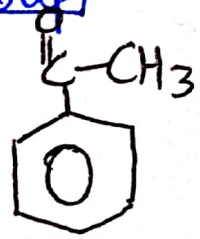
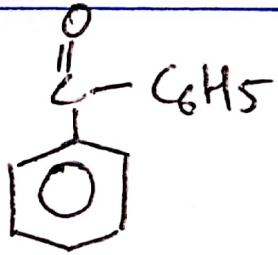
# CARBONYL COMPOUNDS

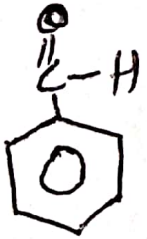
- Functional Group [ $-\overset{O}{\overset{\|}{C}}-$ ]
- Derivatives of formaldehyde [ $H-\overset{O}{\overset{\|}{C}}-H$ ]
- $R-\overset{O}{\overset{\|}{C}}-H$ = Aldehyde
- $R-\overset{O}{\overset{\|}{C}}-R$ = Ketone. (Symmetrical or unsymmetrical)
- General Formula $C_nH_{2n}O$
- Aldehyde group — present in sugars and oils.
- Ketone group — present in camphor, menthone. and sugars.



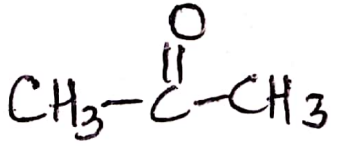
Acetophenone.



Benzophenone.



Benzaldehyde

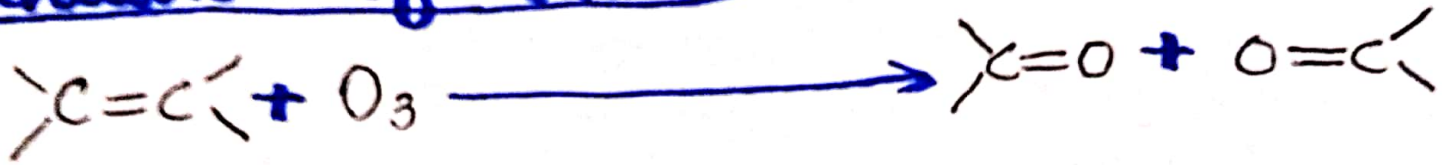


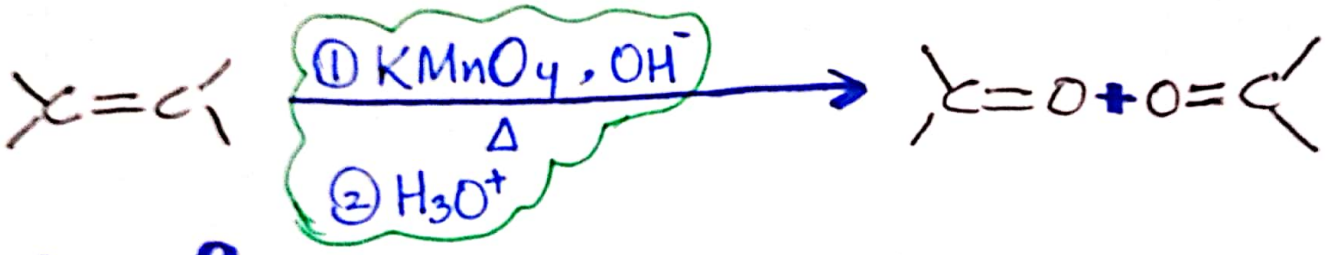
Acetone

# PREPARATORY METHODS

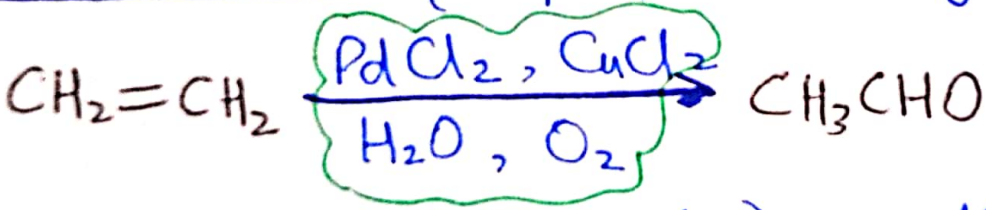
## For Aldehyde and ketone

### 1. Oxidation of alkene:



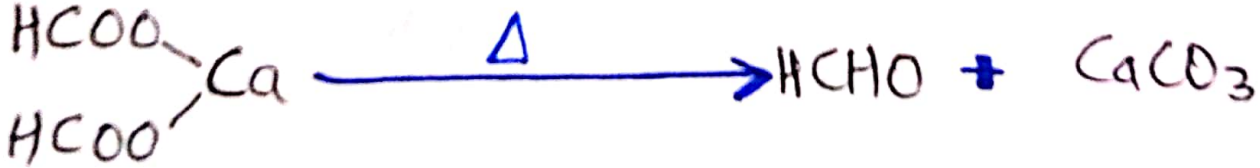



**Wacker Process** (to prepare aldehyde on industrial scale)

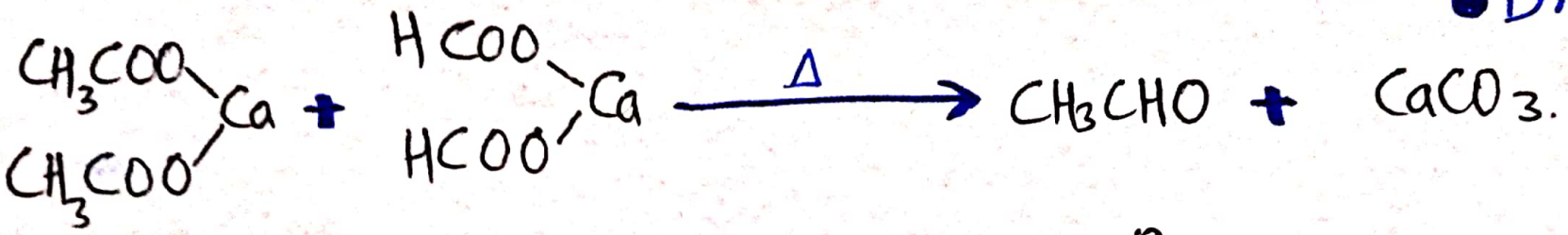


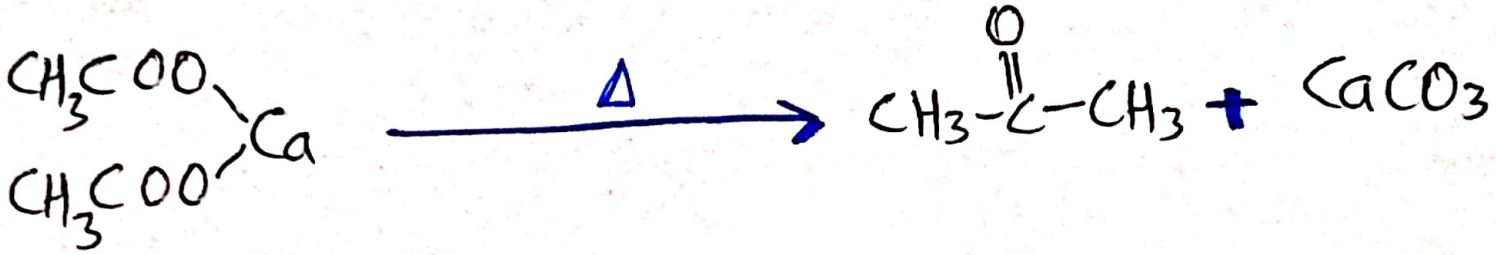

- Cu(II) oxidizes Pd(0) to Pd(II), itself oxidizes back by air.

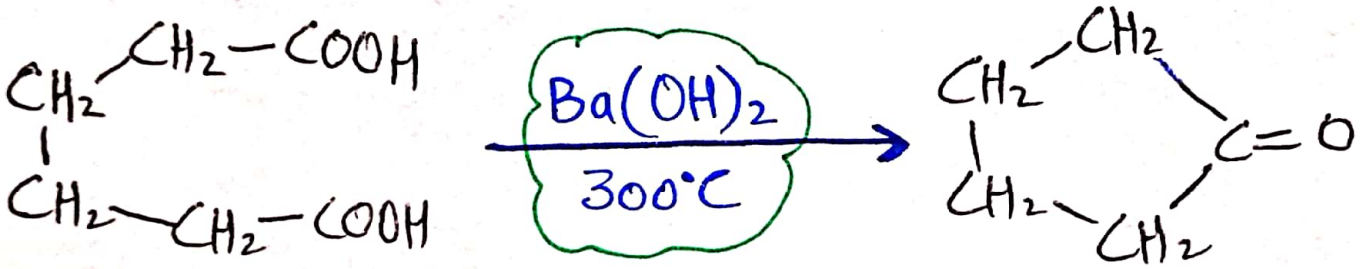
### 2. Pyrolysis of calcium salts of carboxylic acids



● Dry Distillation








## 3. Oxidation of Alcohol:

1° $RCH_2OH \xrightarrow{[O]} RCHO$

2° $RCHR(OH) \xrightarrow{[O]} RCOR$

- In laboratory = $K_2Cr_2O_7/H_2SO_4$
- In industries = $O_2$ (Air)

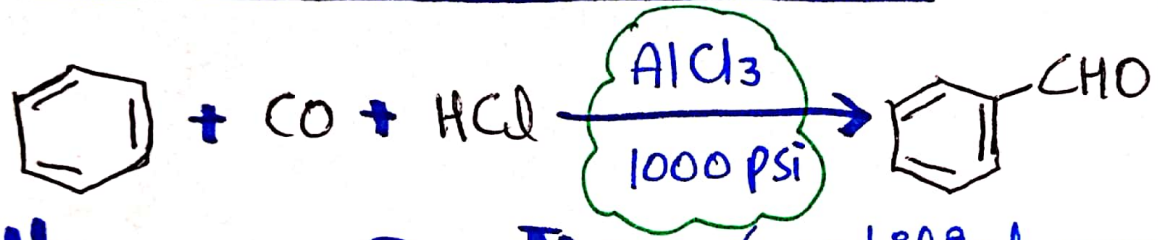
## For Aldehyde:

### 4. Hydroformylation of terminal alkene:

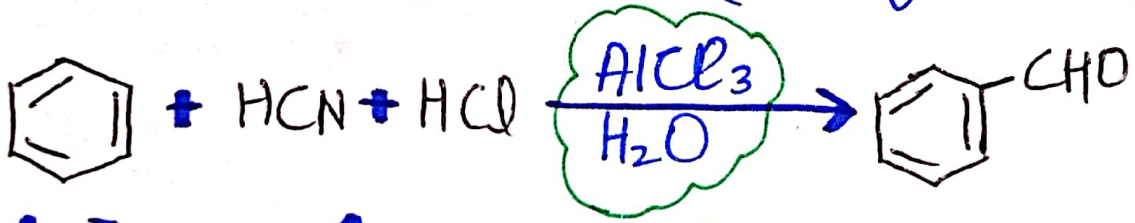
$$CH_3CH=CH_2 + CO + H_2 \xrightarrow[2000\,psi,\,130^\circ C]{HCo(CO)_4} CH_3CH_2CH_2CHO$$

(Oxoprocess)

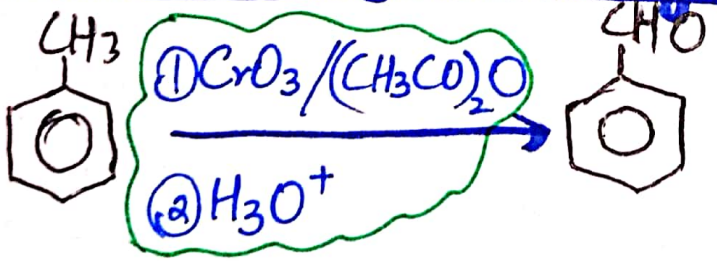
### 5. Gatterman-Koch Reaction



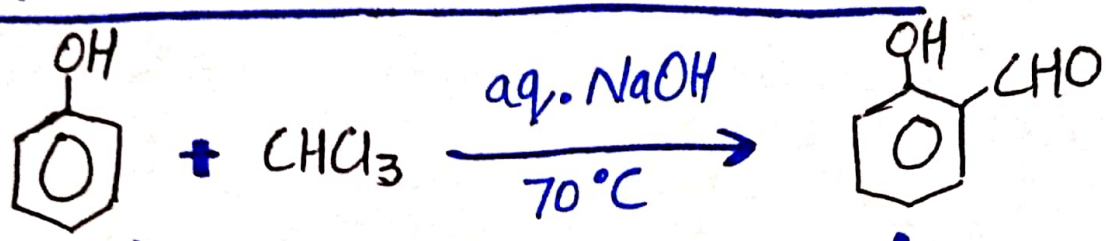

**Gatterman Reaction.** (modified rxn)



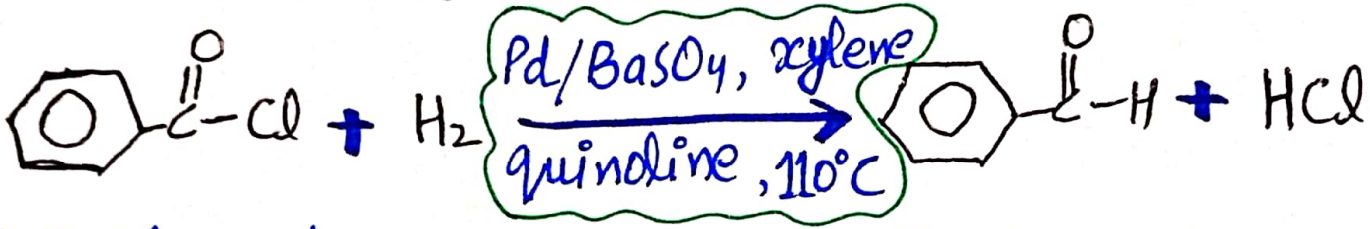

### 6. Oxidation of methylbenzene:



## 7. Reimer Tiamann Reaction:

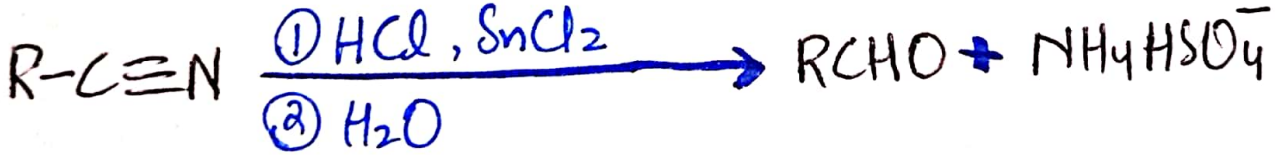



## 8. Reduction of acid cholide: (Rosemund Reduction)



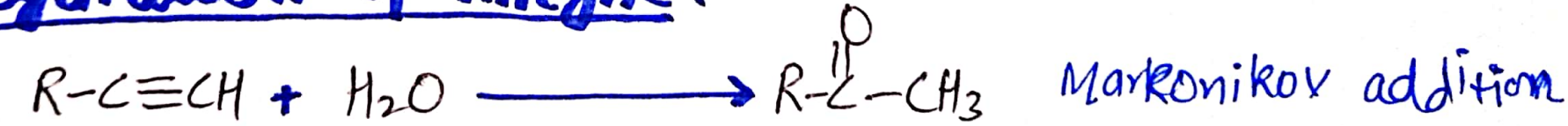

- Suitable reducing agent = $LiAlH(t\text{-}BuO)_3$

## 9. From Nitriles: (Stephen Reaction)




# FOR KETONES

## 10. Hydration of Alkyne:



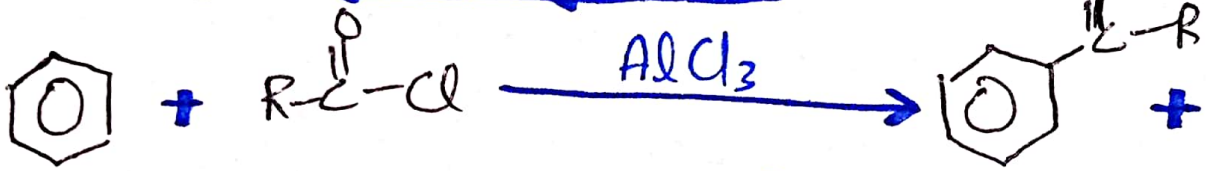

Markonikov addition

## 11. Grignard Synthesis:

$$R\text{-}CN + R'MgX \xrightarrow{\text{(ii) } H_3O^+} \underset{R}{\overset{R}{>}}C=O + NH_3 + Mg\overset{OH}{\underset{X}{}}$$

- $R\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl$ can also be used.

## 12. Friedal craft Acylation:




## 13. From Carboxylic Acid:

$$RCOOH + 2RLi \longrightarrow R\text{-}\overset{O}{\overset{\|}{C}}\text{-}R + H_2O$$

## 14. From Acid chloride:

$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl + R_2CuLi \longrightarrow R\text{-}\overset{O}{\overset{\|}{C}}\text{-}R.$$

less reactive
than Grignard reagent.
It donot react with $-NO_2$, $-CN$, $-CO-$ and $-COOR$.

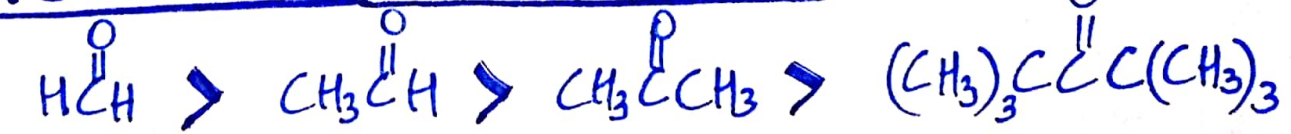
# PHYSICAL PROPERTIES:

- volatile liquids with characteristic odour.
- Simple aldehydes — pungent smell
- Aromatic aldehyde and most ketones — pleasant smell.
- Formaldehyde is a gas.
- B.P° ——— less than alcohol but higher than alkanes.
- Dipole-dipole interactions.
- Soluble in organic solvents.

# CHEMICAL REACTIONS:

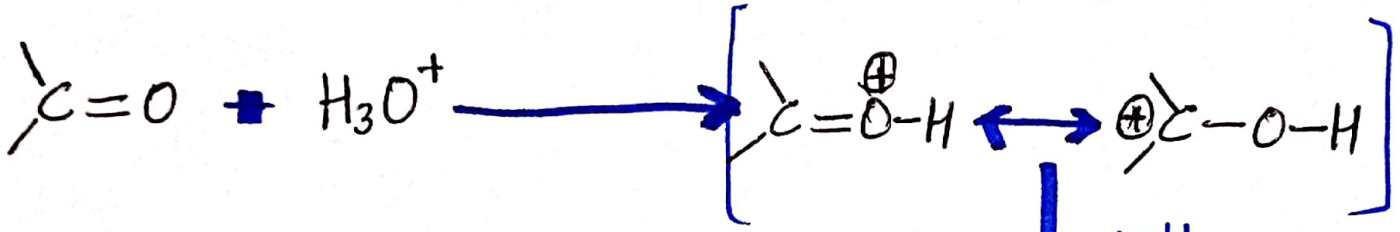
- Nucleophilic addition reactions either acid catalysed or base catalyzed.
- Highly Reactive

## 1. Nucleophilic Addition Reactions:

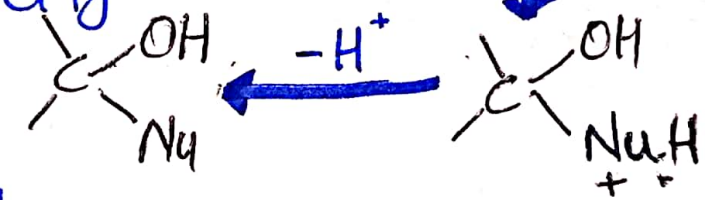
Reactivity order 

# General Mechanisms :-

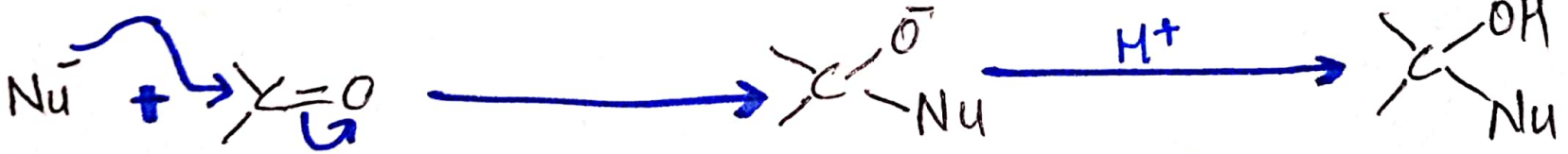
## 1. Acid Catalyzed :-




- Increases electrophilicity of Carbon.

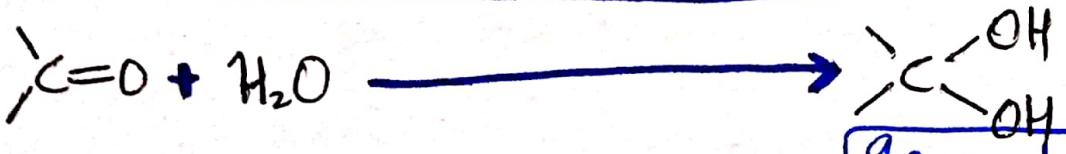



## 2. Base Catalyzed :-


- Increases Nucleophilicity of Nucleophile.

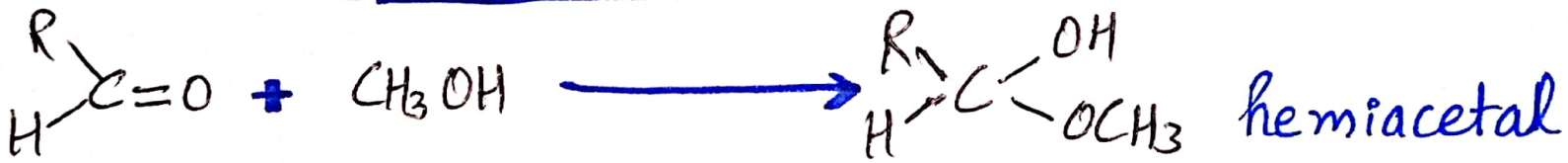
## A- Addition of water:



gem-diol (unstable)
(Stable only in large amount of water)

- HCHO in water —— almost all present in the form of $H_2C(OH)_2$
- $CH_3CHO$ in water —— RCHO and $RCH(OH)_2$ almost in equal amounts.
- $CH_3COCH_3$ in water —— Almost all present in keto form

## B- Addition of Alcohols:-



hemiacetal

hemiketal

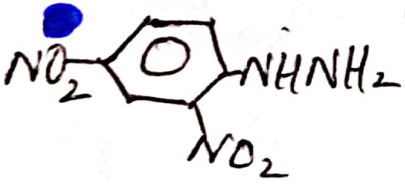
- Hemiacetal and hemiketal are stable in alcoholic soln.

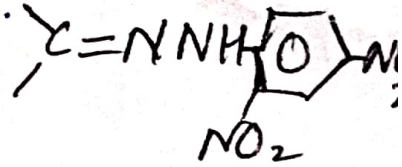
## C. Addition of Ammonia and its derivatives:

$>C=O + NH_2- \longrightarrow >C=N- + H_2O$

Imine derivatives.

- $(NH_3)$ Ammonia $\longrightarrow$ Imine. $(>C=NH)$
- $(NH_2OH)$ Hydroxylamine. $\longrightarrow$ Oxime. $(>C=N-OH)$
- $(NH_2NH_2)$ Hydrazine $\longrightarrow$ Hydrazone. $(>C=NNH_2)$
- $(C_6H_5NHNH_2)$ Phenylhydrazine $\longrightarrow$ Phenyl hydrazone $(>C=NNHC_6H_5)$
- $(NH_2CONHNH_2)$ Semicarbazide $\longrightarrow$ Semi carbazone. $(>C=NNHCONH_2)$
- 2,4-DNPH $\longrightarrow$ 2,4-DNPH Hydrazone.



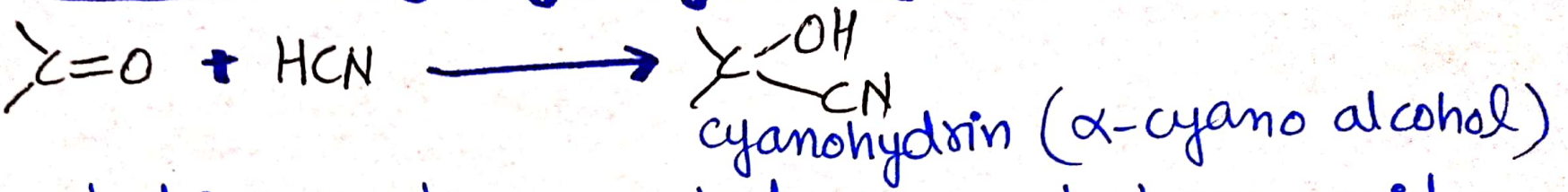


**2,4-DNPH Test** for identification and characterizations of carbonyl compounds —— yellow to red crystalline ppt.

## D. Addition of Grignard Reagent:

- RCHO $\longrightarrow$ 2°-OH
- HCHO $\longrightarrow$ 1°-OH
- RCOR $\longrightarrow$ 3°-OH

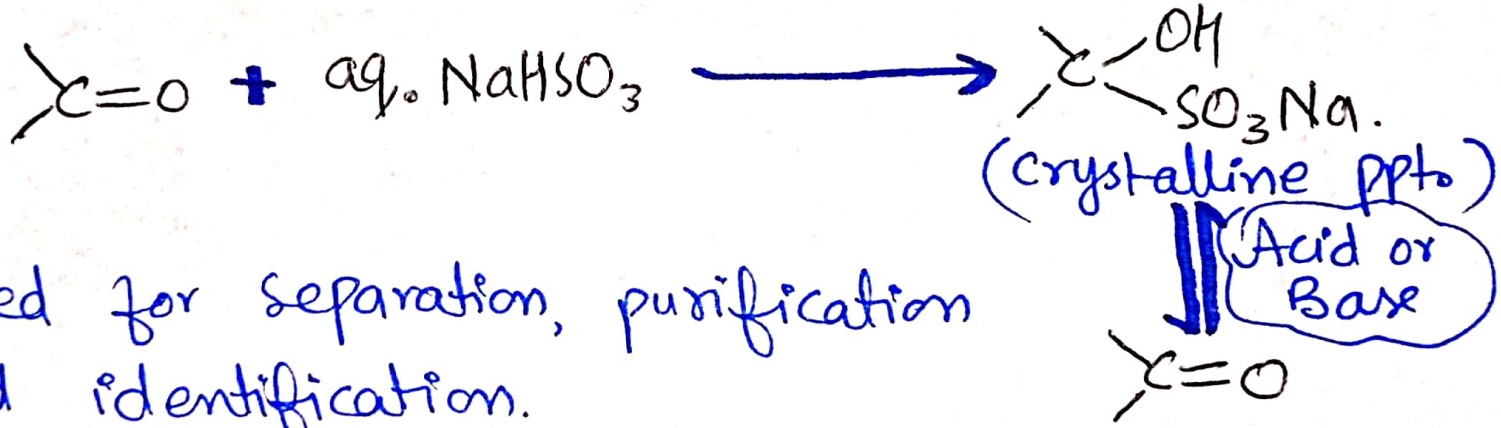
## E. Addition of hydrogen cyanide:-




cyanohydrin (α-cyano alcohol)

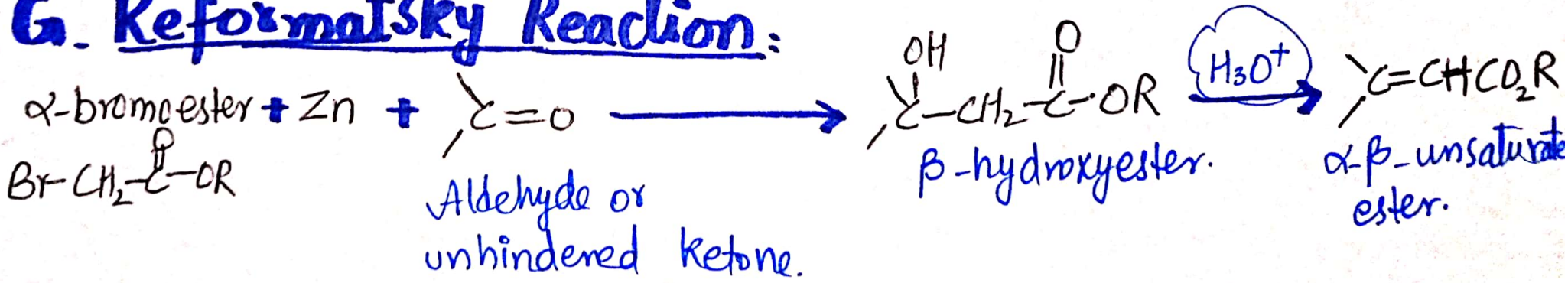
- cyanohydrin can be converted to α-hydroxy acid or α,β-unsaturated acids on acidic hydrolysis.

## F. Addition of Bilsulfite:




- used for separation, purification and identification.

## G. Reformatsky Reaction:



## 2. Aldol Condensation:

$CH_3CHO$ + 10% aq. NaOH ⟶ $CH_3-\underset{OH}{CH}-CH_2CHO$ (Aldol)

↓

Carbonyl compound having α-hydrogen.

3-hydroxyaldehyde.

- can also be catalyzed by strong acids ⟶ dehydration → α, β-unsaturated product.
- to prepare large compound from two simple units.

## 3. Halogenation:

- Catalyzed by both acid or base ⟶ All α-H replaced with halogen. (form haloform)
  - acid → only monohalogenated product formed

Reduced. $CH_3-\overset{O}{\overset{\|}{C}}-H + 3I_2 + 4NaOH \longrightarrow CHI_3 + HCOONa + 3NaI + 3H_2O$

Iodoform.

### Iodoform Test:

- methyl ketones and Acetaldehyde $\xrightarrow{I_2/NaOH}$ yellow ppt. of $CHI_3$
- Methyl ketone ⟶ Carboxylic acid (one C less)

## 4. Oxidation :-

**A. Aldehyde :** (by strong and mild oxidizing agents) even by air (autooxidation)

- Ease of oxidation ⟶ test to distinguish aldehyde from ketones.

### (i) Fehling's Solution Test :

- Alkaline solution of cupric tartarate complex ion.

$$R-\overset{O}{\overset{\|}{C}}-H + Cu(OH)_2 + NaOH \longrightarrow RCOONa + Cu_2O + 3H_2O$$

only aliphatic aldehydes.

brick-red ppt.

### ii) Benedict's Solution Test :

- Alkaline Soln. of cupric citrate complex ion.
- Cuprous oxide ppt. ($Cu_2O$) formed.
- only aliphatic aldehydes give this test.

- To determine glucose in blood or urine.

(iii) **Tollen's Test**: (Ammonical silver nitrate soln.)

$$RCHO + [Ag(NH_3)_2]OH \longrightarrow RCOONa + \underset{\text{Silver mirror.}}{2Ag} + 3NH_3 + H_2O$$

## B. Oxidation of Ketone:

Ketones with α-H $\longrightarrow$ Prolonged heating with strong oxidizing agent. $KMnO_4$ or $Na_2Cr_2O_7$ or conc. $HNO_3$ ↓ oxidative cleavage

$$RCH_2\overset{\overset{O}{\|}}{C}CH_2R' \longrightarrow RCOOH + R'CH_2COOH.$$

## C. Baeyer Villiger Oxidation:

$$CH_3CHO + \underset{\text{Peracetic acid.}}{CH_3COOOH} \longrightarrow 2CH_3COOH.$$

## D. Oxidation of methylene group:

$$CH_3CHO \xrightarrow{SeO_2} CHOCHO$$

$$-CH_2-\overset{\overset{O}{\|}}{C}- \xrightarrow{SeO_2} -\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-$$

## 5. Reduction: (to alcohols or hydrocarbons)

$RCHO \xrightarrow{H_2/Pt \text{ or } LiAlH_4 \text{ or } NaBH_4} RCH_2OH$ 1°-OH

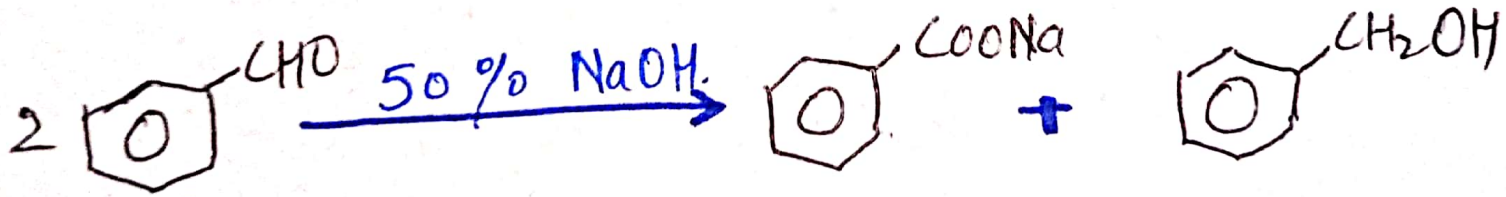
$RCOR \xrightarrow{\text{"}} R-\underset{OH}{CH}-R$ 2°-OH

$RCHO \xrightarrow{NH_2NH_2/KOH} RCH_3$ Wolf-Kishner Red.

$RCOR \xrightarrow{Zn-Hg,\ HCl} RCH_2R$ Clemmenson Red.

## 6. Cannizaro's Reaction: (having no α-H)

$2\ HCHO \xrightarrow{50\%\ NaOH} HCOONa + CH_3OH$




## 7. Willig Reaction:


Aldehyde or Ketone.

Alkene.

## 8. Polymerization :

Addition polymerization —— linear or cyclic polymers.

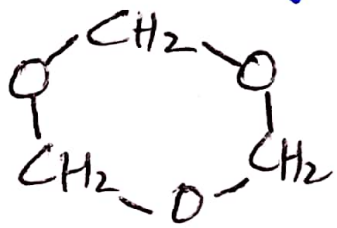
$$n\,CH_2O + H_2O \longrightarrow OHCH_2O(CH_2O)_{n-2}CH_2OH$$

formalin evaporated. Paraformaldehyde.

40 % HCHO

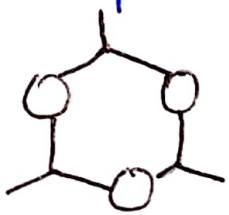
- Conc. aq. soln. of HCHO containing 2 % $H_2SO_4$ distilled.

  metaformaldehyde formed.



- Acetaldehyde treated with few drops of conc. $H_2SO_4$.

  Paraldehyde formed.



- Polymerization is not shown by ketones