

12.1.2 Structure of the Carbonyl Group

The carbonyl carbon atom is sp^2 -hybridised and forms three sigma (σ) bonds. The fourth valence electron of carbon remains in its p -orbital and forms a π -bond with oxygen by overlap with p -orbital of an oxygen. In addition, the oxygen atom also has two non bonding electron pairs. Thus, the carbonyl carbon and the three atoms attached to it lie in the same plane and the π -electron cloud is above and below this plane. The bond angles are approximately 120° as expected of a trigonal coplanar structure (Figure 12.1).

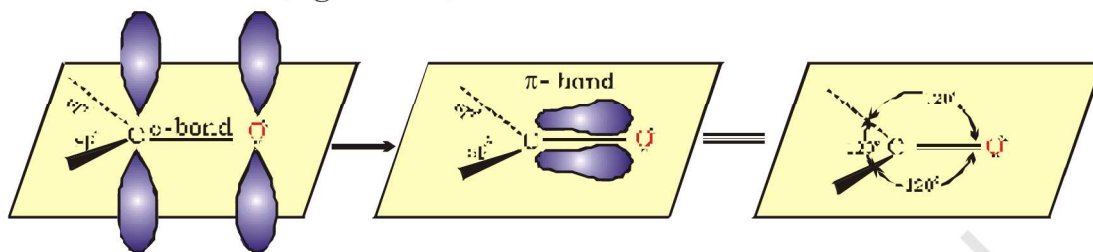
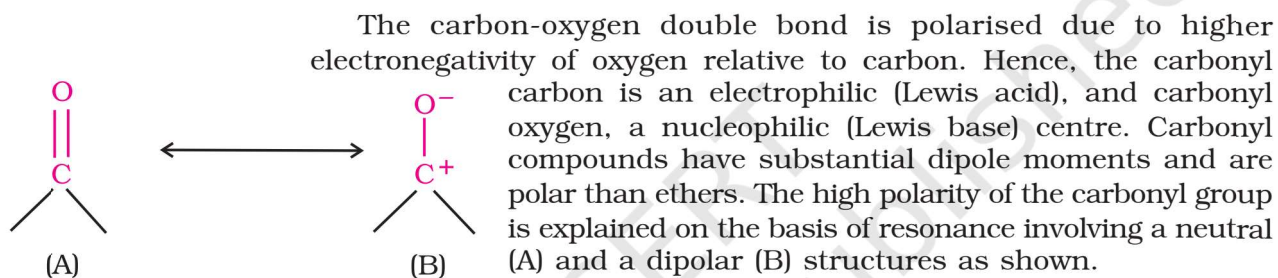


Fig.12.1 Orbital diagram for the formation of carbonyl group



Intext Questions

12.1 Write the structures of the following compounds.

- | | |
|--|---------------------------|
| (i) α -Methoxypropionaldehyde | (ii) 3-Hydroxybutanal |
| (iii) 2-Hydroxycyclopentane carbaldehyde | (iv) 4-Oxopentanal |
| (v) Di-sec. butyl ketone | (vi) 4-Fluoroacetophenone |

12.2 Preparation of Aldehydes and Ketones

Some important methods for the preparation of aldehydes and ketones are as follows:

12.2.1 Preparation of Aldehydes and Ketones

1. By oxidation of alcohols

Aldehydes and ketones are generally prepared by oxidation of primary and secondary alcohols, respectively (Unit 11, Class XII).

2. By dehydrogenation of alcohols

This method is suitable for volatile alcohols and is of industrial application. In this method alcohol vapours are passed over heavy metal catalysts (Ag or Cu). Primary and secondary alcohols give aldehydes and ketones, respectively (Unit 11, Class XII).

3. From hydrocarbons

- (i) *By ozonolysis of alkenes:* As we know, ozonolysis of alkenes followed by reaction with zinc dust and water gives aldehydes,

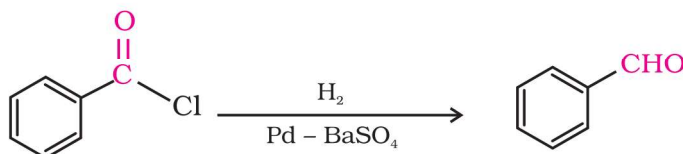
ketones or a mixture of both depending on the substitution pattern of the alkene (Unit 13, Class XI).

(ii) *By hydration of alkynes:* Addition of water to ethyne in the presence of H_2SO_4 and HgSO_4 gives acetaldehyde. All other alkynes give ketones in this reaction (Unit 13, Class XI).

12.2.2 Preparation of Aldehydes

1. From acyl chloride (acid chloride)

Acyl chloride (acid chloride) is hydrogenated over catalyst, palladium on barium sulphate. This reaction is called **Rosenmund reduction**.



Benzoyl chloride

Benzaldehyde

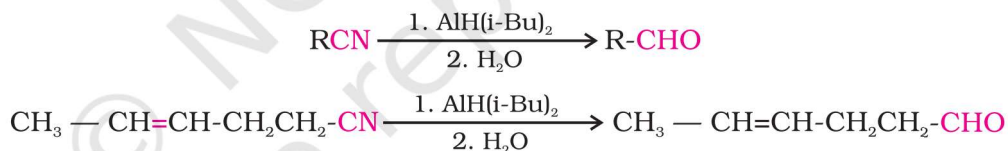
2. From nitriles and esters

Nitriles are reduced to corresponding imine with stannous chloride in the presence of hydrochloric acid, which on hydrolysis give corresponding aldehyde.

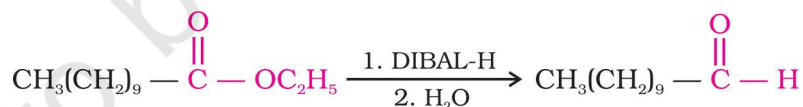


This reaction is called **Stephen** reaction.

Alternatively, nitriles are selectively reduced by diisobutylaluminium hydride, (DIBAL-H) to imines followed by hydrolysis to aldehydes:



Similarly, esters are also reduced to aldehydes with DIBAL-H.



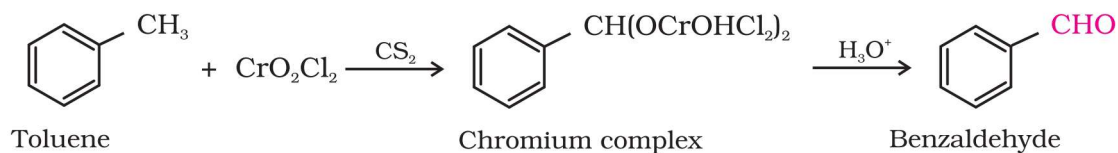
3. From hydrocarbons

Aromatic aldehydes (benzaldehyde and its derivatives) are prepared from aromatic hydrocarbons by the following methods:

(i) *By oxidation of methylbenzene*

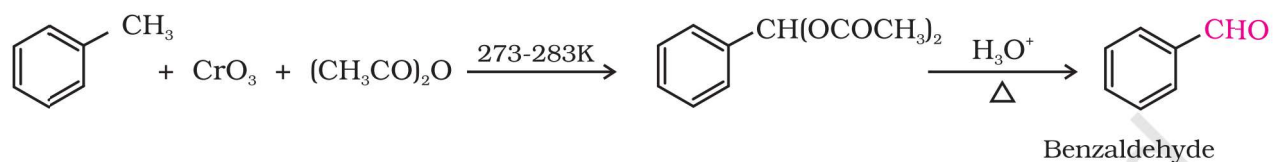
Strong oxidising agents oxidise toluene and its derivatives to benzoic acids. However, it is possible to stop the oxidation at the aldehyde stage with suitable reagents that convert the methyl group to an intermediate that is difficult to oxidise further. The following methods are used for this purpose.

(a) Use of chromyl chloride (CrO_2Cl_2): Chromyl chloride oxidises methyl group to a chromium complex, which on hydrolysis gives corresponding benzaldehyde.



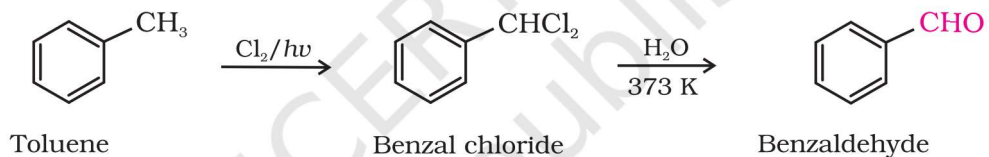
This reaction is called **Etard reaction**.

(b) Use of chromic oxide (CrO_3): Toluene or substituted toluene is converted to benzylidene diacetate on treating with chromic oxide in acetic anhydride. The benzylidene diacetate can be hydrolysed to corresponding benzaldehyde with aqueous acid.



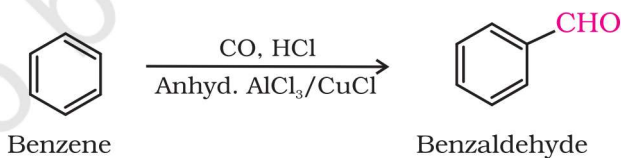
(ii) *By side chain chlorination followed by hydrolysis*

Side chain chlorination of toluene gives benzal chloride, which on hydrolysis gives benzaldehyde. This is a commercial method of manufacture of benzaldehyde.



(iii) *By Gatterman - Koch reaction*

When benzene or its derivative is treated with carbon monoxide and hydrogen chloride in the presence of anhydrous aluminium chloride or cuprous chloride, it gives benzaldehyde or substituted benzaldehyde.

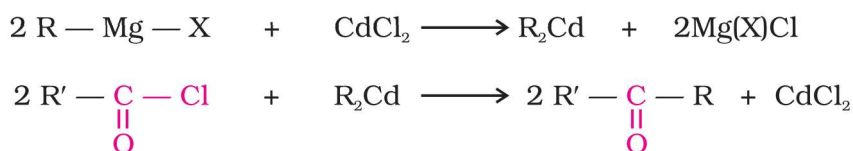


This reaction is known as **Gatterman-Koch** reaction.

12.2.3 Preparation of Ketones

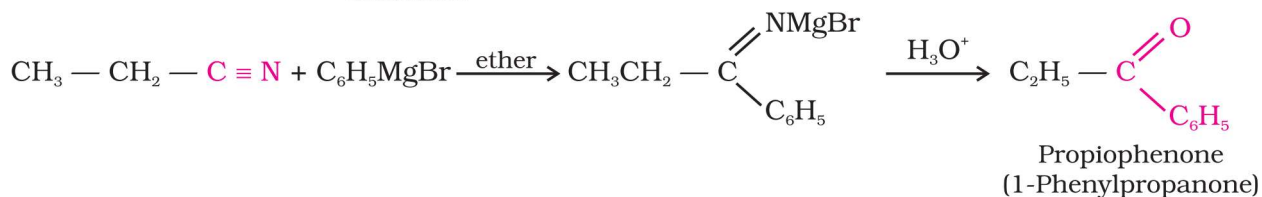
1. From acyl chlorides

Treatment of acyl chlorides with dialkylcadmium, prepared by the reaction of cadmium chloride with Grignard reagent, gives ketones.



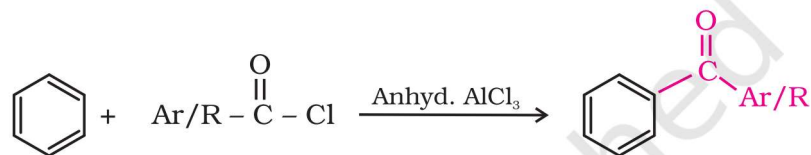
2. From nitriles

Treating a nitrile with Grignard reagent followed by hydrolysis yields a ketone.



3. From benzene or substituted benzenes

When benzene or substituted benzene is treated with acid chloride in the presence of anhydrous aluminium chloride, it affords the corresponding ketone. This reaction is known as **Friedel-Crafts acylation reaction**.



Example 12.1

Give names of the reagents to bring about the following transformations:

- | | |
|---|------------------------------------|
| (i) Hexan-1-ol to hexanal | (ii) Cyclohexanol to cyclohexanone |
| (iii) <i>p</i> -Fluorotoluene to <i>p</i> -fluorobenzaldehyde | (iv) Ethanenitrile to ethanal |
| (v) Allyl alcohol to propenal | (vi) But-2-ene to ethanal |

Solution

- | | |
|---|---|
| (i) $\text{C}_5\text{H}_5\text{NH}^+\text{CrO}_3\text{Cl}$ (PCC) | (ii) Anhydrous CrO_3 |
| (iii) CrO_3 in the presence of acetic anhydride /
1. CrO_2Cl_2 2. HOH | (iv) (Diisobutyl)aluminium hydride (DIBAL-H) |
| (v) PCC | (vi) $\text{O}_3/\text{H}_2\text{O}$ -Zn dust |

Intext Question

12.2 Write the structures of products of the following reactions;

