

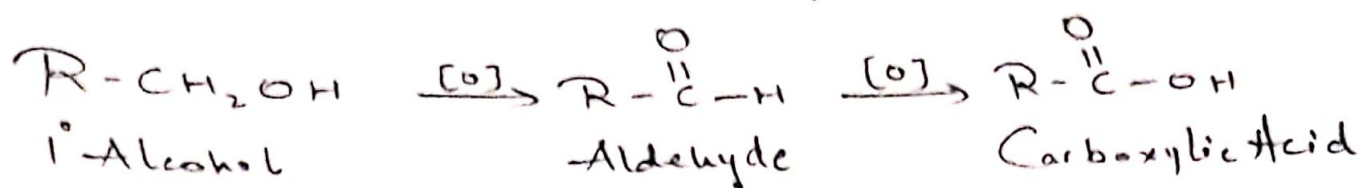
# ORGANIC CHEMISTRY

## Aldehyde & Ketone

≡ Formation of Aldehyde and Ketone :-

≠ Aldehyde

x) Oxidation of Primary Alcohol



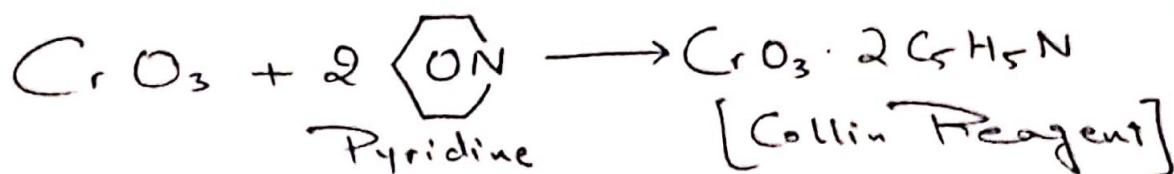
It is difficult to stop the rx<sup>n</sup> at Aldehyde becoz Oxid<sup>n</sup> of Aldehyde to Carboxylic Acid takes place even at Mild Presence of Oxidising agents.

Special Oxidising Agents :-

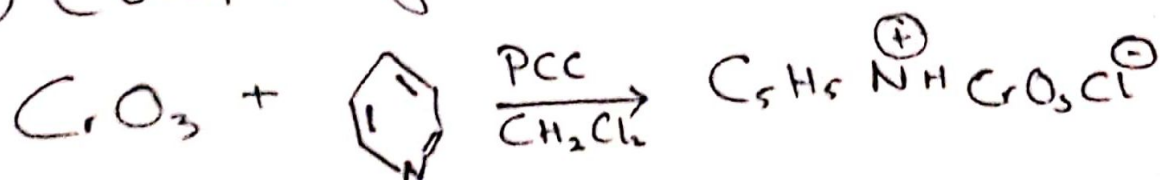
These are specially developed for preparing Aldehydes from Alcohols.

a)\* Sarett's Reagent / Collins' reagent

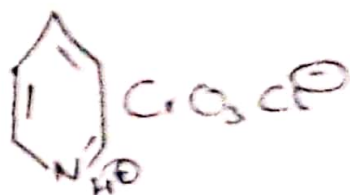
Formed by Addition of  $\text{CrO}_3$  to excess of Pyridine ( $\text{C}_5\text{H}_5\text{N}$ )



b)\* Corey Reagent

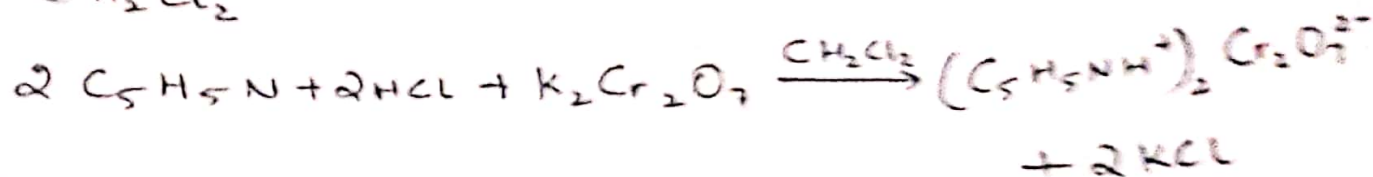


PCC  $\rightarrow$  Pyridinium Chloro Chromate



c) PDC [Pyridinium Dichromate]

Obtained by mixing Pyridine, PDC, HCl in  $\text{CH}_2\text{Cl}_2$



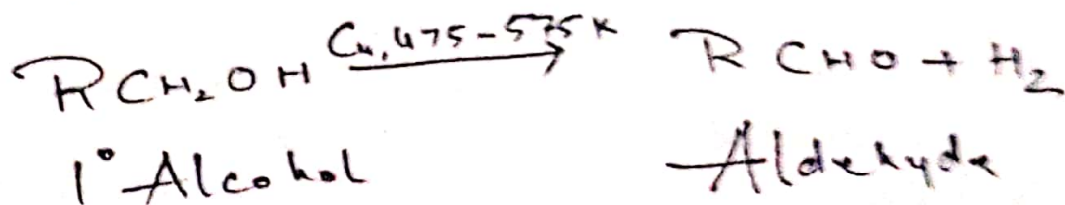
Disadvantages of Using Above Reagents:

- \* They are hazardous to Environment as they are not Eco-friendly.
- \* They are Expensive too, so cannot be used in Laboratory for Oxid. of Alcohols.

Advantages

- \* They are of course helpful in restricting the Rx<sup>n</sup>. to Aldehydes only.
- \* Carbon - Carbon Double Bond if Present in Alcohol, doesn't get Oxidised.

Catalytic Dehydrogenation of Primary Alcohol :-  
It involves direct Elimination of Hydrogen

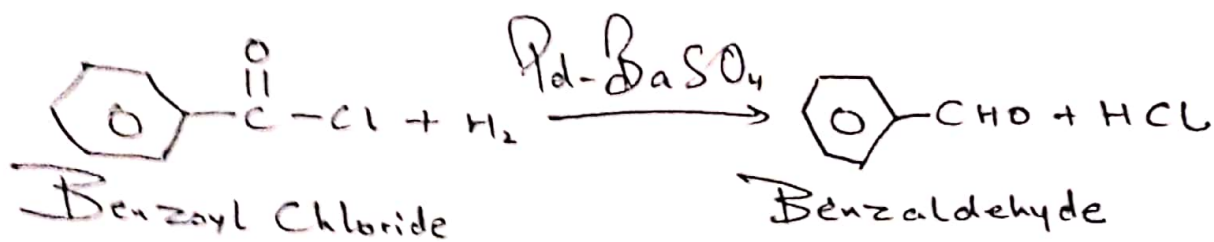
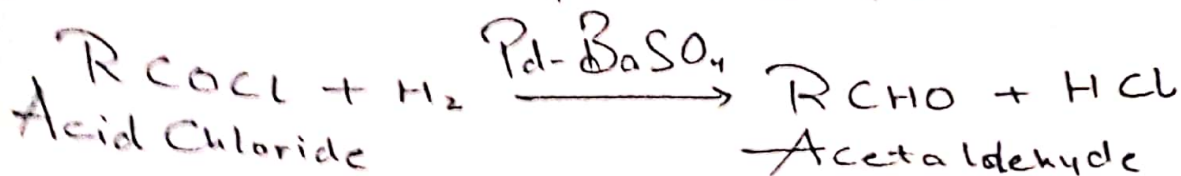


Imp\*

## Reduction of Acid Chlorides :-

### Rosemund's Reaction:

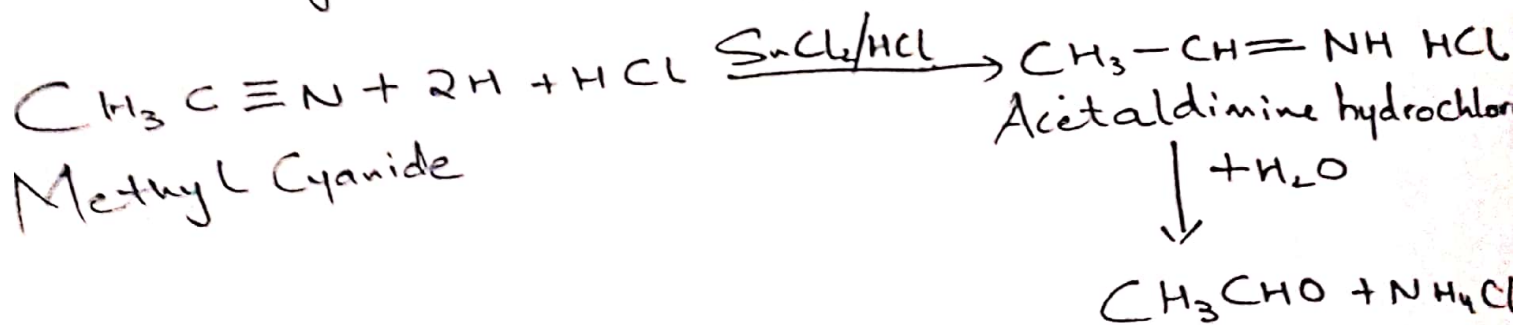
This Rx<sup>n</sup> is usually brought about by passing hydrogen through a hot solution of Acid Chloride in Xylene in the presence of suitable Catalyst.



### METHOD :-

### Stephen's Reaction:

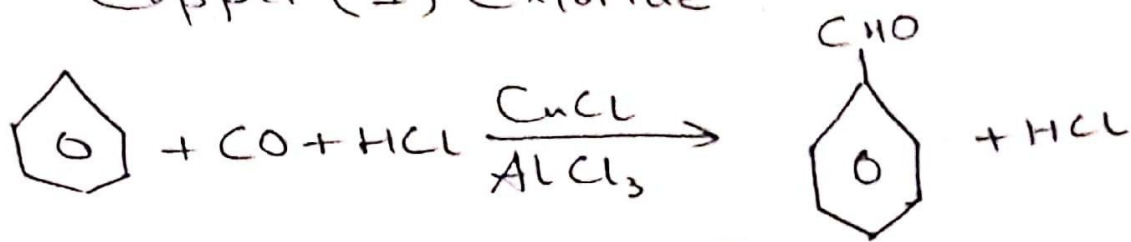
Alkyl Cyanides on Reduction with Stannous Chloride and hydrochloric Acid give rise to Aldimine. The Aldimine get hydrolysed on warming with water to yield an Aldehyde.



### Grattermann - Koch Reaction :-

When Benzene Ring is treated with mixture of CO and HCl in the presence of Lewis Acid

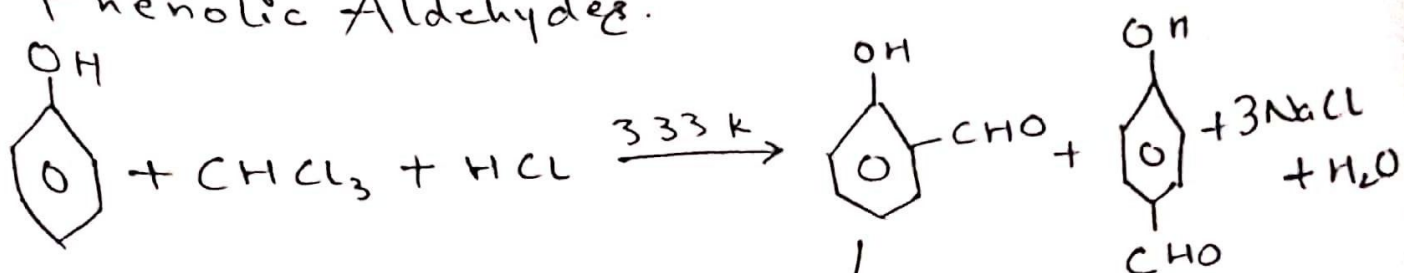
And Copper (I) Chloride



Benzaldehyde

Reimer-Tiemann Reaction

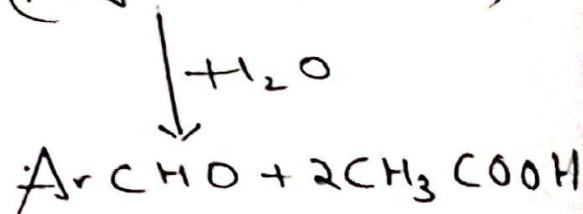
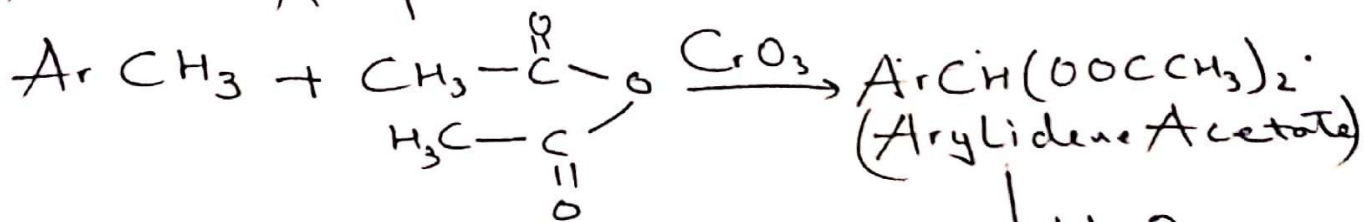
This is a convenient method for the Prep<sup>n</sup> of Phenolic Aldehydes.



Salicylaldehyde  
[Main Product]

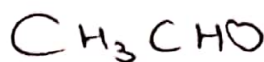
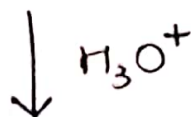
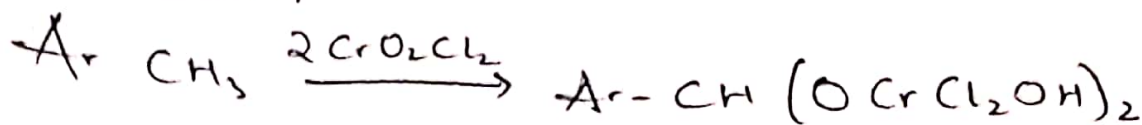
Oxid<sup>n</sup> of Methyl Benzene

o) Oxidation of Methyl Benzene (Toluene) to Aldehyde is usually carried out with Chromium Trioxide in Acetic Anhydride.

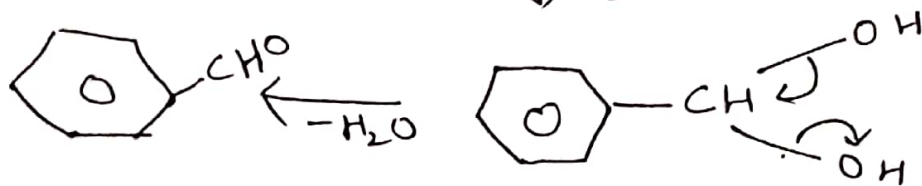
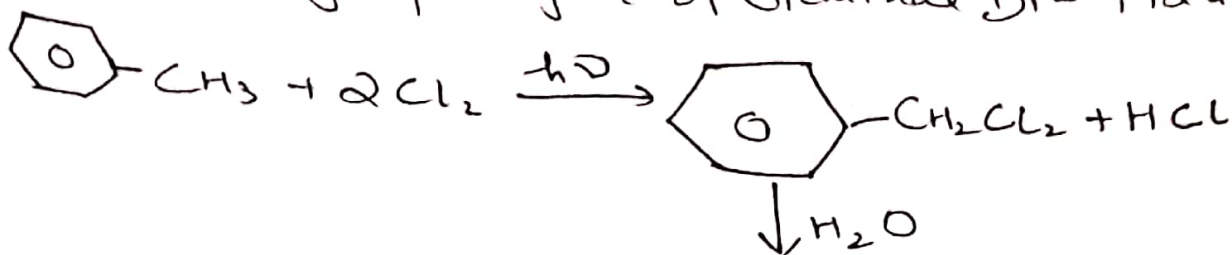


The Controlled Oxid<sup>n</sup> of Methyl Benzene to Aldehyde can also be carried out with Chromyl Chloride and Magnesium dioxide.

The Reaction Involving Chromyl Chloride as Oxidising Agent is also known as Etard Reaction.

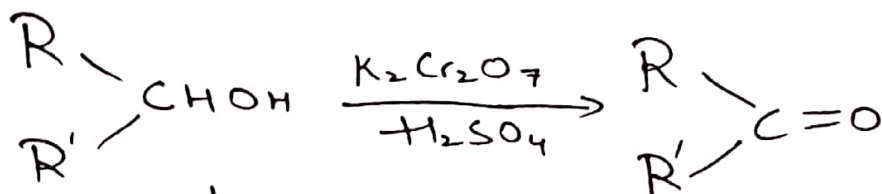


\* Methyl Benzene also converted in Aldehyde by Free Radical Halogenation of Methyl Benzene followed by hydrolysis of Geminal Di-halide



## FORMATION OF KETONES :-

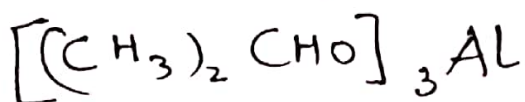
\* Oxid<sup>n</sup> of 2° Alcohols :-

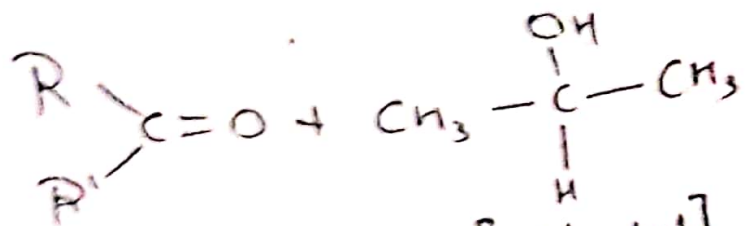
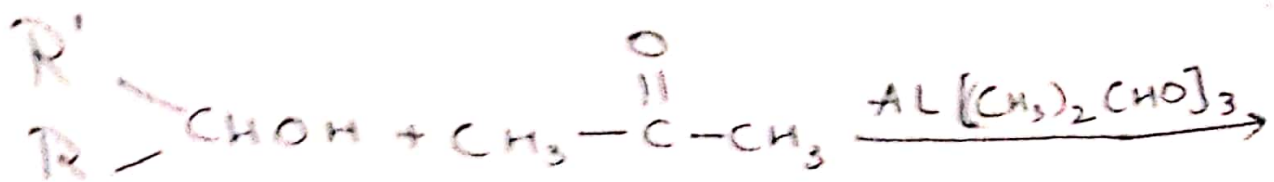


Important \*

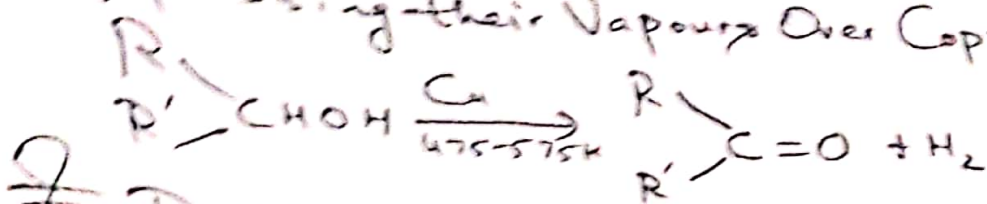
Oppenauer Alcohol Oxidation :-

Secondary Alcohols can also be oxidised in the presence of Aluminium Isopropoxide

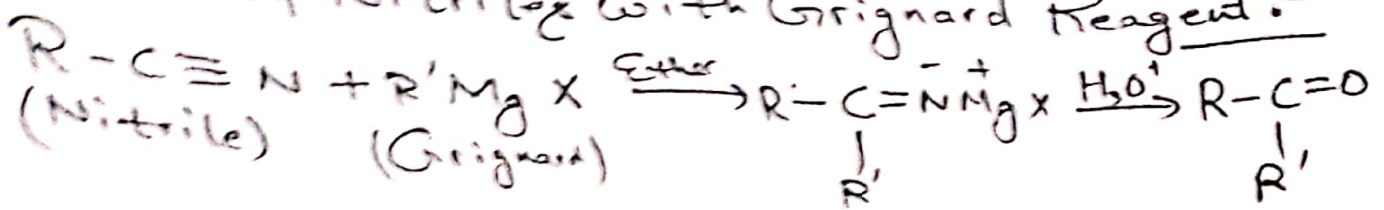




$\frac{1}{2}$  Catalytic Dehydrogenation of 2° Alcohols  $\rightarrow$  Ketones can also be obtained by dehydrogenation of 2° Alcohols by passing their vapours over Copper heated to 475-575 K

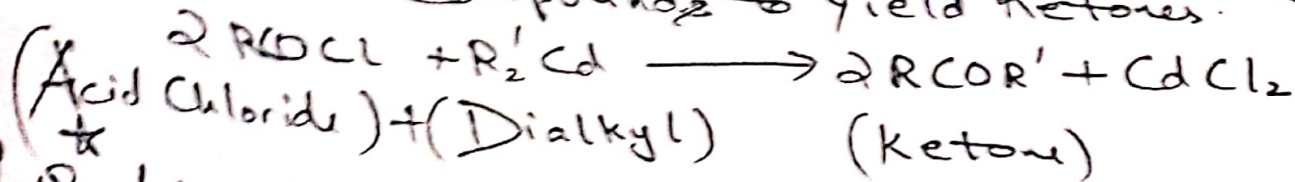


$\frac{1}{2}$  Redn. of Nitriles with Grignard Reagent :-

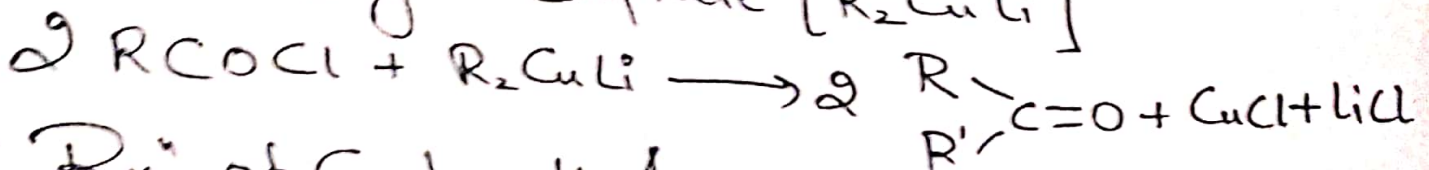


$\frac{1}{2}$  Rxn. of Acid Chloride with Organo Cadmium  $\rightarrow$  Ketone + NH<sub>4</sub><sup>+</sup> + Mg<sup>2+</sup> + X<sup>-</sup>

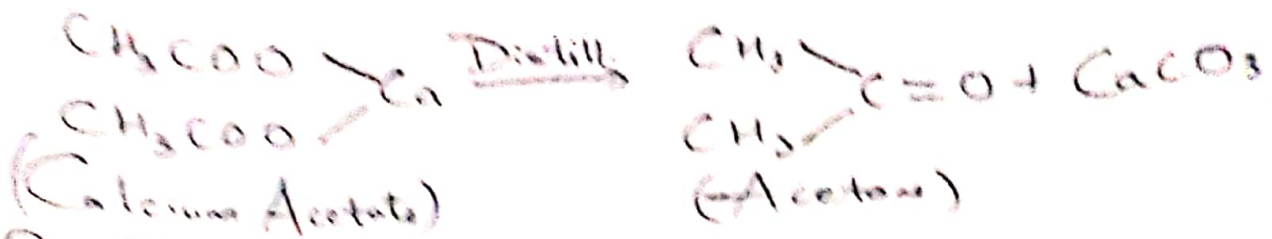
Acid Chloride reacts with suitable Organo Cadmium Compounds to yield Ketones.



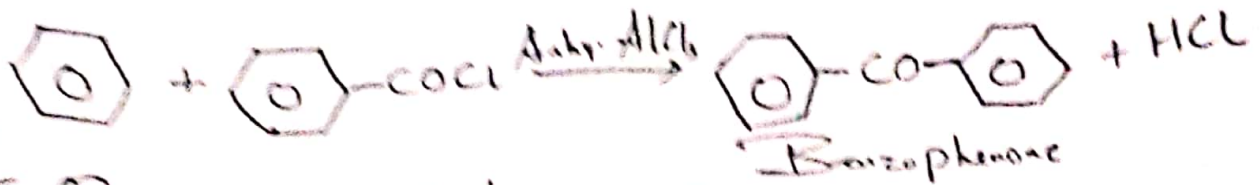
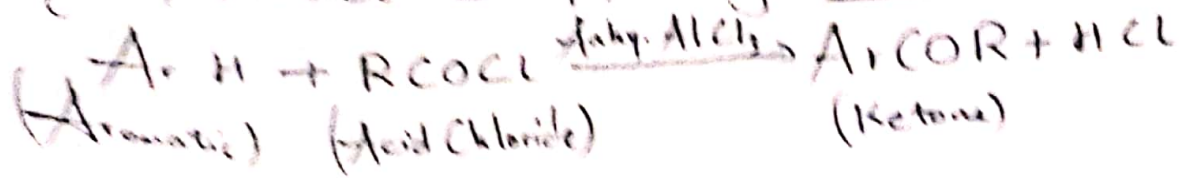
$\frac{1}{2}$  Lithium Organo Cuprate [R<sub>2</sub>CuLi]



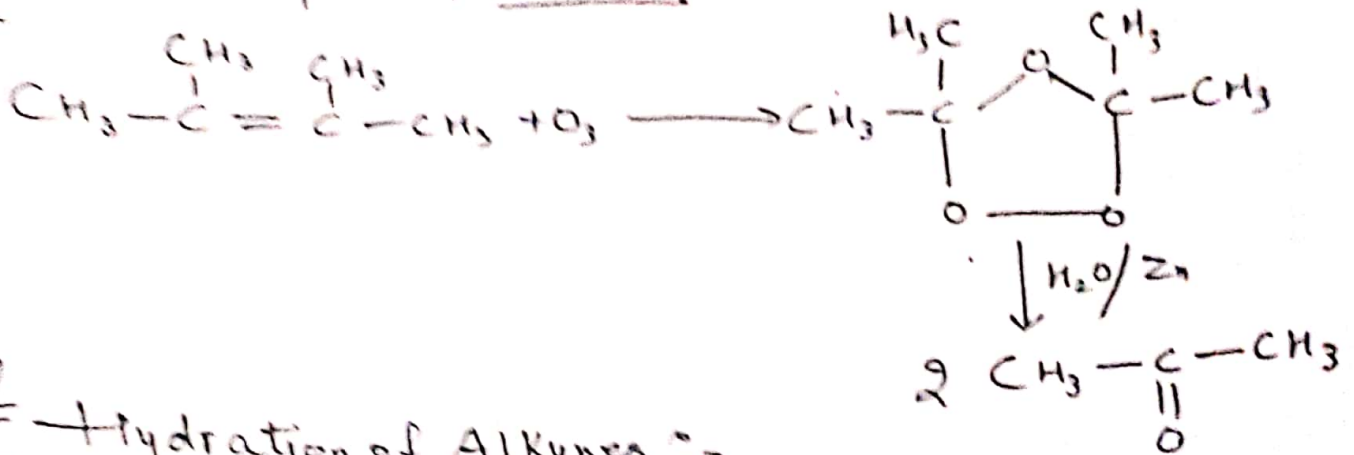
$\frac{1}{2}$  Rxn. of Carboxylic Acid with Alkyl/Aryl Lithium  $\rightarrow$  Ketone can also be obtained by distillation of Calcium Salt of Carboxylic Acid other than formic.



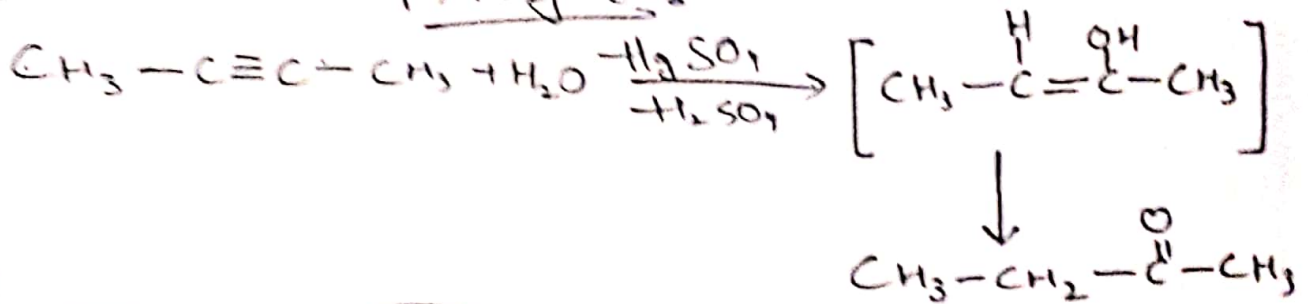
### Friedel-Crafts Acylation :-



### Ozonolysis of Alkenes :-



### Hydration of Alkyne :-



## PHYSICAL PROPERTIES

a) Physical State :- With Exception of formaldehyde commonly Aldehyde and Ketone are liquids at Room temp.

b) Boiling Point :- Due to their high Polarity, there is less Intermolecular Attraction between them.

Hence, they have low Boiling Point than those of Alcohols And Carboxylic Acids.

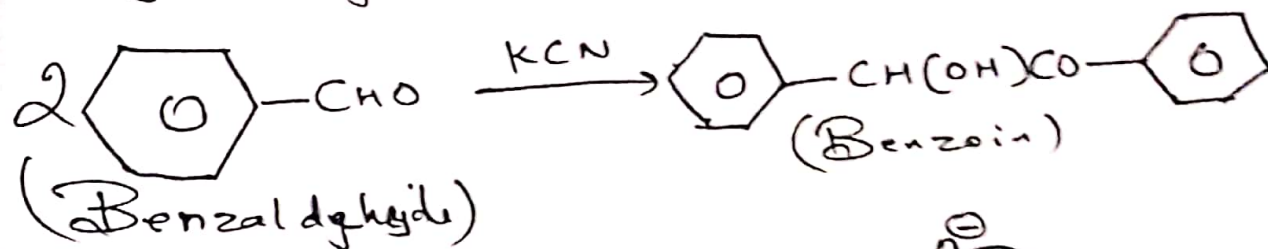
c) Melting Point :- They do not show any regular trend in M.P.

d) Solubility :- Solubility of these, are increasing in trend with increasing Molecular Weight. However, all aldehydes and ketones are readily soluble in Organic Solvents.

## MECHANISM :-

### Benzoin Condensation

Aromatic Aldehydes, which do not contain  $\alpha$ -hydrogen cannot go simple Condensation. However, in the presence of potassium Cyanide, they undergo self Condensation to form Benzoin.



### Mechanism

