

# Unit 12

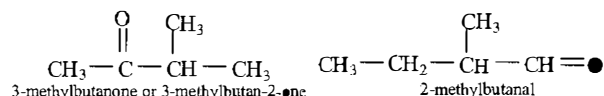
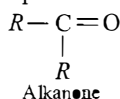
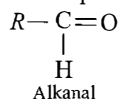
# Aldehydes, Ketones and Carboxylic Acids

## ALDEHYDES AND KETONES

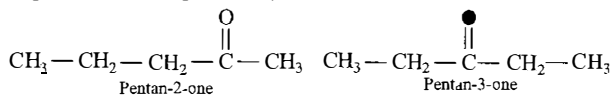
- Compounds containing  $\text{>C=O}$  (carbonyl) group are collectively known as carbonyl compounds. If one of the valencies is satisfied by H-atom then the compounds are known as aldehydes and have general formula  $RCHO$  (Where  $R$  may be H or alkyl group), if both the valencies are satisfied by alkyl group then the compound is said to be ketone ( $RCOR$ ). Both aldehydes and ketones have general formula  $C_nH_{2n}O$ .

### Nomenclature

- According to IUPAC name 'e' of alkane is replaced by 'al' in case of aldehyde and 'one' of alkane is replaced by 'one' in case of ketone. Aldehyde is always at terminal hence position of aldehydic group is normally not indicated. In case of ketone we use position of carbonyl group whenever it is needed.

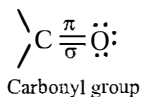
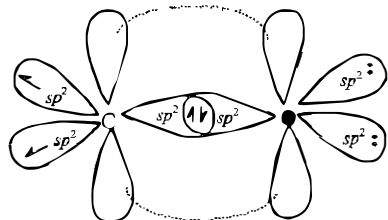


(Here we may write position '2' or may not because other position is not possible.)



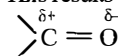
### Nature of Carbonyl group

- Carbonyl group consists of one  $\sigma$  and one  $\pi$  bond like  $\text{>C=C<}$ . Here both carbon and oxygen are in  $sp^2$  hybridized state. One of the  $sp^2$  hybrid orbitals of C-atom forms  $\sigma$  bond by overlapping of one of  $sp^2$  hybrid orbitals of O-atom and  $\pi$  bond is formed by sidewise overlapping of unhybrid orbitals of both the atoms.

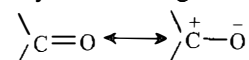


Carbon atom is joined to three atoms by  $\sigma$ -bonds. Since, these bonds utilize  $sp^2$ -orbitals, they lie in the same plane and are  $120^\circ$  apart. Hence, carbonyl group is planar.

The electrons in the  $\pi$  bond of the carbonyl group are not equally shared i.e. they are pulled towards the more electronegative oxygen atom. This results in polarization of bond as

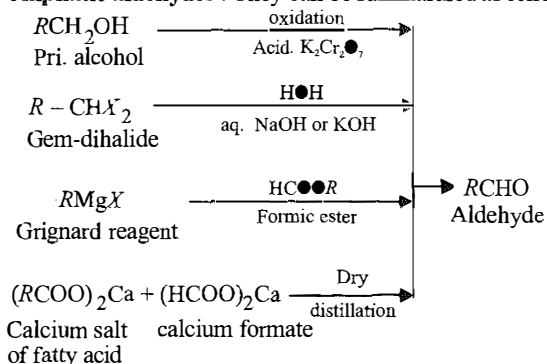


Alternatively the polar nature of the carbonyl group can also be indicated by the following resonating structures:

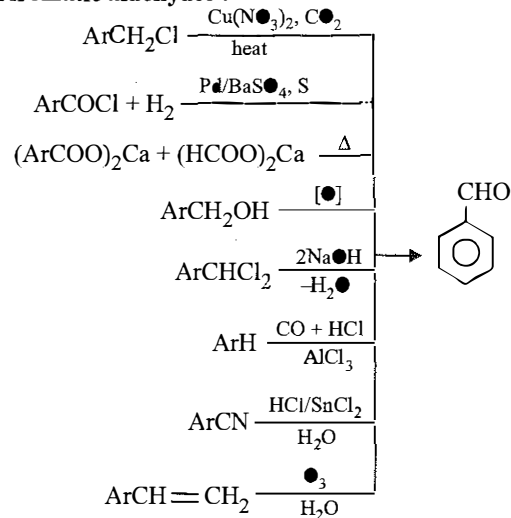


### General Methods of Preparation

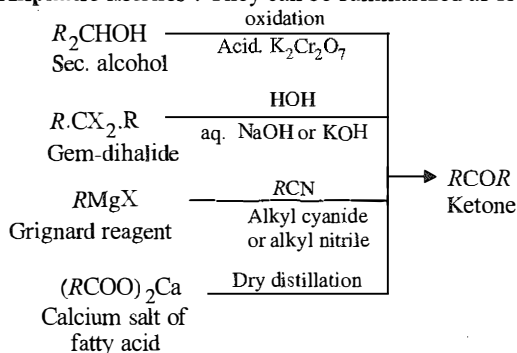
- Aliphatic aldehydes** : They can be summarized as follows.



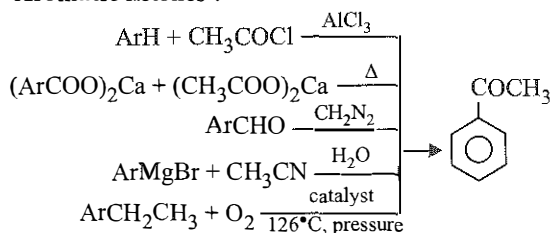
- Aromatic aldehydes** :



- **Aliphatic ketones :** They can be summarized as follows.

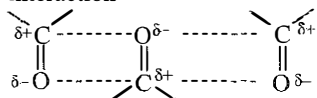


- **Aromatic ketones :**



### Physical Properties

- Carbonyl compounds are held together by dipole-dipole interaction

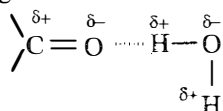


Dipole-dipole interactions are weaker forces than H-bonding and stronger than the van der Waal's interactions. Thus boiling points of aldehydes and ketones are somewhat higher than those of hydrocarbons and lower than those of alcohols of comparable molecular mass.

alcohol > carbonyl compounds > alkane

**Note:** Among the carbonyl compounds, ketones have slightly higher boiling points than the isomeric aldehydes because of presence of two electrons releasing groups around the carbon atom of carbonyl group which makes them more polar *i.e.* they also have more dipole moment than aldehydes.

- Lower members are water soluble as they can form hydrogen bonding with water as

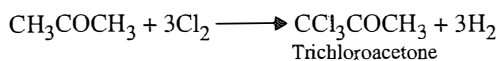
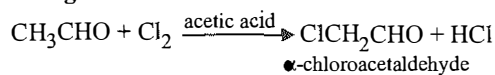


- The solubility in water decreases with increase in molecular mass.
- Carbonyl compounds have lower density than water.

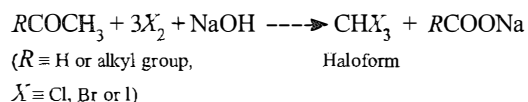
### Chemical Properties

- **Substitution reactions of alkyl group :**

#### ➤ Halogenation :



#### ➤ Haloform reaction :



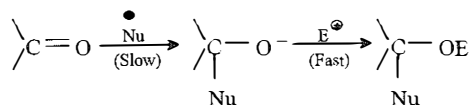
**Note :** Haloform reaction is given by the carbonyl compounds contain  $CH_3CO-$  group, thus, this reaction is used to diagnose the presence of  $CH_3-C(=O)-$  group and

also to distinguish methyl ketones from others.

- **Addition reactions of carbonyl group :** Carbonyl compounds have  $>C=O$  group which are polar because of more electronegative oxygen atom. This results in polarization of  $\pi$ -electrons as

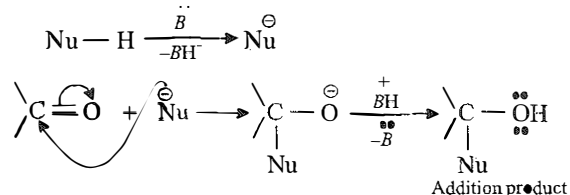


By resonating structure it is clear that there is nucleophilic addition over carbonyl compounds. The attack of nucleophile precedes the attack of electrophile as anion formed here after nucleophilic attack is more stable than the cation. Thus rate determining step is attack of nucleophile over carbonyl carbon atom.

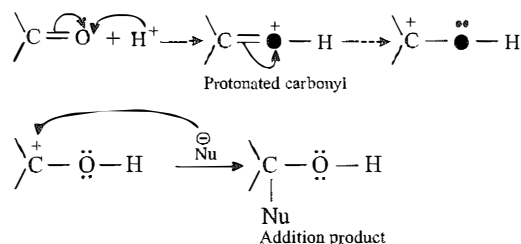


- **Mechanism of addition reactions :** Addition reaction over carbonyl compound may be base catalyzed and acid catalyzed.

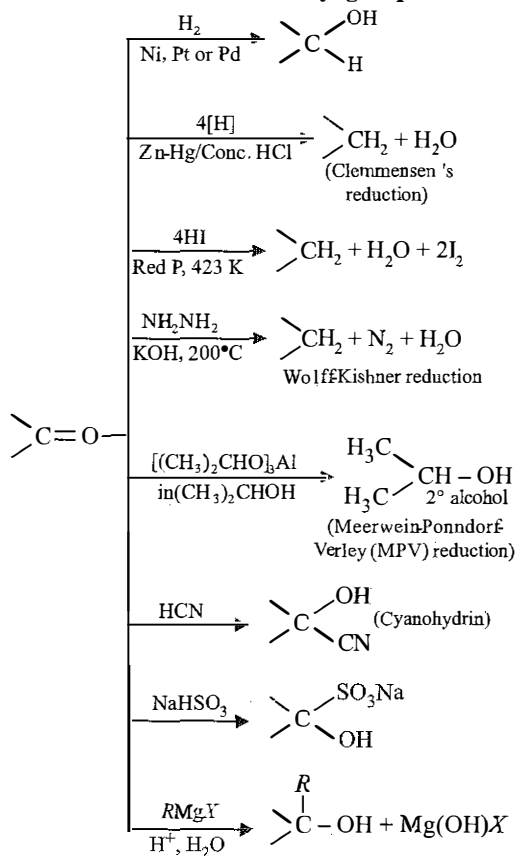
– **Base catalysed addition :** During the addition, base converts the weak neutral nucleophile to a strong one by removing a proton which adds over carbonyl carbon. The reaction is summarized as



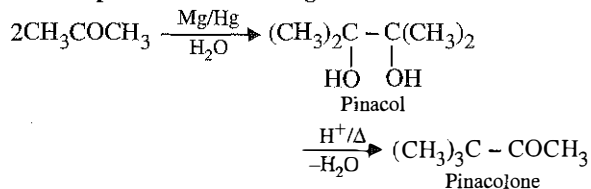
– **Acid catalysed addition :** In this condition oxygen atom of carbonyl group becomes protonated which in turn, increases the positive charge on the carbonyl carbon. Because of this, the weak nucleophile readily attacks the carbonyl carbon. The reaction is summarized as



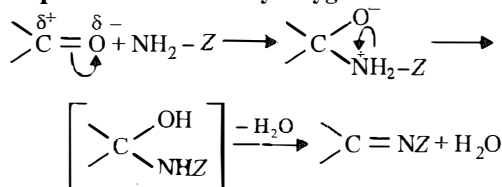
➤ **Addition reactions of carbonyl group :**



• **Pinacol pinacolone rearrangement :**



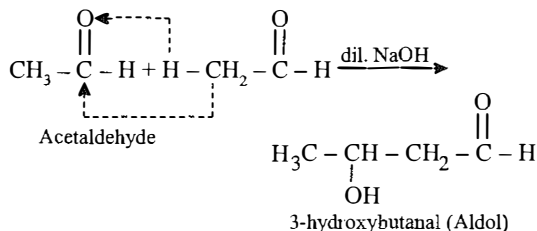
• **Replacement of carbonyl oxygen :**



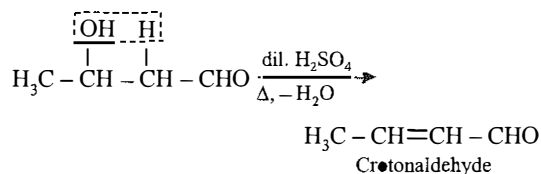
Where Z = OH, NH<sub>2</sub>, NHC<sub>6</sub>H<sub>5</sub>, NHCONH<sub>2</sub>, etc.

• **Condensation reactions :**

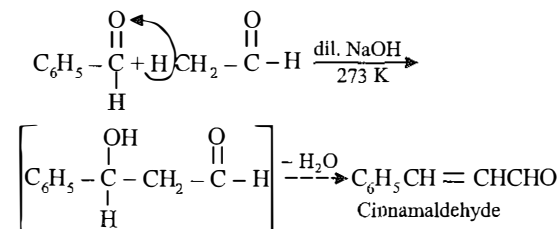
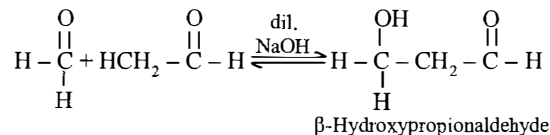
➤ **Aldol condensation :**



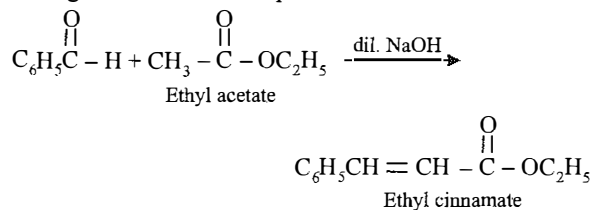
– **Significance :** The products of aldol condensation on heating with dilute acid undergo dehydration to form α, β-unsaturated carbonyl compounds.



➤ **Crossed Aldol Condensation :** When condensation takes place between two different aldehydes or ketones, or between one aldehyde and one ketone, it is called as crossed aldol condensation.

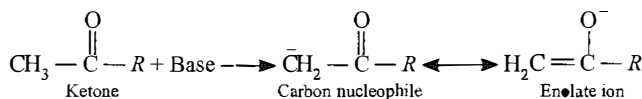
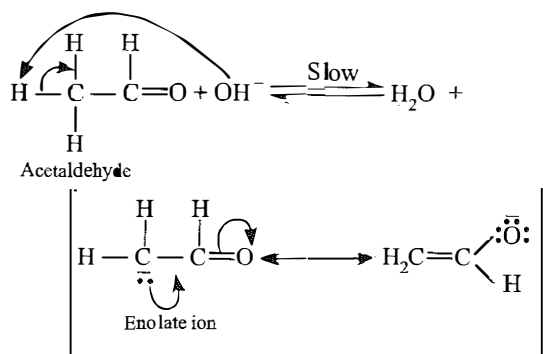


Such a base catalysed aldol condensation between an aromatic aldehyde and an aliphatic aldehyde or ketone is called as **Claisen-Schmidt** or **Claisen-Condensation**. Aliphatic esters containing α-hydrogen atoms can also undergo such reactions in presence of a base.



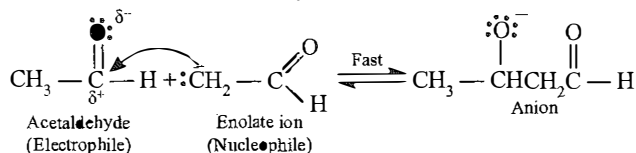
➤ **Mechanism of aldol condensation (Acidify of α-hydrogen) :** Aldol condensation involves the following steps through the formation of carbanion or the enolate which is stabilized by resonance in Step 1.

**Step 1:** The base (OH<sup>-</sup>) ion removes one of the α-hydrogen atom (which is somewhat acidic) from aldehydes and ketones to form a carbanion or the enolate ion.

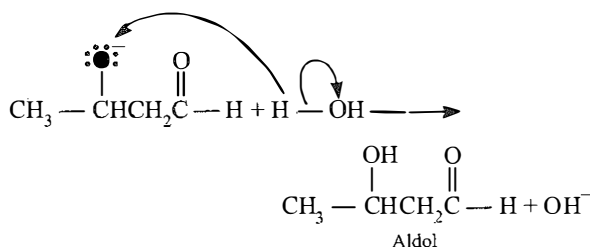


The acidity of  $\alpha$ -hydrogen is due to resonance stabilization of enolate anion.

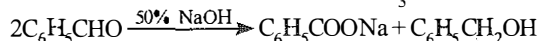
**Step 2 :** The enolate ion (nucleophile) attacks the carbonyl carbon of another aldehyde molecule to form the anion.



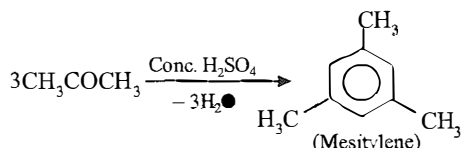
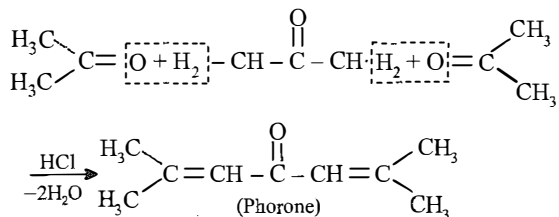
**Step 3 :** A proton from water is accepted by anion to form aldol and the  $\text{OH}^-$  ion is regenerated.



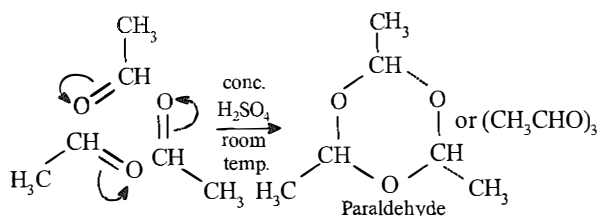
➤ **Cannizzaro's reaction :** It is shown by aldehydes which do not have  $\alpha$ -H atom. The aldehydes undergo disproportionation *i.e.*, self oxidation-reduction process.



➤ **Condensation of acetone :**

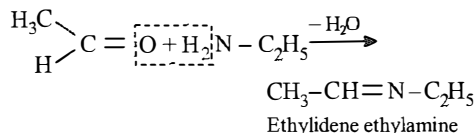


➤ **Polymerisation of acetaldehyde:**

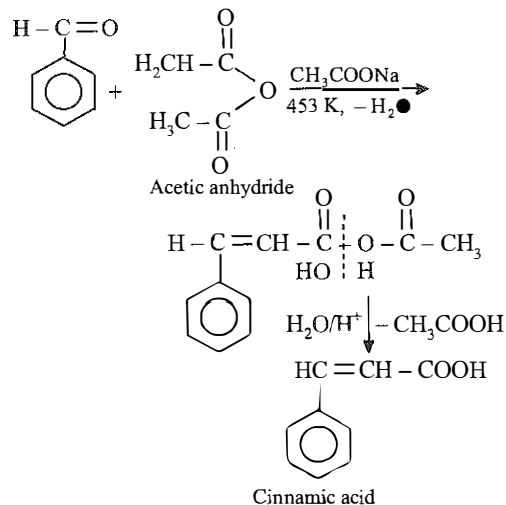


Paraldehyde is used as hypnotic, *i.e.* sleep inducing agent.

➤ **Reaction with primary amines :** Schiff's base or anils are formed.



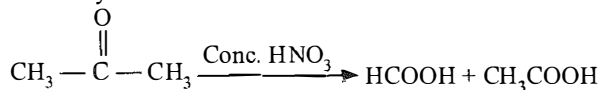
➤ **Perkin reaction :**



• **Oxidation reactions :** Aldehydes differ from ketones in their oxidation reactions. Aldehydes can be easily oxidised to carboxylic acids due to the presence of a hydrogen atom on the carbonyl group which can be converted to  $-\text{OH}$  group without undergoing cleavage of any other bond. Thus the carboxylic acids formed contain the same number of carbon atoms as the aldehyde.



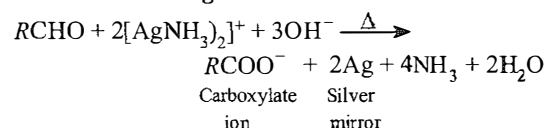
While ketones are not easily oxidised, under drastic condition ketones undergo cleavage of  $\text{C}-\text{C}$  bond gives carboxylic acids of lower number of C-atoms.



Thus, oxidation reactions can be used to distinguish between aldehydes and ketons.

Aldehydes can be oxidised by mild oxidising agent.

➤ **With Tollen's reagent :**



➤ **With Fehling's solutions :**  $\text{RCHO} + 2\text{Cu}^{2+} + 5\text{OH}^- \longrightarrow \text{RCOO}^- + \text{Cu}_2\text{O} + 3\text{H}_2\text{O}$   
Red ppt

### Tests of Aldehydes and Ketones

	Tests	Aldehydes	Ketones
1.	With Schiff's reagent	Give pink colour	No colour
2.	With Fehling's solution	Give red precipitate	No precipitate is formed
3.	With Tollen's reagent	Black precipitate of silver or silver mirror is formed	No black precipitate or silver mirror is formed