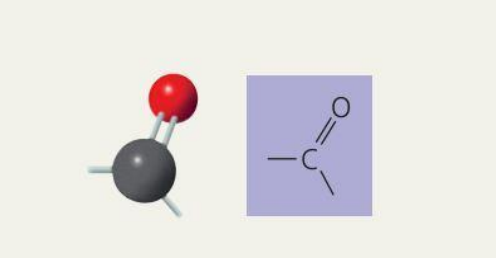
# Aldehyde and Ketones

*Dr Sadique Akhtar Javed*
*Faculty of Pharmacy*
*Jazan University*

# Aldehydes and Ketones

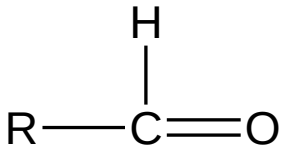
- Aldehydes and ketones are classes of compounds both of which contain a carbon doubly bonded to oxygen, known as carbonyl group.



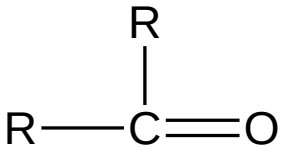

Carbonyl group (Carbon-oxygen double bo

- The compounds with this group are collectively known as ***carbonyl compounds***.
- In *aldehydes* the carbonyl carbon is linked to one **hydrogen atom and one aliphatic or aromatic organic group.** Formaldehyde is an exception in which the carbonyl group is linked to two H atoms.
- In *ketones* it is linked **to two other carbon atoms.**

# Aldehydes and Ketones

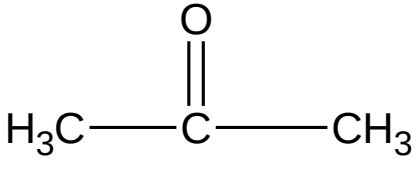



Aldehyde



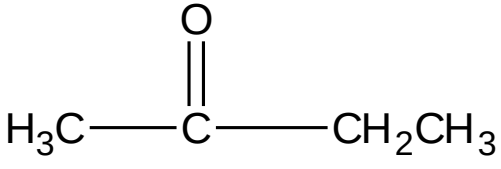

Ketones

- The ketones may be ***symmetrical*** or ***unsymmetrical*** according to the two alkyl groups attached to the carbonyl group are same or different.




Dimethyl ketone

(Symmetrical)




Ethyl methyl ketone

(Asymmetrical)

# Nomenclature

## Aldehydes

- The **Common Names** of aldehydes are derived from those of the carboxylic acids to which they are oxidized.
- The portion ***'-ic acid'*** of the name of the corresponding acid is replaced by the suffix ***'-aldehyde'.***
- Thus **$CH_3CHO$** is oxidized to acetic acid and is named as **acetaldehyde**.

*Acetic acid - ic acid + aldehyde = acetaldehyde*

# Aldehydes and Ketones

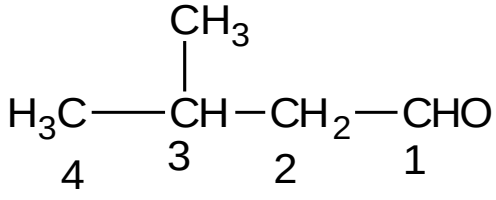
- In the **IUPAC system**, aldehydes are named as ***alkanals***.
- The name of the individual aldehyde is obtained by dropping the terminal ***'e'*** of the name of the parent hydrocarbon and adding the suffix ***'-al'***.
- Thus **HCHO** is called as **methanal**, the parent hydrocarbon being **methane.**

*Methane - e + al = methanal*

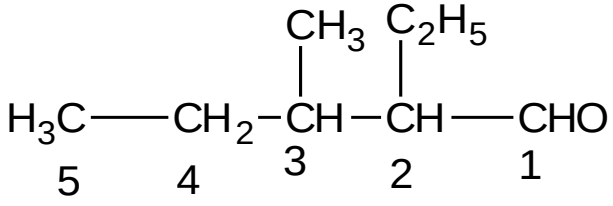
| Formula | Common name | IUPAC name |
|---|---|---|
| HCHO | Formaldehyde | Methanal |
| $CH_3CHO$ | Acetaldehyde | Ethanal |
| $CH_3CH_2CHO$ | Propionaldehyde | Propanal |
| $CH_3CH_2CH_2CHO$ | Butyraldehyde | Butanal |

# Aldehydes and Ketones

- While assigning IUPAC names to complex aldehydes, the longest carbon chain containing the –CHO group is selected as parent chain.
- It is numbered from the carbon of the –CHO group which assigned as **number 1**.
- The substituents on the chain are given positional numbers and named in the usual fashion.
- *Since the aldehyde group –CHO is always at the end of the chain, it is unnecessary to specify its position.*




3-methylbutanal

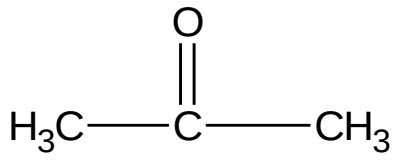
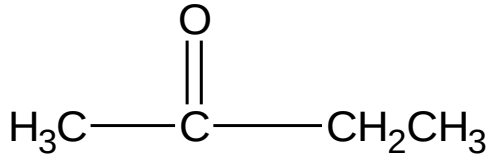
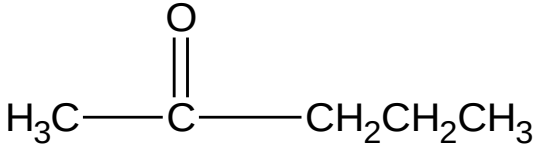



2-ethyl-3-methylpentanal

# Ketones

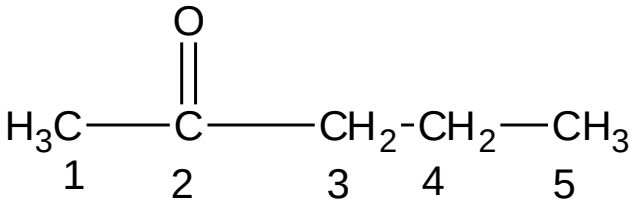
- According to the ***Common System***, symmetrical ketones are named as ***dialkyl ketones***.
- First member of the series is *dimethyl ketone* ($CH_3COCH_3$), popularly known as **acetone**.
- The common names of unsymmetrical ketones are obtained by naming the alkyl groups as separate words in alphabetic order and adding the third word ketone.
- The ***IUPAC name*** of ketone is ***alkanone*** and the name of an individual member is derived by dropping the final ***'e'*** of the parent hydrocarbon and adding the suffix ***'one'***.

# Aldehydes and Ketones

| Formula | Common name | IUPAC name |
|---|---|---|
|  | Dimethyl ketone (acetone) | Propanone |
|  | Ethyl methyl ketone | Butanone |
|  | Methyl propyl ketone | 2-Pentanone |

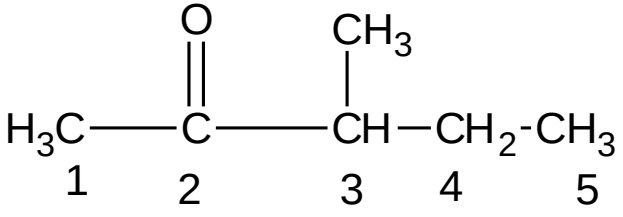
# Aldehydes and Ketones

- While naming the higher ketones, it becomes necessary to assign positional number to the carbonyl group (lowest possible).

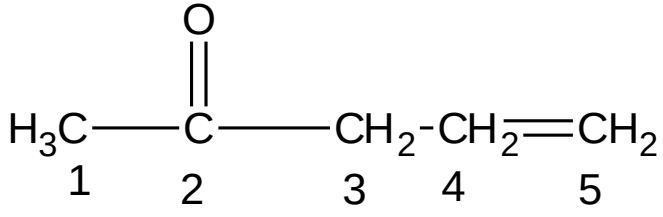



2-Pentanone

- In complex compounds, where prefixing of the positional number to the ketone name gives rise to confusion it is inserted before the suffix ***–one***.




3-Methyl pentan-2-one

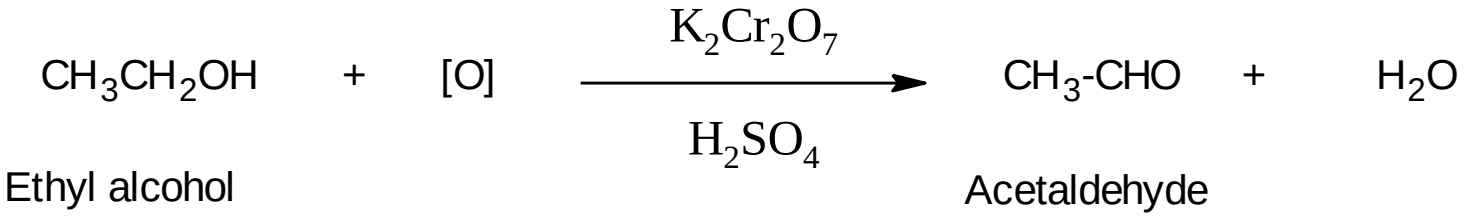



4-Penten-2-one

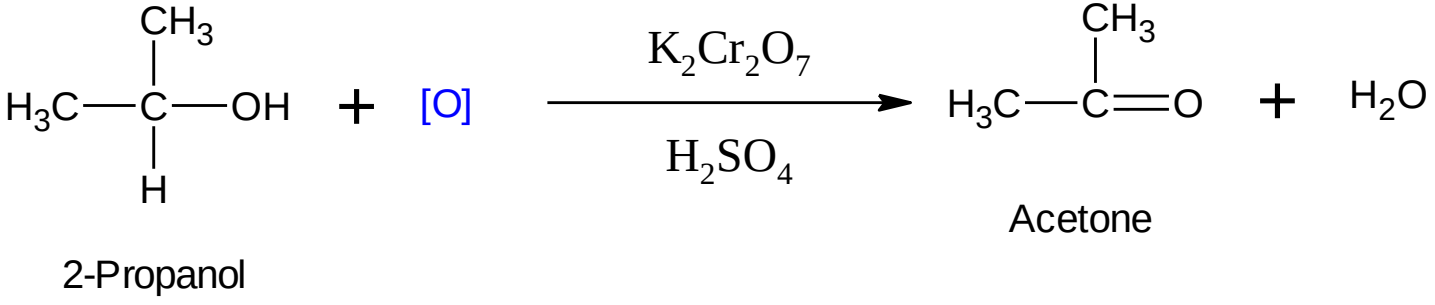
# Methods of Preparation

## 1. Oxidation of alcohols

- Aldehydes are prepared by the oxidation of primary alcohols with potassium dichromate in sulfuric acid.

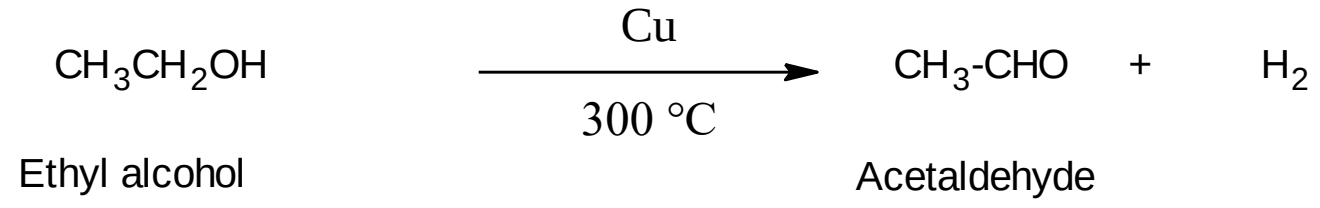


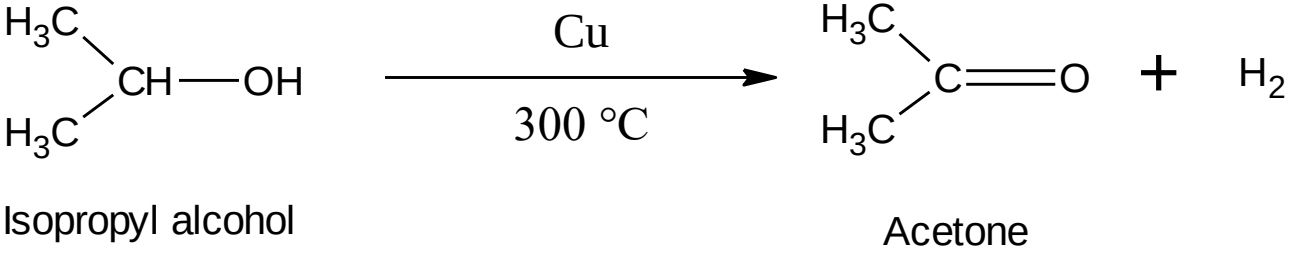

- Ketones are prepared by the oxidation of secondary alcohols with same method



# 2. Catalytic dehydrogenation of alcohols

- When vapour of a primary alcohol is passed over a catalyst such as reduced copper at 300℃, the alcohol is dehydrogenated to give an aldehyde.
- Similarly ketones can be prepared from secondary alcohols.



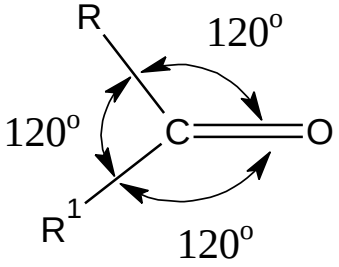



## Physical Properties

- Formaldehyde, the first member of the aldehyde series is a gas at ordinary temperature.
- The next 10 member (C2-C11) are liquids and higher members are solids.
- Similarly, ketones upto C11 are colouless liquids and higher members are solids.
- Lower memebers of the aldehydes have an unpleasant odour.
- Ketones are pleasant smelling. The higher aldehydes and ketones are used in perfumery.
- The first few members of the aldehyde and ketone are soluble in water, but the solubility decrease with increase in the size of the hydrocarbon group attached to carbonyl group.

## The Carbonyl group

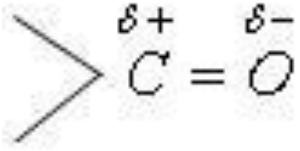
- The carbon-oxygen double bond consists of a sigma (σ) bond and a pi (π) bond. The carbon atom is $sp^2$ hybridized. The three atoms attached to the carbonyl carbon lie in a plane with bond angles of 120°. There are two unshared electron pairs on the oxygen atom.




- Since, oxygen is more electronegative than carbon, the electrons of the bond are attracted towards oxygen.

# Aldehydes and Ketones

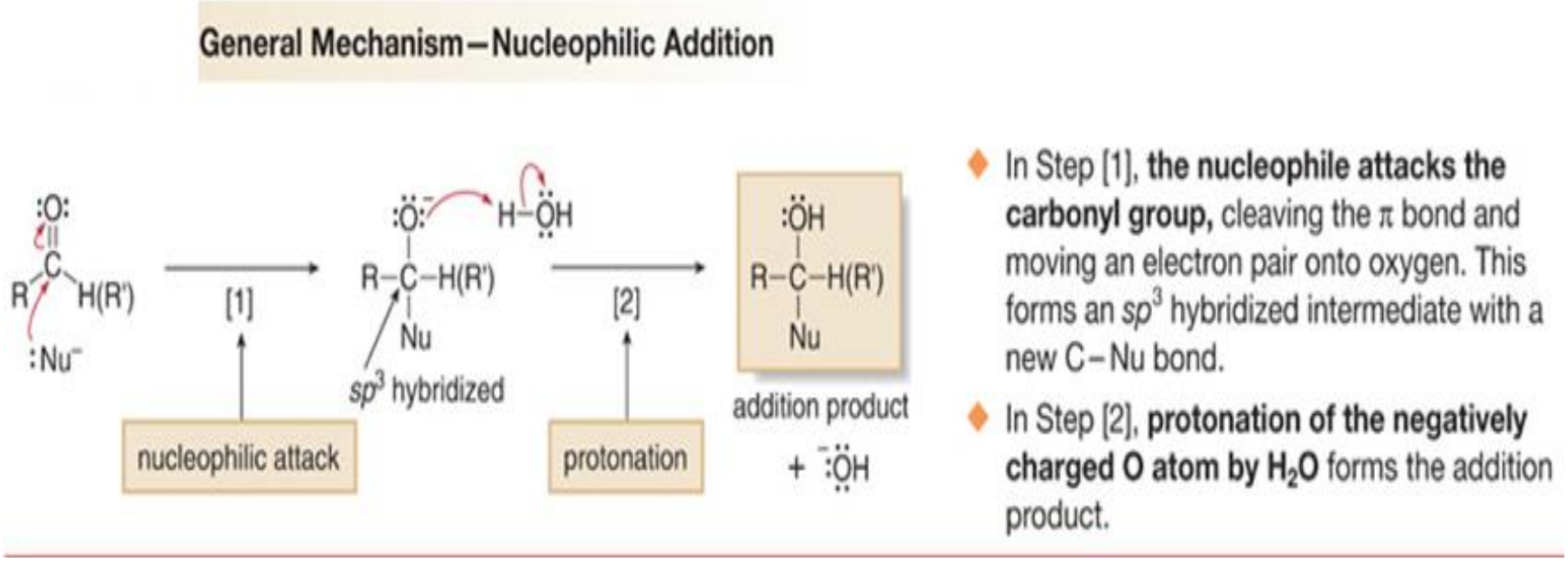
- *Consequently, oxygen attains a partial negative charge and carbon a partial positive charge producing a polarized bond.*
- Thus carbon becomes slightly positive and oxygen slightly negative. The carbon atom of the carbonyl group is electron deficient, while the oxygen atom is electron rich.



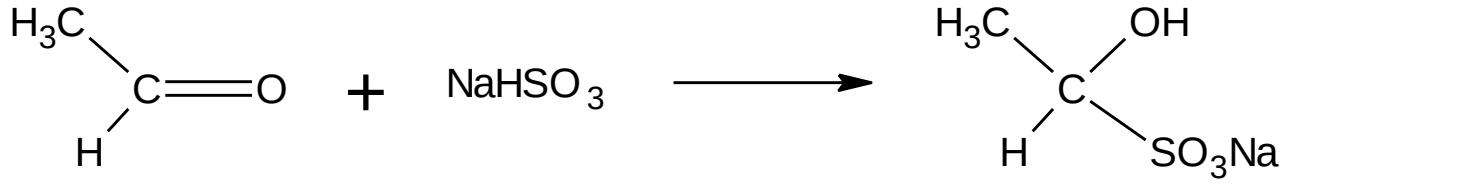

- As a result of this polarization, **most carbonyl reactions involved nucleophilic attack** at the carbonyl carbon, often accompanied by addition of a H atom to the oxygen.

# 1. Nucleophilic addition reactions

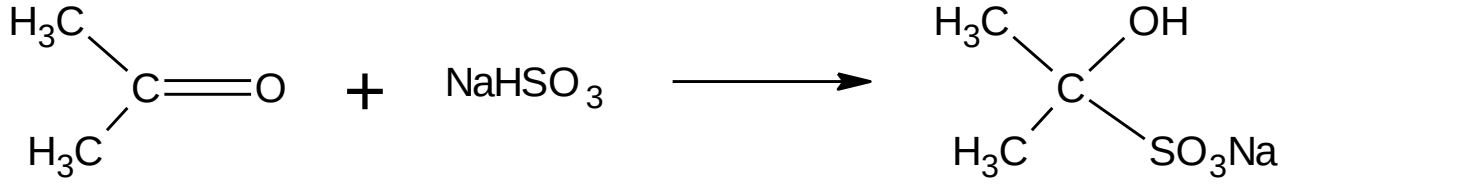
The electron deficient carbon of the carbonyl group is easily attacked by a nucleophile which can supply an electron pair.



**a) Addition of sodium bisulfite:** Saturated solution of sodium bisulfite ($NaHSO_3$) in water, when mixed with aldehydes and ketones forms crystalline 'bisulfite addition compounds'.

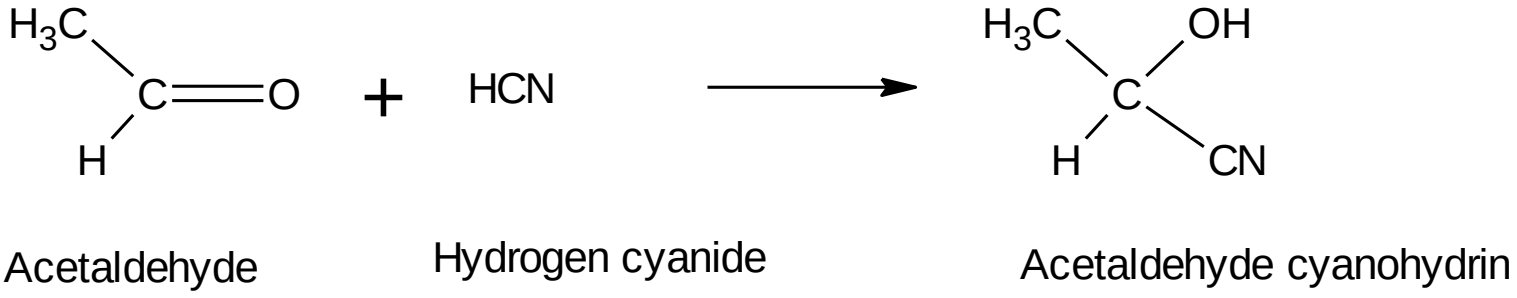



Acetaldehyde  Sodium bisulfite  Bisulfite addition compound

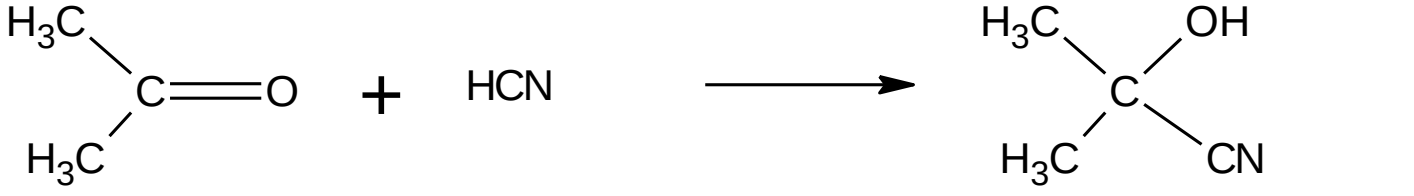



Acetone  Sodium bisulfite  Bisulfite addition compound

**b) Addition of Hydrogen cyanide:** Hydrogen cyanide adds on to all aldehydes and methyl ketones to yield ***Cyanohydrins***.



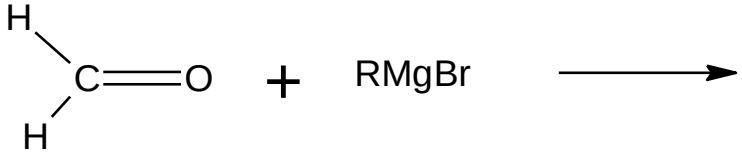

Acetaldehyde + Hydrogen cyanide → Acetaldehyde cyanohydrin



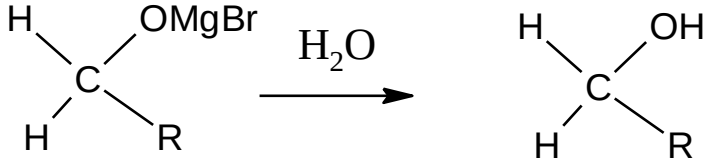

Acetone + Hydrogen cyanide → Acetone cyanohydrin

## c) Addition of Grignard Reagents:

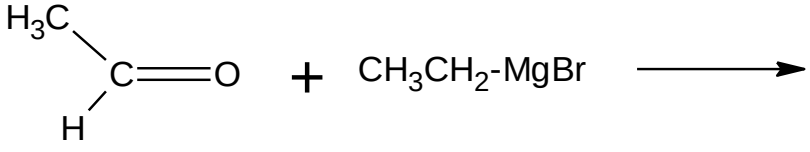
Aldehydes and ketones react with Grignard reagent to form alcohol. Formaldehyde gives a primary alcohol. Other aldehydes give secondary alcohols and ketones give tertiary alcohols.



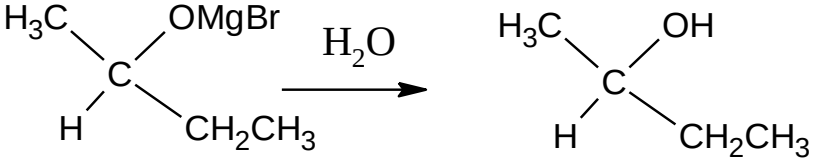

Formaldehyde Grignard reagent



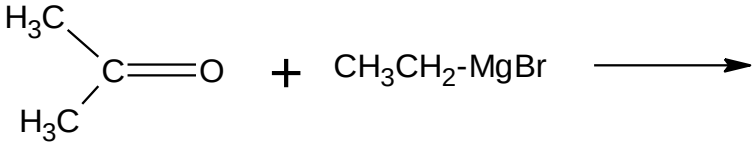

Adduct Primary alcoho



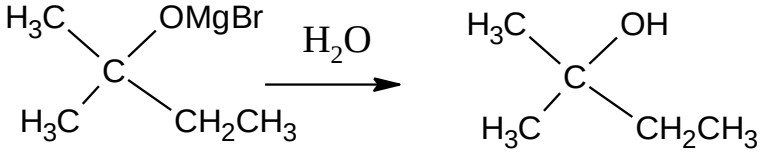

Acetaldehyde Grignard reagent




Adduct Secondary alcohol



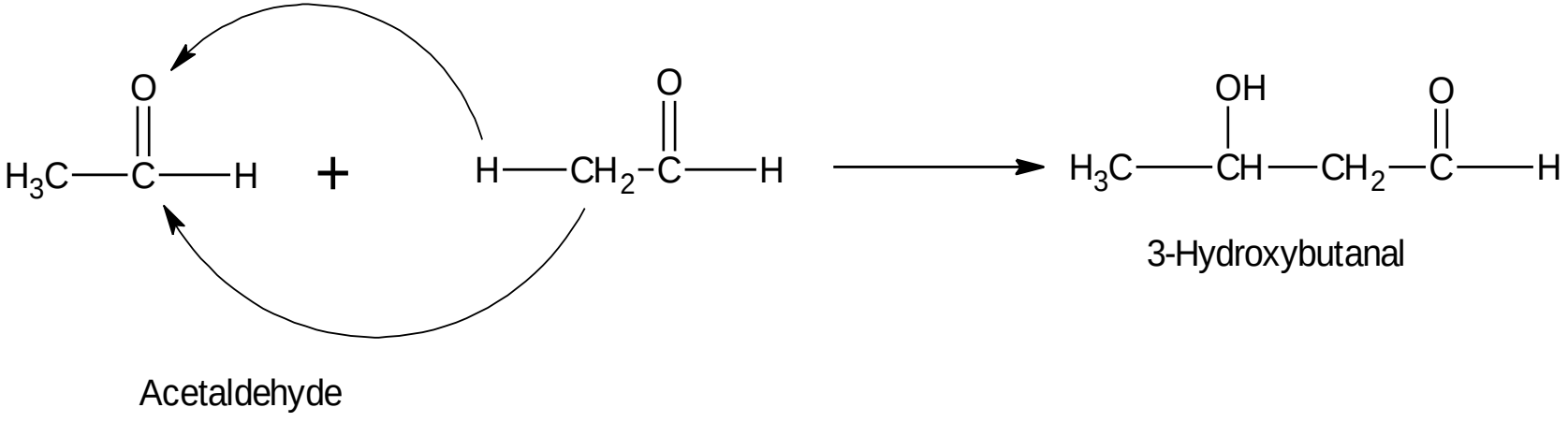

Acetone Grignard reagent



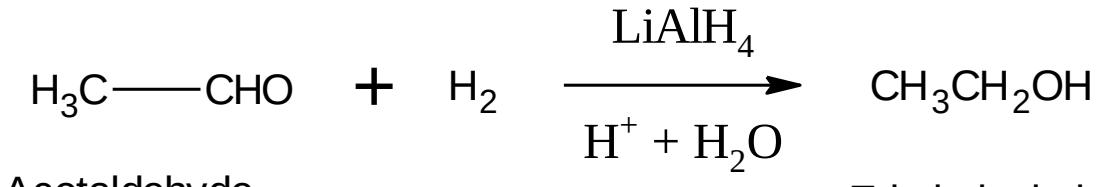

Adduct Tertiary alcohol

## 2. Aldol Condensation:

- Aldehydes undergo self addition in presence of dilute base to give condensation product which is both an aldehyde and alcohol. This is called ***aldol*** and the reaction is known as ***aldol-condensation***.

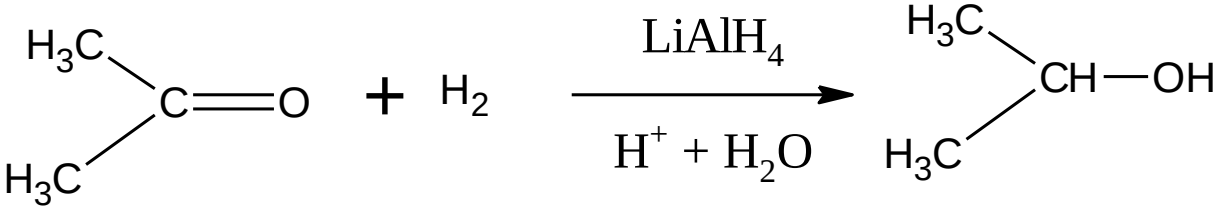


**3. Reduction to Alcohol:** The carbonyl group of aldehydes and ketones are reduced to primary and secondary alcohols by hydrogen in the presence of metal catalyst like Lithium Aluminium Hydride ($LiAlH_4$).




Acetaldehyde

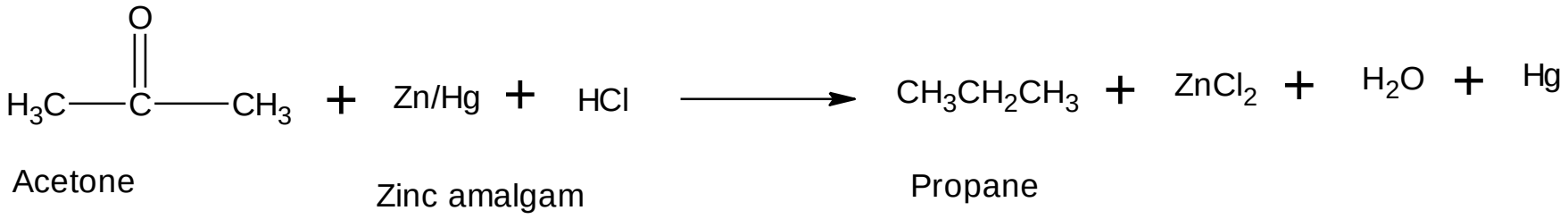
Ethyl alcohol (primary alcohol)




Isopropyl alcohol (Secondary alcohol)

## 4. Clemmensen Reduction:

Aldehyde and ketones are reduced to hydrocarbon using Zinc amalgam and HCl as reducing agent.



# Aromatic Aldehydes and Ketones

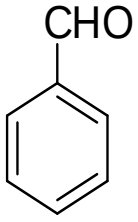
## Aldehydes:

- When the aldehyde group is directly attached to the carbon of the aromatic ring is referred as aromatic aldehydes.
- Examples: Benzaldehyde, salicylaldehyde, tolualdehyde etc.

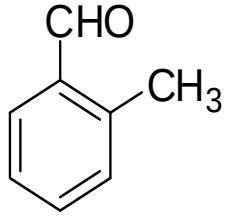
## Nomenclature:

- They are generally called by their ***common names*** which are derived from the names of the corresponding carboxylic acids by replacing the ***–ic*** or ***–oic*** acid by ***–aldehyde***.

- Thus the name of the **benzaldehyde** is derived from **benzoic acid**, **o-tolualdehyde** is derived from **o-toluic acid** and **salicylaldehyde** is derived from **salicylic acid**.
- The ***IUPAC name*** of the aromatic aldehyde is derived by dropping the ending ***–ene*** of the name of the hydrocarbon and adding the suffix ***–al***.

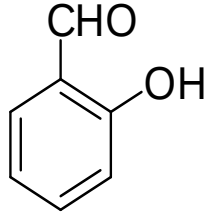



Benzaldehyde




o-Tolualdehyde

(2-Methylbenzaldehyde)

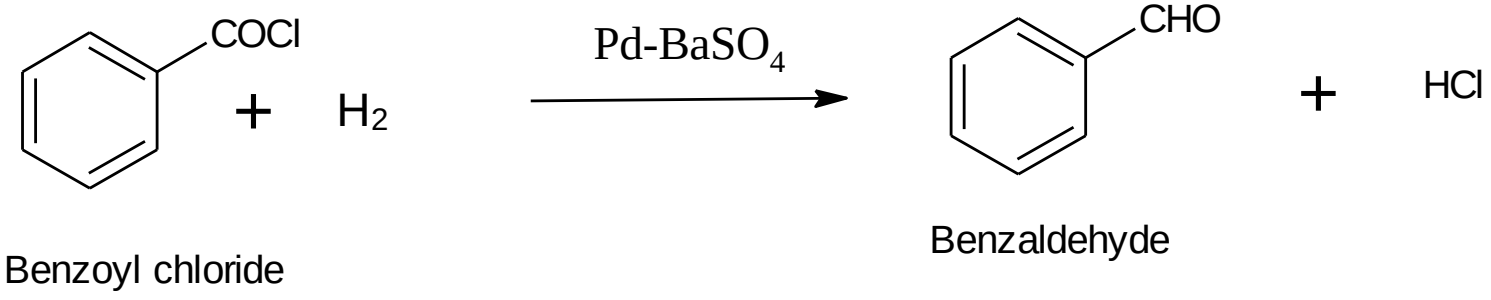



Salicylaldehyde

(2-Hydroxybenzaldehyde)

## Method of Preparation

- **Rosenmund Reaction:** Aromatic aldehydes may be produced by reduction of aromatic acid chloride with palladium-barium sulfate as catalyst.

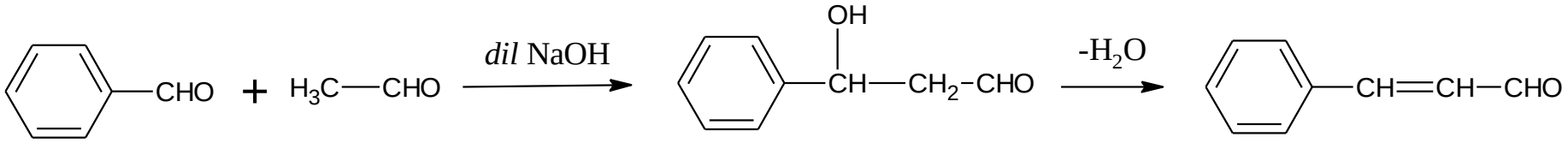



Benzoyl chloride

Benzaldehyde

## Reactions of Aromatic aldehydes:

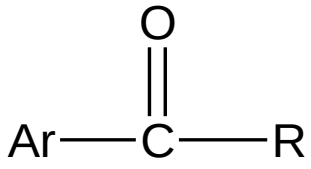
- Most of the reactions due to –CHO group are similar to as discussed in aliphatic aldehydes. For example, addition reactions, oxidation and reduction.
- **Claisen-Schmidt Condensation:** Benzaldehyde condenses with aliphatic aldehyde or methyl ketones in the presence of dilute alkali to from unsaturated aldehydes or ketones. This reaction is known as ***Claisen-Schmidt condensation.***



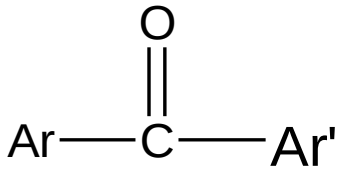

Benzaldehyde Acetaldehyde mixed aldol (unstable) Cinnamaldehyde

## Aromatic Ketones

- Ketones in which one or both the hydrocarbon moieties attached to the carbonyl group (-CO-) are aryl, are referred at as ***Aromatic ketones***.
- These could be designated as ***alkaryl*** or ***diaryl ketones***.



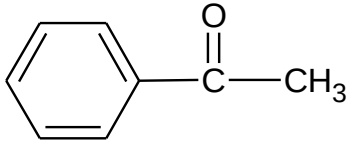

Alkaryl ketone




Diaryl ketone

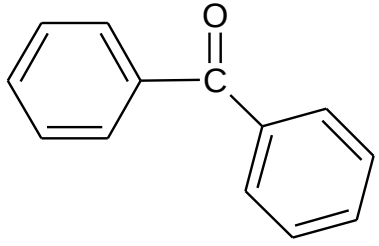
## Nomenclature

- Ketones containing the carbonyl group attached to a benzene ring are named ***phenones***.
- The name of such a ketone is derived by adding ***–phenone*** or ***–ophenone*** to the stem formed by removing ***–ic acid*** from the name of the corresponding acid.
- The common names of the aromatic ketones are obtained as usual by naming the alkyl or aryl groups attached to the carbonyl group, followed by the word ***ketone***.




acetophenone

(methyl phenyl ketone)

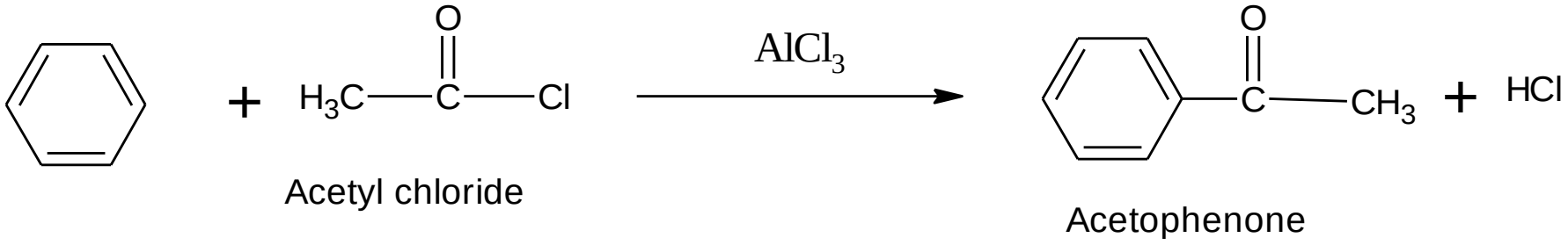



benzophenone

(diphenyl ketone)

## Methods of Preparation:

- Aromatic ketones are obtained by Friedel-Craft reaction from benzene and acid chlorides.




Acetyl chloride

Acetophenone

## Reactions of Aromatic ketones:

- Aromatic ketones give most of the reactions of aliphatic ketones.