

13.2 AROMATIC ALDEHYDES AND KETONES

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Learning outcomes

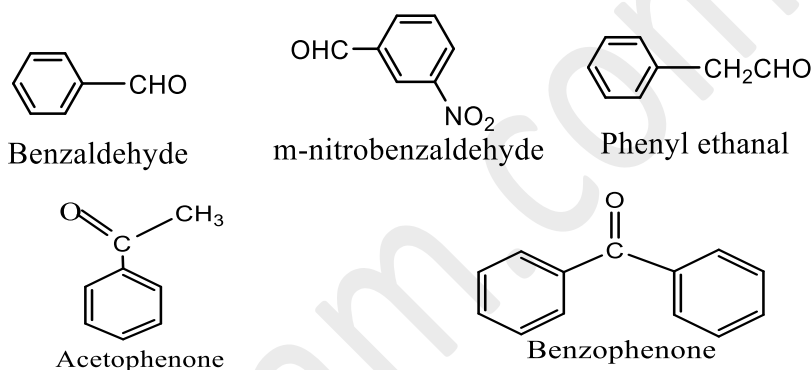
by the end of the chapter, students should be able to:

- Show the preparation of benzaldehyde from toluene and acetophenone from benzene.
- Explain the chemical properties of benzaldehyde, i.e. Perkin condensation, Benzoin condensation, Cannizzaro's reaction and electrophilic substitution reaction.

Introduction

In aromatic aldehydes and ketones, the carbonyl group is attached directly or indirectly to at least one aryl group. Aromatic aldehydes and ketones are of two types.

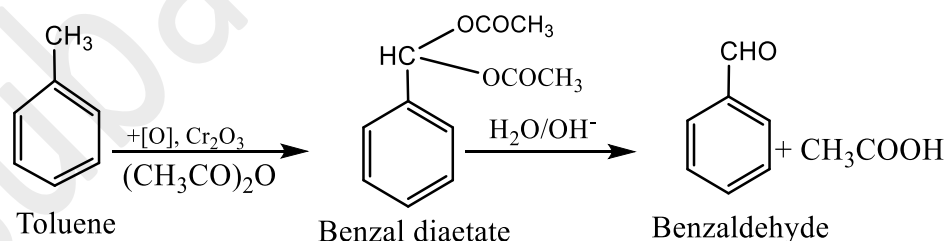
- The aromatic aldehydes in which the $-\text{CHO}$ group is directly attached to the benzene ring. e.g., Benzaldehyde
- The aromatic aldehydes in which the $-\text{CHO}$ group is in the side chain. e.g., phenyl acetaldehyde



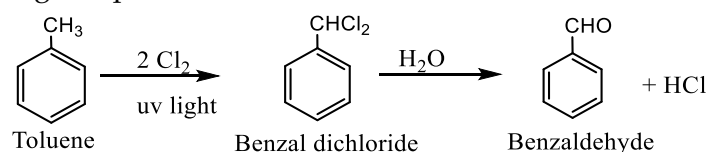
Preparation of Aromatic Aldehydes and Ketones

1. Preparation of Benzaldehyde from Toluene

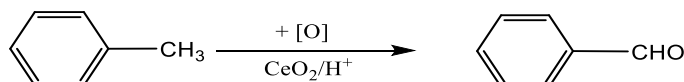
Benzaldehyde is prepared by the oxidation of methylbenzene (toluene) with chromium trioxide in acetic anhydride.



Benzaldehyde is commercially prepared by the side chain chlorination of toluene followed by the hydrolysis of the resulting compound.

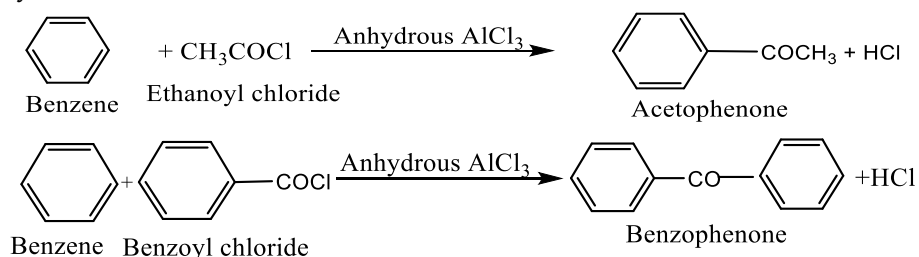


Benzaldehyde can also be prepared by oxidation of Toluene with Cerium oxide in an acidic medium.



2. Preparation of Acetophenone from benzene (Friedel-Crafts acylation)

Aromatic ketones are prepared by treating aromatic hydrocarbons with acid chlorides in the presence of anhydrous AlCl_3 .



Chemical properties of Aldehydes and ketones

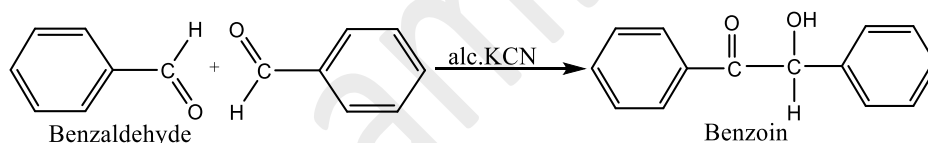
Most reactions of the carbonyl group ($>\text{C}=\text{O}$) in both aliphatic and aromatic aldehydes and ketones are almost the same, except for the fact that aromatic aldehydes and ketones are less reactive.

Therefore, aromatic aldehydes and ketones give similar reactions with HCN , NaHSO_3 , PCl_5 , 2,4-DNP, hydrazine, phenylhydrazine, hydroxylamine, Semicarbazide, and most other reagents.

Benzaldehyde gives some special reactions not shown by aliphatic aldehydes. Viz:

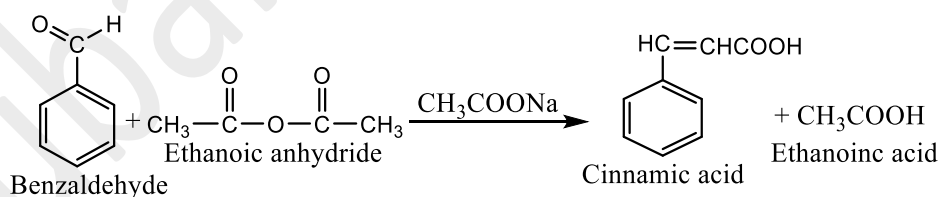
1) Benzoin condensation

When Benzaldehyde is heated with an alcoholic KCN solution, two molecules of Benzaldehyde join to form an α -hydroxy ketone known as *Benzoin*.



2) Perkin condensation

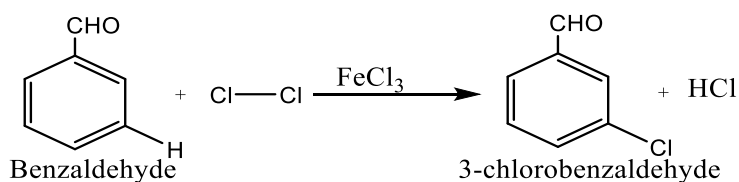
When an aromatic aldehyde, like Benzaldehyde, is condensed with aliphatic acid anhydride, like acetic anhydride, in the presence of a salt of the corresponding acid such as sodium acetate, α - β unsaturated acid is formed. This reaction is known as the Perkin condensation reaction.



Electrophilic aromatic substitution reactions

The reaction characteristic of the benzene ring is electrophilic substitution. The aldehyde group is a deactivating group and a meta-directing group. Hence, meta-substituted products are formed. E.g.,

1) Halogenation



Similarly, sulphonation, nitration, Friedel-Crafts alkylation, Friedel-Crafts acylation, etc. occur at the meta position.

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