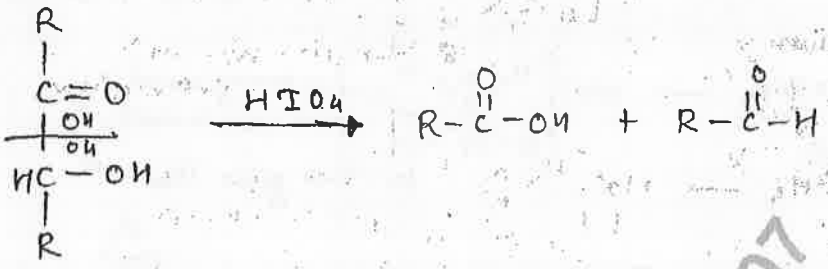
$R-\overset{O}{\overset{\|}{C}}-H$ → Again pink colour reappear

$R-\overset{O}{\overset{\|}{C}}-R$ → Again No colour pink colour

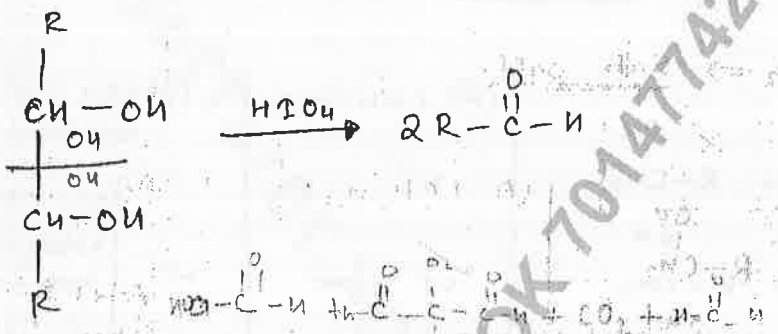
⑦ Oxidation by HIO_4 (Per-iodic Acid) :-

($HIO_4 \cdot H_2O$)

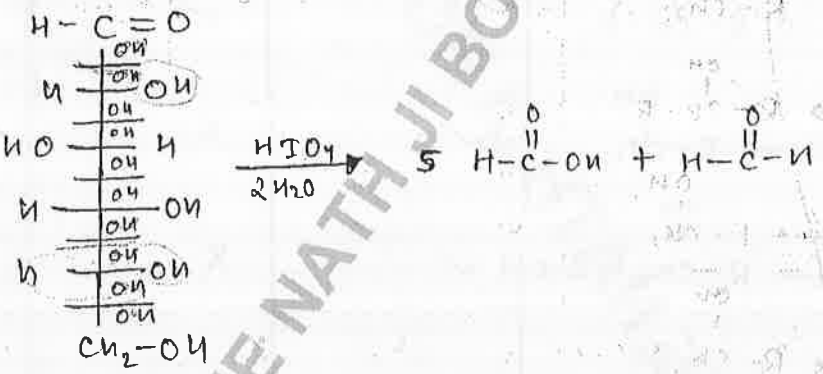
(I)



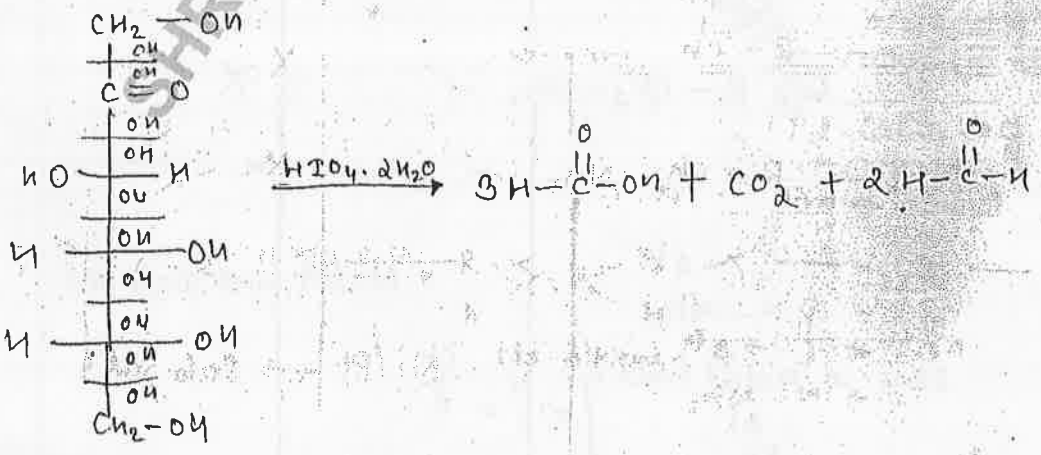
(II)



(III)



(IV)



Reduction of OC

Ⓐ LAH → $LiAlH_4$ → $Li^+[H_4Al^{\ominus}]$ → weak bond, more break

Lithium Aluminium hydride

Is → give more $H^{\ominus}$ in Rxn medium.

Ⓑ SBH → $NaBH_4$ → $Na^+[H_4B^{\ominus}]$ → strong bond, less break

Sod. Borohydride

Is → give less $H^{\ominus}$

Ⓒ Ni / Pt / Pd / H_2 ⇒ Sab SaFP.

	Ⓐ LAH/H_2O	Ⓑ SBH / C_2H_5-OH	Ⓒ Ni/Pt/Pd / H_2O
) $R-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow R-CH_2-OH$	✓	✓	✓
) $R-\overset{O}{\overset{\|}{C}}-H \longrightarrow R-CH_2-OH$	✓	✓	✓
) $R-\overset{O}{\overset{\|}{C}}-R \longrightarrow R-CH(OH)-R$	✓	✓	✓
) $R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R \longrightarrow R-CH_2-OH$	✓	X	✓
) $R-\overset{O}{\overset{\|}{C}}-OR \longrightarrow R-CH_2-OH + R-OH$	✓	X	✓
) $R-\overset{O}{\overset{\|}{C}}-OH \longrightarrow R-CH_2-OH$	✓	X	✓
) $R-\overset{O}{\overset{\|}{C}}-NH_2 \longrightarrow R-CH_2-NH_2$	✓	X	✓
— X — X — X — X — X — X —			
) LAH ⇒ $\overset{O}{\overset{\|}{C}}-OH$ ⇒ $N-NH_2$	Ni/Pt → Sab Saf!		
SBH ⇒ Acid halide, Aldehyde, Ketone ⇒ $\overset{O}{\overset{\|}{C}}=\overset{OH}{C}$			

Acid halide, Aldehyde, Ketone

Δ

	Ⓐ LAH/H2O	② SBH/C_2H_5OH	③ Ni/Pt/Pd/H_2
⑧ $R-C\equiv N \longrightarrow R-CH_2-NH_2$	✓	×	✓
⑨ $R-N\overset{+}{\equiv}C^{-} \longrightarrow R-NH-CH_3$	✓	×	✓
⑩ $R-NO_2 \longrightarrow R-NH_2$	✓	×	✓
⑪ $R-CH_2-CH_2-X \longrightarrow R-CH_2-CH_3$ (1° & 2°)	✓	×	✓
⑫ $R-CH=CH-R$ or $R-C\equiv C-R \longrightarrow R-CH_2-CH_2-R$	×	×	✓

② Strong Reducing agent Red/P/HI →

① $R-CH_2-CH_2-OH$, $R-CH_2-\overset{O}{\overset{\|}{C}}-H$, $R-CH_2-\overset{O}{\overset{\|}{C}}-OR$ $\xrightarrow{\text{Red P/HI}}$ $R-CH_2-CH_3$

⑪ $R-CH_2-CH_2-I \xrightarrow{\text{Red P/HI}} R-CH_2-CH_3$

⑪ Glucose $\xrightarrow{\text{Red P/HI}}$ n-hexane.

C= → inner
alcohol → Alkene
alkyne → cis Alkene

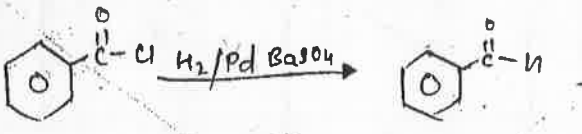
③ Partially Reduction by $H_2/Pd-BaSO_4$ / $Pd-CaCO_3$ →
(जहरीला) lindlar catalyst.

① $R-C\equiv C-R \xrightarrow{H_2/Pd-BaSO_4} \underset{H}{R}\!>\!C=C\!<\!\overset{R}{H}$

cis-Alkene.

(2) $R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{H_2/Pd-BaSO_4} R-\overset{O}{\overset{\|}{C}}-H$

Acid halid



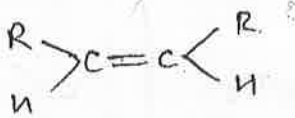
ROSSENMUND Reduction.

Can't + Form formal aldehyde

(3) $R-C\equiv N \xrightarrow{H_2/Pd-BaSO_4} R-CH=NH$

Imine.

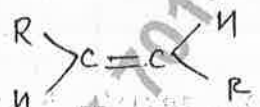
NCERT

$R-C\equiv C-R \xrightarrow[H_2]{Pd,\ charcoal}$ 

Alkyne

Cis-Alkene

(4) Birch Reduction → colloidal soln

(1) $R-C\equiv C-R \xrightarrow{Na-Liq.\ NH_3}$ 

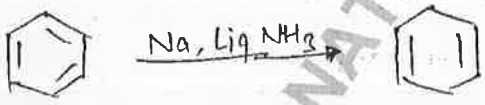
Alkyne

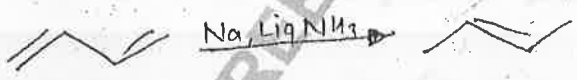
Trans-Alkene

(11) $R-CH_2-C\equiv C-H \xrightarrow{Na,\ Liq\ NH_3} R-CH_2-C\equiv C^{\ominus}Na^{+} + \frac{1}{2}H_2$

or

$CH\equiv C-H$

(111) 

(IV) 

(5) Stephan Reaction →

Stephan Reagent $SnCl_2+HCl \rightarrow SnCl_2+H_2$

$R-C\equiv N \xrightarrow[(11)\ H_2O]{(1)\ SnCl_2+HCl} R-\overset{+\delta\ OH}{CH}=\overset{-\delta\ H^+}{NH} \xrightarrow{H_2O} R-\overset{O}{\overset{\|}{C}}-H + \ddot{N}H_3$

(6) MENDIUS Rxn →

$$R-C\equiv N \xrightarrow{Na + C_2H_5OH} R-CH_2-NH_2$$

(7) Bouveoult Blanc Rxn.

$$R-\overset{O}{\overset{\|}{C}}-OR \xrightarrow{Na + C_2H_5OH} R-\overset{OH}{CH_2} + R-OH$$

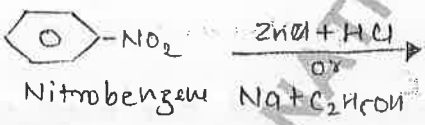
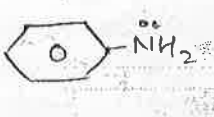
(8) Reduction of Alkyl halide →

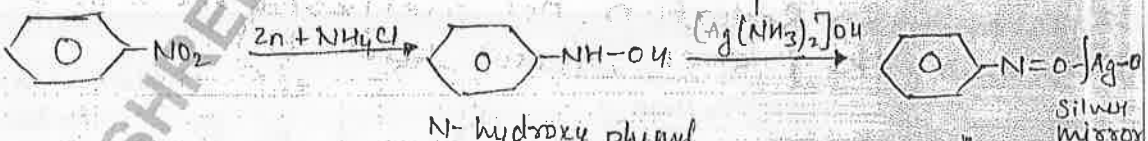
Heavy + HCl ⇒ Reduction

$$R-CH_2-CH_2-X \xrightarrow[\text{or } Sn+HCl \text{ or } Na+C_2H_5OH]{Fe+HCl} R-CH_2-CH_3$$

(9) Reduction of Nitro comp:-

(I) $R-NO_2 \xrightarrow[\text{or } Sn+HCl \text{ or } Na+C_2H_5OH]{Fe+HCl} R-\ddot{N}H_2$ 1° Amine.

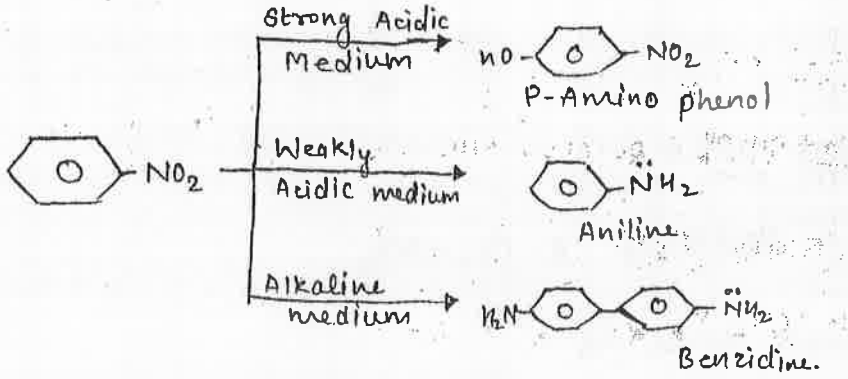
(II)  Nitrobenzene $\xrightarrow[\text{or } Na+C_2H_5OH]{Zn+HCl}$ 

(III) 

N-hydroxy phenyl amine

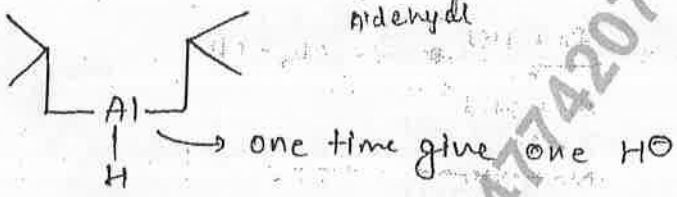
Baker nuliean test

(IV) Electrolytic Reduction of Nitro comp:-

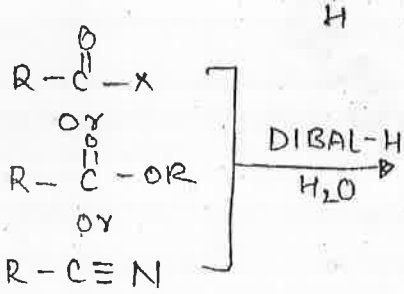


(c) Partially Reduction by DIBAL-H / H_2O →

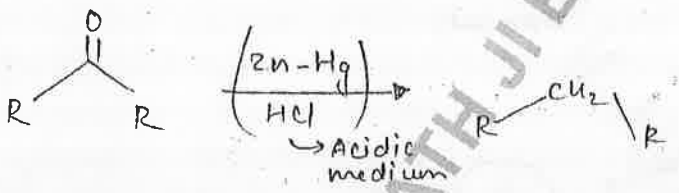
↓ Aldehyde



(i)



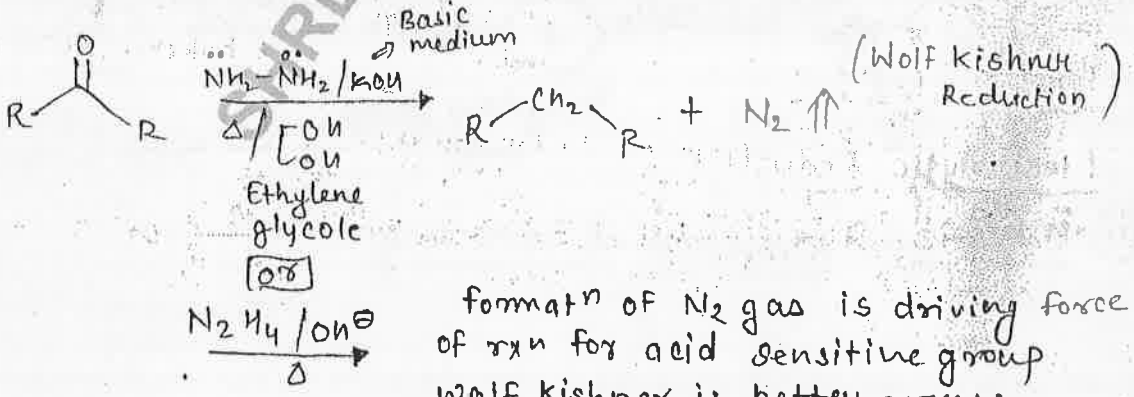
(ii)



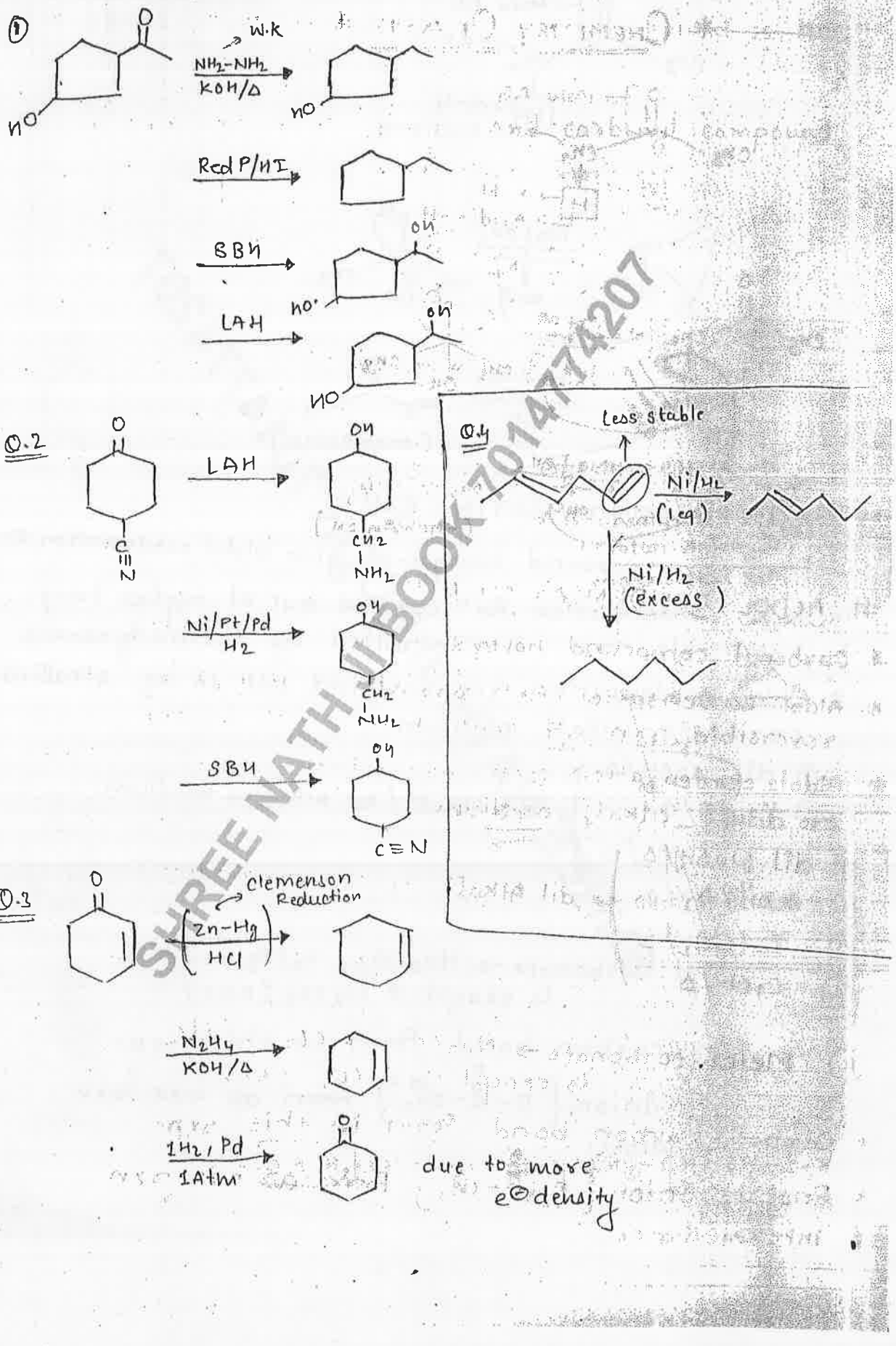
(Clemenson Reduction)

Clemenson Reduction not preffered for acid sensitive group like (R-OH , Acetal ketal etc).

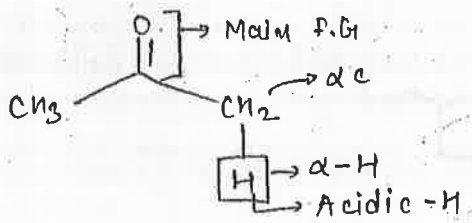
(i)

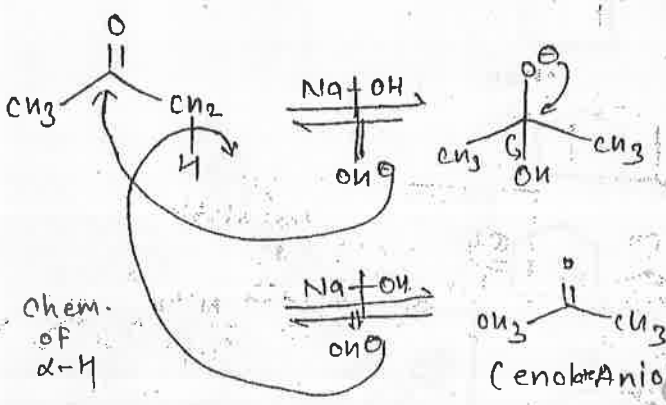


formatn of N_2 gas is driving force of rxn for acid sensitive group wolf kishner is better process.



* CHEMISTRY OF α-H *





#1 ALDOL CONDENSATION RXN :-

* Carbonyl compound having α-H give aldol condensation Rxn.
* Aldol condensation Rxn carried out at higher temp; reversible rxn, & controlled by thermodynamics
* Aldol condensation rxn carried out in aq. alkaline or dilute alkali medium.

① dil NaOH/Δ
② KOH/Δ
③ $Ba(OH)_2$/Δ
④ CsOH/Δ

→ dil Alkali / Aq Alkaline medium.

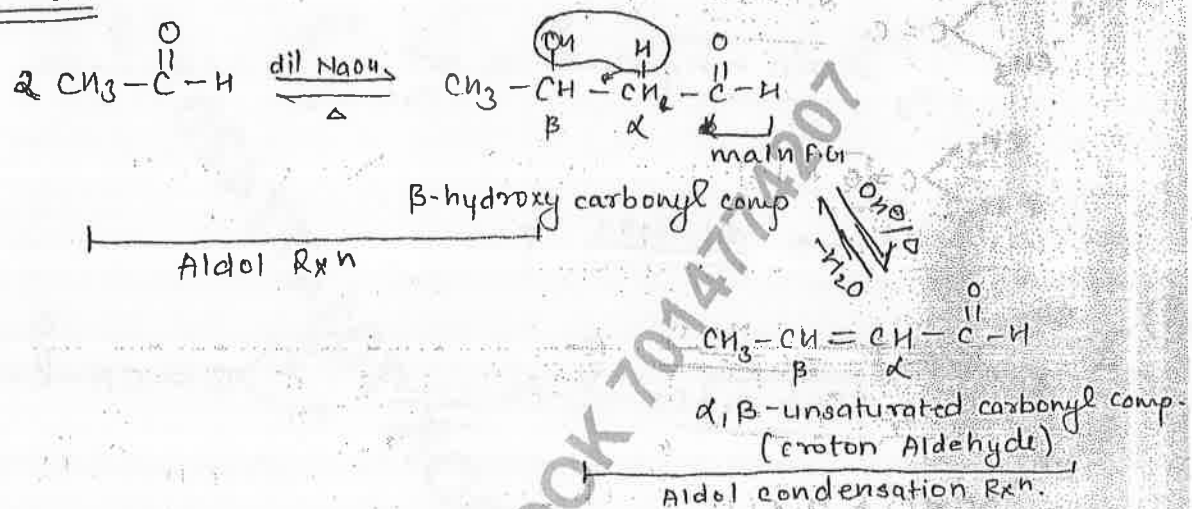
⑪ Metal carbonate → Na_2CO_3, K_2CO_3 - - - etc.
↳ except ⇒ Li_2CO_3 (×××)

* Carbon-carbon bond form in this rxn.
* Enolate anion $\left[R-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{C}H_2\right]$ form as rxn rxn intermediate.

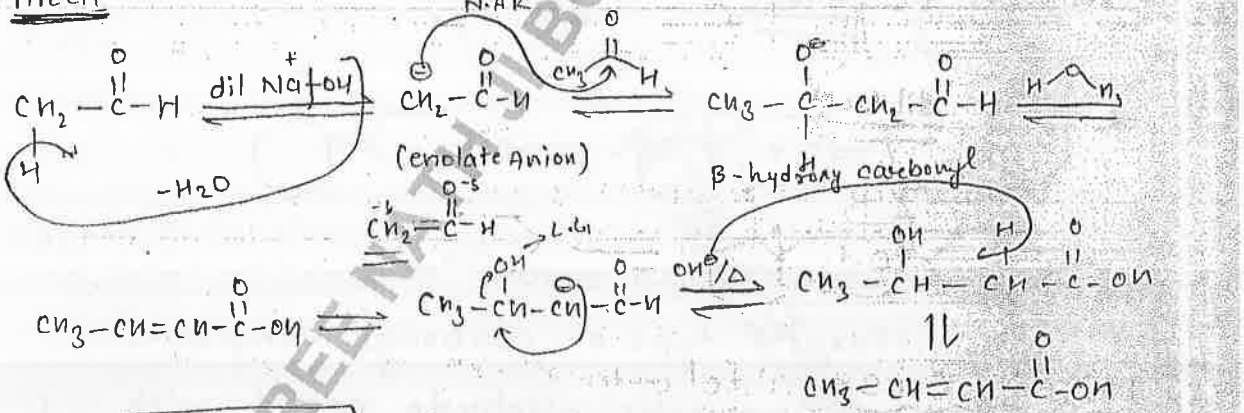
* formation of β-Hydroxy carbonyl compound is known as aldol rxn.

* formation of α, β unsaturated carbonyl compound is known as aldol condensation rxn.

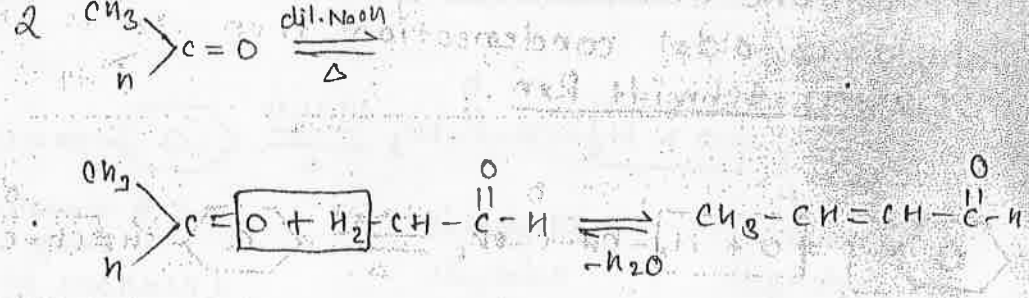
NET RXN



MECH



KEY POINT



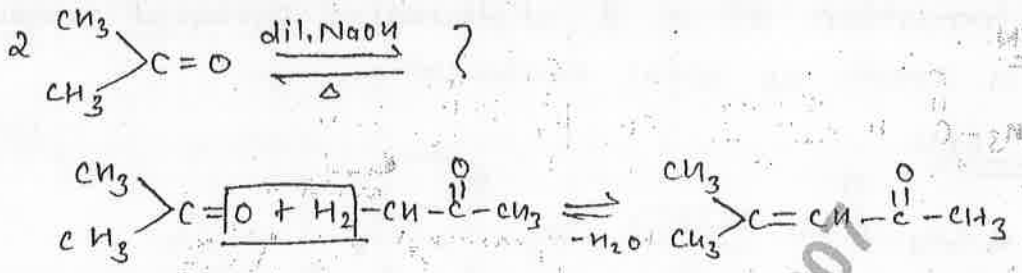
Ek Ke ॥ & Dusre Ke H_2 behidale

Type of aldol condensation :-

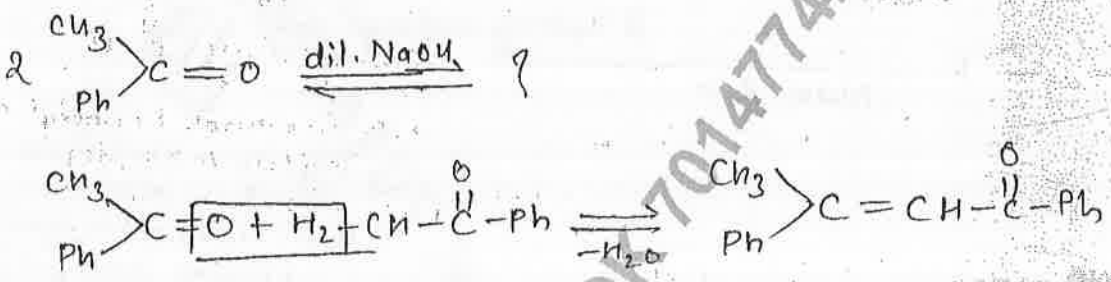
① Simple aldol condensation.

→ Two same ~~time~~ type of carbonyl compound.

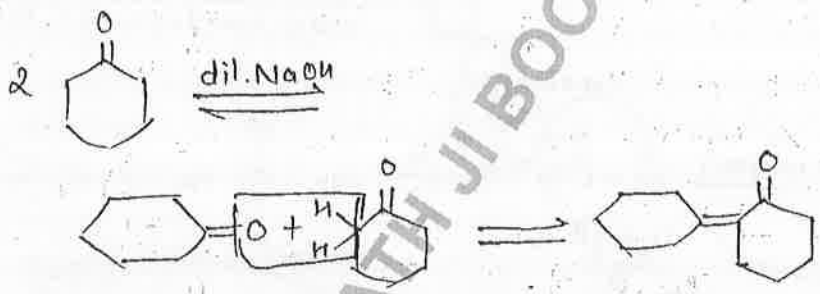
①



②



③



② Mixed / Cross aldol condensation rxn

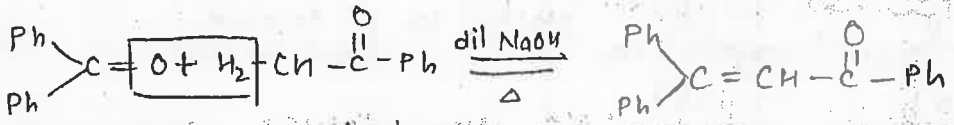
→ Two different type of carbonyl compound.

Whenever one aromatic aldehyde react with aliphatic aldehyde in aldol condensation then rxn is known as Classen Schmidt Rxn.

①

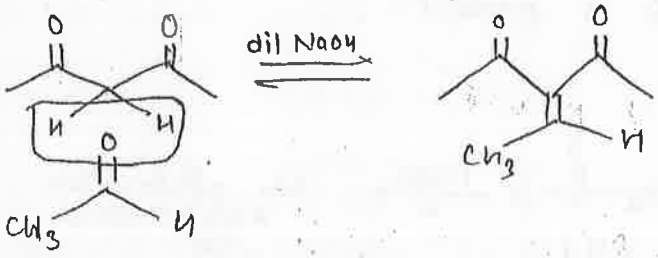
Aromatic Aldehyde — Aliphatic Aldehyde — α-β-unsaturated carbonyl comp (Cinnam Aldehyde)

(2)



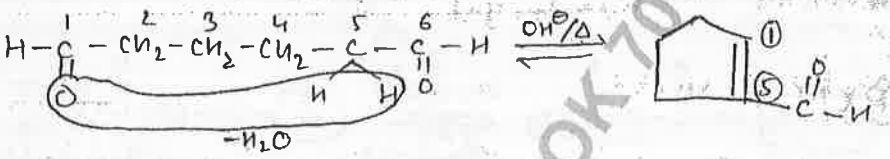
Benzophenone Acetophenone

(3)

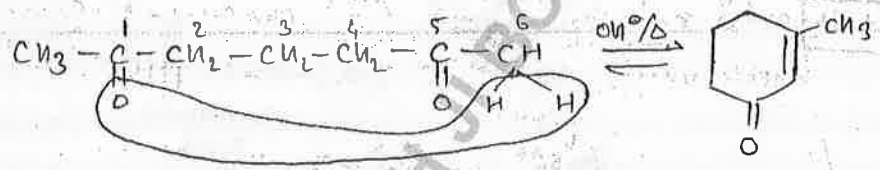


(3) Intramolecular aldol condensation →

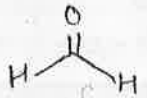
(i)

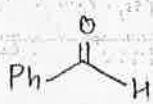


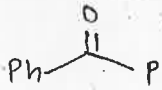
(ii)

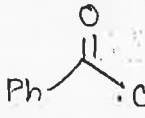


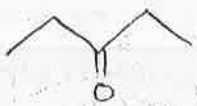
Q Which of the following compounds give aldol condensation Rxn.? [α-H Hona chahia]

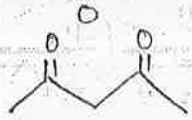
(1)  X

(2)  X

(3) 

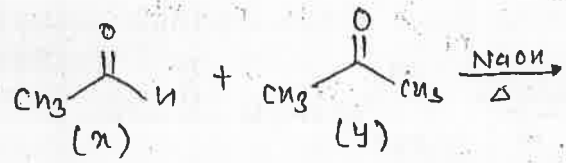
(4)  ✓

(5)  ✓

(6)  ✓

No. of possible aldol product :-

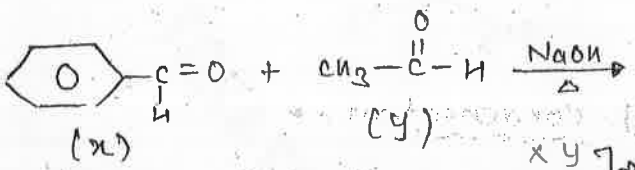
Q.1



No. of Possible Aldol Product.

X X
X Y
Y X
Y X
] ⇒ 4 product.

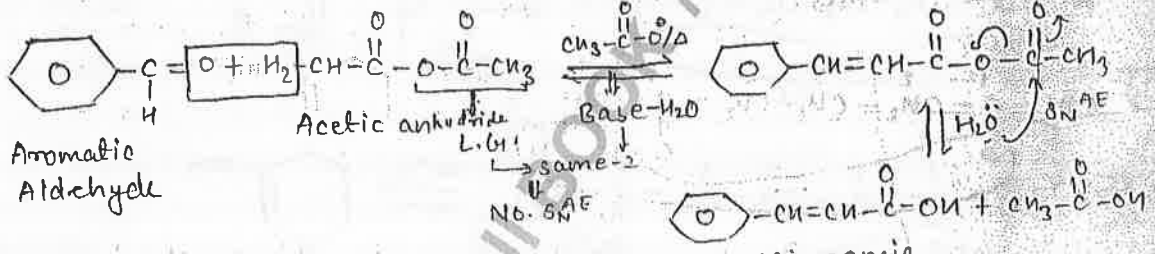
Q.2



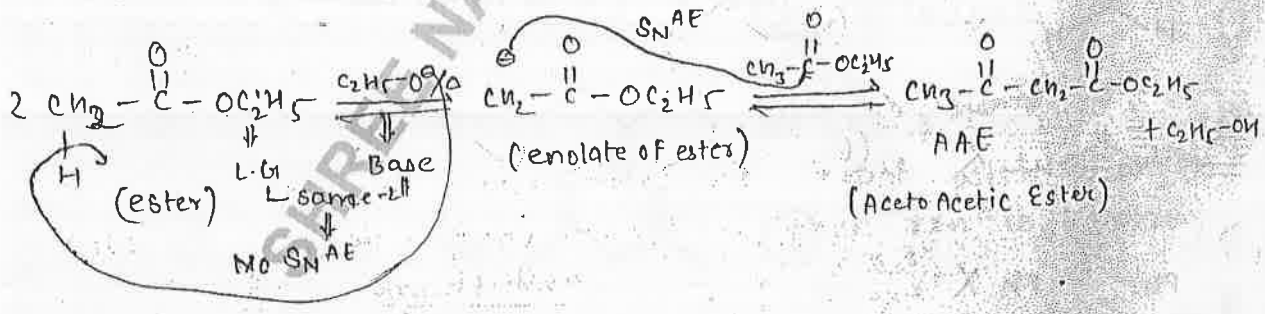
No. of Possible Aldol Product.

x y
y y
] ⇒ 2 product.

(2) PERKIN RXN :-



(3) CLAISENESTER CONDENSATION RXN :-

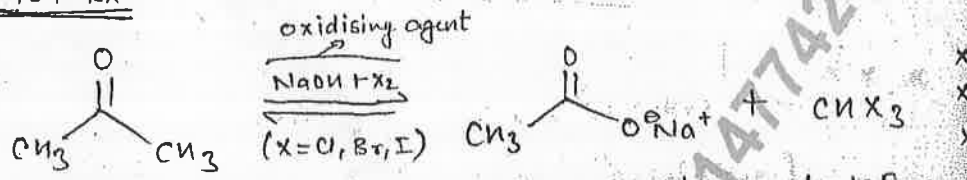


$CH_3 \rightarrow CH_3$

Halo Form Rxn / Iodo Form Rxn / α-halogenation Rxn.

		colour	use	test	
①	$CHCl_3$	colourless	Anasthetic	C–Cl → strong bond	Does not give white ppt with $AgNO_3$
②	CHI_3	Yellow	Antiseptic	C–I → Weak bond ⇒	give yellow ppt with $AgNO_3$

NET Rxn

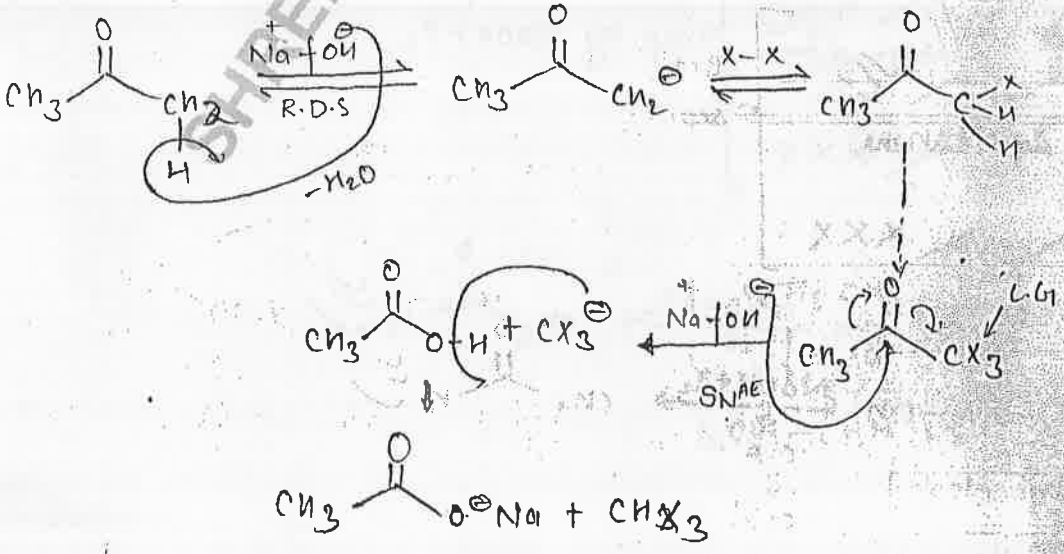


X = Cl (chloroform)
X = Br (Bromoform)
X = I (Iodoform)

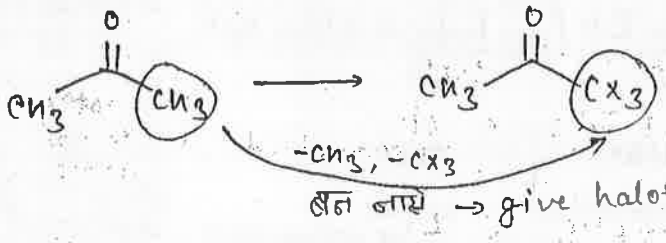
Salt of Acid — haloform

Reagent →
(I) X_2 + Alkaline medium (NaOH, KOH --- etc)
(II) $NaOH + I_2$
(III) NaOI (sod. hypohalide)
(IV) $\overset{\ominus}{O}I$
(V) $X_2 + Na_2CO_3 + H_2O$
(VI) $CaCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$

Mech

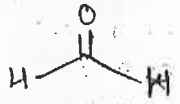


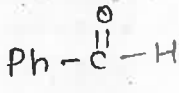
KEY POINT संभार रोगे comp $CH_3 \rightarrow CX_3$ बन जाए Give haloform rxn.

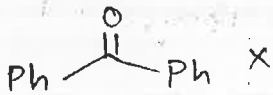


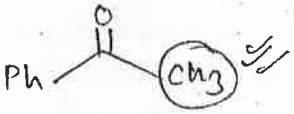
बन जाये → give haloform Rxn.

Q. Which of the following compound give positive test Iodoform test with $NaOH + I_2$:-

(1)  × × ×

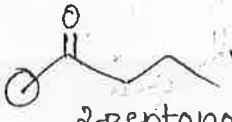
(2)  × × ×

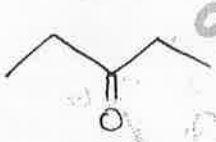
(3)  × × ×
Benzophenone

(4) 
Acetophenone

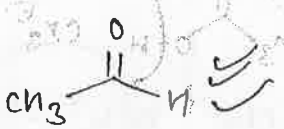
→ Both can be sep. by $NaOH + I_2$

(5)  × × ×

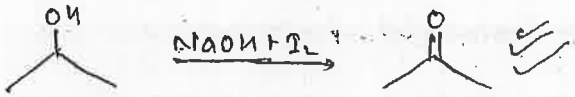
(6) 
2-pentanone

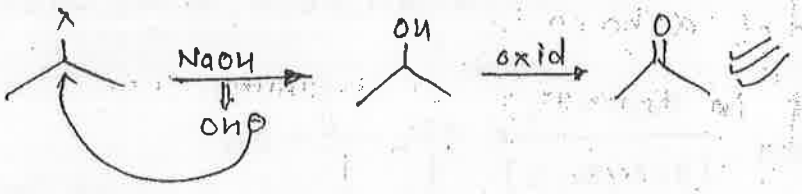
(7)  × × ×

→ Both can be sep. by $NaOH + I_2$

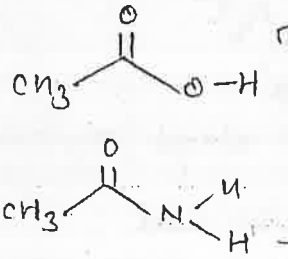
(8) $CH_3-CH_2-OH \xrightarrow{NaOH+I_2}$ 
ethyl Alcohol

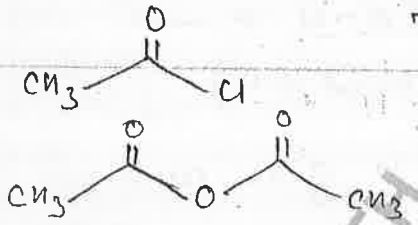
O.A
⇓
oxid

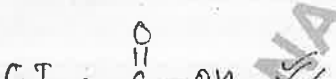
(9) 

(10) 

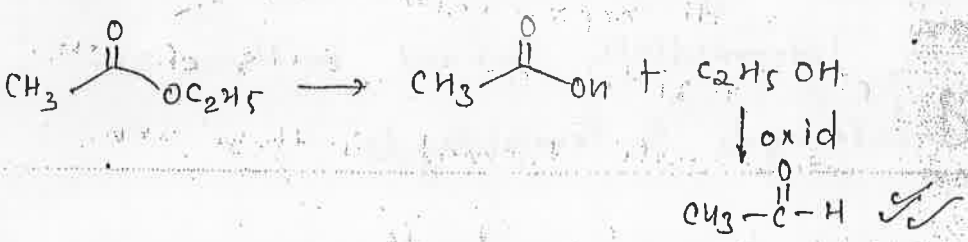
#Generally acid & acid derivaties does not give haloform Rxn due to presence of. L.G.

(11) 
→ No haloform Rxn
(First give Acid base)

(12) 
→ No halo form.
[L.G]

(13) 

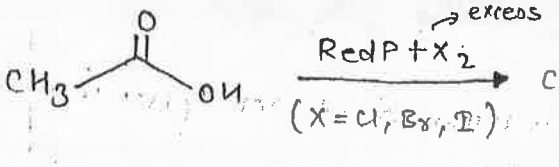
(14) 
(Active methylene)

(15) 

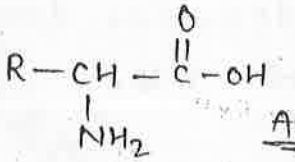
⑤ Hell Volhard zilensky (HVZ) Rxn →

Aim ⇒ Formation of α-haloacid.

Use ⇒ Rxn used in formation of α-amino acid.



α-halo Acid



Amino acid

‡ Total α-amino acid = 20

‡ All α-amino acid are optically active except Glycine

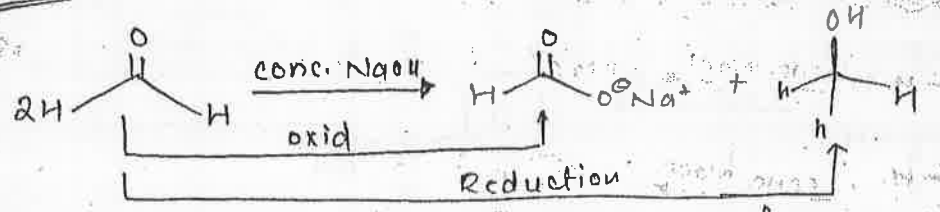
‡ All α-amino acid are naturally amino acid.

* CHEMISTRY WITHOUT α-H *

CANNIZARO RXN :- (Aldehyde without α-H)

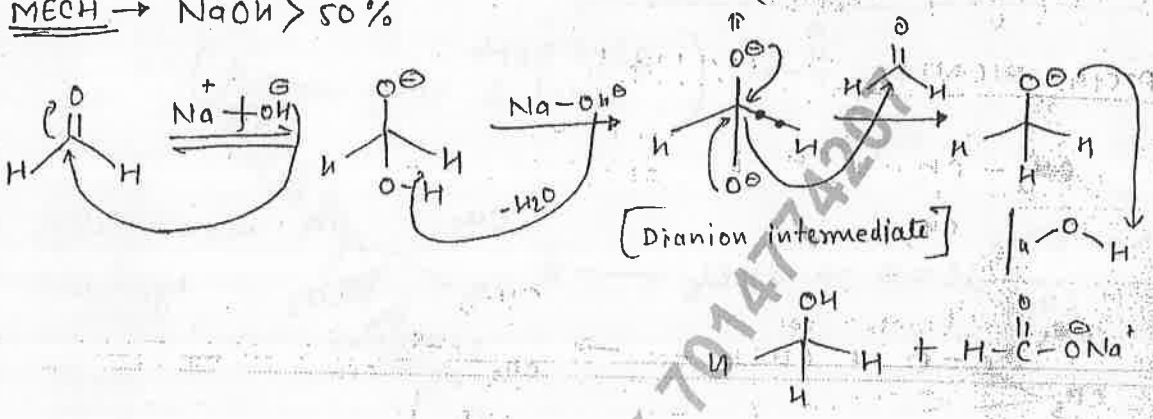
* Aldehyde don not having α-H give cannizaro Rxn
* It is carried out in conc. alkaline medium.
* . Conc. NaOH
  excess NaOH
  50% NaOH
  ⇒ conc. alkaline medium.
* Cannizaro is a disproportination rxn
* Shifting of hydride ion is RDS of rxn.
* Dianion intermediate Formed in these rxn.
* Eg. benzaldehyde & formaldhyde

NET Rxn



MECH → NaOH > 50 %

oxid = $(H-\overset{O}{\overset{\|}{C}}-O^{\ominus})$



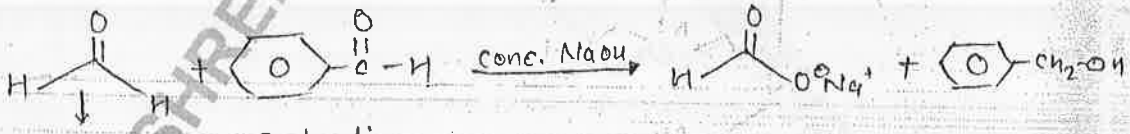
* Type of Cannizaro Rxn

(A) Simple cannizaro Rxn

Same type of aldehyde.

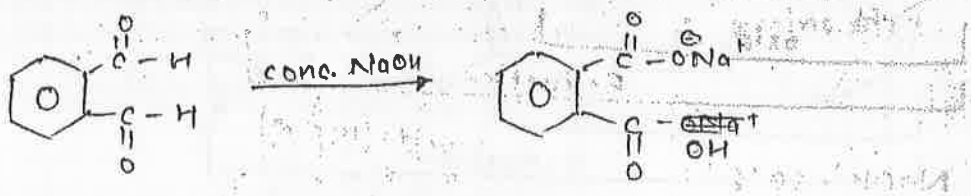
(1) 2 

(B) Mixed / cross cannizaro Rxn :-

(1) 

(III) Intramolecular cannizaro Rxn :-

(i) $H-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H \xrightarrow{\text{conc. NaOH}} Na^{\oplus}O^{\ominus}-\overset{O}{\overset{\|}{C}}-CH_2-OH$

(ii) 

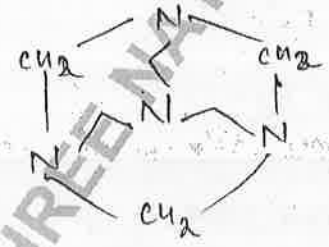
SPECIAL POINTS TO REMEMBER

(1) $CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{O}{\overset{\|}{C}}-H$ (give both Aldol & cannizaro Rxn)

(2) $(CH_3)_2C=O + CCl_3 \longrightarrow (CH_3)_2C(OH)CCl_3$ chlorotone — use ⇒ sedative & hypnotic.

(3) $CHCl_3 + HNO_3 \longrightarrow CCl_3-NO_2$
Tear gas / chloropicrin / Nitro chloro methane

(4) $6\,HCHO + 4\,NH_3 \longrightarrow (CH_2)_6N_4$ use ⇒ Diuretics
↓
UROTROPINE



* AROMATIC COMPOUNDS *

Reagent of Aromatic compounds :-

① ① n-hexane → Al_2O_3/Δ / Cr_2O_3/Δ / Mo_2O_3/Δ (Ar, Cr, Mo) → Aromatising agent

② n-heptane → (Ar, Cr, Mo) → CH_3

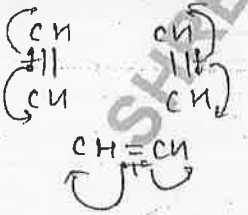
③ n-butane → $AlCl_3 + HCl$ → (iso-butane)

Branching (Isomerisation) → Both are C.I

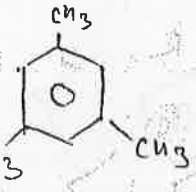
② OH → Zn Dust → Deoxygenation

Fenton Reagent ($Fe^{+2} + H_2O_2$)

③ $3\ CH \equiv CH$ → Red hot Fe tube



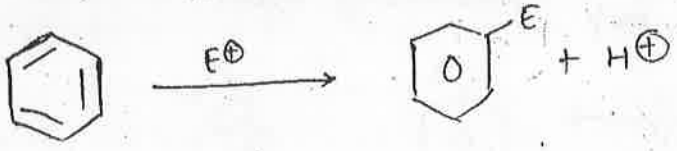
④ $CH_3 - C \equiv CH$ → Red hot Fe tube → Mesitylene



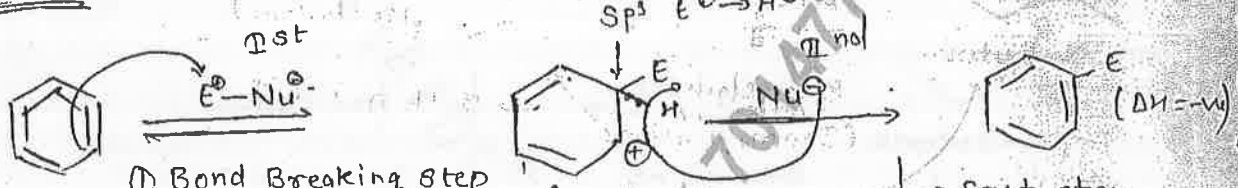
* Aromatic compound mainly give ESR - rxn.
FSR - is characteristick of rxn of Aromatic comp.

E.S.R / S_E - Rxn

[Electrophillic Substitution Rxn].



MECH



① Bond Breaking step
★② Slowest Step
★③ RDS
④ Aromaticity Break

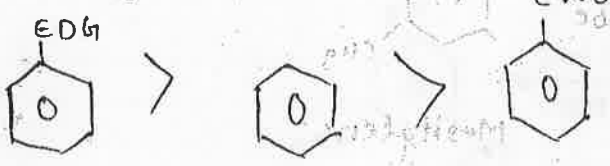
(N.A)
⇒ σ - complex
⇒ Arrenium Complex
⇒ Wheland complex

→ Fast step
→ Bond forming step
→ Aromatic

* Reactivity of ESR ∝ stability of intermediate
(c+ intermediate)
(σ-complex)

$$\propto \frac{+M/+H/+I}{-M/-H/-I}$$

* Reactivity of E.S.R



* Two step rxn

* Generally in ESR 1st step (Aromaticity break) is the RDS of rxn but in case of sulphonation & iodination 2nd step is R.D.S of rxn.

* In case of sulphonation & iodination rxn give K.I.E.

* Rate expression (r) =

$$r_{C_6H_6} = r_{C_6D_6} = r_{C_6T_6}$$

→ Ist step is R.D.S

Eg. halogination, Nitration, FCR

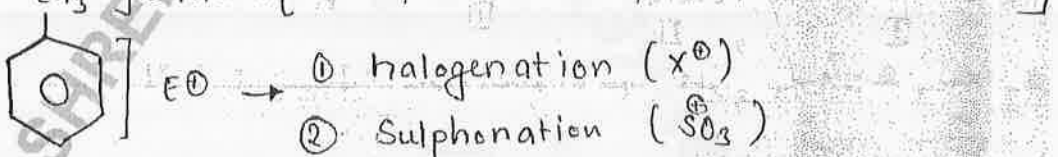
rate expression (r)

$$r_{C_6H_6} > r_{C_6D_6} > r_{C_6T_6}$$

⇒ IInd step is R.D.S

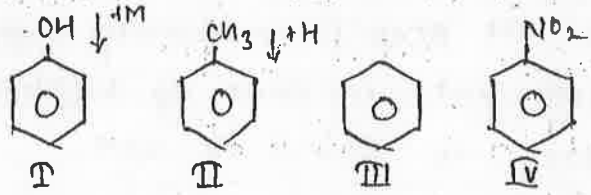
Eg. Sulphonation, Iodination Rxn.

KEY POINT



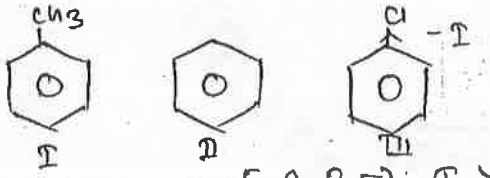
Q. Find correct reactivity order for ESR in given compounds:

(1)



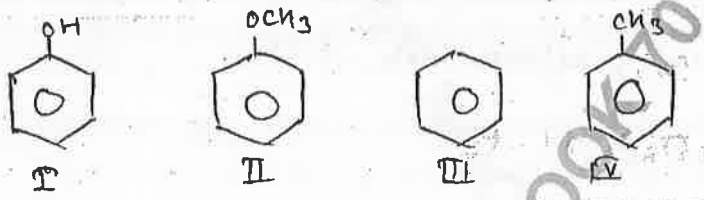
Reactivity of ESR ⇒ I > II > III > IV

(2)



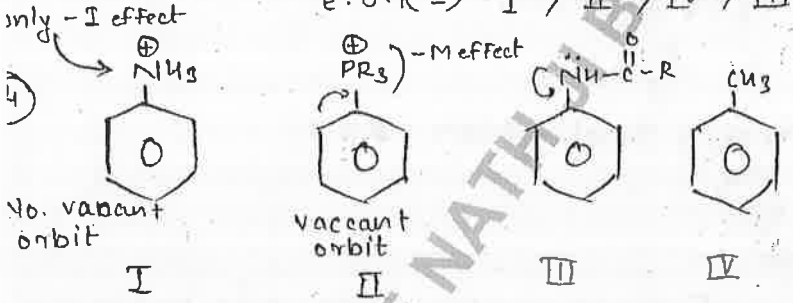
E.S.R ⇒ I > II > III

(3)



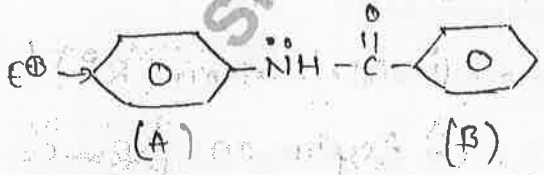
E.S.R ⇒ I > II > IV > III

(4)



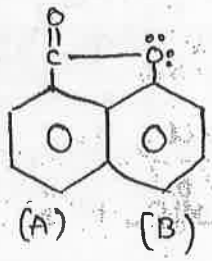
E.S.R ⇒ III > IV > I > II

(5)



Reactivity ⇒ A > B

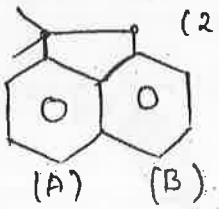
(6)



(A) (B)

E.S.R ⇒ B > A

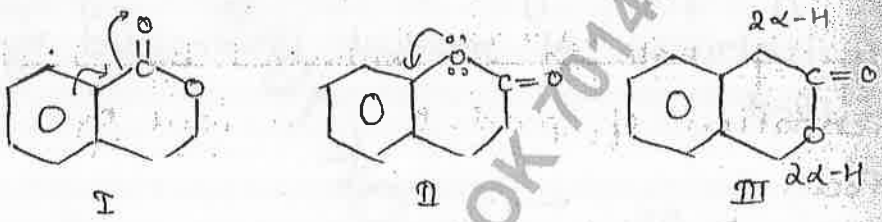
(7)



(A) (B)

E.S.R ⇒ B > A

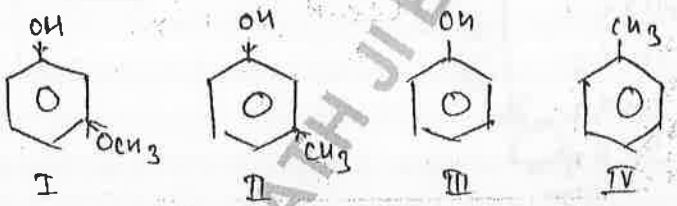
(8)



I II III

Reactivity order ⇒ II > III > I

Q9



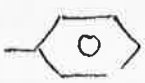
I II III IV

E.S.R ⇒ I > II > III > IV

NOTE

Activating group

- Strong Activating group ⇒ $-O^{\ominus}$, $-\ddot{N}\begin{matrix}R\\R\end{matrix}$, $-\ddot{N}H-R$, $-NH_2$ etc
- Moderate Activating group ⇒ $-OR$, $-\ddot{N}H-\overset{O}{\overset{\|}{C}}-R$, $-O-\overset{O}{\overset{\|}{C}}-R$
- Weakly Activating group ⇒ $-CH_3$, $-CH_2-CH_3$, $-CH\begin{matrix}CH_3\\CH_3\end{matrix}$, $-CH=CH$

 ... etc.

Deactivating group

- Strong deactivating group ⇒ $-\overset{\oplus}{N}R_3$, $-\overset{\oplus}{N}H_3$, $-NO_2$, $-C\equiv N$, $-CCl_3$ etc.
- Moderate deactivating group ⇒ $-\overset{O}{\overset{\|}{C}}-OH$, $-\overset{O}{\overset{\|}{C}}-H$, $-\overset{O}{\overset{\|}{C}}-Cl$, $-\overset{O}{\overset{\|}{C}}-OR$. etc.
- Weakly deactivating group ⇒ $-F$, $-Cl$, $-Br$, $-I$

* All halogens are Weakly deactivating group but ortho, para-directing group.

* Reactivity of halogen is controlled by $-I$ effect but orientation of product is decided by $+M$ effect.

Strong Lewis Acid ⇒ BX_3, BeX_2, AlX_3, SbX_5, ZnX_2, SnX_4

Weak L.A ⇒ FeX_3

HALOGENATION RXN

$E^{\oplus} \Rightarrow X^{\oplus}$

Rxn

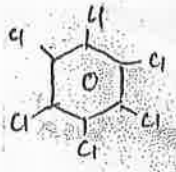
formation of $E^{\oplus}$ →

① $X-X \xrightarrow[(Anhyd)]{AlX_3} X^{\oplus} + AlX_4^{\ominus}$

(II) $X-X \xrightarrow[(Anhyd)]{FeX_3} X^{\oplus} + FeX_4^{\ominus}$

(III) $2Fe + 3X_2 \longrightarrow 2FeX_3$ (Same-2)

(IV) $X-\ddot{O}H \xrightarrow{H^{\oplus}} X-\overset{+}{O}\begin{matrix}H\\H\end{matrix} \longrightarrow X^{\oplus}$

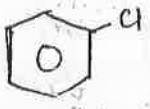


(E.S.R)

Hexachloro benzene

Q.1

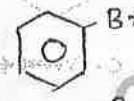
$\xrightarrow[Cl^{\oplus}]{Cl-Cl/AlCl_3\ (Anhyd)}$



(E.S.R)

Chlorobenzene

$\xrightarrow[Br^{\oplus}]{2Fe + 3Br_2}$

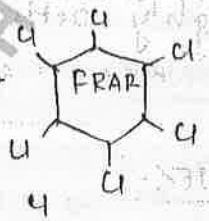


(E.S.R)

Bromobenzene

$\xrightarrow[\text{or } Cl_2 \text{ Non-polar medium}]{Cl_2,\ In\ Dark}$ No Rxn.

$\xrightarrow[High\ temp]{Cl_2,\ h\nu}$

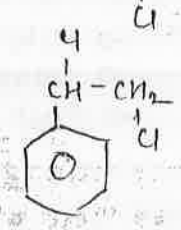


BHC / Gamexene / 666

Q.2

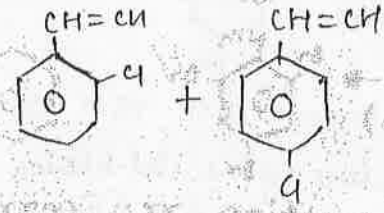
styrene

$\xrightarrow{Cl_2, CCl_4}$



(Anti Addition)

$\xrightarrow[Cl^{+}]{Cl-Cl/AlCl_3\ (Anhyd)}$



$Br_2, Cl_2, HBr + KBrO_3 \rightarrow$ Weak or Neutral $E^{\oplus}$

$\Downarrow$

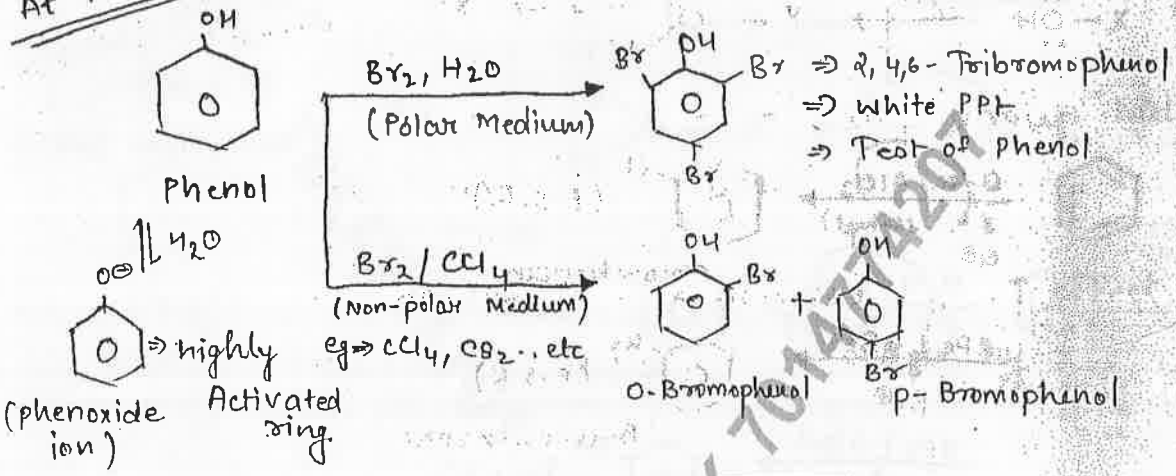
Br_2

$\Downarrow$

Only attack at highly activated ring

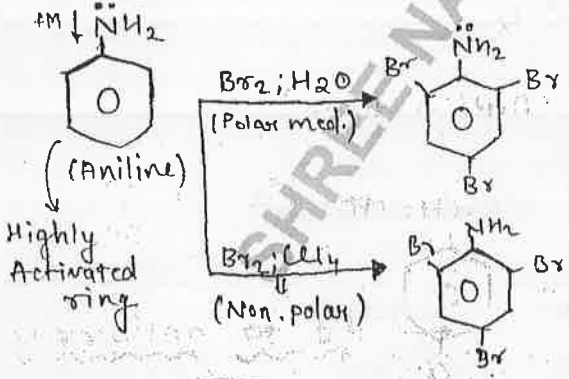
1.3

Halogenation At Phenol



* Whenever halogenation Rxn carried out at phenol in aq medium then due to acid-base rxn phenol change into phenoxide ion & Ring will be highly activated give tribromo product this rxn is known as test of phenol.

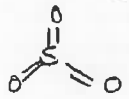
HALOGENATION AT ANILINE:-



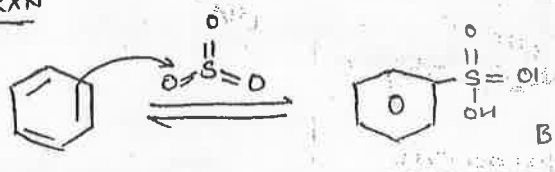
⇒ 2,4,6-Tribromo Aniline
⇒ White PPt
⇒ Test of Aniline

* Whenever halogenation rxn carried out at aniline then ative aniline give tri-bromo product in both polar & Non-polar medium becoz $[\ddot{N}H_2]$ having strong Activating group.

② SULPHONATION RXN :

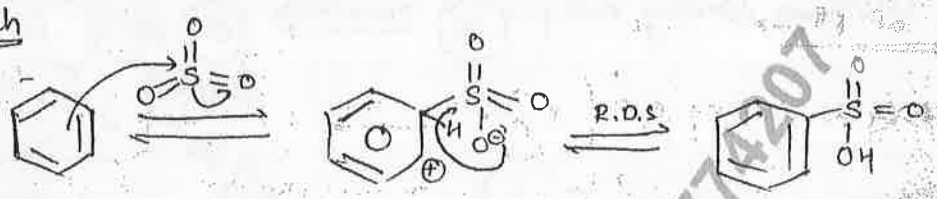
$E^{\oplus} \Rightarrow$ 

NET RXN



Benzen sulphonic acid

Mech

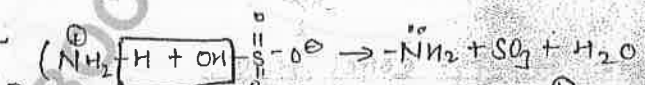


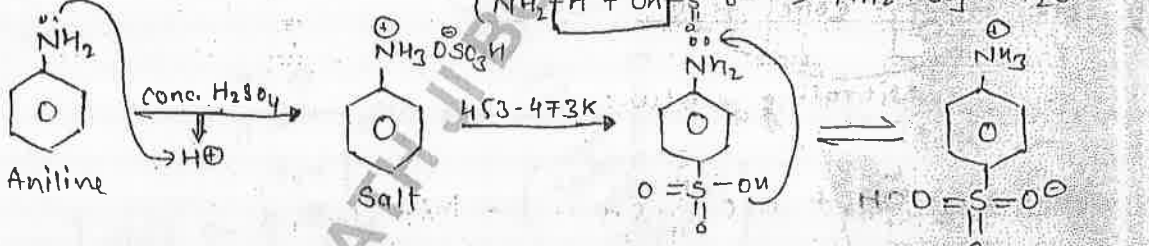
formation of $E^{\oplus} \Rightarrow$

① $H_2S_2O_7 \xrightarrow{\Delta} SO_3 + H_2SO_4$ (best)

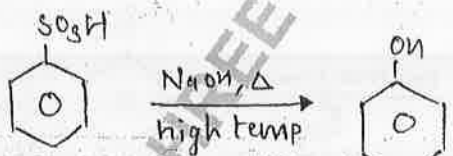
② Conc. H_2SO_4

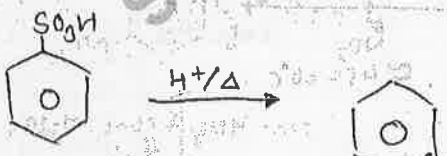
Sulphonation of aniline





Aniline — Salt — p-sulphonic Acid — (zwitter ion)

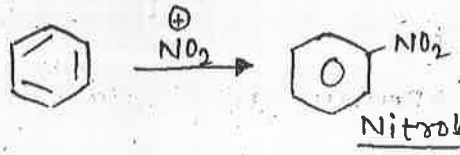




③ NITRATION Rxn :-

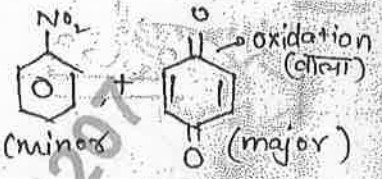
$E^{\oplus} \Rightarrow \overset{\oplus}{N}O_2$

NET Rxn



Nitrobenzene

formation of $E^{\oplus}$ →

① conc. HNO_3 ⇒ Strong O.A ( $\xrightarrow{\text{conc. } HNO_3}$ 

P-Benzoquinone

② conc. $HNO_3 \rightarrow$ conc. $NO_2-\ddot{O}H + H-O-NO_2 \longrightarrow$ conc. $NO_2-\overset{+}{O}(H)(H)$

Auto/self ionisation.

$\downarrow H_2O$

$NO_2^{\oplus}$ ⇒ Rate ⇓

③ conc. HNO_3 + conc. H_2SO_4

Nitrating mixture.

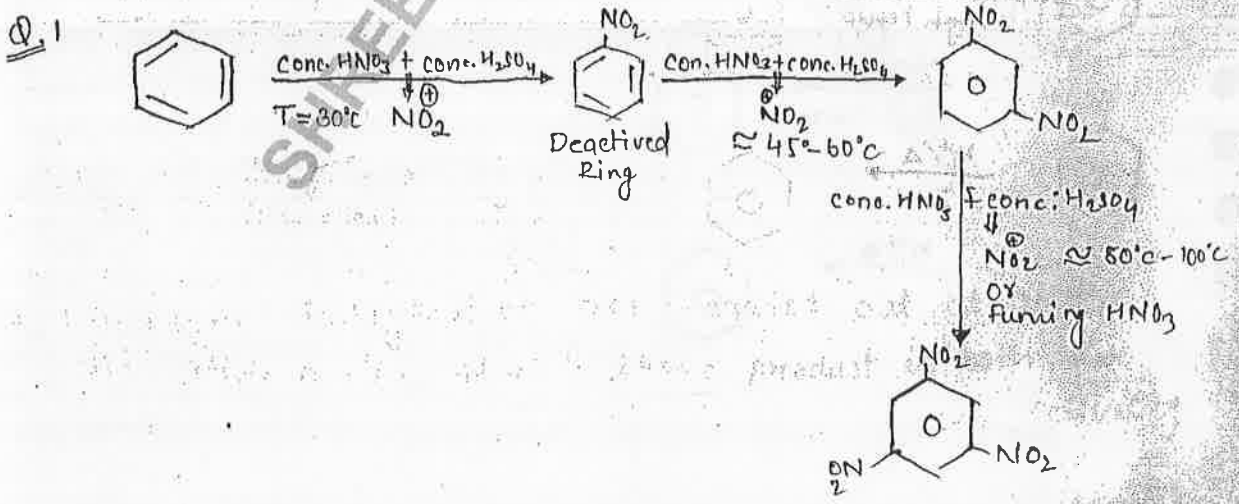
conc. $NO_2-\ddot{O}H$ + $H-O-\overset{O}{\underset{O}{S}}(=O)-OH$ $\longrightarrow$ $NO_2-\overset{\oplus}{O}(H)(H)$

(Behave as Base) (Behave as Acid)

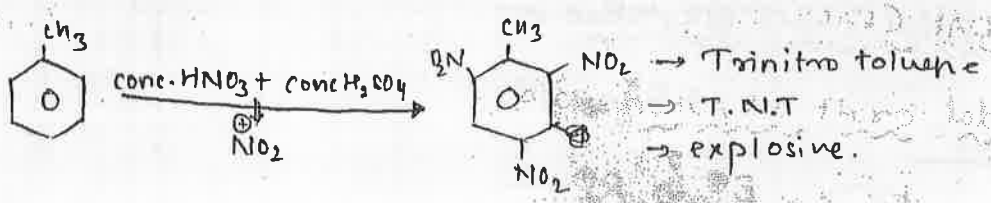
$\downarrow H_2O$

$NO_2^{\oplus}$ ⇑ ⇒ Rate ↑

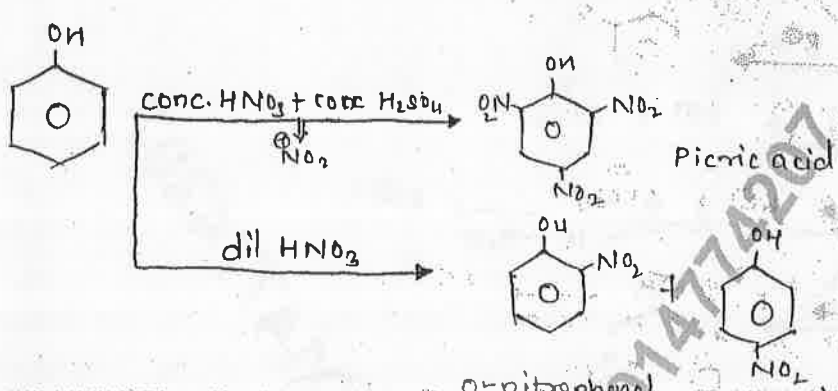
conc. $HClO_4$ ⇒ Rate ⇑

Q.1 

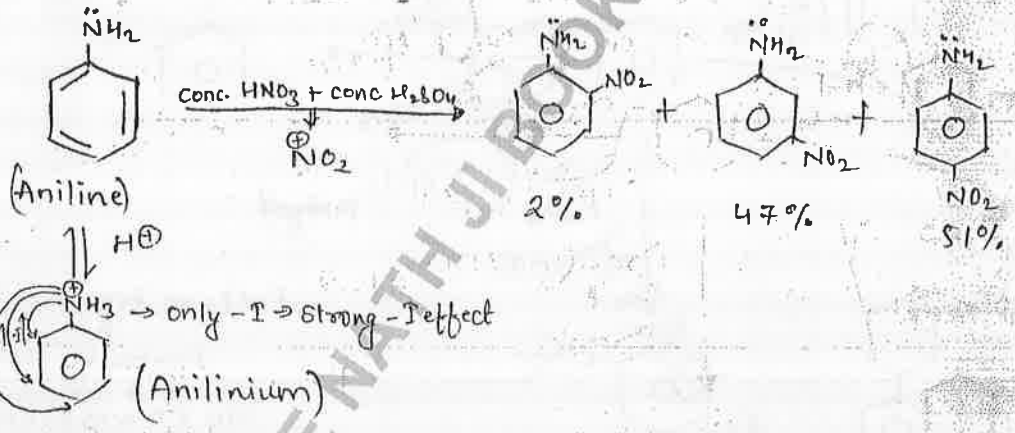
Q.2



Q.2



Q.4 Nitration At Aniline :-



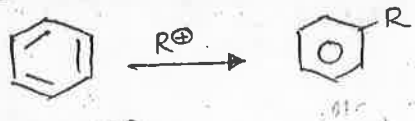
* Whenever ~~halogenat~~ nitration rxn carried out at aniline then due to acid base rxn b/w lone pair of nitrogen atom & H^+ aniline change into anilinium ion. & ring will be highly deactivated.

④ FRIEDAL CRAFT Rxn :-

Ⓐ friedal craft alkylation ⇒

$E^{\oplus} \Rightarrow R^{\oplus}$

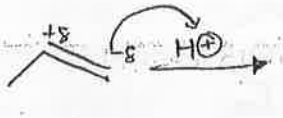
NET Rxn

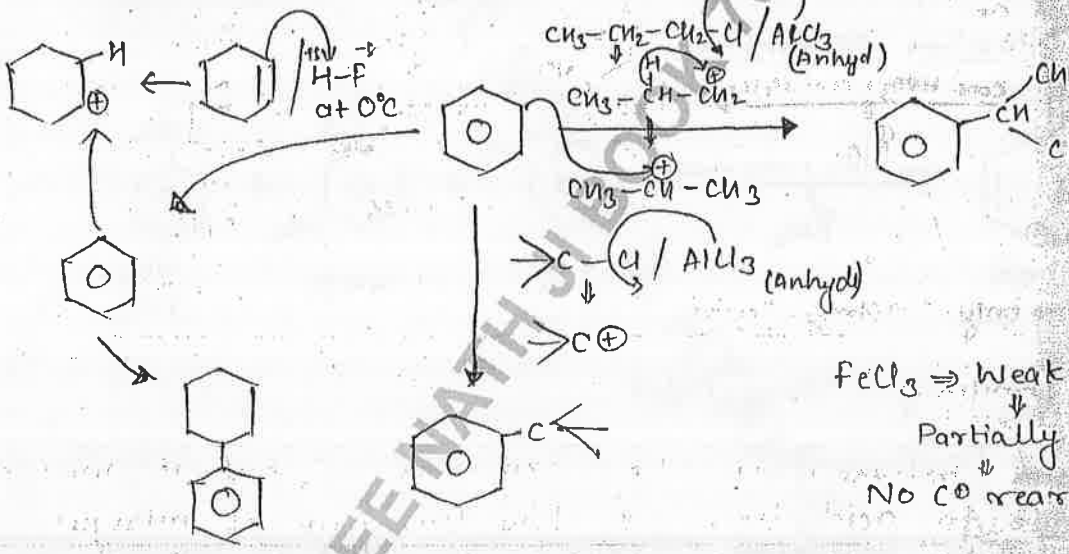


Formation of $E^{\oplus}$ ⇒

① $R-Cl \xrightarrow[(Anhyd)]{AlCl_3} R^{\oplus} + AlCl_4^{\ominus}$

② $R-\ddot{O}H \xrightarrow{H^{\oplus}} R-\overset{\oplus}{O}(H)(H) \xrightarrow{-H_2O} R^{\oplus}$

③ 



$FeCl_3$ ⇒ Weak L.A
⇓
Partially $c^{\oplus}$
⇓
No $c^{\oplus}$ rearrangement

Ⓑ friedal craft Acylation Rxn :-

$E^{\oplus} \Rightarrow R-\overset{\oplus}{C}=O$ / $R-C\equiv O^{\oplus}$

Acyliniun ion

$\{ >C-\overset{\oplus}{C}=\ddot{O} \Rightarrow >C^{\oplus} + CO \}$

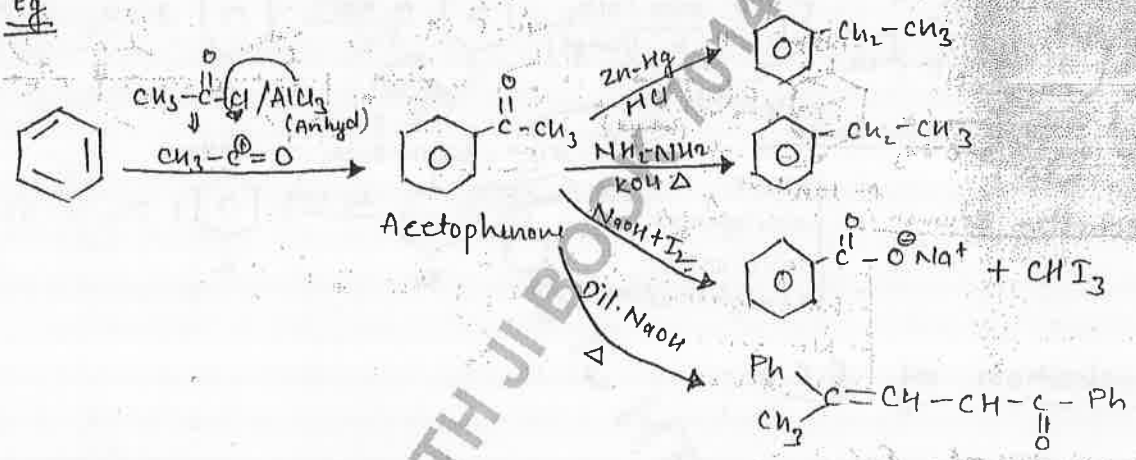
formation of $E^{\oplus}$ →

(i) $R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[(Anhyde)]{AlCl_3} R-\overset{\oplus}{C}=O + \overset{\ominus}{AlCl_4}$

(ii) $R-\overset{O}{\overset{\|}{C}}-\ddot{O}H \xrightarrow{H^{\oplus}} R-\overset{O}{\overset{\|}{C}}(\overset{\oplus}{OH}H) \longrightarrow R-\overset{O}{\overset{\|}{C}}\oplus + H_2O$

(iii) $R-\overset{O}{\overset{\|}{C}}-\ddot{O}-\overset{O}{\overset{\|}{C}}-R \xrightarrow[(Anhyd)]{AlCl_3} R-\overset{O}{\overset{\|}{C}}(\overset{\oplus}{O}-\overset{\ominus}{AlCl_3})-\overset{O}{\overset{\|}{C}}-R \longrightarrow R-\overset{O}{\overset{\|}{C}}\oplus$

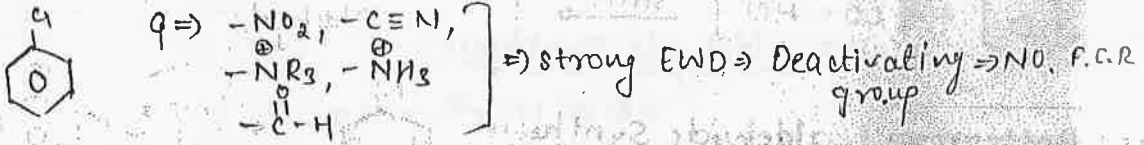
Eg.



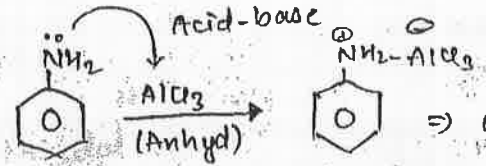
* FCR rxn used for formation of DDT, bakelite polymer & phenopthalin indicator.

Diadvantage of FCR :-

* Highly deactivated ring does not give F.C.R rxn because $R^{\oplus}$, $R-\overset{\oplus}{C}=O$ is a weak electrophile [$E^{\oplus}$]



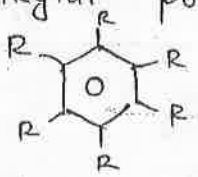
* Aniline does not give f.c.R rxn Due to Acid-base rxn b/w lone pair of nitrogen atom & lewis Acid aniline change into anilinium ion & ring will be deactivated.

(11) 

⇒ N.D. F.C.R

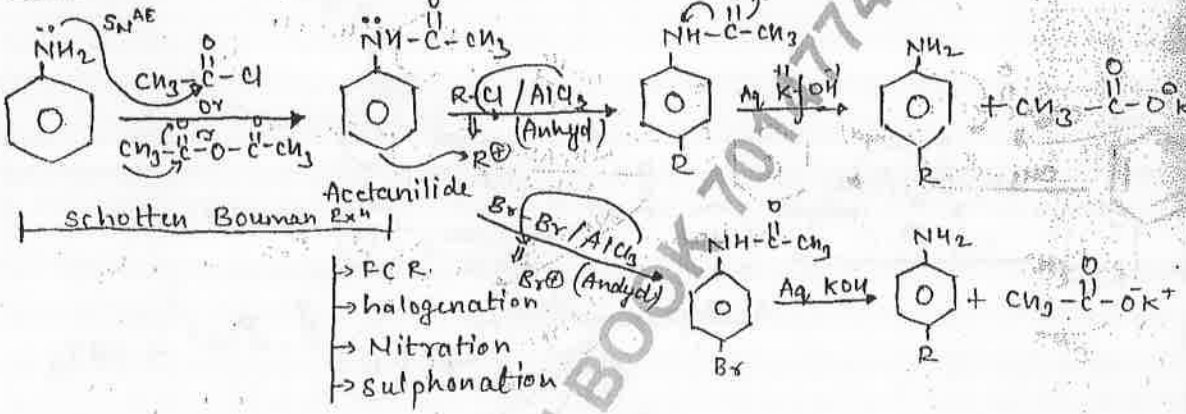
Anilinium.

) In ~~F.C~~ F.C alkylat^n polyalkylated product formed



Nitro-benzene used as a solvent in f.c.R rxn :-

Protection of Aniline →



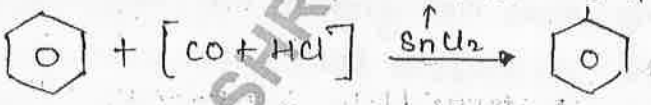
Application of F.C.R :-

) Formylation Rx^n :-

(A) Gatterman's Koch Rx^n →

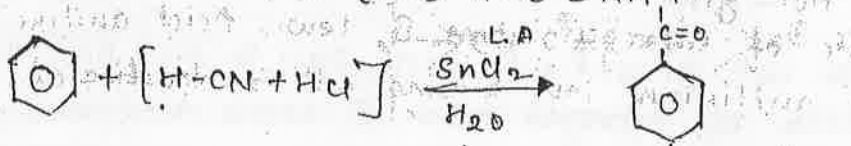
$[CO]$

$E^{\oplus} \Rightarrow H-\overset{\oplus}{C}=O \longleftrightarrow H-C\equiv O^{\oplus}$



) Gatterman's aldehyde Synthesis :-

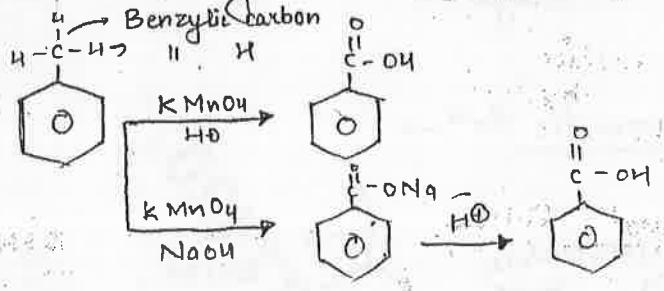
$E^{\oplus} \Rightarrow H-C^{\oplus}=NH\,H$



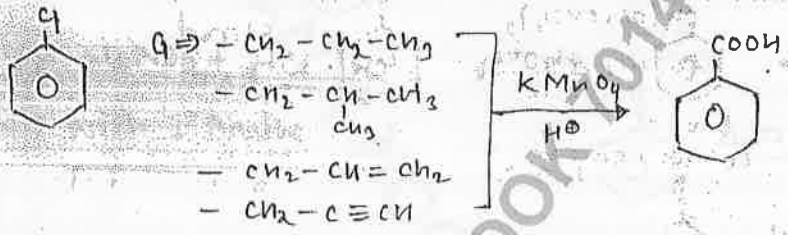
Oxidation of Aromatic Compound.

(A) Oxidⁿ by Strong Oxidising agent.

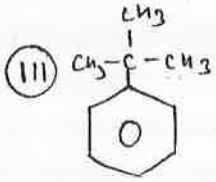
(I) Oxidation by $KMnO_4$ [H^+/NaOH] →



(II)



(III)



No Rxⁿ.

(IV)

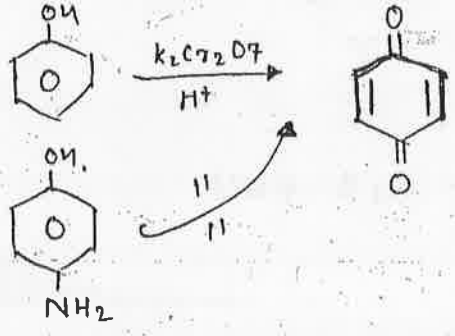
No Rxⁿ

(B) Oxidation by $K_2Cr_2O_7$ →

(I)

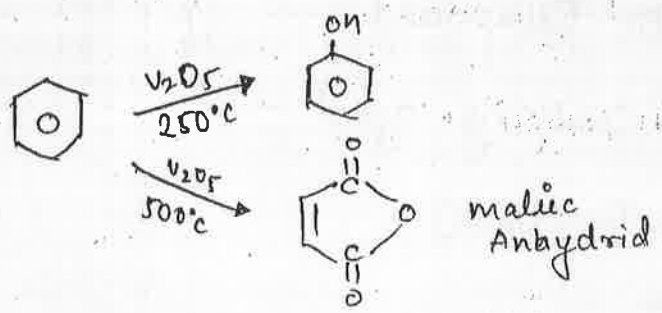
No Rxⁿ

(II)

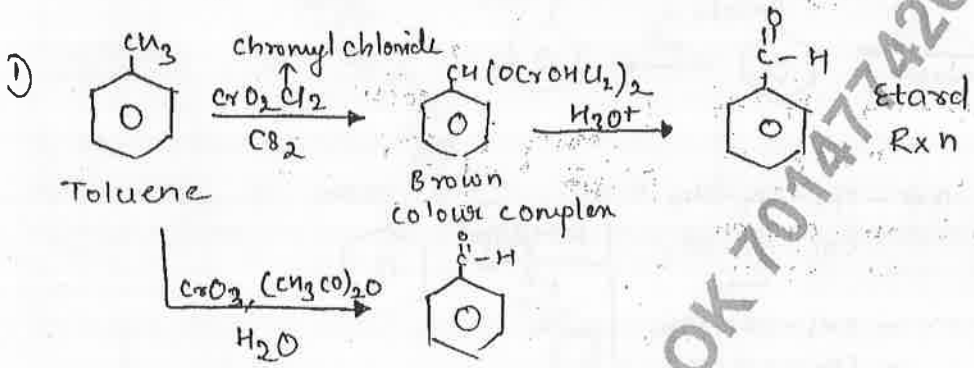


P-Benzoquinone

③ Oxidation by $V_2O_5/\Delta \rightarrow$



② Partially oxidⁿ of Aromatic Rxⁿ →



AMINE

* Test of Amine.

+ Diazotisation Rxn

$-NH_2 \xrightarrow[(0°-5°C)]{NaNO_2+HCl} -\overset{\oplus}{N_2}\ (-N\equiv N) \longrightarrow N_2\uparrow$

Poor L.G — Best L.G — (stable gas)

Reagent

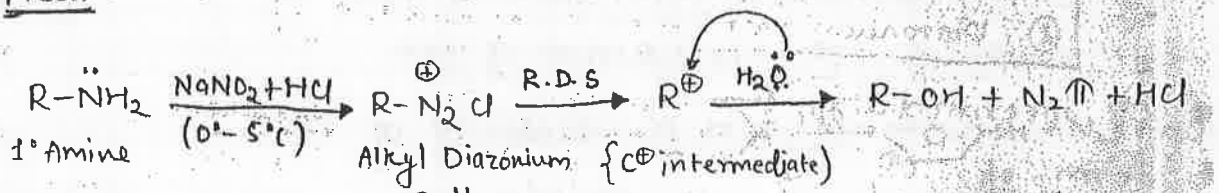
$NaNO_2 + HCl$
or
$HNO_2 + HCl$ ⇒ दोनों
or
HNO_2

NET Rxn

$R-\ddot{N}H_2 \xrightarrow[(0°-5°C)]{NaNO_2+HCl} R-OH + N_2\uparrow + HCl$

1° Amine — (major)

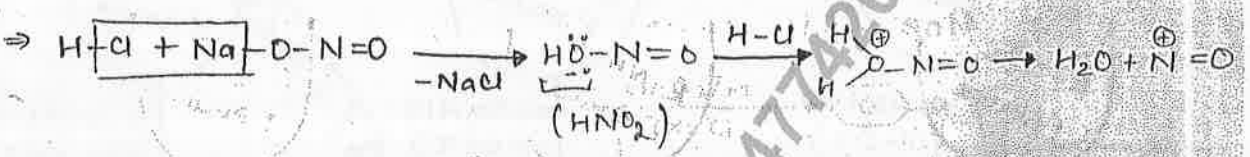
Mech



$NaNO_2 + HCl \rightarrow \overset{\oplus}{N}{=}O \;/\; H_2O$

↓

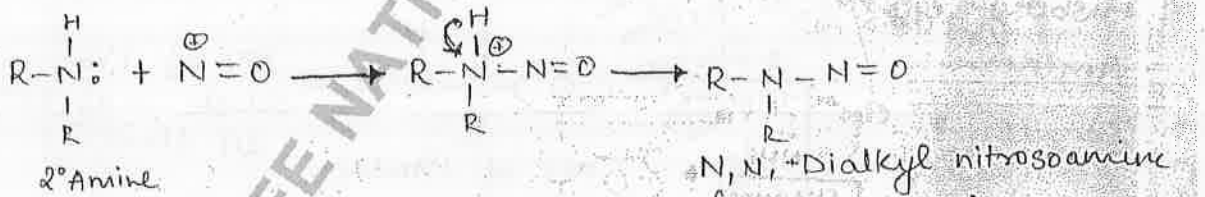
Nitrosonium ion → Behave as $E^{\oplus}$



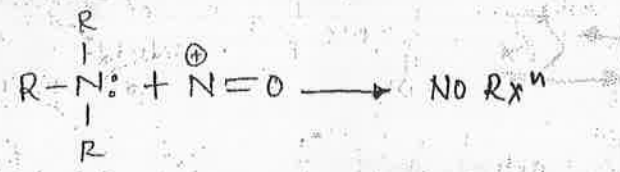
Rxn of $NaNO_2 + HCl$ with diff. Amine →

① Rxn with 1° Amine :-

② Rxn with 2° Amine :-



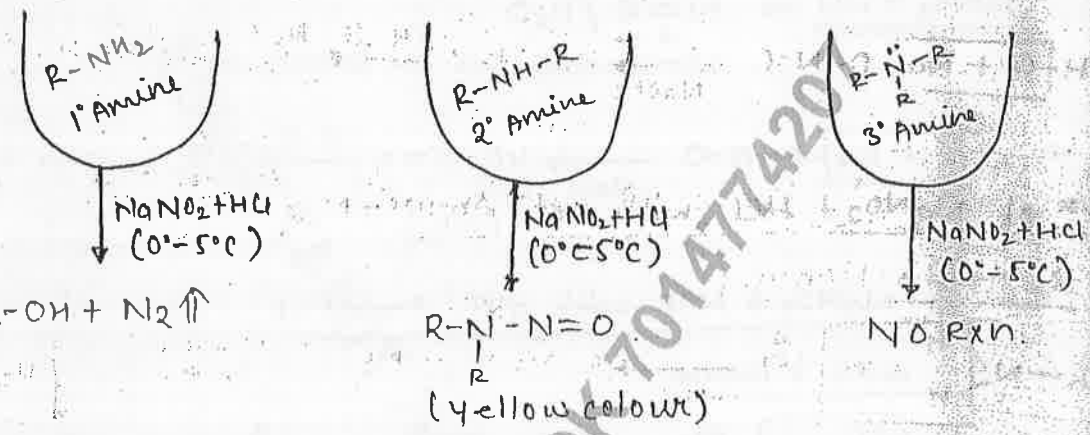
③ Rxn with 3° Amine :-



① ESR rxn in Aromatic comp → C⊕

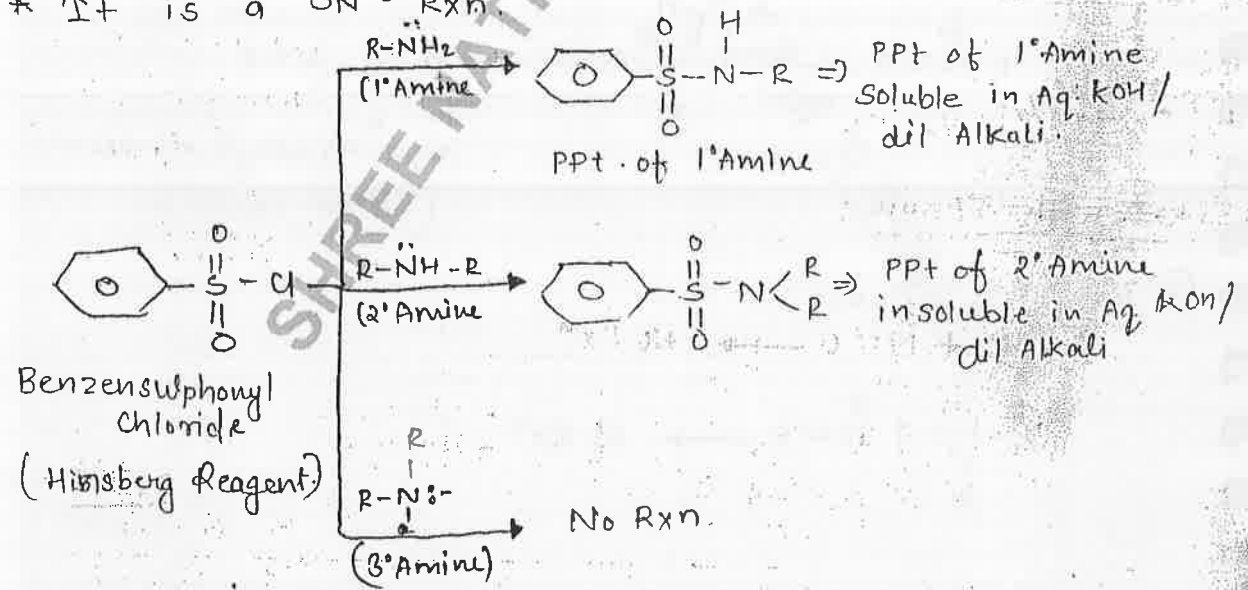
② Diazonium salt → C⊕ intermediate

* C⊕ intermediate form in this rxn.
* form of C⊕ is R.D.S of rxn.
* Reactivity of rxn ∝ Stability of C⊕
* C⊕ rearrangement possible.

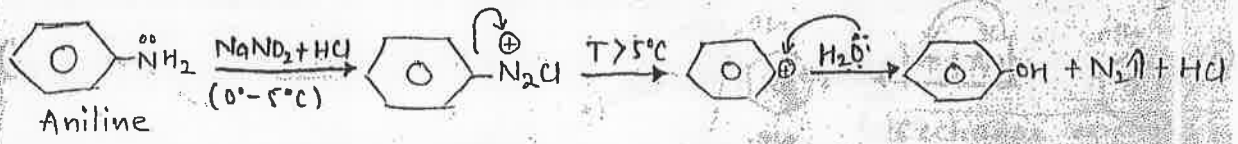


Rxn of Amine with Hinsberg Reagent:-

* Hisberg reggent, used for identification of 1°, 2°, 3° Amine.
* It is a S_NAE Rxn.

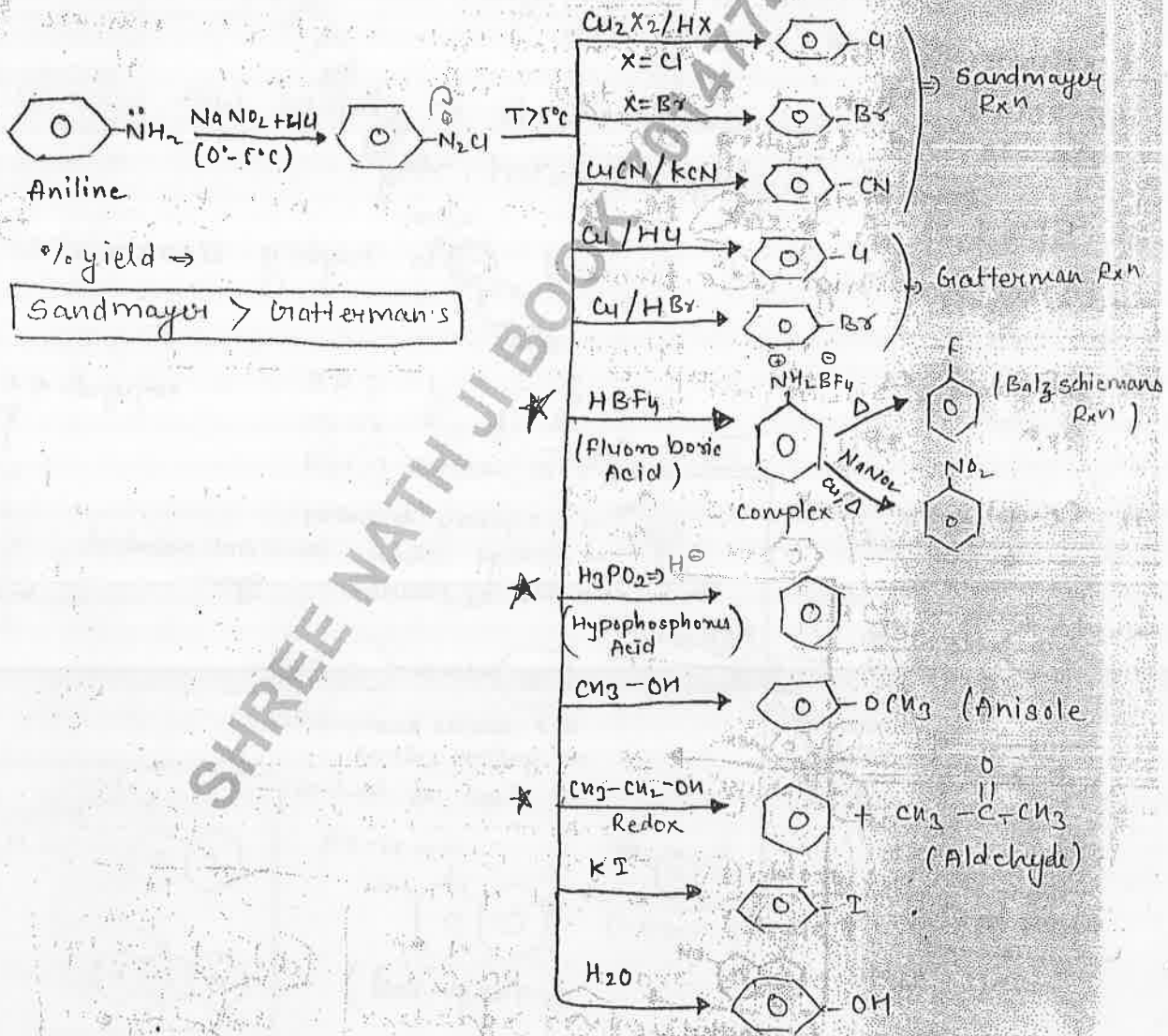


CHEMISTRY OF BENZENE DIAZONIUM SALT



Aniline — Benzendiazonium Salt. (Reso. Satablised) — Arylcation ($S_N{}^{1}Ar$)

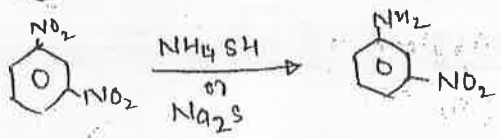
* Rxn completed with $S_N{}^{1}Ar$ Mech. This is rare mech. and only observed in Benzendiazonium salt.



% yield ⇒ Sandmayer > Gattermann's

(i) $CH_3-NH_2 \xrightarrow[(0^\circ-5^\circ C)]{NaNO_2+HCl} CH_3-O-CH_3$

(ii) 

(iii) 

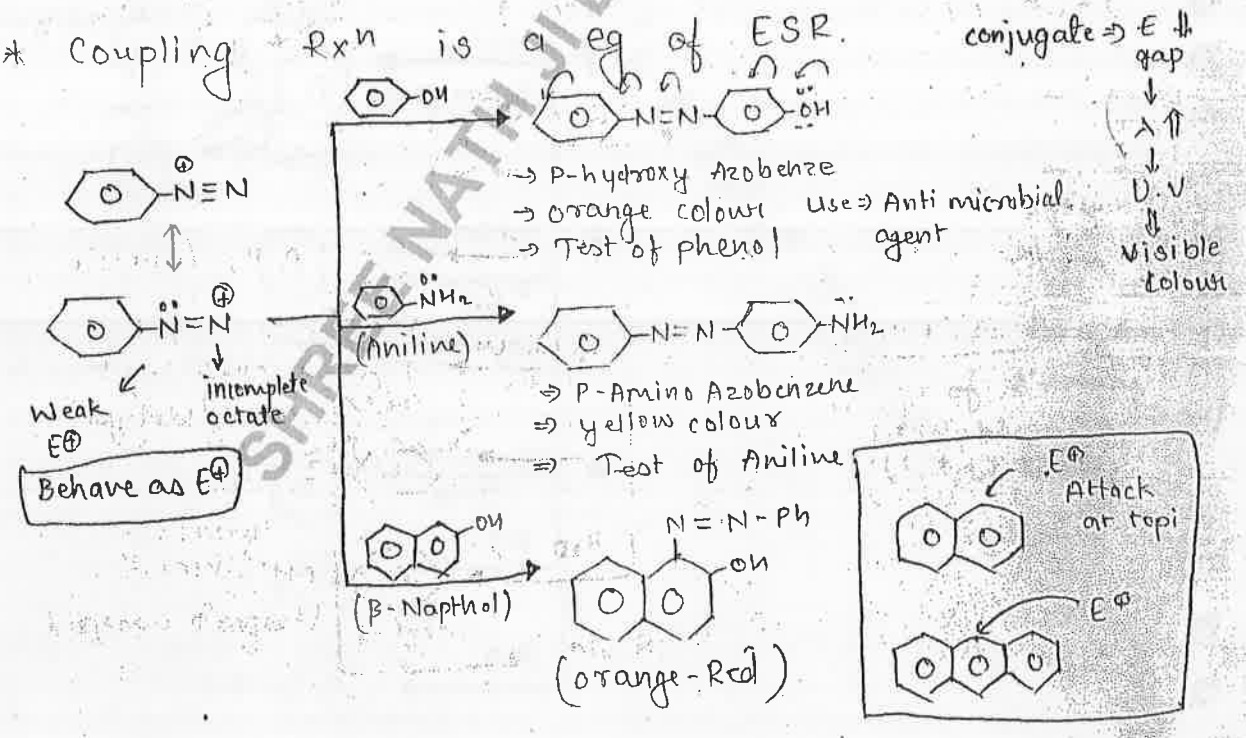
COUPLING RXN

* Whenever Benzene diazonium salt react with aromatic compound then it form dyes / indicator product. This rxn is cld Coupling rxn.

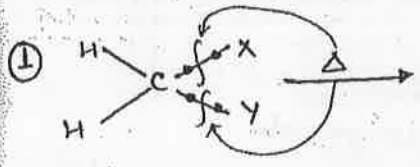
* BDS is a weak $E^{\oplus}$ so it coupled with benzene Ring or highly activated ring.

* BDS does not coupled with highly deactivated Rxn

* Coupling Rxn is a eg of ESR.



CHEMISTRY OF CARBENE

① 

/ $\overset{\uparrow}{\underset{\uparrow}{CH_2}}$

Exchange energy

→ Triplet carbene

→ spin multiplicity ⇒ (2s+1) • $+\frac{1}{2}, +\frac{1}{2}$ ✓, $-\frac{1}{2}, -\frac{1}{2}$ ✓, $+\frac{1}{2}, -\frac{1}{2}$ ✗] S=1

S=1

⇒ 3 ⇒ triplet carbene

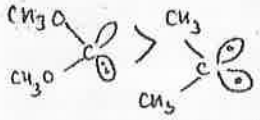
→ formation by homolytic cleavage.

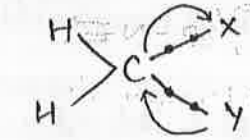
→ In complete octate.

→ hyb ⇒ sp

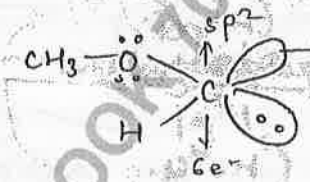
→ Behave as $E^{\oplus}$

Q Stability ⇒ $\overset{\uparrow}{CH_2} > \overset{\downarrow}{CH_2}$ (Generally)

Q 

② 

हमारा SYLLABUS



catora khali / $:CH_2$ / $\overset{\downarrow}{CH_2}$ singlet carbene

Singlet carbene

→ form by heterolytic cleavage

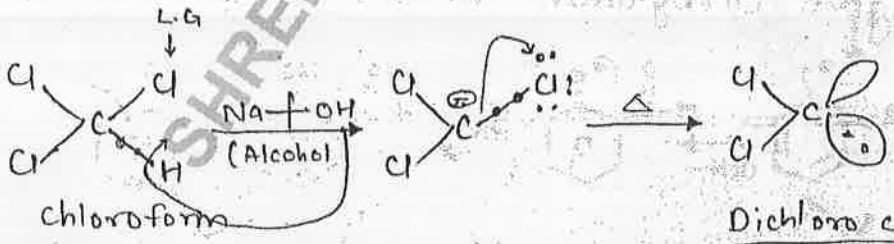
→ In complete octate

→ Behave as $E^{\oplus}$

→ hyb ⇒ sp^2

★

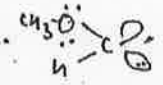
* Formation of carbene in O.C ⇒ $CHCl_3 + NaOH$



Dichloro carbene (singlet carbene)

Generally triplet carbene is more stable than singlet carbene due to exchange energy.

Singlet carbene may be more stable then triplet carbene if backbonding is tnt in singlet carbene

Eg. 

Rxn of Carbene

① Carbylamine Rxn / Isocyanide test:-

NET Rxn

$$R-\ddot{N}H_2 + CHCl_3 \xrightarrow{NaOH} R-N\equiv C$$

Alkyl isocyanide

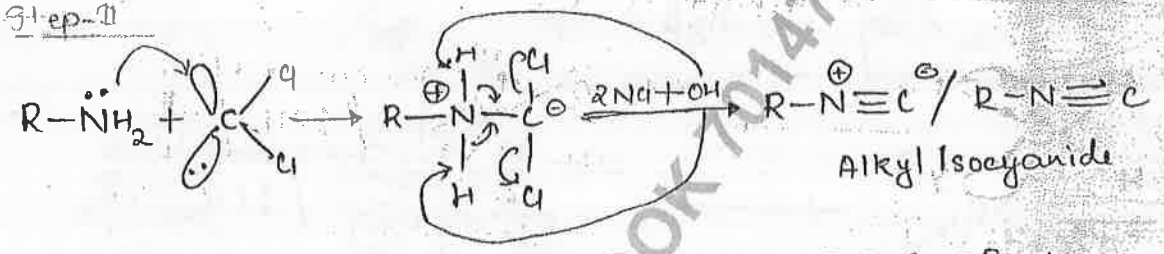
Mech

Step-I

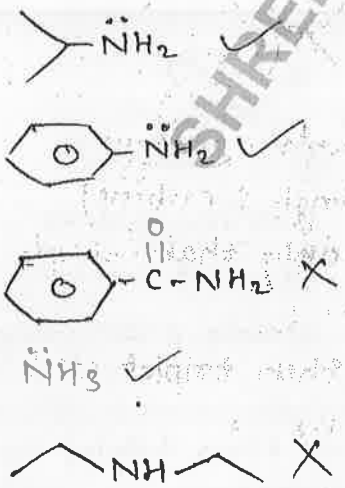
$$CHCl_3 + NaOH \xrightarrow{R.D.S} \text{Cl}_2\text{C}: + \text{Cl}^- + H_2O$$

Dichloro carbene

Step-II

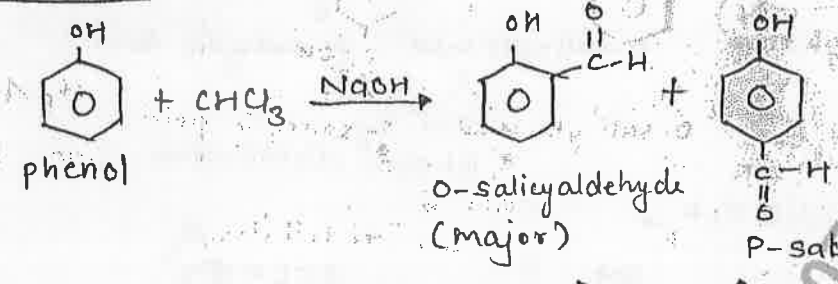


* formation of dichloro carbene is R.D.S of rxn.
* 1° Amine ($R-NH_2$), Aniline ($C_6H_5NH_2$) & Ammonium ($\ddot{N}H_3$) give carbylamin / Isocyanide test.
* 2° Amine ($R-\ddot{N}H-R$), 3° Amine ($R-\overset{R}{\underset{|}{N}}-R$) & Amide ($R-\overset{O}{\overset{||}{C}}-\ddot{N}H_2$) does not give carbylamine Rxn or Isocyanide test.



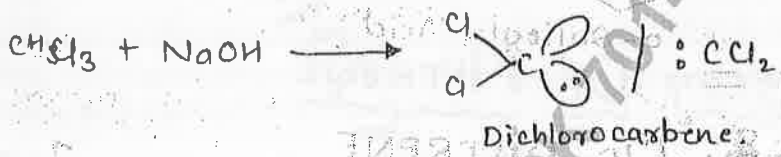
(2) Riemer tiaman's Rxn :-

NET Rxn

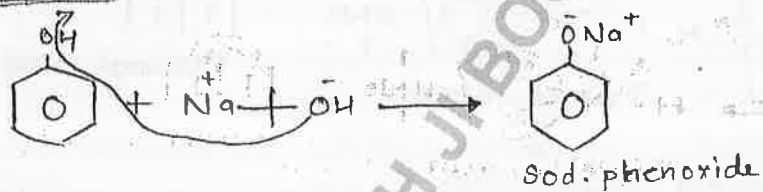


Mech →

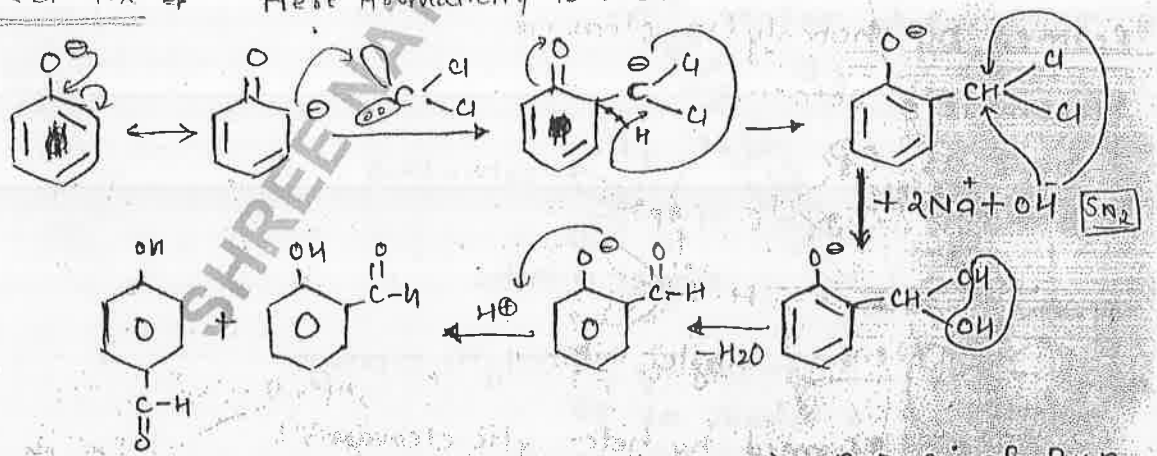
Step-I → formation of E⊕ → (R.D.S) of Rxn



Step-II → formation of Nu →

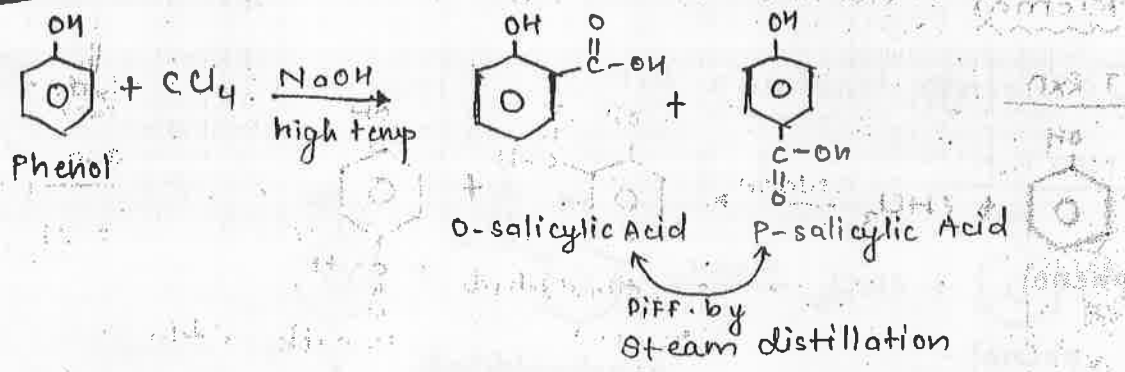


Net Rxn → Here Aromaticity is break

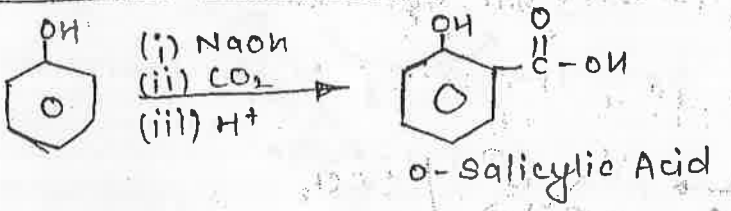


* formation of Dichloro carbene is R.D.S. of Rxn.
* In Riemer tiaman's Rxn if we use CCl_4 in the of $CHCl_3$ then Rxn carried out at high temp & O & P salicylic acid form as a product

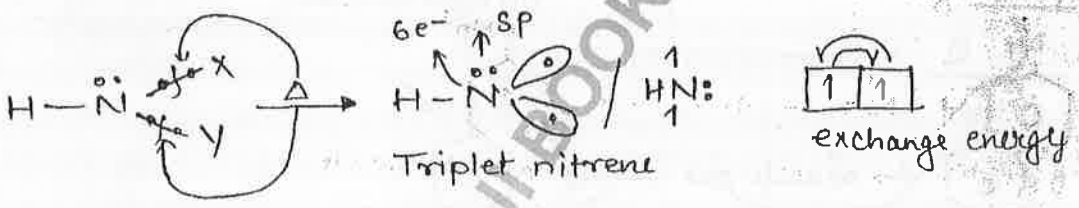
Net Rxn



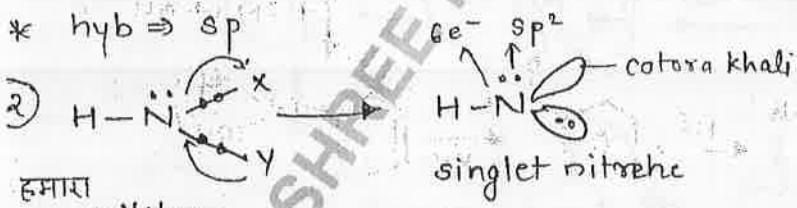
Kolbe - Schmidth Rxn →



CHEMISTRY OF NITRENE

① 

* formed by homolytic cleavage.
* Incomplete octate.
* Behave as $E^\oplus$
* hyb ⇒ sp

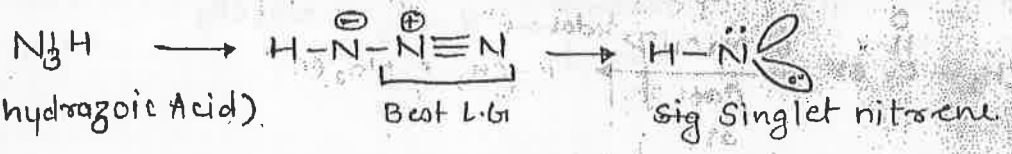
② 

हमारा Syllabus

* formed by heterolytic cleavage
* Behave as $E^\oplus$
* Incomplete octate
* hyb ⇒ sp^2

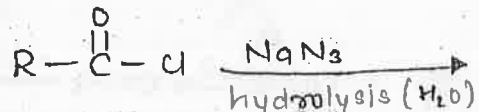
Reagent →

Formation of nitrene in O.C → N_3H (Hydrazoic Acid)

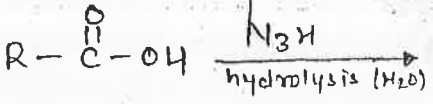


* Degredation Rxn of Nitrene (step-down Rxn)

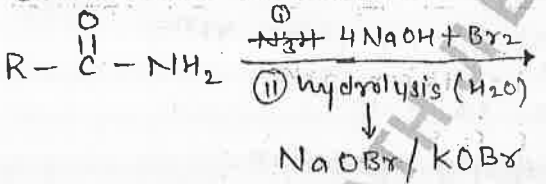
(i) Curtius Rxn →

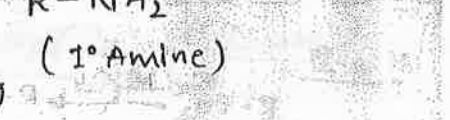


(ii) Schmidt Rxn →

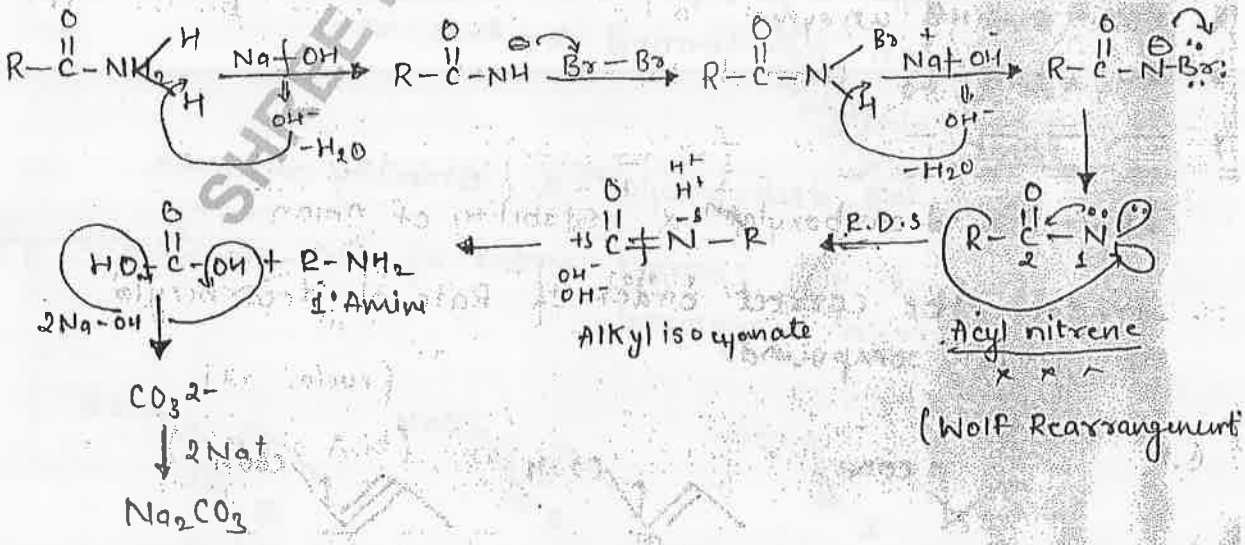


(iii) Hoffman's Bromomide Rxn →





Mech. of Hoffman Bromomide Rxn:-



★ Alkane

① Sodalime decarboxylatn Rxn :-

Net Rxn.

$$R-CH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[CaO]{\text{① NaOH, sodaline}} R-CH_3 + Na_2CO_3$$

3:1

Mech

Step-I

$$R-CH_2-\overset{O}{\overset{\|}{C}}-O-H \xrightarrow[-H_2O]{Na^+ \; ^-OH} R-CH_2-\overset{O}{\overset{\|}{C}}-O^{\ominus}$$

Step-II

$$R-CH_2-\overset{O}{\overset{\|}{C}}-O^{\ominus} \xrightarrow[R.D.S]{\Delta} R-CH_2^{\ominus} + CO_2 \xrightarrow{CaO} CaCO_3 \xrightarrow{NaOH} Na_2CO_3$$

(Anion intermediate)

Step-III

$$R-CH_2^{\ominus} \xrightarrow{H-\ddot{O}-H} R-CH_3$$

* It is step down rxn.
* carbanion intermediated form in these rxn
* formation of carbanion is R.D.S
* Reactivity of Rxn ∝ stability of anion.
* Both sym & unsymm. alkane can be formed by this rxn.
* CH_4 can be formed by this rxn.
* KEY Point
  - Rate of decarboxylatn ∝ Stability of Anion

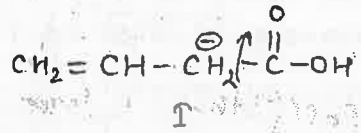
Ex. findout the correct order of Rate of decarboxylatn in given compound.

Q.1

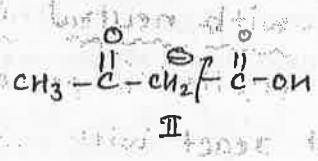
I II III

Rate of Decarboxylatn ⇒ III > II > I

Q.2



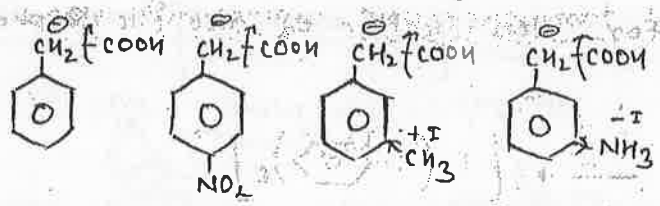
I



II

Rate of Decarboxylⁿ ⇒ II > I

Q.3

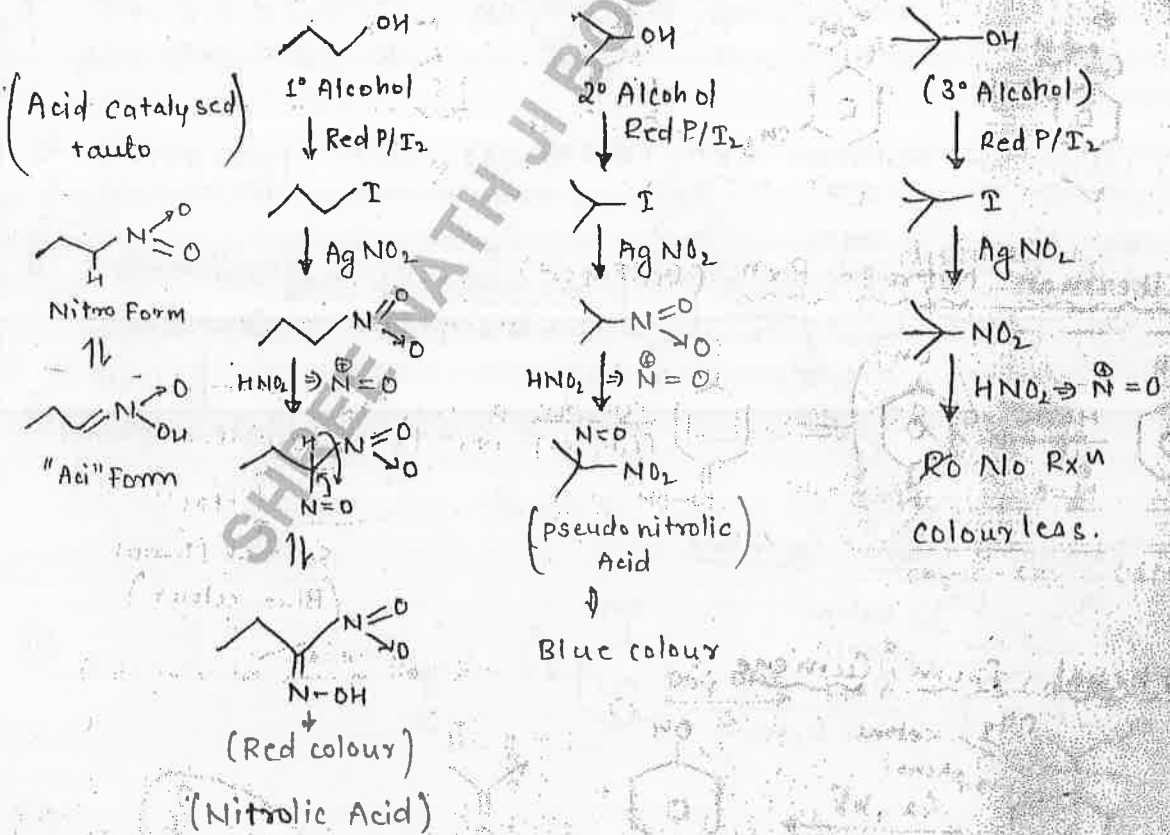


Rate of Decarboxylⁿ ⇒ II > IV > I > III

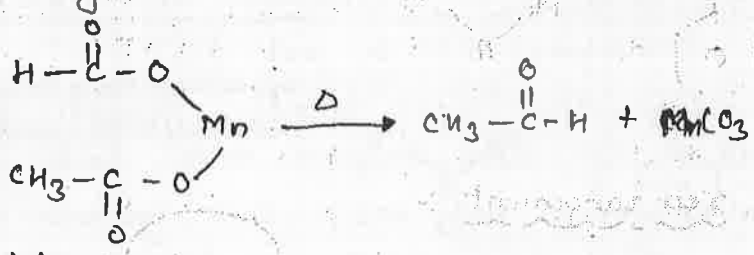
Alcohol, Phenol & Ether

① Victor Mayer test (RBC):-

* Victor Mayer test used for identificatⁿ of 1°, 2°, 3° Alcohol



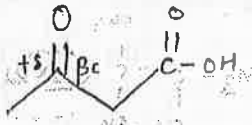
Heavy with MnO →



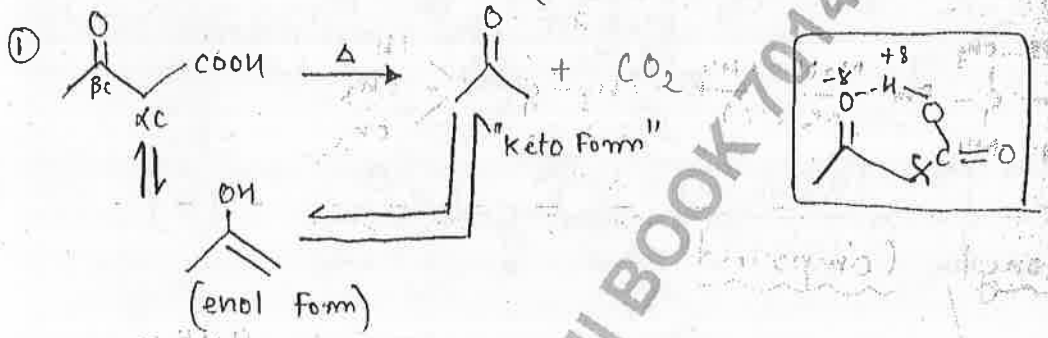
***

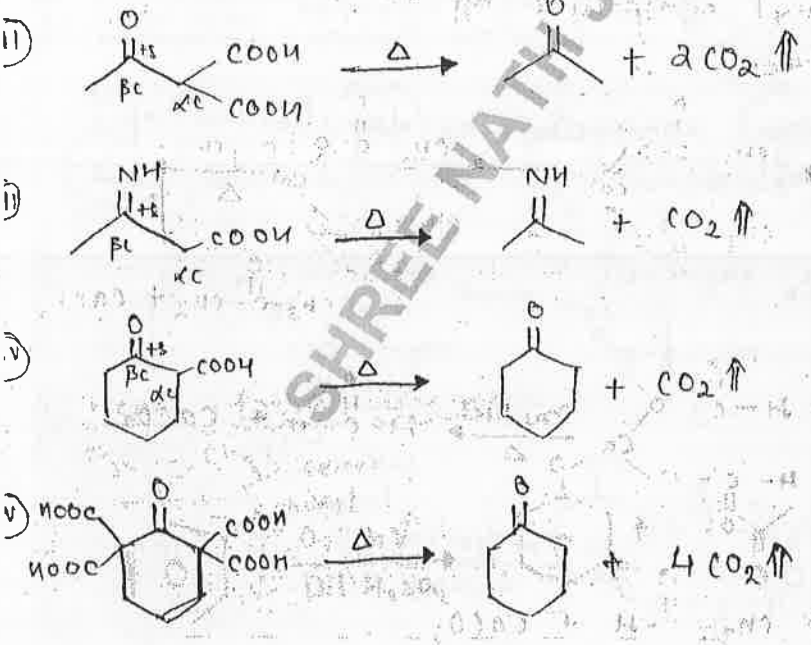
② Heating effect →

Ⓐ Heating effect at β- keto Acid →



(β-Keto Acid)





No Rxn
No Decarboxylation
Because Bredist rule is violated.

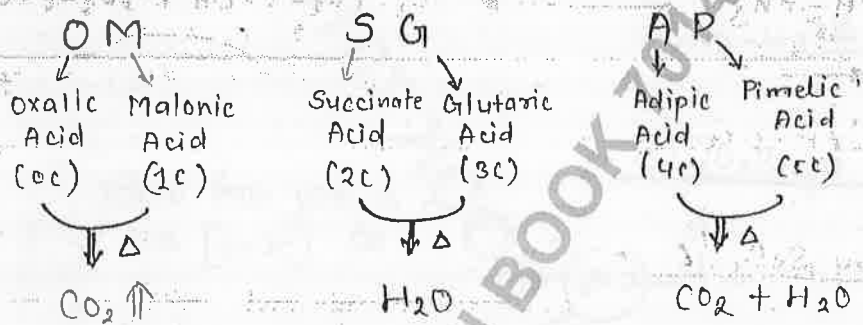
* In case of β-keto acid if partially +ve charge developed at β-position of β-keto acid then on heating it release CO_2

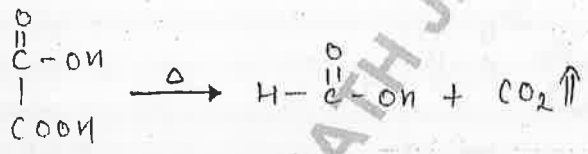
* In case of β-keto acid 1st form enol then it convert into keto form.

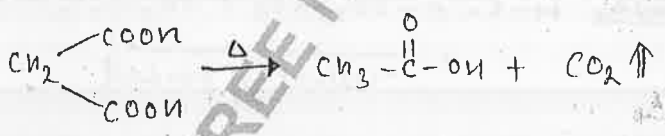
* 6 MCTS formed in this rxn.

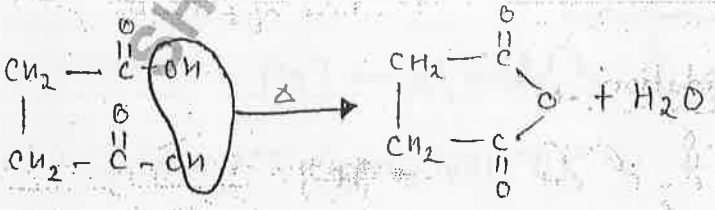
(B) Heating effect of Dicarboxylic Acid →

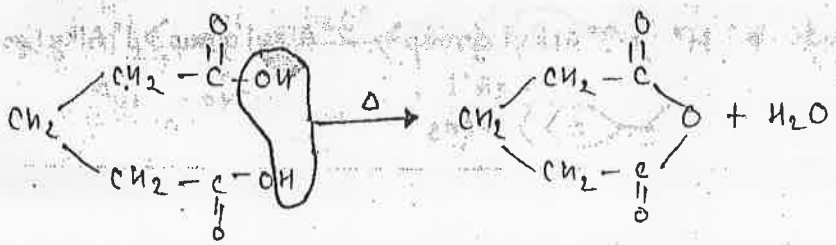
OMSGAP



① 

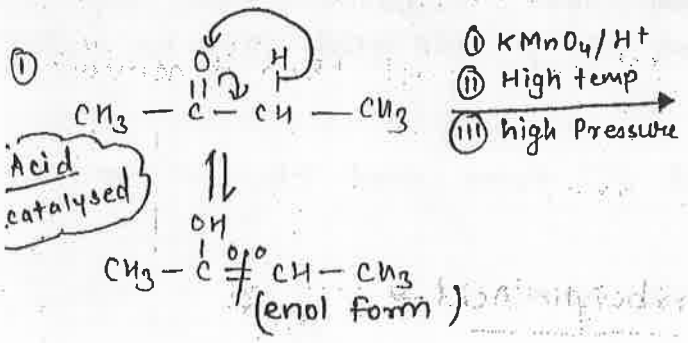
② 

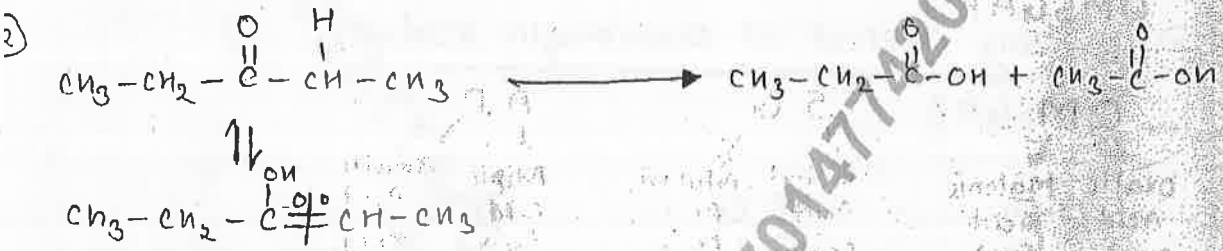
③ 

④ 

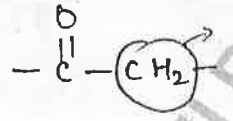
③ Popoff's Rule →

★ More stable enol will be formed major product

① 

② 

④ Oxidation by SeO_2/Δ →

KEY POINT :- 

>C=O के बाजू वाले कार्बन को [>C=O] बना देता है।

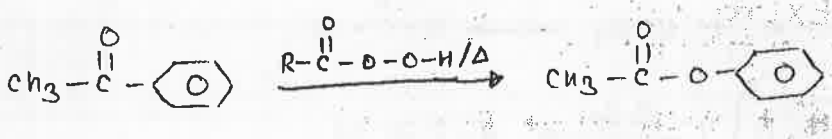
① $CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{SeO_2/\Delta} CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H$

② $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3 \xrightarrow{SeO_2/\Delta} H-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_2-CH_3 + CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$

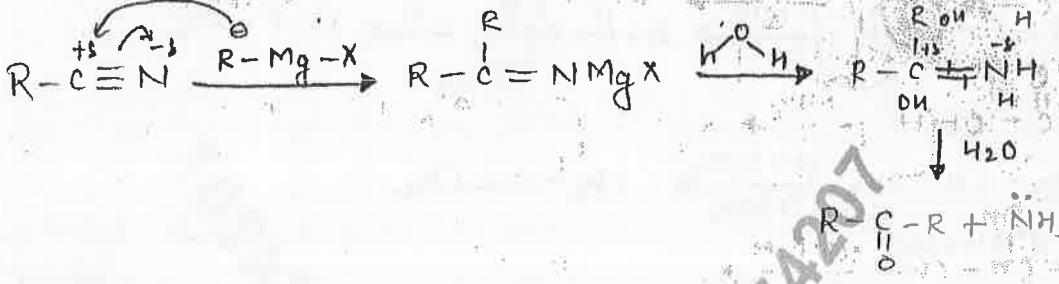
\+ Mixture of product.

⑤ Bayer villiger oxidation →

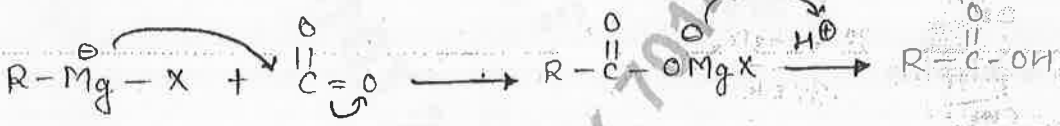
Migratory Aptitude → H° > 3° Alkyl group > 2° Alkyl group > 1° Alkyl group >  > $-CH_3$

Eg. 

(6) Rxn of R-Mg-X with Cyanide →



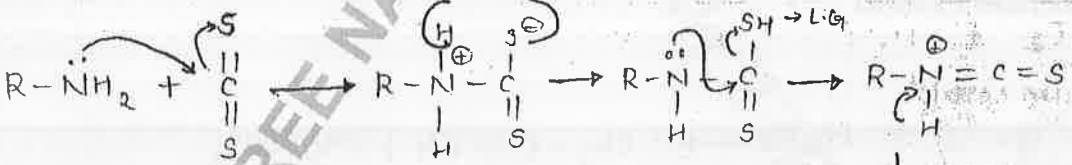
(7) Rxn of R-Mg-X with CO_2 ⇒



AMINE

(1) Hoffman mustard oil Rxn →

* Rxn also k/as test of Amine
* 1° Amine & Aniline give Hoffman mustard oil Rxn.

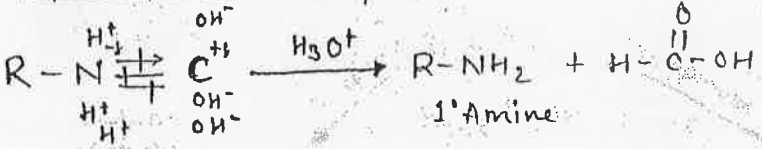


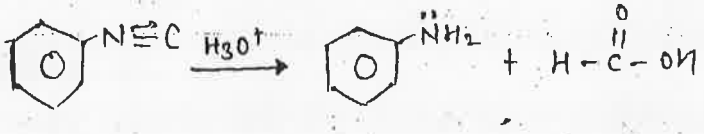
$R-N=C=S$

Alkyl isothiocyanate

(Smell like mustard oil)

(2) Hydrolysis of Isocyanide →

(i) 

(ii) 

Some Extra Point :-

① $R-\overset{O}{\overset{\|}{C}}-O-H + SOCl_2 \longrightarrow R-\overset{O}{\overset{\|}{C}}-Cl$

② $R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\Delta]{P_2O_5} R-C\equiv N$

③ $R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{NH_3} R-\overset{O}{\overset{\|}{C}}-O^{\ominus}\,NH_4^{\oplus} \xrightarrow{\Delta} R-\overset{O}{\overset{\|}{C}}-NH_2 + H_2O$

④ $CH_3-\underset{OH}{\underset{|}{CH}}-CH_3 \xrightarrow[440K]{80\%\ H_3PO_4} CH_3-CH=CH_2$

2° Alcohol

⑤ $CH_3-\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_3 \xrightarrow[358K]{20\%\ H_3PO_4} \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C=CH_2$

3° Alcohol

CHEMISTRY OF CARBIDE →

① $Al_4C_3 + 12\,H_2O \longrightarrow 3CH_4 + Al(OH)_3$

Aluminium carbide

⑪ $CaC_2 + H_2O \longrightarrow CH\equiv CH + Ca(OH)_2$

Calcium carbide

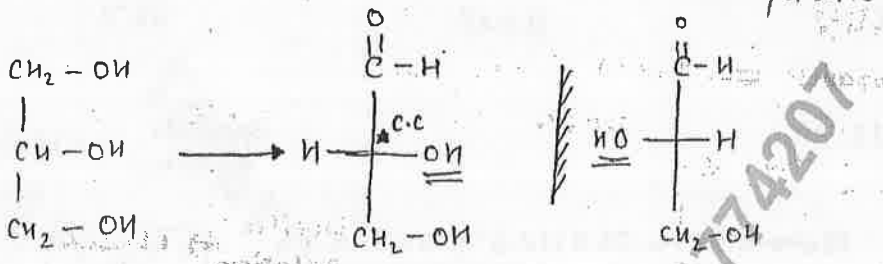
⑪⑪ $Mg_2C_3 + H_2O \longrightarrow CH_3-C\equiv CH + Mg(OH)_2$

Magnesium carbide

BIOMOLECULE [NCERT]

★ CARBOHYDRATE:-

Polyhydroxy Aldehyde or ketonic compound with minimum 1-chiral center is known as carbohydrate.



* D & L configuration is standard relative configuration of glyceraldehyde there is no relation with optical activity.

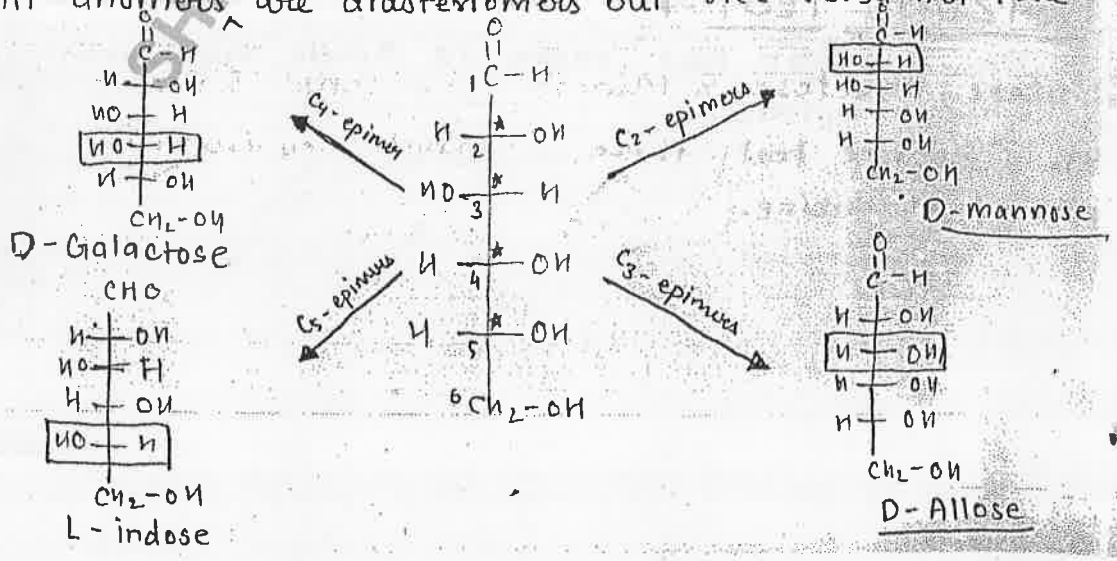
★ D, L Configuration → See in Steriochemistry.

Epimers → Whenever 2 monosaccharides are differ from each other in their configuration around a single specific carbon then compound is klas epimers of each other.

All epimers are diasteriomers. but vice-versa not true.

[α & β]

☆ All anomers are diasteriomers but vice-versa not true



★ Anomers → See in NAR

★ Hemiacetal → See in NAR

★ POC of carbohydrate → See in Ord^{n} of OC & NCERT

★ MUTAROTATION →

β-D-(+)-Glucopyranose ⇌ D-(+)-Glucose ⇌ α-D-(+)-Glucopyranose

64% 0.02% 36%

Specific rotation → +18.7°

Specific rotation → +112.2°

$$\text{Mutarotat}^{n} = \frac{36 \times 112.2^{\circ} + 64 \times 18.7^{\circ}}{100} = \boxed{+52.2^{\circ}}$$

: All monosaccharide & Disaccharide except sucrose give phenonmenon of mutarotation due to ence of Hemiacetal group.

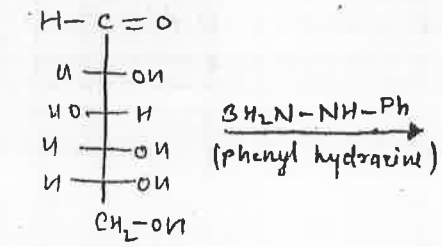
: β-D-(+)-glucose is more stable than α-D-glucose

: change in optical rotation whenever pure 100% α-D glucose & β-D-glucose introduced in aq. sol^{n} then the Avg. rotation is known as mutarotation

★ OSAZONE TEST →

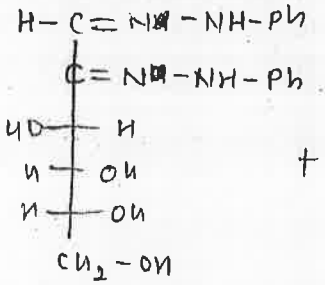
ε Glucose, Fructose & Manose form same Osazone.

ε In Osazone test there is 3 mole requirement of phenyl hydrazine.



D-Glucose

$3H_2N-NH-Ph$ (phenyl hydrazine)



Glucosozone

+ $Ph-NH_2$ & NH_3 Side product.

★ MOLISH TEST :-

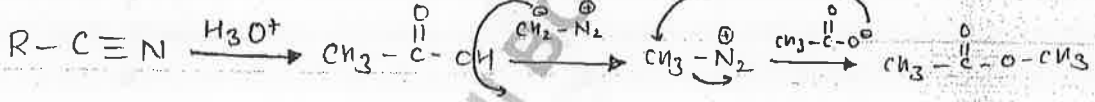
- primary test for carbohydrate = Molish test

Molish Reagent ⇓

(5% α-Napthol in excess of C_2H_5-OH)

* 1° test for fat - Solubility Test

* 1° test for peptide bond / protein - Biuret test



POLYMERS

SARVOTTAM CAREER INSTITUTE
Premier Institute for Pre-Medical Exams

Classification Based on :-

Source

(1) Natural Polymers found in plants & Animals
- Starch
- Protein
- Cellulose
- Glycogen
- Resins
- Natural Rubbers
  Ex. Isoprene

(2) Semi-Synthetic Polymers
- Cellulose derivatives
  Cellulose acetate (Rayon)
  Cellulose nitrate
- Vulcanised rubber

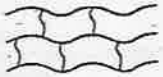
(3) Synthetic polymers
- Nylon –6, 6
- Buna-N
- Buna-S

Structure

(1) Linear Polymers
- High density Polythene
- Poly vinyl chloride

(2) Branched polymers
- Low density polythene

(3) Cross linked or Network Polymers / Thermosetting Polymer
- Bakelite
- Melamine
- Urea formaldehyde



IMF

(1) Elastomers
- Natural rubber
- Vulcanised rubbers
- Buna - N
- Buna - S
- Neoprene — Synthetic rubber

(2) Fibres
- Polyamides
- Plolyesters

(3) Thermoplastic polymers
- Polystyrene, Polyvinyls
- Polythene
- Taflon

Mode of Polymerisation

(1) Addition Polymers (Chain Growth Polymer's)

Homopolymer	Co-polymer
1. Polythene	1. Buna - S
2. Polystyrene	2. Buna - N
3. Poly vinyl chloride (PVC)	
4. Poly acrylonitrite (PAN) or Orlon or acrilan	
5. Teflon	
6. Poly cis-Isoprene - Natural rubber	
7. Neoprene - Synthetic rubber	

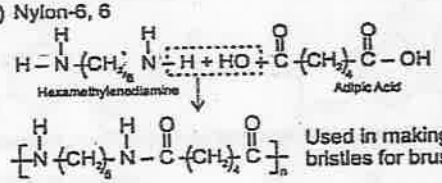
Monomer	Polymer
1. Ethene $CH_2 = CH_2$	Polyethene $-[CH_2 - CH_2]_n-$
2. Styrene $CH_2 = CH$ (C$_6$H$_5$)	Polystyrene $-[CH_2 - CH(C_6H_5)]_n-$ → Used as an insulator, wrapping mat, Toys, Radio & TV Cabinets
3. Acrylonitrile $CH_2 = CH(CN)$	Polyacrylo nitrile $-[CH_2 - CH(CN)]_n-$ → Used as a substitute for wool in making commercial fibres
4. Vinyl chloride $CH_2 = CHCl$	Poly vinyl chloride $-[CH_2 - CH(Cl)]_n-$ used in manufacture of Rain coats, Hand bags, water pipes.
5. Tetra floro ethene $CF_2 = CF_2$	Teflon $-[CF_2 - CF_2]_n-$ Used in making oil seals & gaskets & also for non-stick surface coated utensils. Insulating in electric wire.

(2) Condensation Polymer (Step Growth Polymers)

Homopolymer	Co-polymer
Nylon-6	1. Nylon-6, 6
	2. Terylene or Dacron
	3. Glyptal
	4. Bakelite
	5. Melamine

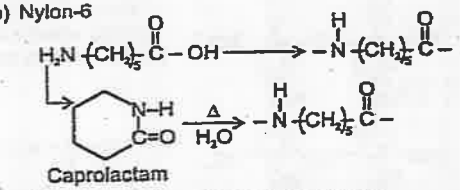
(1) Polyamides $-\overset{O}{\overset{\|}{C}}-OH + NH_2-$ (Acid + Amine = Amide)

(a) Nylon-6, 6



Used in making sheets, bristles for brushes

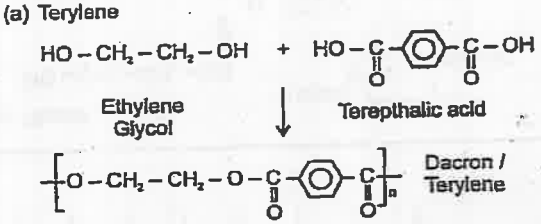
(b) Nylon-6



Used for manufacture of tyre cords, fabrics & ropes.

(2) Polyesters $-\overset{O}{\overset{\|}{C}}-OH + -OH$ (Acid + Alcohol = Ester)

(a) Terylene



(4) Thermosetting polymers
- Bakelite
- Melamine
- Urea-Formaldehyde resins

⇒ Order of Strength

Fibres > Thermoplastic polymers > Elastomers

		c	b/w
O	– Oxalic acid	0	C
M	– Malonic acid	1	C
S	– Succenic acid	2	C
G	– Glutamic acid	3	C
A	– Adipic acid	4	C
P	– Pivalic acid	5	C

COOH
|
COOH unit

- Carbon ring = Lactum + amide
- Carbon ring = Lacton + ester

6. Isoprene ⟶ Poly cis-Isoprene

$CH_2 = C(CH_3) - CH = CH_2 \longrightarrow -[CH_2 - C(CH_3) = CH - CH_2]_n-$

7. Chloroprene ⟶ Neoprene

$CH_2 = C(Cl) - CH = CH_2 \longrightarrow -[CH_2 - C(Cl) = CH - CH_2]_n-$

8. 1, 3-Butadiene + Styrene ⟶ Butudiene – styrene Copolymer (Buna-s)

$CH_2 = CH - CH = CH_2 + CH_2 = CH(C_6H_5) \longrightarrow -[CH_2 - CH = CH - CH_2 - CH_2 - CH(C_6H_5)]_n-$

9. 1, 3-Butadiene + Acrylonitrile ⟶ Buna - N

$CH_2 = CH - CH = CH_2 + CH_2 = CH(CN) \longrightarrow -[CH_2 - CH = CH - CH_2 - CH_2 - CH(CN)]_n-$

used to make oil seals tank lining.

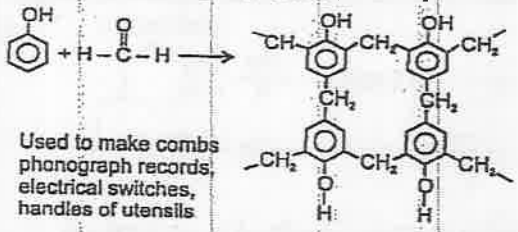
(b) Glyptal

$HO - CH_2 - CH_2 - OH$ + HOOC, COOH pthalic acid

$\Rightarrow -[O - CH_2 - CH_2 - O - C(=O) - C_6H_4 - C(=O)]-$

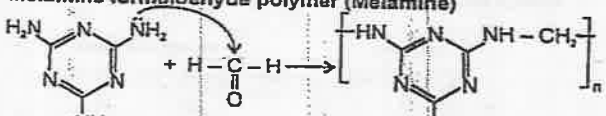
Used in manufacturing of paints & lacquers.

(3) Phenyl formaldehyde polymer (Bakelite)



Used to make combs phonograph records, electrical switches, handles of utensils

(4) Melamine formaldehyde polymer (Melamine)



Used in manufactor of unbreakable crockery

Biodegradable polymers

These polymers contain functional group similar to the functional groups present in biopolymers.

(1) Poly-β-hydroxybutyrate-Co-β- hydroxy valerate
(PHBV) use-Bacterial degradation used in speciality packaging orthopaedic devices & in controlled release of drugs.

$HO - CH(CH_3) - CH_2 - COOH + HO - CH(CH_2 - CH_3) - CH_2 - COOH$

$-[O - CH(CH_3) - CH_2 - C(=O) - O - CH(CH_2 - CH_3) - CH_2 - C(=O)]_n-$

(2) Nylon-2-Nylon-6

$H - NH - CH_2 - C(=O) - OH + H_2N - (CH_2)_5 - C(=O) - OH$

Glycine ↓ Amino caproic acid

$-[NH - CH_2 - C(=O) - NH - (CH_2)_5 - C(=O)]_n-$

Vucanisation of rubber

Vulcanised rubber-semisynthetic rubber Row rubber + sulphur = Vulcanised rubber. In manufacture of tyre rubber 5% of suphur is used as a cross linking agent

Characteristics :-

(1) Resistance against oxidising agent
(2) Water holding capacity ↓es
(3) Stability ↑es
(4) Hardness ↑es
(5) Softness ↓es

Range of mixing sulphur 3–10%

DDT – non-biodegradable

Polythene

(1) Low density polyethene
- By polymerisation of ethene in high pressure & at a temperature of 380 K - 570 K in presence of traces of dioxygen or a peroxide inittator (catalyst).
- Obtained by free radical addition & H-atom abstraction has highly branched structure.
- Chemically inert, tough but flexible.
- Used in manufacture of toys, flexible pipes, squeeze bottles & insulators

(2) High density polyethene
- By polymerisation of ethene in a hydrocarbon solvent in presence of catalyst as zeigler - Natta Catalyst.
- Chemically inert, tough, hard
- Used to make buckets, dustbins, bottles, pipes etc.

Zeigler – Natta Catalyst $(C_2H_5)_3Al + TiCl_4$