Cyanide & isocyanide :-

$H-C\equiv N$ $R-CN$ $Ar-CN$

$R-NC$ $Ar-NC$

$R-\overset{\curvearrowright sp}{C}\equiv\overset{\curvearrowright sp}{\ddot{N}}$

$R-\overset{\oplus}{N}\equiv\overset{\ominus}{C}$

Preparation of cyanide :-

① $R-X + \underset{\substack{NaCN \\ (\text{ionic})}}{KCN} \xrightarrow[S_N2]{\text{aq. Ethanol}} R-CN\,(\text{major}) + (R-NC\ \text{minor})$

$1^\circ, 2^\circ$

$R-X + \underset{(\text{covalent})}{Ag-CN} \xrightarrow[S_N1]{\text{aq. ethanol}} \underset{(\text{minor})}{R-CN} + \underset{(\text{major})}{R-NC}$

$$H-C\equiv \ddot{N} \rightleftharpoons H^{\oplus} + :C^{\ominus}\equiv \ddot{N}$$

$$:\overset{\ominus}{C}\equiv N: \longleftrightarrow :C=\overset{\ominus}{\ddot{N}}:$$ (major contributing canonical structure)

ambident nu⊖

c-centre is more nucleophilic as it is bigger in size & electronegetivity is less.

$$N\equiv \overset{\ominus}{C} + R-X \longrightarrow R-C\equiv N$$

Ag is more halophilic than the cyanide.

$$R-X + AgCN \longrightarrow R^{\oplus} + AgX\downarrow + \overset{\ominus}{CN}$$

$$AgCN \rightleftharpoons Ag^{\oplus} + \overset{\ominus}{CN}$$

$$R-X + Ag^{\oplus} \xrightarrow{S_N1} R^{\oplus} + AgX\downarrow$$ [ppt. of AgX favours the formation of R⊕]

carbocation

$$\downarrow C=N^{\ominus}$$ (as it is present in major amount)

$$R-\overset{\oplus}{N}\equiv\overset{\ominus}{C}$$

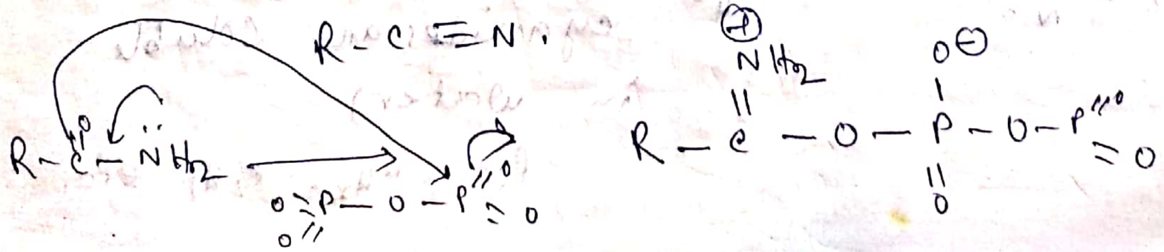
hard.

or $R^{\oplus}$ + $\ddot{N}\equiv C-Ag$

hard (covalent)

② $$\underset{\text{(aldoxime)}}{R-\underset{|}{\overset{}{C}}H=N-OH} \xrightarrow[-H_2O]{Ac_2O} R-C\equiv N$$

$$\underset{\text{(amide)}}{R-\overset{O}{\overset{\|}{C}}-NH_2} + PCl_5 \xrightarrow[-H_2O]{P_2O_5} R-C\equiv N + POCl_3 + HCl$$



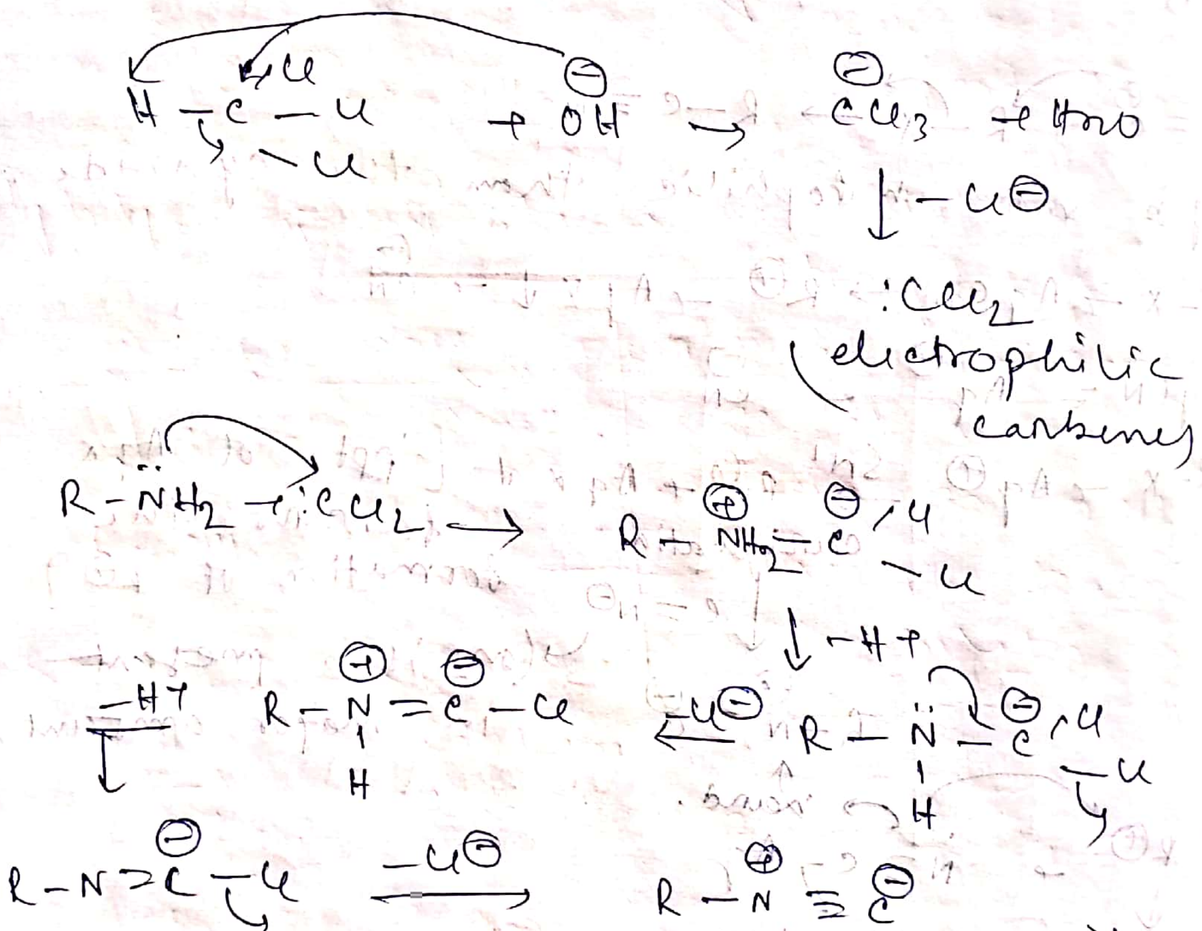
③ $(CH_3)_3C-MgCl + ClCN$ (cyanogen chloride) or $(CN)_2$

$$\downarrow$$

$$(CH_3)_3C-CN.$$

Carbylamine rxn :—

$$\underset{\text{(Only 1° amines)}}{R-NH_2} + \underbrace{KOH + CHCl_3}_{:CCl_2} \rightarrow R-\overset{\oplus}{N}\equiv\overset{\ominus}{C}$$



(volatile & with characteristics smell)

(iii)

$$R-C\equiv N \overset{\Delta}{\rightleftharpoons} R-\overset{\oplus}{N}\equiv C^{\ominus}.$$

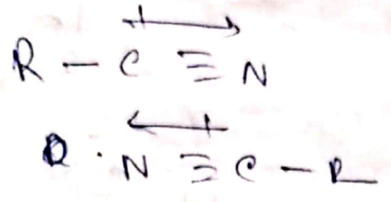
$$R-\overset{+\!\!\rightarrow}{C\equiv N}\cdots H-O-H$$

(lower membered cyanides are soluble in water)

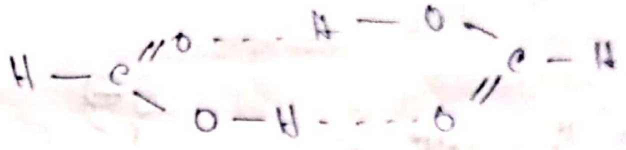
$R = -CH_3, -C_2H_5$ etc.

$CH_3-C\equiv N \rightarrow 41$ b.p ~80°C

Ⓝ $HCOOH \rightarrow 46$ ~100°C

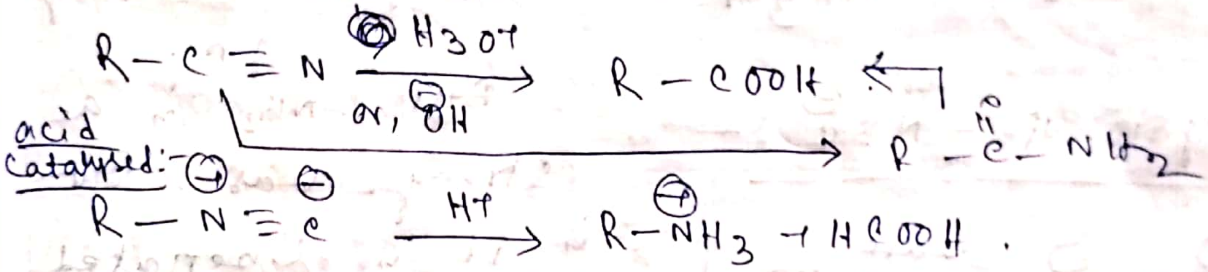


(dipole-dipole interaction)



(dimer)

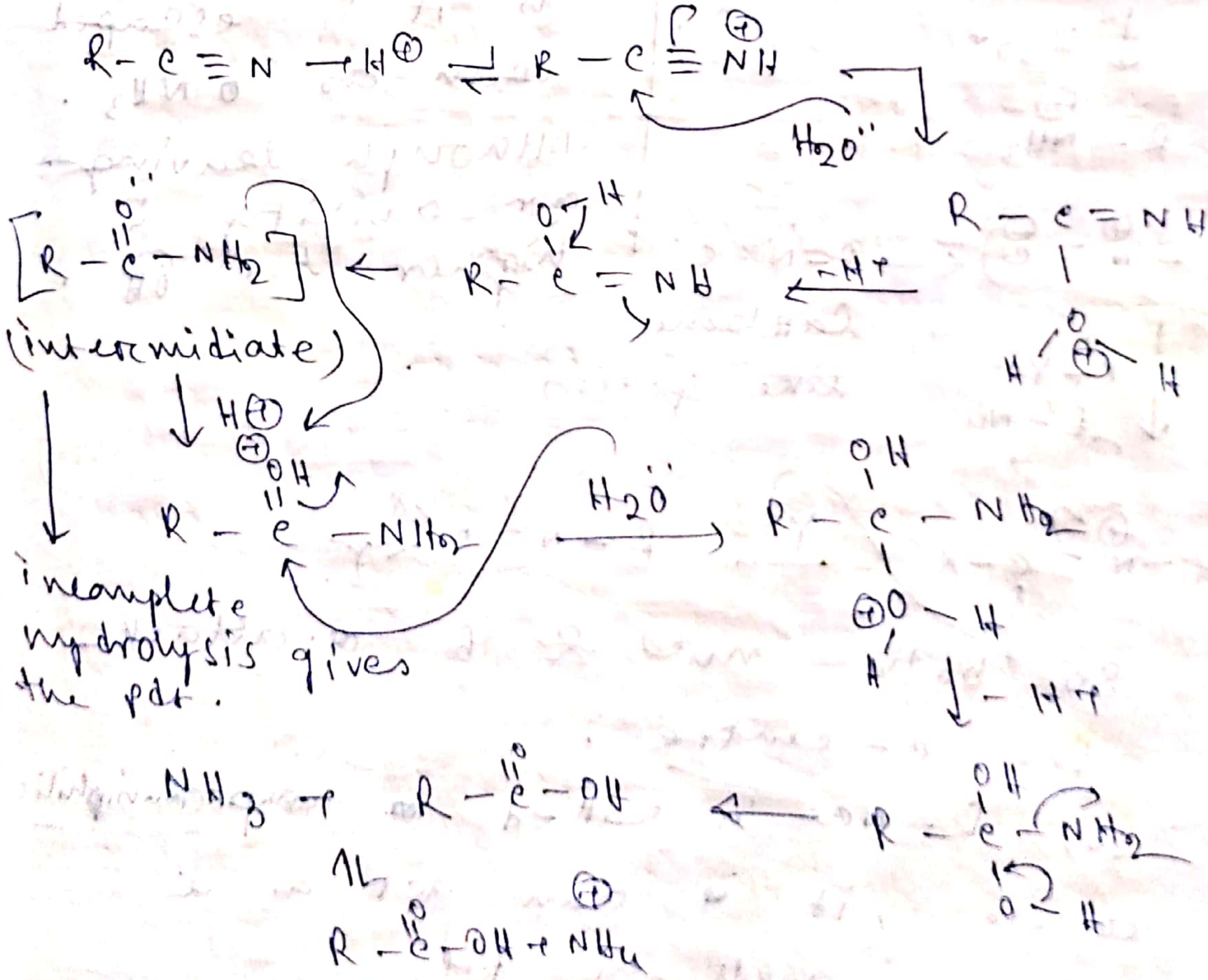
Reactions :-



$$R-C\equiv N \xrightarrow[\text{or, } \overset{\ominus}{O}H]{\overset{\oplus}{H_3O}} R-COOH \leftarrow R-\overset{O}{\overset{\|}{C}}-NH_2$$

acid catalysed:-

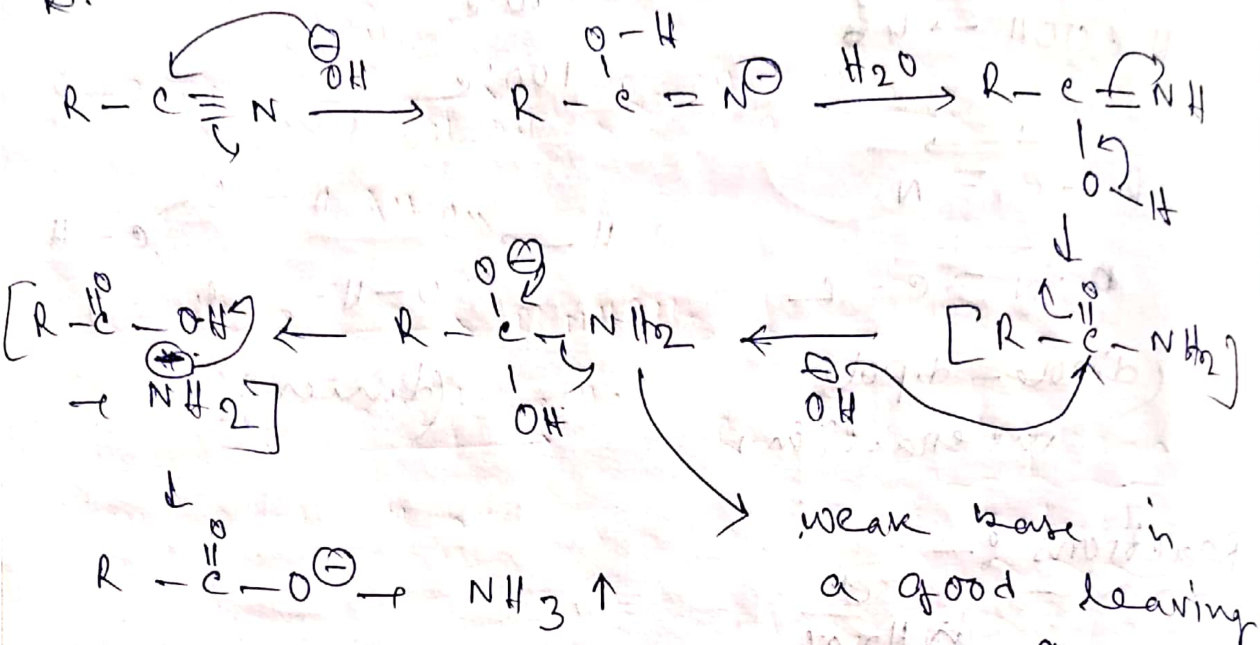
$$R-\overset{\oplus}{N}\equiv\overset{\ominus}{C} \xrightarrow{H^+} R-\overset{\oplus}{N}H_3 + HCOOH.$$



(intermidiate)

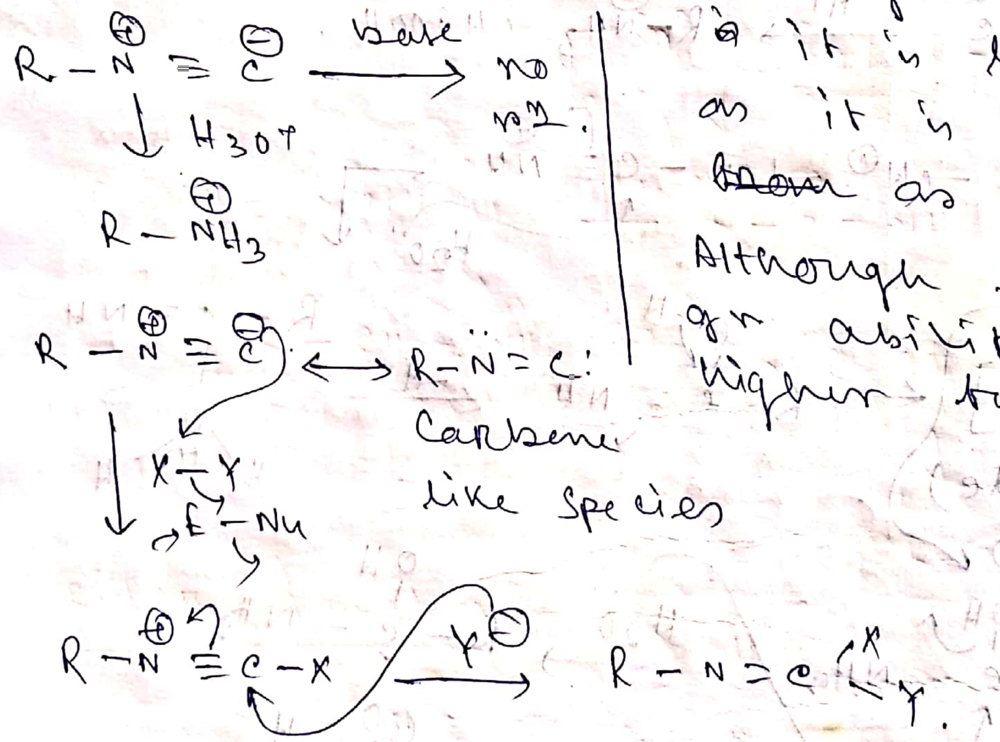
incomplete hydrolysis gives the pdt.

b. base catalysed:—



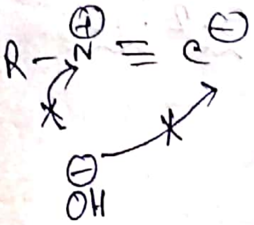
weak base is a good leaving gr. But –NH_2 is a strong base. But as it is liberated as it is escaped ~~[illegible]~~ as NH_3. Although leaving gr ability is higher for $\overset{\ominus}{OH}$.

Hydrolysis of $-\overset{\oplus}{N}\equiv\overset{\ominus}{C}$:—



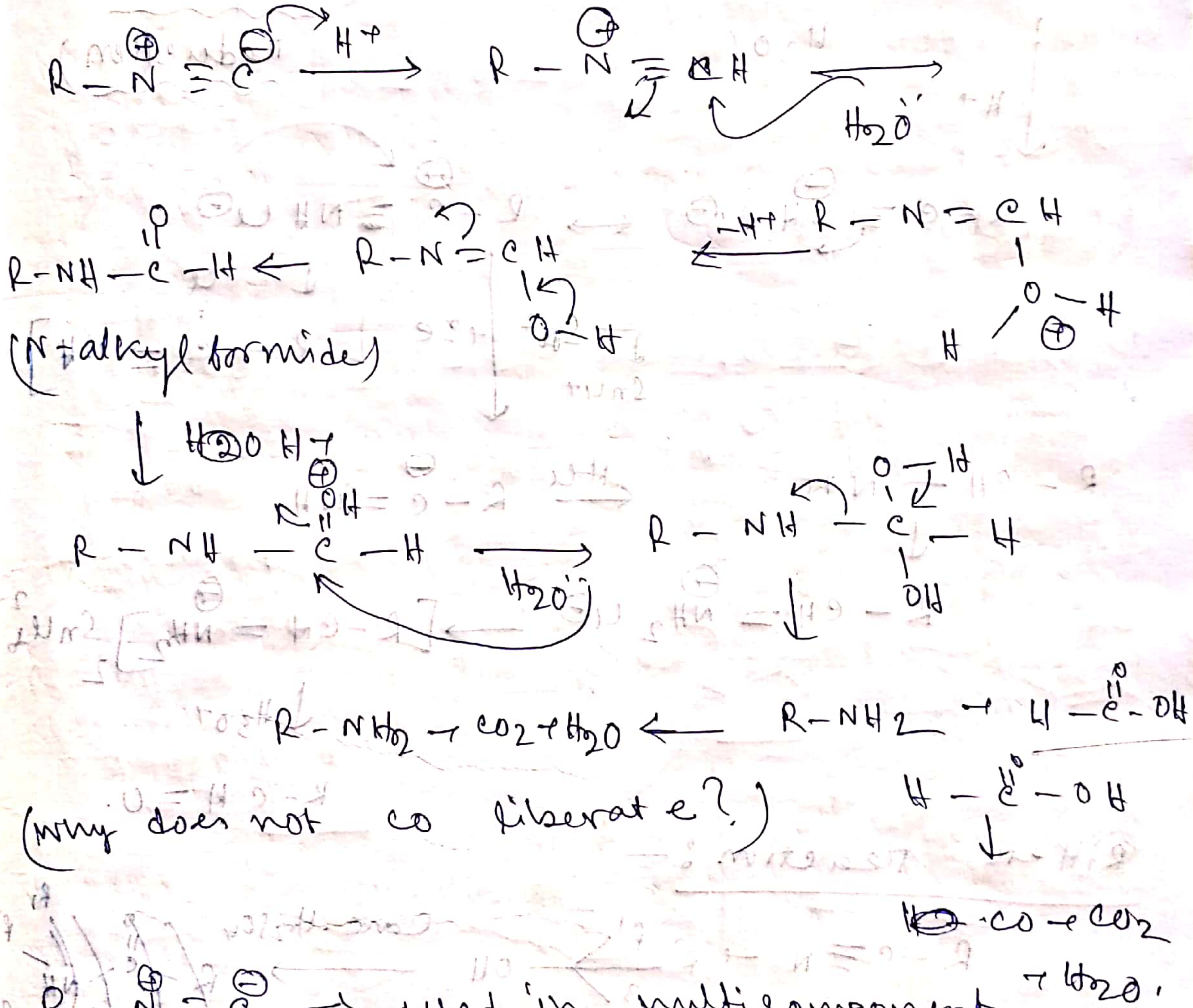
So, both nu⊖ & E⊕ attack the c-centre.

So, R–NC is called ~~[illegible]~~ ~~group~~ ambiphilic ~~so~~ as, it ~~is~~ can act as a nu⊖ as well as E⊕.



as nitrogens contain 4 bonds already, so it can't further increase it's valency so, $\overset{\ominus}{OH}$ can't attach the N.

so, base catalysed hydrolysis of isocyanide is not possible.



$R-\overset{\oplus}{N}\equiv\overset{\ominus}{C} \Rightarrow$ used in multicomponent rxn.

Reduction of cyanide:-

$$R-C\equiv N \xrightarrow{[H]} R-CH_2-NH_2$$

(1° amine)

i) Na/C_2H_5OH

ii) LAH

iii) Ni/H_2.

$$R-C\equiv N \xrightarrow[Na/C_2H_5OH]{Ni/H_2} R-CH_2-NH_2$$

LAH

$$R-N\equiv C \longrightarrow RNHCH_3$$

$$R-C\equiv N \xrightarrow{SnCl_2/conc.HCl} R-CHO$$ (Stephen's reduction)

H_3O^+

$$\downarrow H^+$$

$$R-C\equiv\overset{\oplus}{N}H\ Cl^{\ominus} \longleftrightarrow R-\overset{\oplus}{C}=NH\ Cl^{\ominus}$$

$$\downarrow \quad [R-\overset{Cl}{\overset{|}{C}}=NH]$$

$$Sn^{2+} \to Sn^{4+} \quad +2e \downarrow$$

$$R-CH=NH \xleftarrow{HCl} R-\overset{\ominus}{C}=NH$$

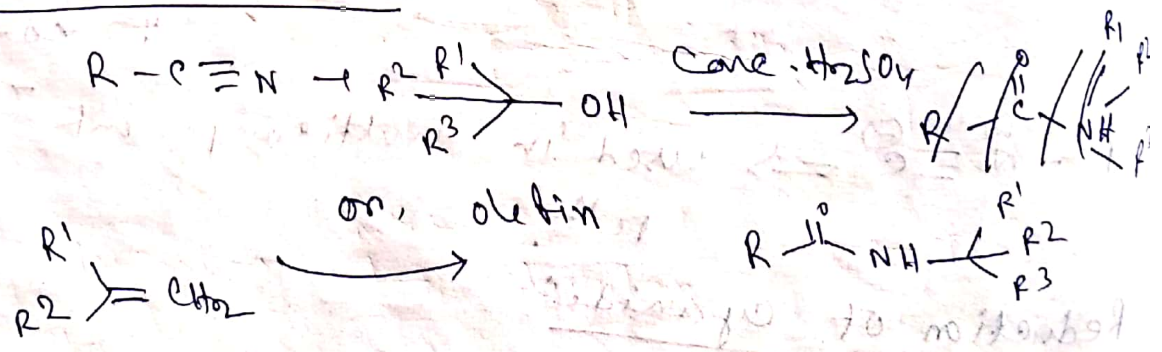
$$\downarrow$$

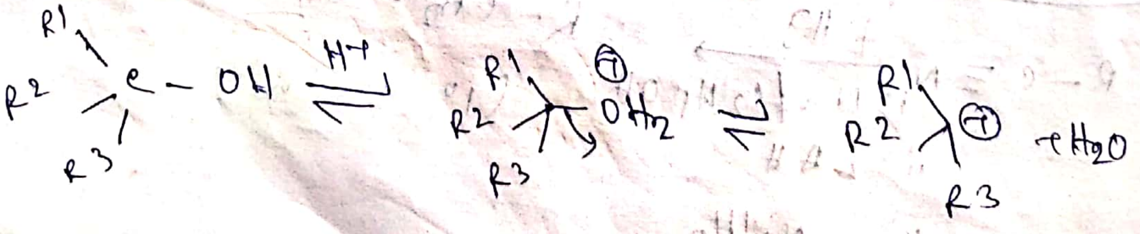
$$R-CH=\overset{\oplus}{N}H_2\ Cl^{\ominus} \longrightarrow [R-CH=\overset{\oplus}{N}H_2]_2\ SnCl_6^{2-}$$

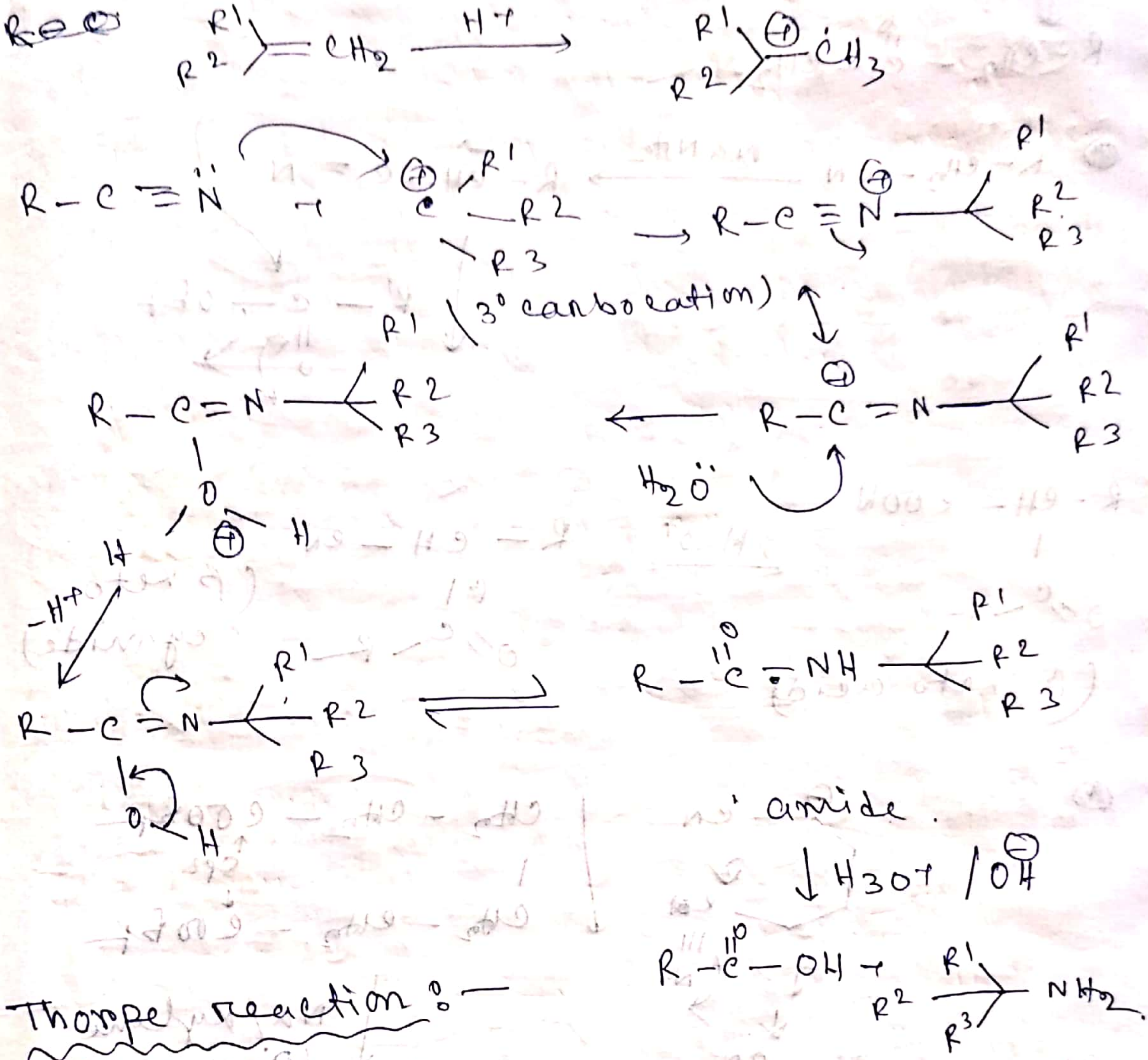
$$\downarrow H_3O^+$$

$$R-CH=O.$$

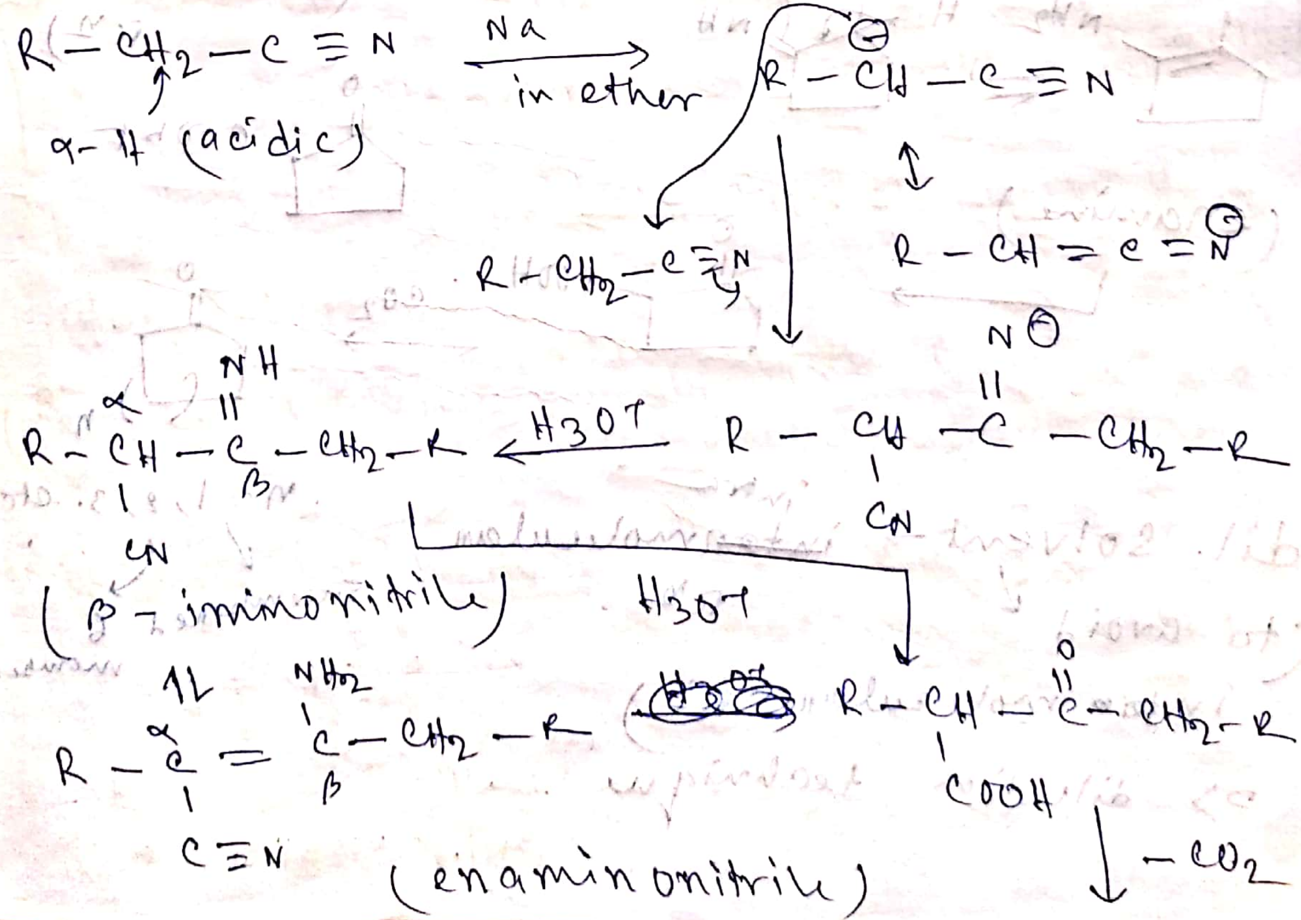
Ritter reaction :-

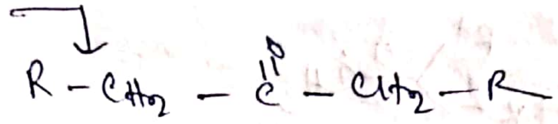






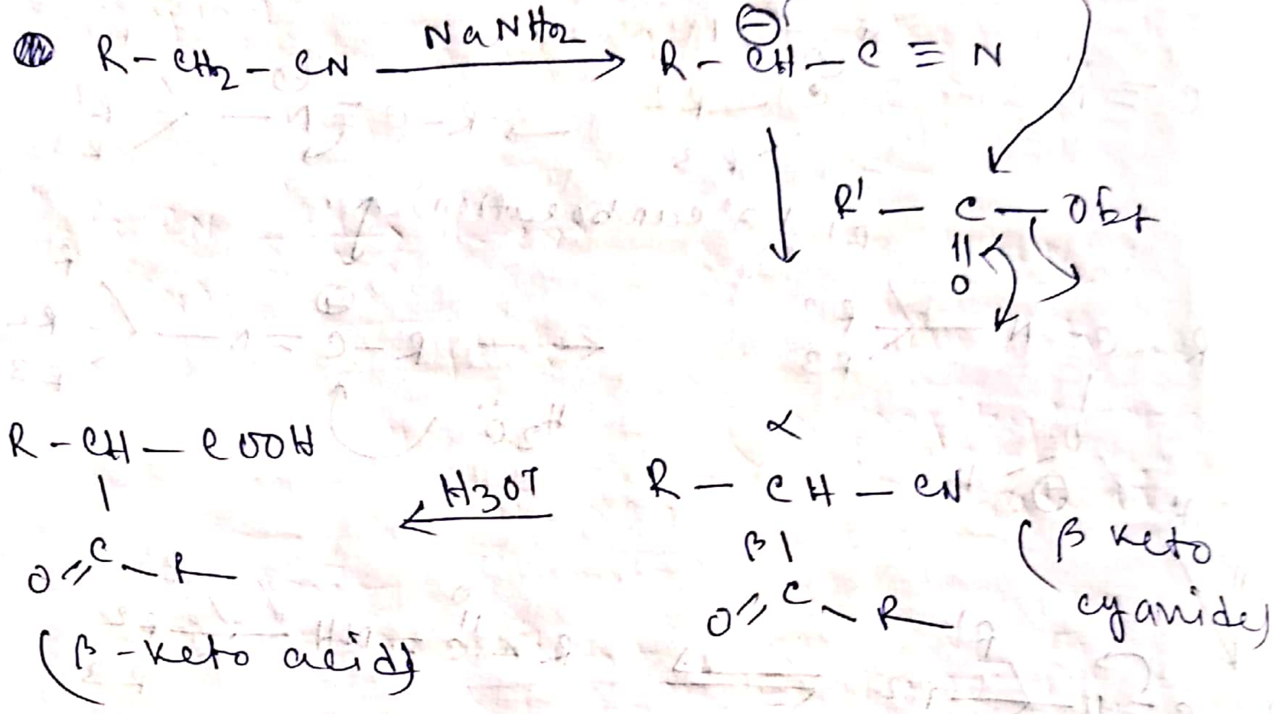
Thorpe reaction :-



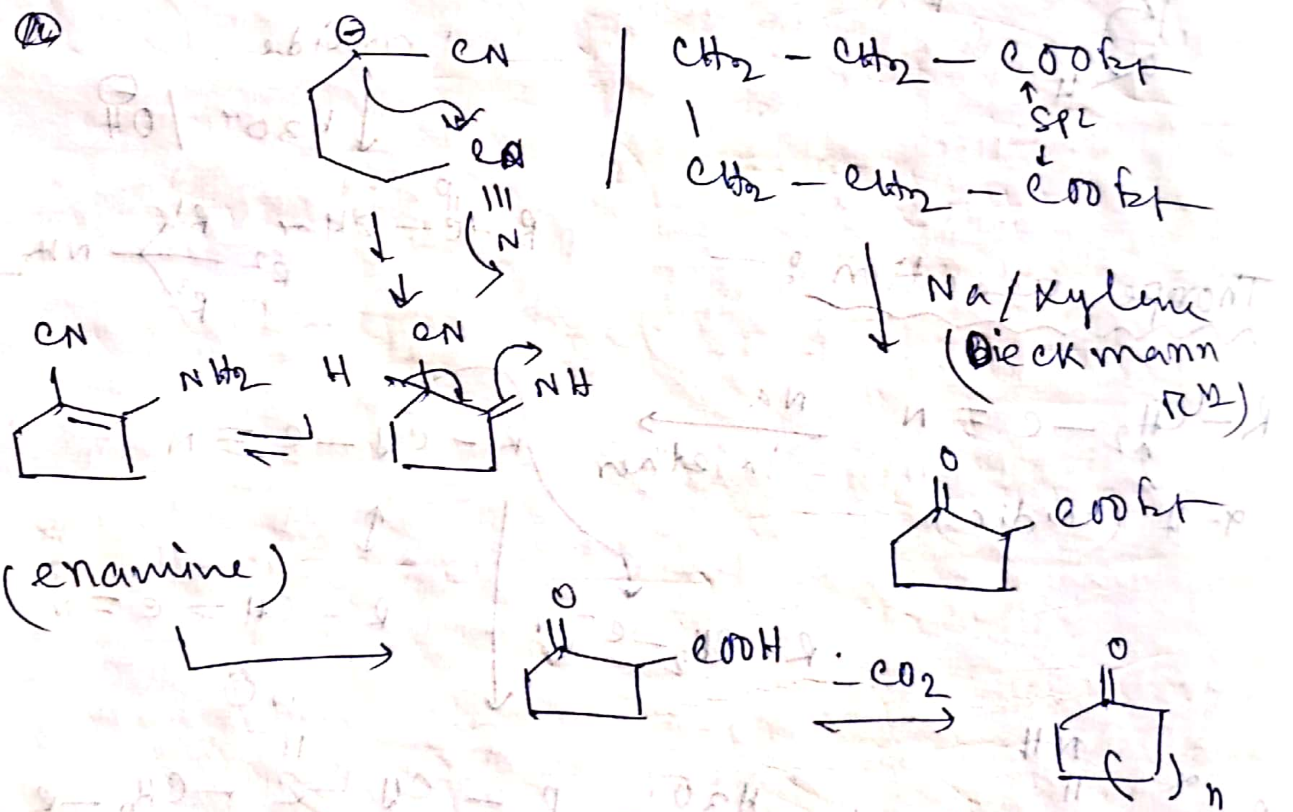


$R-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-R$

(iii)



(iv)



n = 1, 2, 3. etc → 5 membered, 6 membered

dil. solvent → ~~inter~~ intramolecular rxn.

(to avoid intermolecular rxn)

=> dilution technique.

(dihalo isocyanate)

$$R-\overset{\oplus}{N}\equiv\overset{\ominus}{C}\xrightarrow{X_2}R-N=C<^{X}_{X}$$

$$\xrightarrow{S}R-N=C=S$$ (isothiocyanate)

$$R-\overset{\oplus}{N}\equiv\overset{\ominus}{C}\quad {}^{+2}Hg=O\xrightarrow{HgO}R-N=C=O+Hg\downarrow.$$

$R-N=C=O+\overset{\circ}{Hg}$

(alkyl isocyanate) MIC → methyl isocyanate

$$N\equiv C-C\equiv N\longleftrightarrow\overset{\oplus}{N}=C=C=\overset{\ominus}{N}\updownarrow\overset{\ominus}{N}=C=C=\overset{\oplus}{N}$$

(b.p = −39°C)

$$X-CN\xrightarrow{KOH}K^{\oplus}O^{\ominus}-CN.$$

$$X-C\equiv N\xrightarrow{\overset{\ominus}{O}H}HO-CN\longrightarrow K^{\oplus}O^{\ominus}-C\equiv N\xrightarrow{R-X}R-N=C=O$$

[C−C ⟹ C=C less energy required
C−O ⟹ C=O here more energy is required]

$R-N=C=O$ → reactive (react with H_2O, $R-SH$, $R-NH_2$)

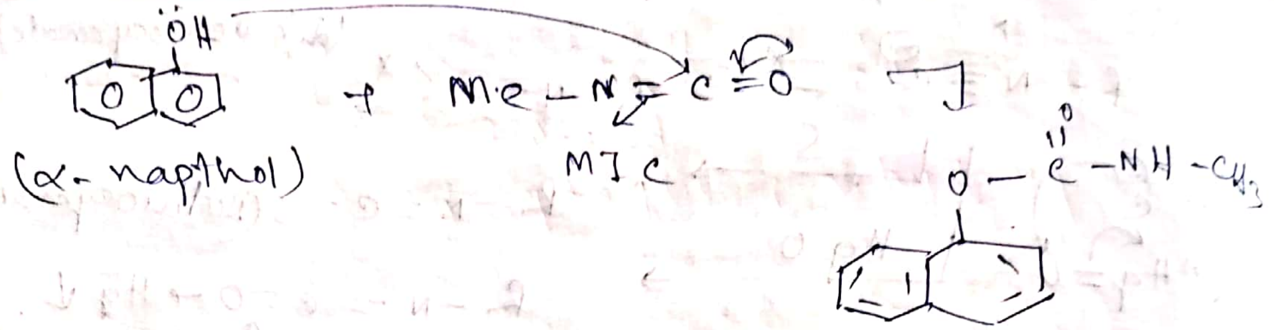
(toxic) → very dense (density 2 times higher than air).

(exothermic rxn)

$$R-N=C=O\xrightarrow{H_2O}R-NH-\overset{O}{\overset{\|}{C}}-OH$$ (carbamic acid)

$\downarrow R'-\ddot{N}H_2$

$$R-NH-\overset{O}{\overset{\|}{C}}-NH-R'$$ (N,N-dialkyl urea)



SEVIN

(insectiside)

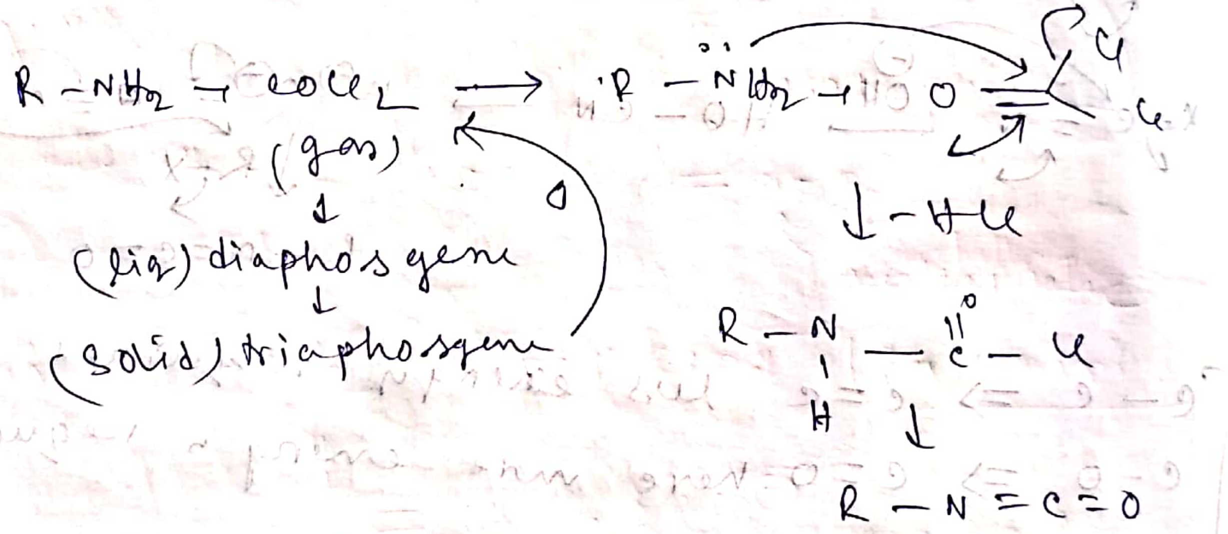
(α-napthyl - N- methyl carbamate)

① $X-CN \xrightarrow{H_2O} H-CN$

$(CN)_2 \xrightarrow{H_2O}$ H – CN + H – NCO

isocyanic acid (oxamite)

$(CONH_2)_2 \equiv HCOO^- NH_4^{\oplus}$



(gas)

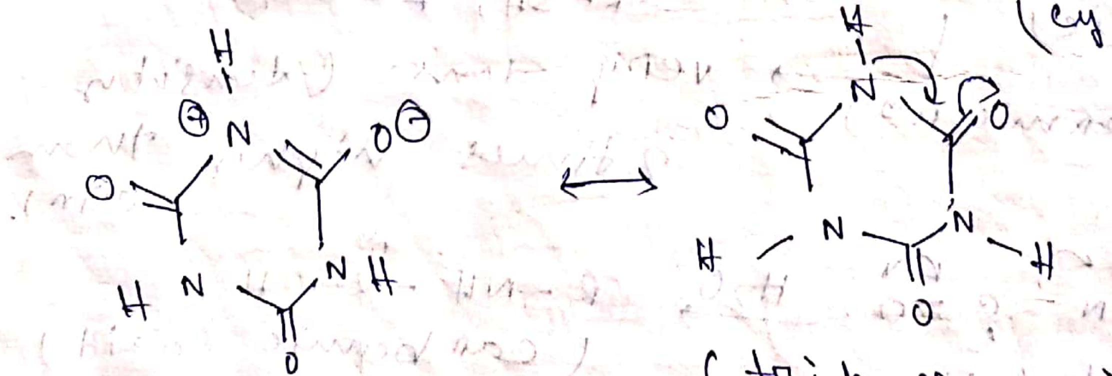
↓

(liq) diaphosgene

↓

(solid) triaphosgene

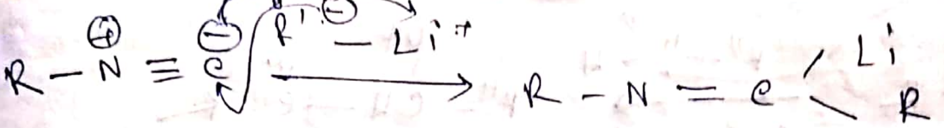
② $H-N=C=O \xrightarrow{\Delta} H_3N_3C_3O_3$ (cyanuric acid)



(tribasic acid)

used as acid catalyst.

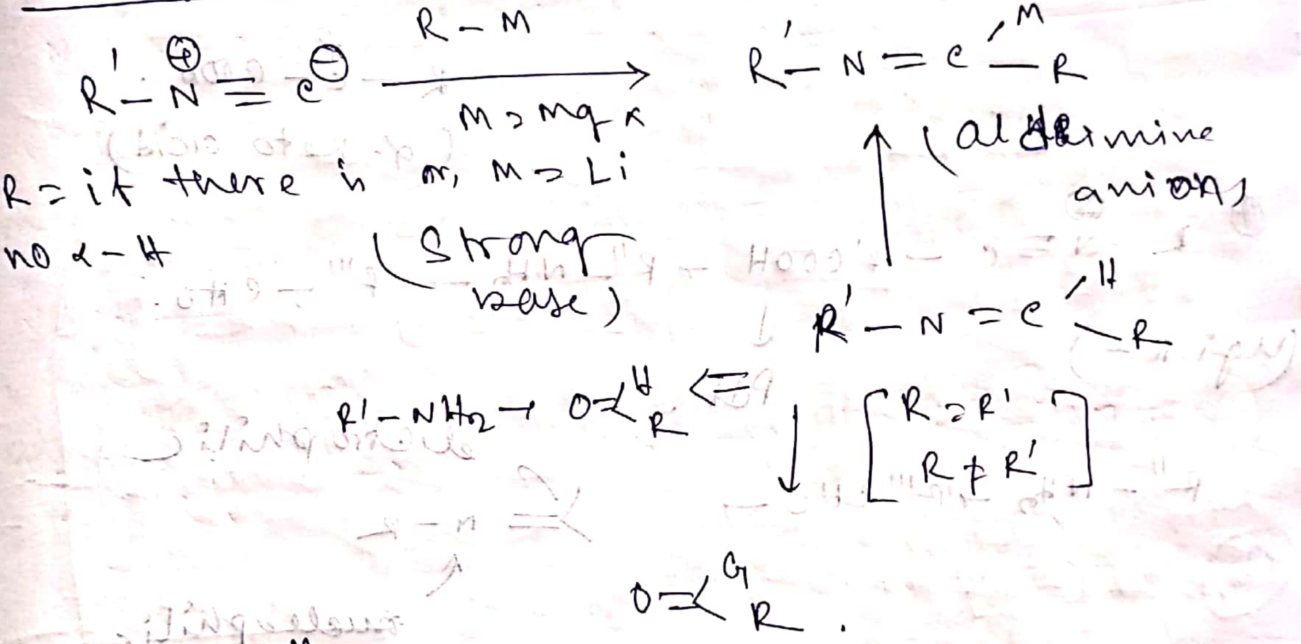
(this is an acid which contain no –OH gr, no – COOH gr.)



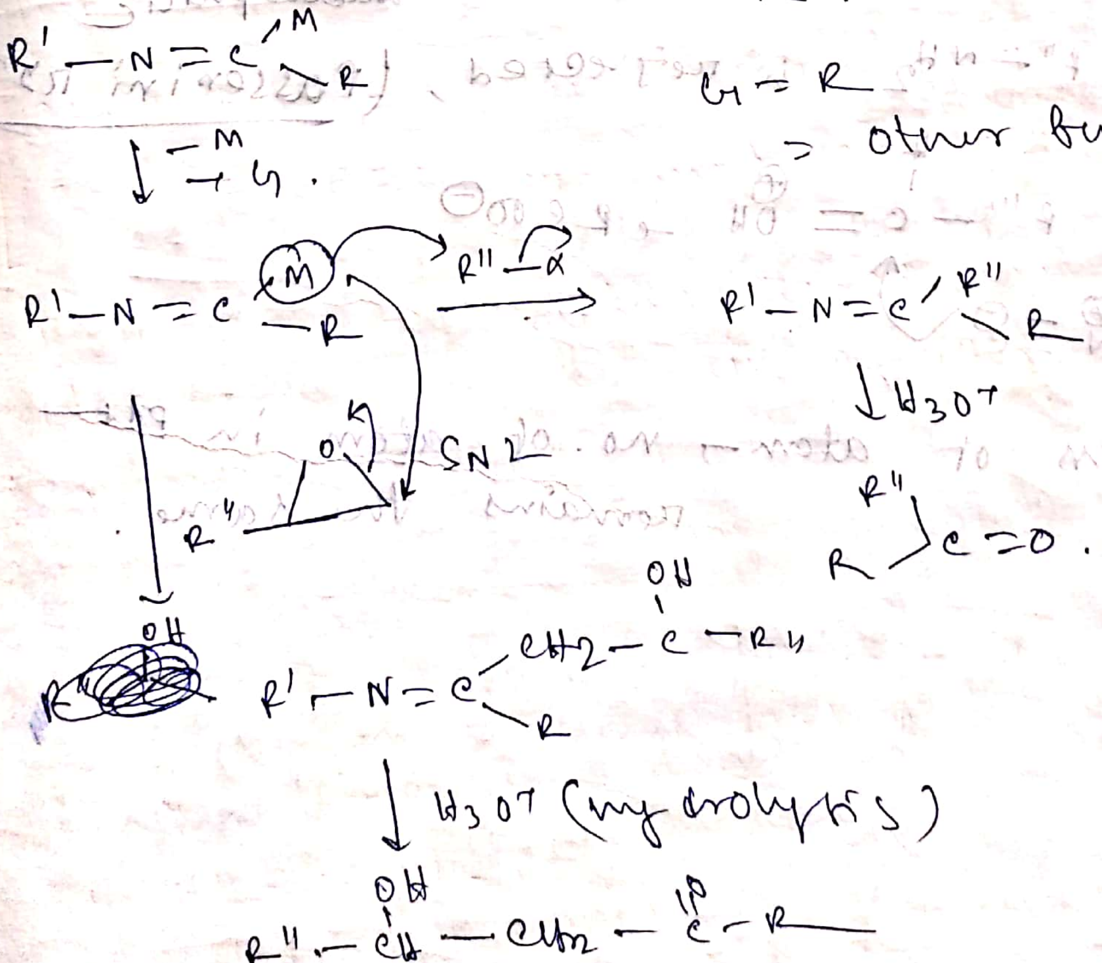
(used as synthetic reagent)

7.2.13

Isocyanide



R = if there is no α-H



G = R
= other functional gr.

β-hydroxy ketone

$$R'-N=C\begin{matrix}\nearrow M\\ \searrow R\end{matrix} \xrightarrow[\text{followed by hydrolysis}]{R''-\overset{O}{\overset{\|}{C}}-H} R''-\overset{OH}{\overset{|}{C}H}-\overset{O}{\overset{\|}{C}}-R$$

(α-hydroxy ketone)

$$R'-N=C\begin{matrix}\nearrow M\\ \searrow R\end{matrix} \xrightarrow{CO_2} R-\overset{\overset{O}{\overset{\|}{C}}-O^{\ominus}}{\overset{|}{C}}=N-R'$$

$$\downarrow H_3O^+$$

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

(α-keto acid)

③ $R-\overset{\oplus}{N}\equiv C + R'COOH + R''-NH_2 + R'''-CHO.$

$$\downarrow$$

Pdt.

(Ugi Rn)

$R''-NH_2 + R'''CHO \rightarrow \;>\!=N-R$

electrophilic

nucleophilic

②

if $R''-NH_2$ is rejected, (Passerini Rn)

$$R'''-\overset{H}{\overset{|}{C}}=\overset{\oplus}{O}H + RCOO^{\ominus}$$

$$R-\overset{\oplus}{N}\equiv\overset{\ominus}{C}$$

No loss of atom → no. of atom in pdt remains the same.