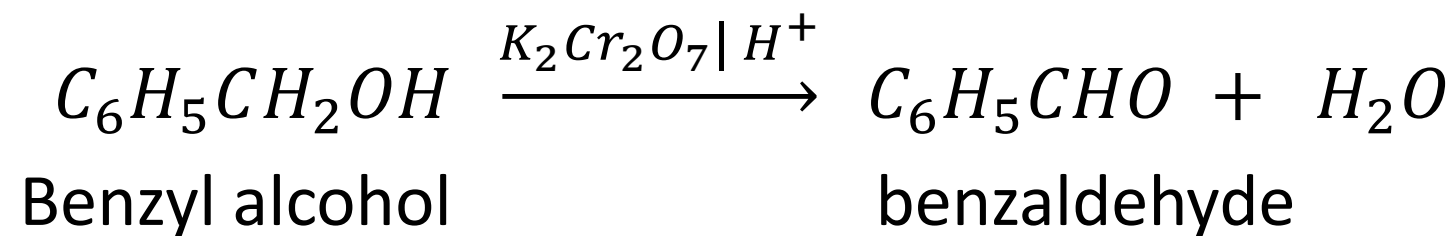


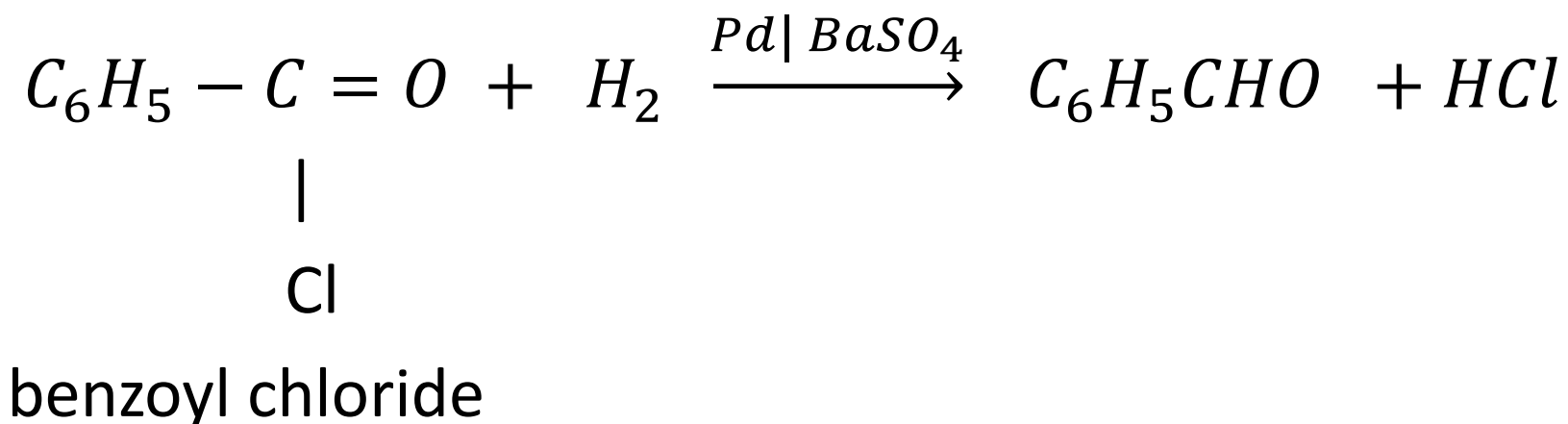
AROMATIC ALDEHYDE AND KETONE

Preparation of aromatic aldehyde (benzaldehyde)

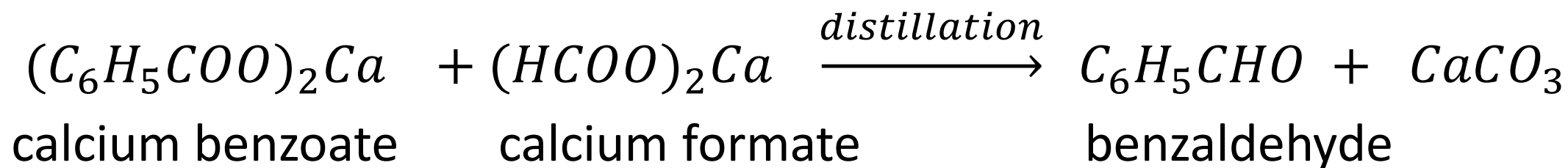
a) By oxidation of benzyl alcohol.



b) By Rosenmund reduction –



c) By distillation of calcium benzoate with calcium formate



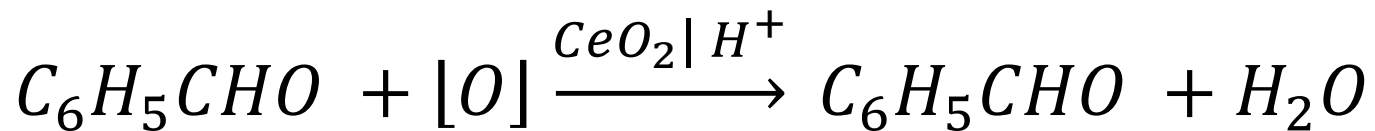
d) By Gattermann – Koch reaction:



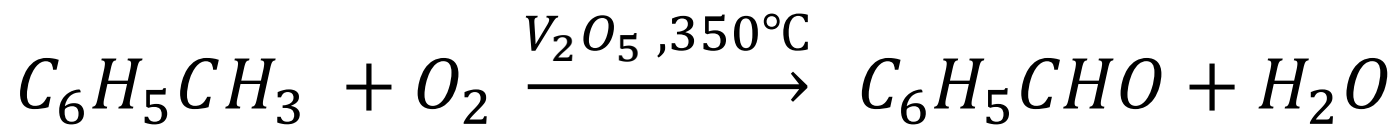
benzene

e) From toluene :

i) By reacting toluene with cerium oxide in acidic medium.



ii) By reacting toluene with air.



toluene

iii) By reacting toluene with chromium trioxide in acetic anhydride.



Preparation of aromatic ketone (acetophenone):

Acetophenone can be prepared by acylation of benzene.



Benzene acetyl chloride acetophenone

Chemical properties:

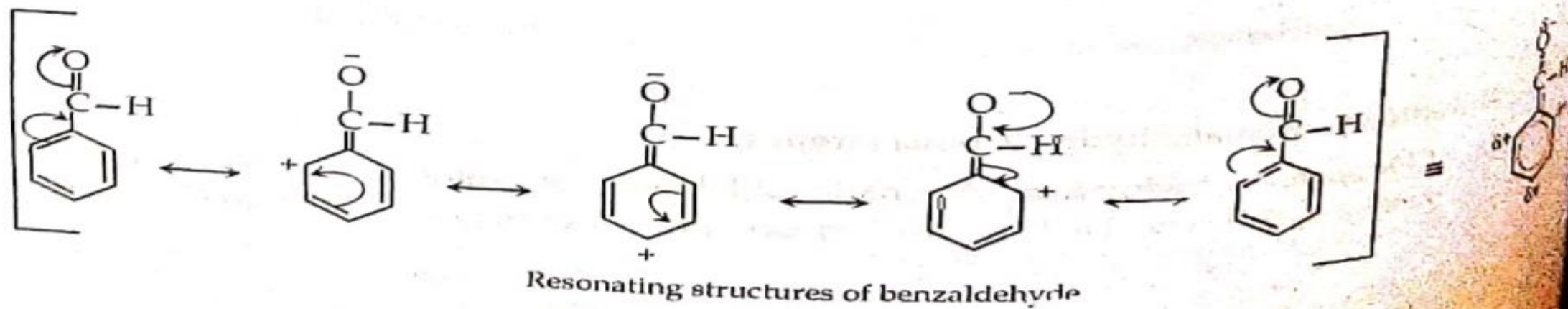
Aromatic aldehyde and ketone are less reactive than aliphatic aldehyde and ketone towards nucleophilic addition reaction. This is due to the resonance effect. The aryl or phenyl group acts as electron releasing group by resonance so it tends to decrease the extent of positive charge on the carbonyl group.

Resonance in benaldehyde,

D. Reaction given by aromatic benzene ring: Electrophilic aromatic substitution reaction

Benzaldehyde is less reactive than aliphatic aldehydes towards nucleophilic addition reaction. This can be explained on the basis of electron-releasing resonance effect of benzene ring. The carbonyl ($>\text{C}=\text{O}$) group is an electron-withdrawing group, which pulls the electron density from the aromatic benzene ring towards the carbonyl oxygen of the $>\text{C}=\text{O}$ group. As a result of which a negative charge is developed on the carbonyl oxygen and a positive charge is developed in the aromatic benzene ring. Therefore, the electron-withdrawing carbonyl ($>\text{C}=\text{O}$) group always deactivates the benzene ring towards electrophilic substitution reaction.

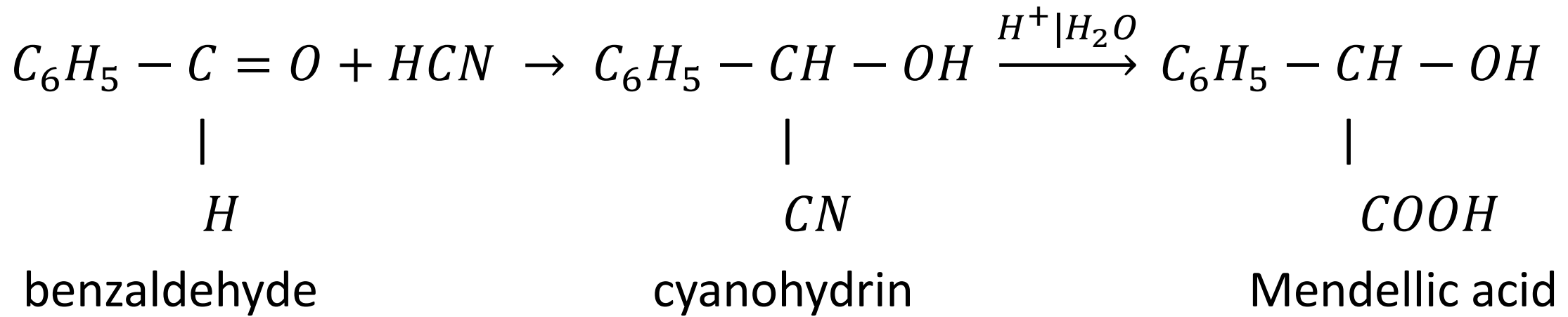
The positive charge so developed on the benzene ring is delocalized in the aromatic benzene ring to give the resonance hybrid structures. In these resonance structures, the positive charge (δ^+) appears in *ortho*- and *para*-positions rather than in *meta*-positions, which makes *ortho*- and *para*-positions less reactive than *meta*-positions towards electrophilic substitution reaction. Therefore, aromatic aldehydes and ketones are *meta*-directing towards electrophilic substitution reaction and hence the reaction takes place slowly at *meta*-positions to give *meta*-substituted products.



Most of the chemical reactions of benzaldehyde and acetophenone are similar to aliphatic compounds. Eg,

A) Nucleophilic addition reactions :

i) Addition of HCN

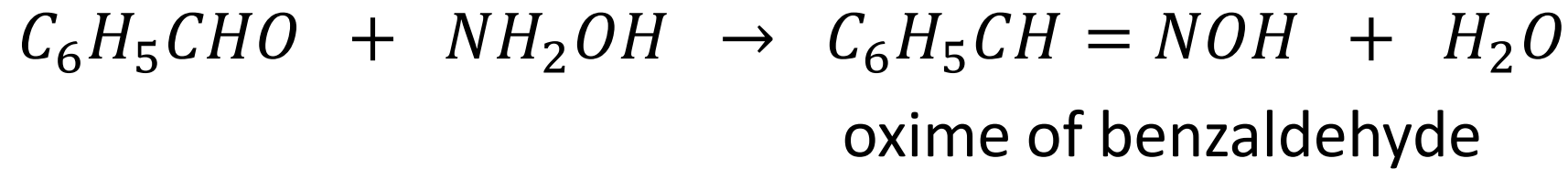


Benzaldehyde also reacts with sodium hydrogen sulphite and Grignard reagent.

B) Nucleophilic addition followed by elimination reaction.

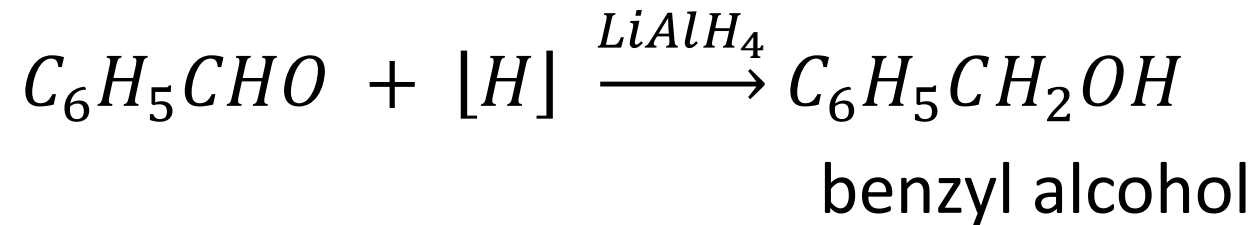
Benzaldehyde reacts with ammonia and derivatives of ammonia.

Eg, with hydroxylamine, it gives oxime.

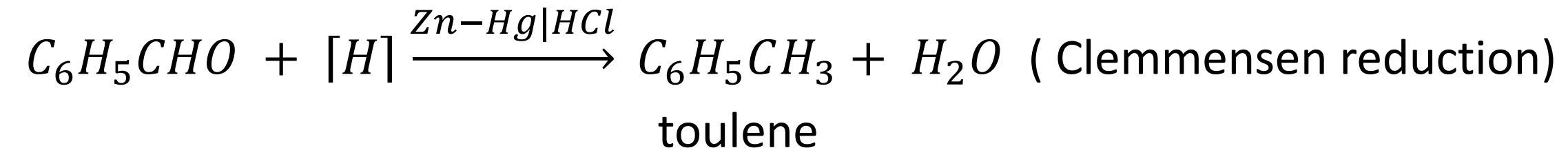


C) Reduction :

On partial reduction, benzaldehyde gives benzyl alcohol.

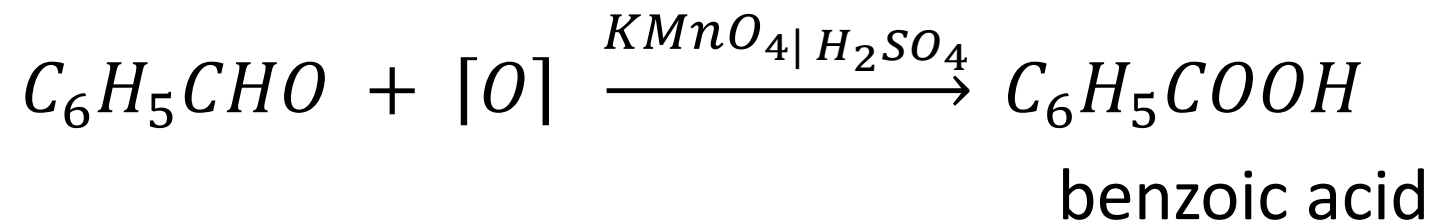


On complete reduction, benzaldehyde gives toluene.

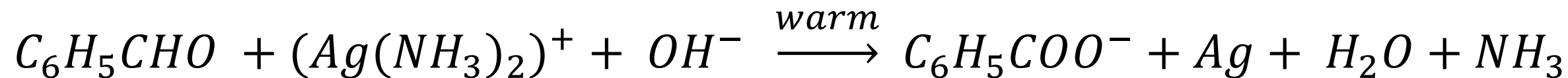


D) Oxidation :

Benzaldehyde is oxidized to benzoic acid .



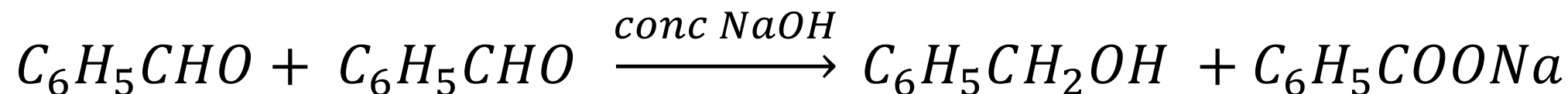
Benzaldehyde is also oxidized by Tollen's reagent.



But it is not oxidized by Fehling's solution.

Some special reactions of benzaldehyde.

a) Cannizzaro reaction-



Two molecules of ben