# Unit - V

## Metal hydride

When metal is fushed with the anionic form of hydrogen ion then they form metal hydride.

Ex -;

$H \rightarrow H^+ \rightarrow$ Hydronium

$H \rightarrow H^- \rightarrow$ Hydride

Metal -;

| Alkali metal (+) | Alkalene earth (+2) | Boron family (+3) |
|---|---|---|
| $Li \rightarrow LiH$ | $Be \rightarrow BeH_2$ | $B \rightarrow BH_3$ |
| $Na \rightarrow NaH$ | $Mg \rightarrow MgH_2$ | $Al \rightarrow AlH_3$ |
| $K \rightarrow KH$ | $Ca \rightarrow CaH_2$ | $Ga \rightarrow GaH_3$ |
| $Rb \rightarrow RbH$ | $Sr \rightarrow SrH_2$ | $In \rightarrow InH_3$ |
| $Cs \rightarrow CsH$ | | |

$LiAlH_4 \rightarrow$ Lithium aluminium tetra hydride

$NaBH_4 \rightarrow$ Sodium hydro borate.

# $LiAlH_4$ (Lithium Aluminium tetra hydride)

$LiAlH_4$ is a strong reducing agent with chemical formula $LiAlH_4$.

* The m.wt. of this is 36.
* This is used for reducing the different functional group like aldehyde, ketone, ester, carboxylic acid and CN etc.

## Method of preparation

1- Laboratory method :-

In laboratory method, LiH is reacted with $AlCl_3$ to produce $LiAlH_4$.

$$4LiH + AlCl_3 \longrightarrow LiAlH_4 + 3LiCl$$

2- Industrial method -;

In industrial method, it is synthesized into 2 step.

Step-1 → Sodium and aluminium metal is treated with $H_2$ which form $NaAlH_4$.

Step-2 → Further, $NaAlH_4$ is react with LiCl which produce $LiAlH_4$.

$$Na + Al + 2H_2 \longrightarrow NaAlH_4$$

$$NaAlH_4 + LiCl \longrightarrow LiAlH_4 + NaCl$$

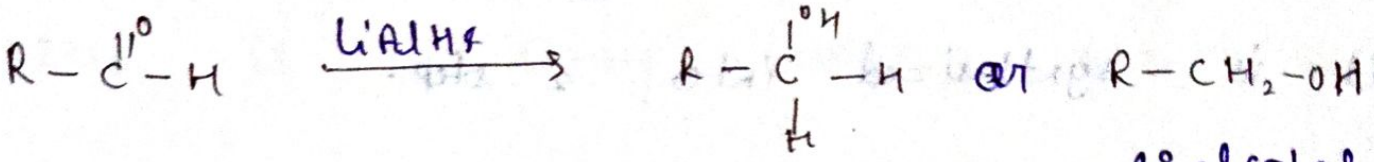
## Chemical rxn of $LiAlH_4$

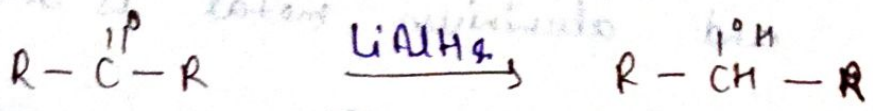
1- Reduction of aldehyde and ketone -;

* $LiAlH_4$ is a strong reducing agent and it converts aldehyde and ketone into alcohol.

After reduction aldehyde is convert into primary alcohol and ketone is convert

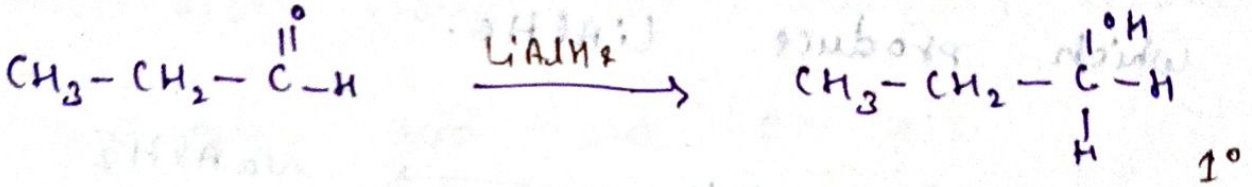
into secondary alcohol.

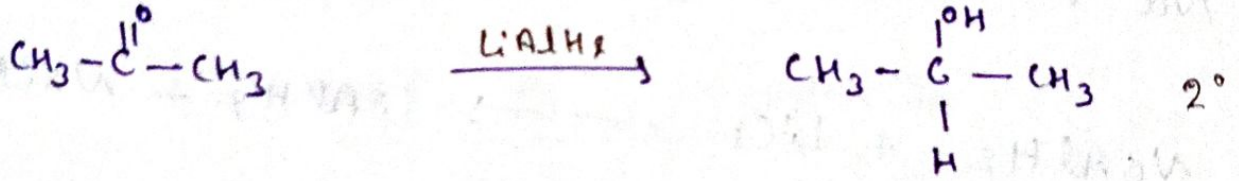


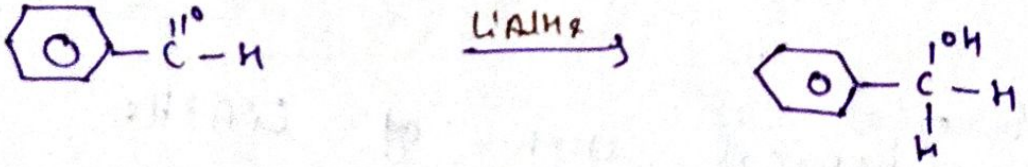




2° alcohol

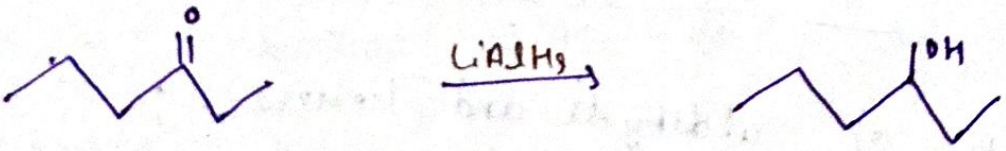
Ex-1




Benzyl alcohol




Hexan ol -3

2 - Rxn with carboxylic acid :-

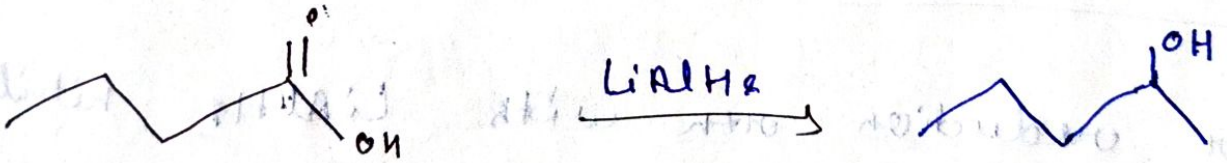
When acid reacts with $LiAlH_4$ then after reduction acid is convert into alcohol and release water.

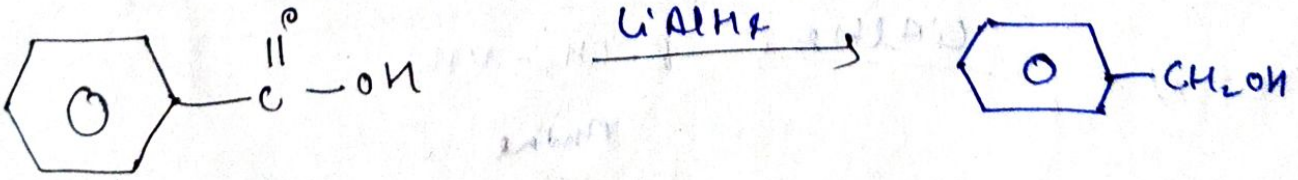
$$R-\overset{\overset{O}{\|}}{C}-OH \xrightarrow{LiAlH_4} R-CH_2-OH + H_2O$$

1° alcohol

Ex :-

$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OH \xrightarrow{LiAlH_4} CH_3-CH_2-CH_2OH$$



3- Reduction of ester and amides →

After reduction with with $LiAlH_4$ ester is dissociated into two molecules of alcohol and amide convert into amines.

$$R-\overset{O}{\overset{\|}{C}}-O-R \xrightarrow{LiAlH_4} R-CH_2-OH + R-OH$$

Ester Alcohol Alcohol

$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{LiAlH_4} R-CH_2-NH_2 + H_2O$$

Amide amines

4- Reduction of nitriles (cyanides) →

After reduction with with $LiAlH_4$ nitrile gives amine product.

$$R-C\equiv N \xrightarrow{LiAlH_4} R-CH_2-NH_2$$

Amine

# $NaBH_4$ (sodium boro hydrade)

* It is more specific and reduces only ketones and aldehyde and convert it into alcohol.

* These rxn are perform in the polar solvent like THF, DME, water and ethanol.

## Chemical rxn of $NaBH_4$

1- Reduction of aldehyde and ketone →

$$R-\overset{O}{\overset{\|}{C}}-H \xrightarrow{NaBH_4} R-\underset{H}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-H$$

$$R-\overset{O}{\overset{\|}{C}}-R \xrightarrow{NaBH_4} R-\overset{OH}{\overset{|}{CH}}-R$$

2- Rxn with carboxylic acid →

$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{NaBH_4} R-CH_2-OH + H_2O$$

3- Reduction of ester and amide :

$$R-\overset{O}{\overset{\|}{C}}-OR \xrightarrow{NaBH_4} R-CH_2-OH + R-OH$$

Ester — Alcohol

$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{NaBH_4} R-CH_2-NH_2 + H_2O$$

Amide — Amines

4- Reduction of nitriles (cyanides) :

$$R-C\equiv N \xrightarrow{NaBH_4} R-CH_2-NH_2$$

# Naming orth

## 1- Clemmenson reduction orth -:

* CRR is used to reduce the aldehyde and ketone into alkane.

* In CRR the carbonyl group of aldehyde and ketone is convert into methylene grp when it is reacted with Amlegated zinc in acidic medium.

$$R-\overset{O}{\overset{\|}{C}}-H \xrightarrow[HCl]{CRR\ Zn/Hg} R-CH_3 + H_2O$$

Aldehyde

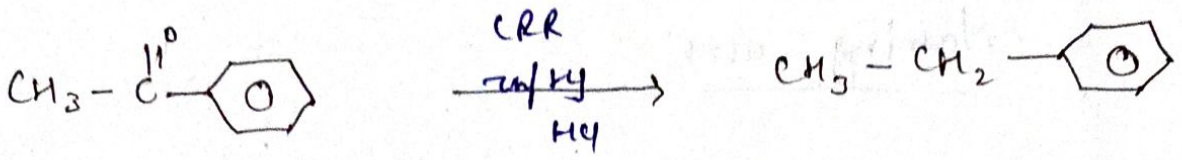
$$R-\overset{O}{\overset{\|}{C}}-R' \xrightarrow[HCl]{CRR\ Zn/Hg} R-CH_2-R' + H_2O$$

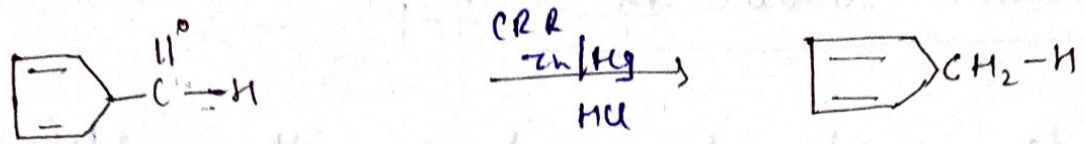
ketone

Ex -:

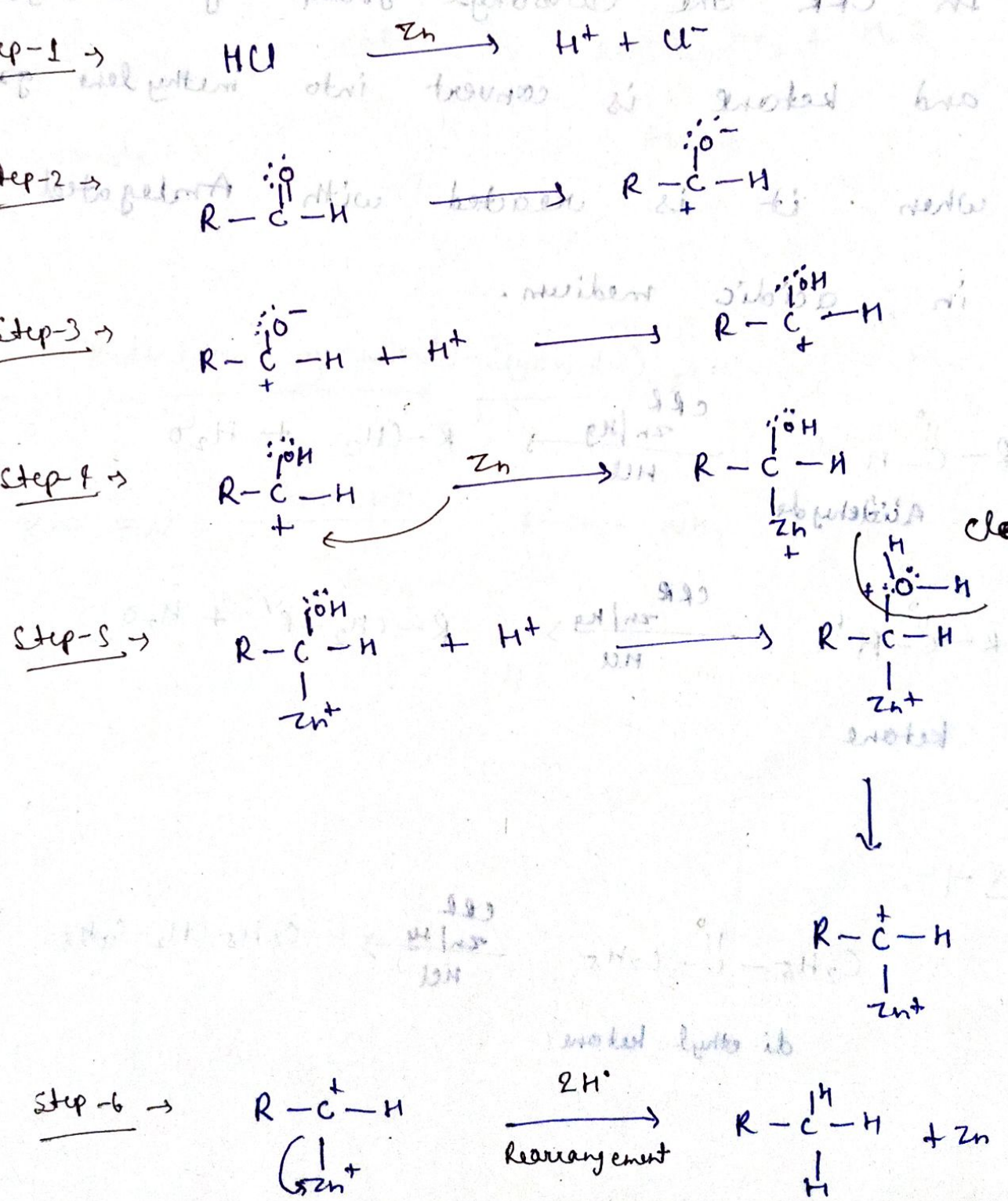
$$C_2H_5-\overset{O}{\overset{\|}{C}}-C_2H_5 \xrightarrow[HCl]{CRR\ Zn/Hg} C_2H_5CH_2-C_2H_5$$

di ethyl ketone


CRR
Zn/Hg
HCl


CRR
Zn/Hg
HCl

## Mechanism


Step-1 →
HCl
Zn
H+ + Cl−
Step-2 →
Step-3 →
Step-4 →
Zn
Cleavage
Step-5 →
Step-6 →
2H+
Rearrangement
+ Zn

## Application of CKR

* It is used to reduce aliphatic and mixed aliphatic aromatic carbonyl compound.
* Reduction of keto acid with α-β keto acids are generally not reduced by CKR.

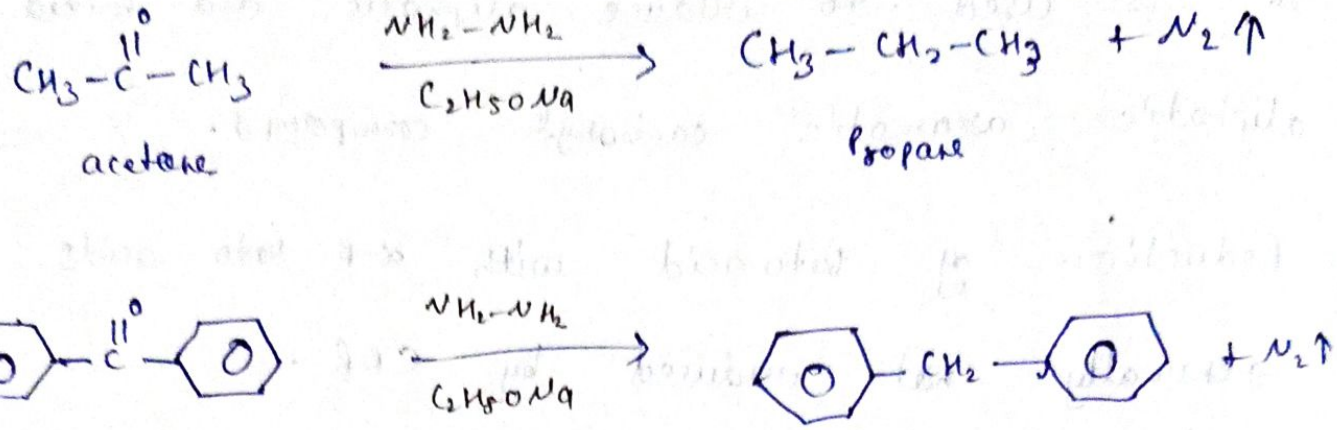
## 2- Wolff kishner reduction rxn

* WKR rxn are these rxn in which the ketone compounds are reduced into n-alkane.
* In this rxn ketone are heated with hydrazin and 180° C in the presence of sodium ethoxide solvent and ketone is reduced to form alkane.
* After this rxn water and nitrogen gas is release.

$$R-\overset{O}{\overset{\|}{C}}-R \xrightarrow[\text{Hydrazine, } 180^\circ C]{NH_2-NH_2} R-\overset{N-NH_2}{\overset{\|}{C}}-R + H_2O \xrightarrow[\text{Sodium ethoxide}]{C_2H_5ONa} R-CH_2-R + N_2\uparrow$$

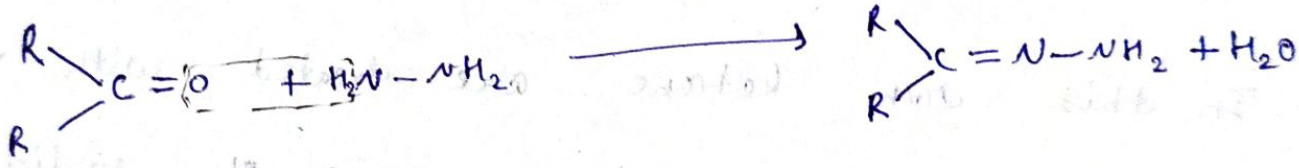
alkane

Ex -:

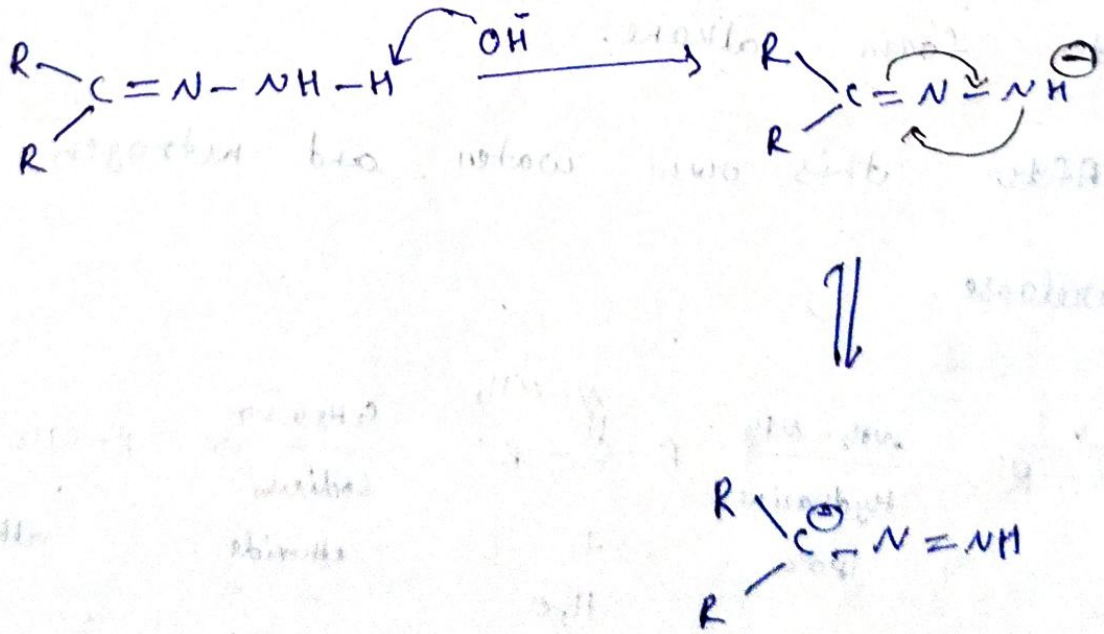



## Mechanism of WKR with

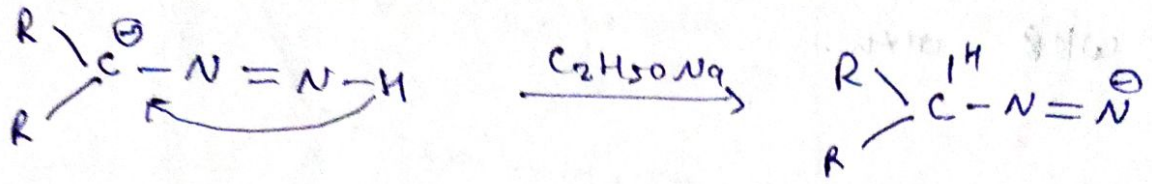
Step-1 →



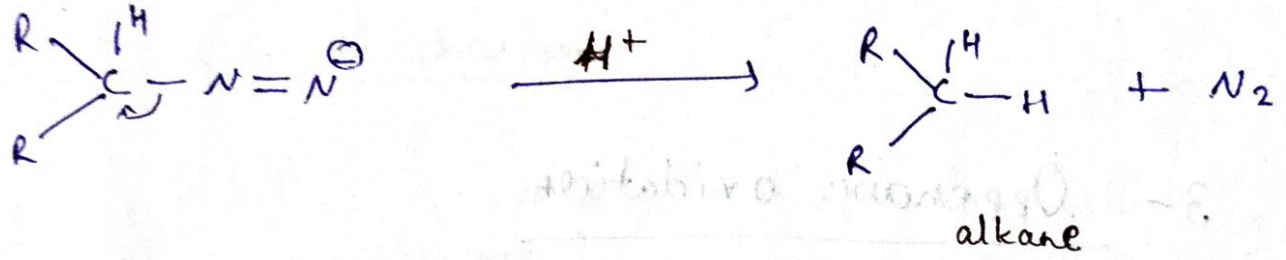

Step-2 →



Step-3 →

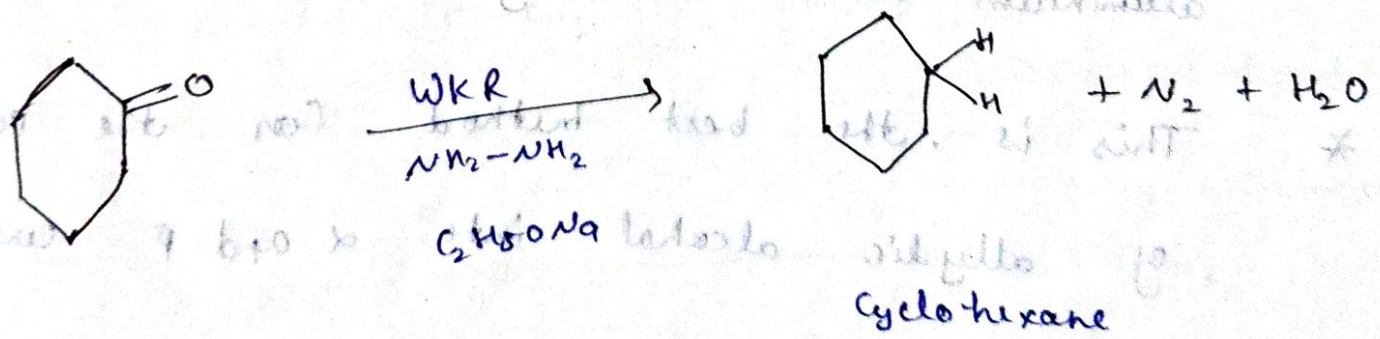



Step-4 →




## Application of WKR

* Cyclohexanone is convert into cyclohexane by this rxn.

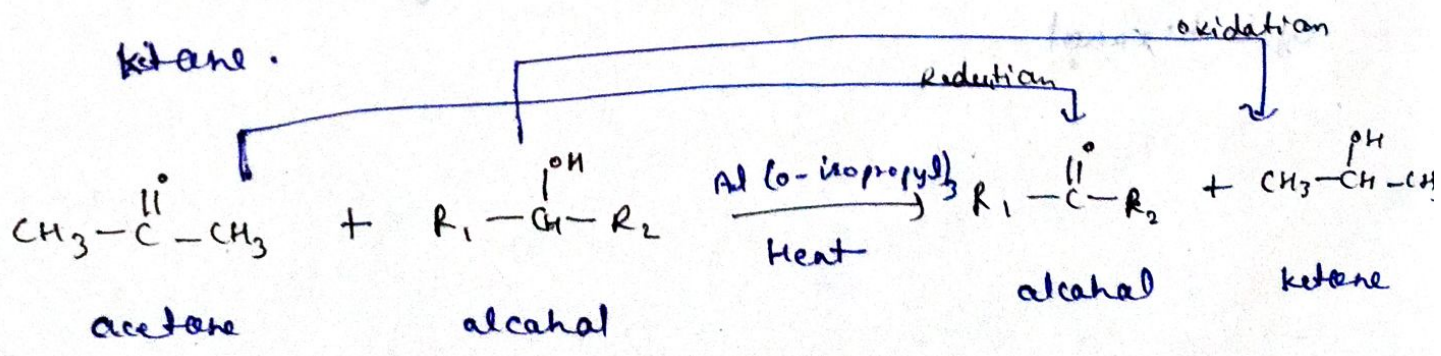


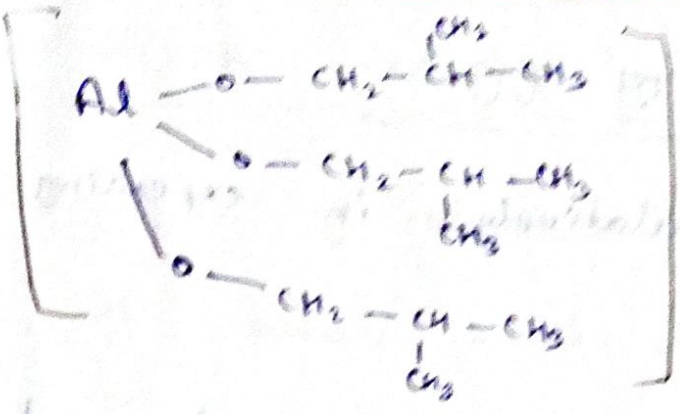

Cyclohexanol

* Acetophenone is convert into methyl benzene by WKR rxn.

## 3- Oppenauer oxidation

* OO is an aluminium alkoxide catalysed oxidation of secondary alcohol into corresponding ketone.
* This rxn is opposite to MPB rxn.
* In this rxn aluminium tri iso propoxy or aluminium tri iso butoxy is used as catalyst.
* This is the best method for the conversion of allylic alcohol into α and β unsaturated ketone.

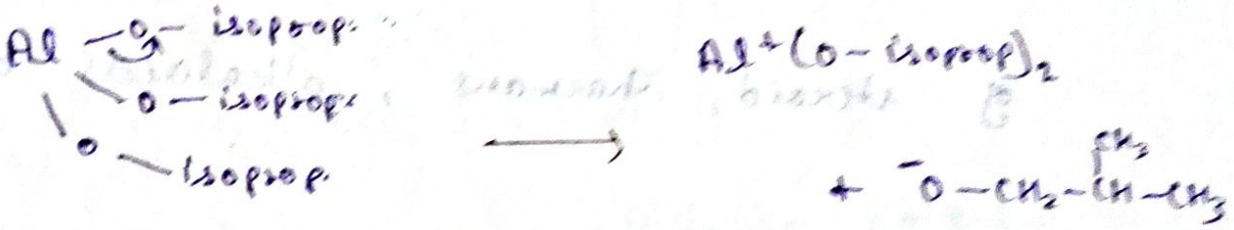




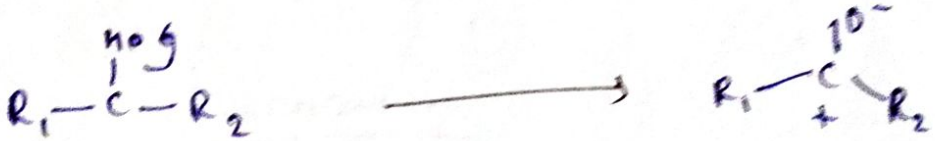
Aluminium isopropoxy

## Mechanism

Step-1 →



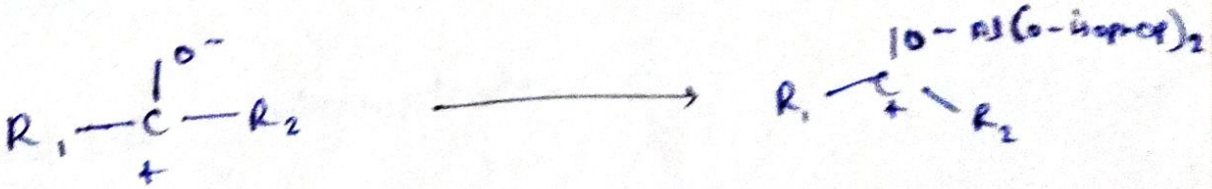
Step-2 →



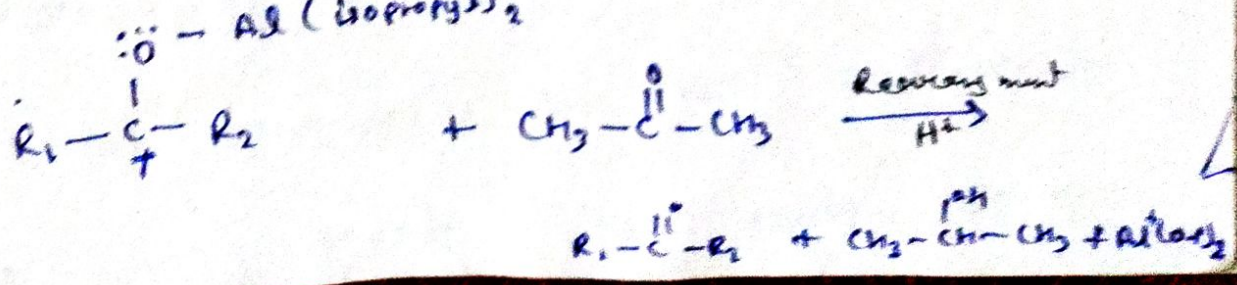
Step-3 →

iso propyl alcohol

Step-4 →



Step-5 →

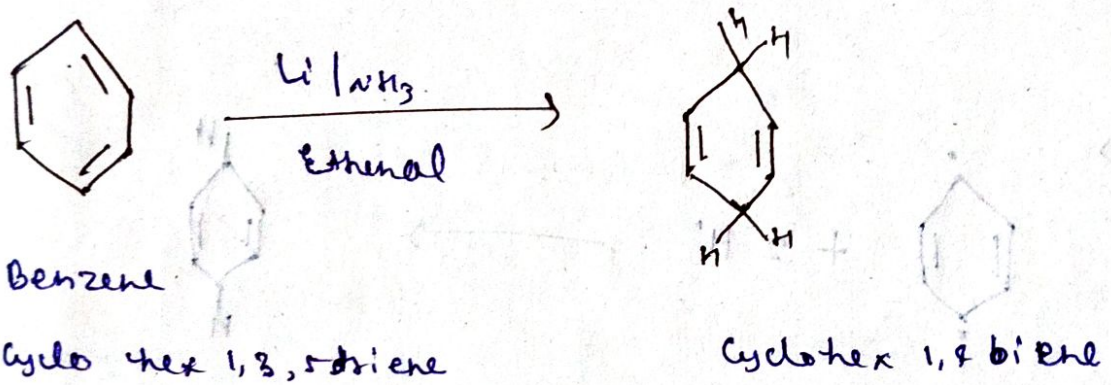


# Uses of OO

* OO used as relatively in expessing and non toxic reagents.
* This rxn utilized mild and gentle rxn.
* This rxn is used for vrabile substance.
* This rxn is commonly used in varrious industrial process such as the synthesis of steroid, harmons, alkaloids and terbens.

# 4- Birch reduction rxn

The reduction of aromatic compound in the presence of alkali metal, liquid ammonia and alcohol into cyclohex-1,4-diene compound is called birch reduction rxn.




## Mechanism

* The solvated $e^-$ accept an $e^-$ and generate the free radical anion which then takes a proton from the alcohol and form a free radical intermediate.

* The role of alcohol is to supply the $H^+$ beco2 ammonia is not sufficient acidic to supply the proton to all

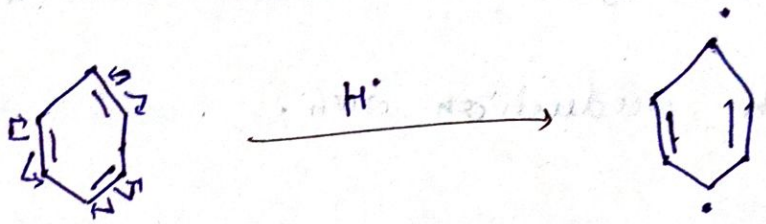
intermediate action.

(11)

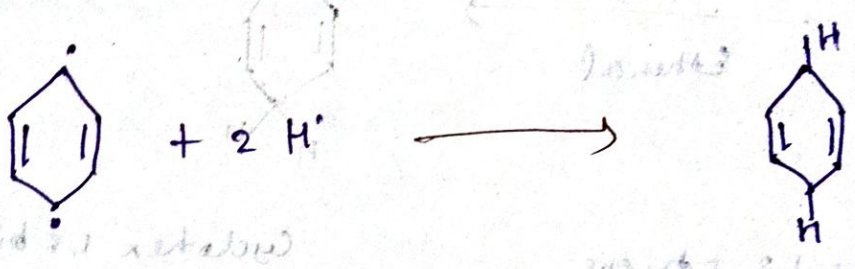
Step-1 → $NH_3 + 2R-O-H \longrightarrow 2R-O^{\cdot} + 2H^{\cdot}$

Base

Step-2 →



Step-3 →



Step-4 →

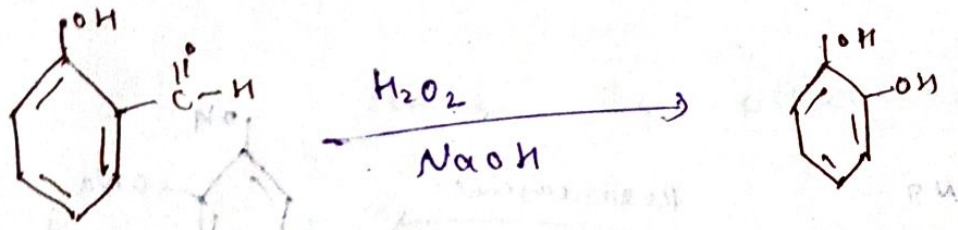
$R-O^{\cdot} + {}^{\cdot}O-R \longrightarrow R-O-O-R$

alkyl peroxide

## 5- Dakin rxn ✓

* This rxn is proposed by henary drystale 'dakin.

* Dakin rxn involves the replacement of aldehyde group of ortho and para hydroxy benzaldehyde in the present of base and $H_2O_2$.




o - hydroxy benzeldehyde

catehal

### Mechanism

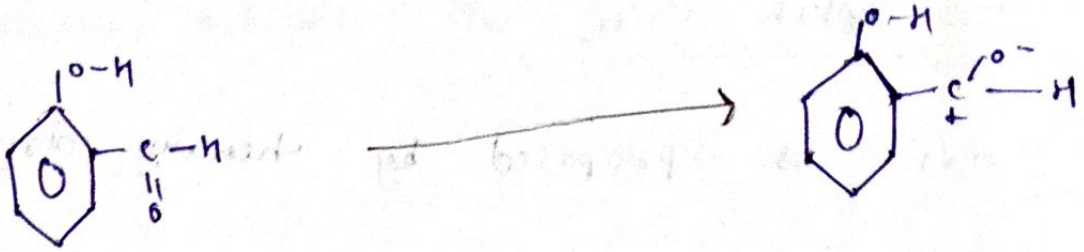
Step-1 → $H-O-O-H \longrightarrow H-O-O^- + H^+$

$NaOH \longrightarrow Na^+ + OH^-$

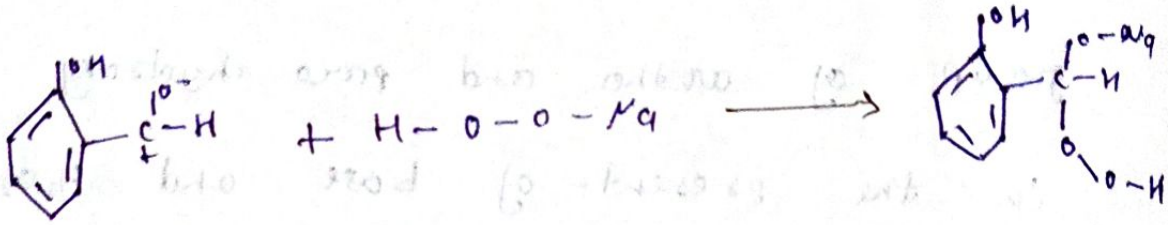
Step-2 → $H-O-O^{\ominus} + Na^+ \longrightarrow H-O-O-Na$

$H^+ + OH^- \longrightarrow H_2O$

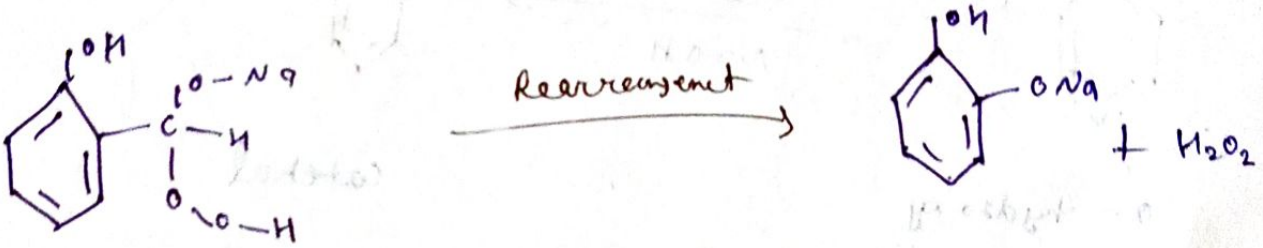
Step-3 →



Step-4 →



Step-5 →




Step-6 →

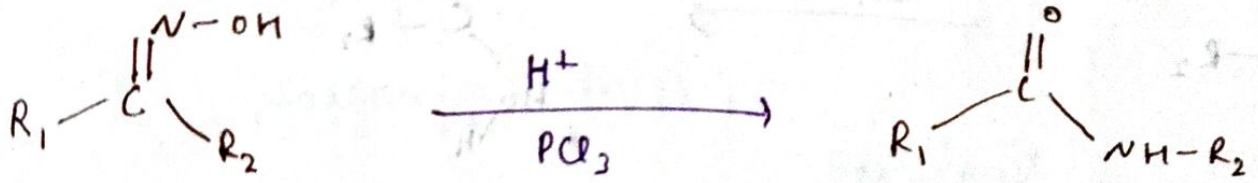
## Usep

* Dakin rxn is most commonly used to synthesise benzene diol and alkoxy phenol. Ex. Catechol
* Dakin rxn is also used to synthesise guaiacol which is a precursor of several flavours.

* Dakin rxn is also used to synthesise hydroquinone which is a common photograph developing agent.

## 6- Bechmann Rearrangement rxn

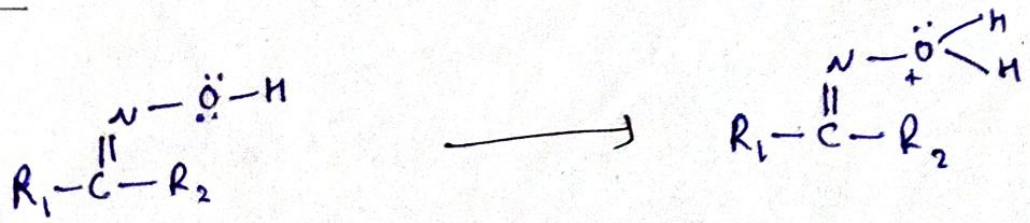
Bechmann rearrangement rxn is an acid catalyst rxn in which ketoxim is convert into N- alkyl amide by rearrangement.



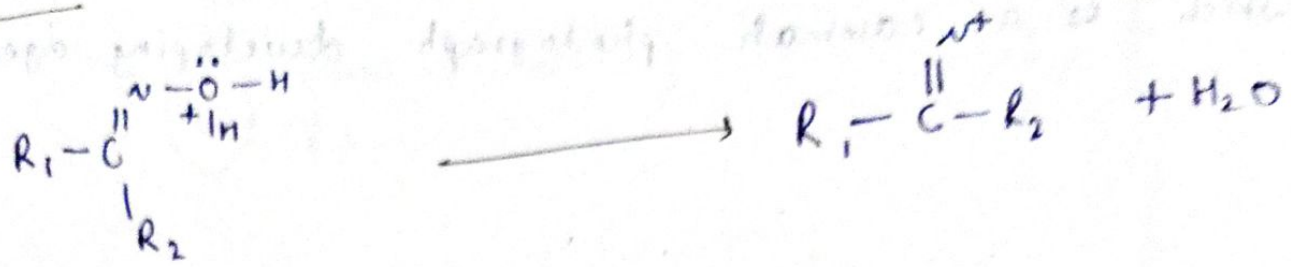

ketoxim Amide

### Mechanism

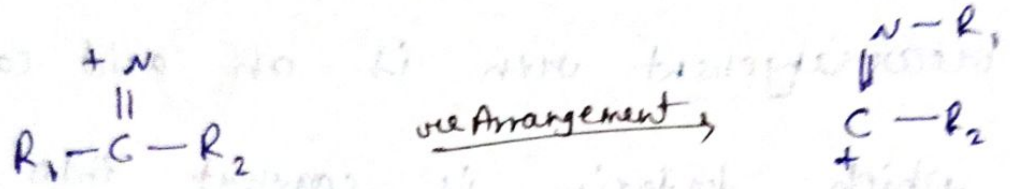
Step-1 :-



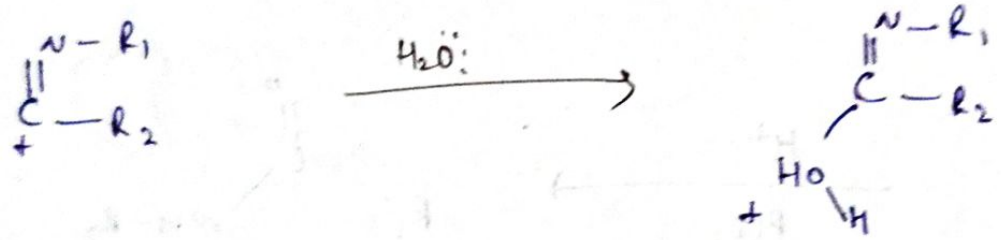
Step-2 →



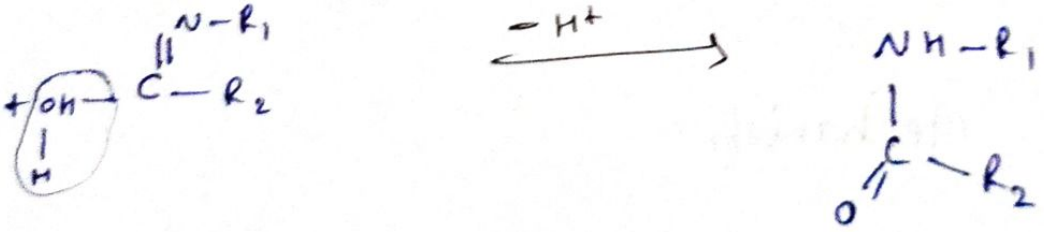
Step-3 →



Step-4 →



Step-5 →



## Uses

* The bechmann rearrangement synthesis is helpful in the production of some of the chiro bicyclic lactams.

* This rxn is used for industrial synthesis of PCM.

* This synthesis rxn is used in the synthesis of following drugs—

Benzepril

Cefaramide

Etazepine.

Prazepine

Enprazepine

## 7 - Schmidt rxn

Schmidt rxn is a type of rearrangement rxn in which carboxyllic acid, aldehyde or ketone is react with hydrazoic acid and gives different rearrangement product.

$$R-\overset{O}{\overset{||}{C}}-OH + N_3H \xrightarrow{H_2SO_4} R-NH_2 + CO_2 + N_2$$

Hydrazaic acid — Amine

$$R-\overset{O}{\overset{||}{C}}-R + N_3H \xrightarrow{H_2SO_4} R-\overset{O}{\overset{||}{C}}-\overset{H}{\overset{|}{N}}-R + N_2$$

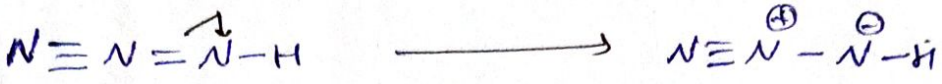
ketone — Amide

$$R-\overset{O}{\overset{||}{C}}-H + N_3H \longrightarrow R-C\equiv N + R-\underset{H}{\underset{|}{N}}-\overset{O}{\overset{||}{C}}-H$$

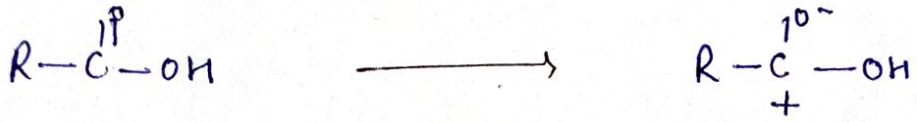
Alkyl nitrile — Formyl amide

# Mechanism

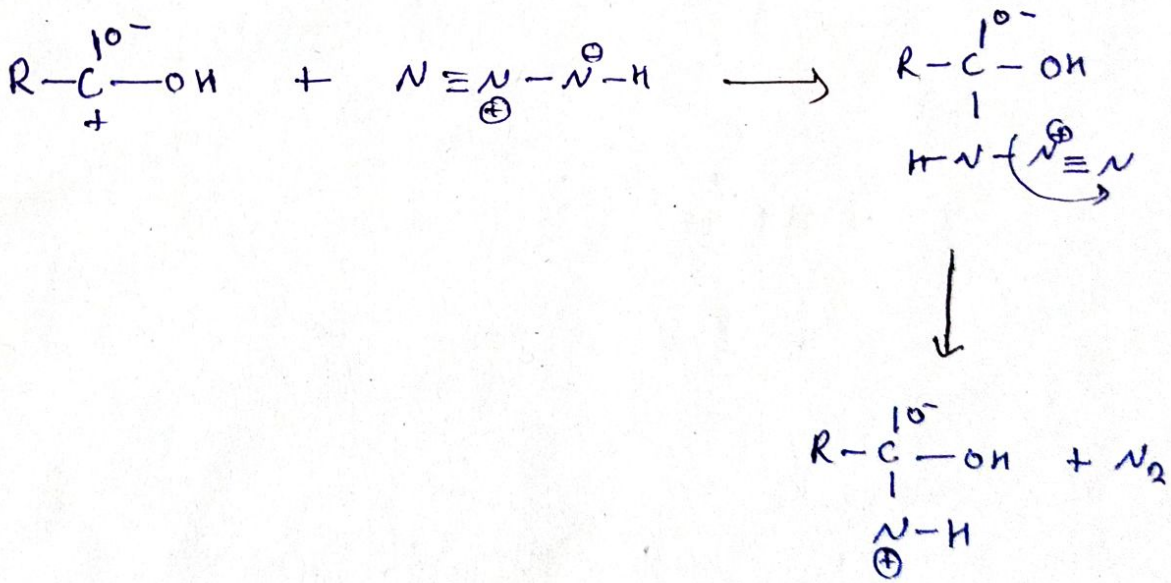
Step-1 →



Step-2 →



Step-3 →



Step-4 →