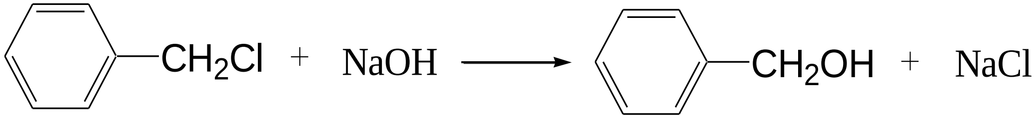
Aromatic Alcohols

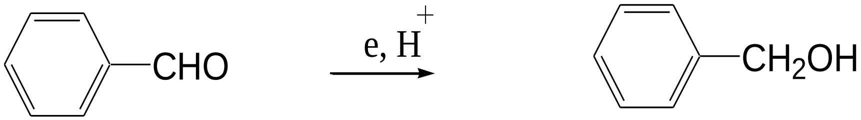
Aromatic alcohols are compounds containing a hydroxyl group in a side-chain, and may be regarded as aryl derivatives of the aliphatic alcohols

Preparation

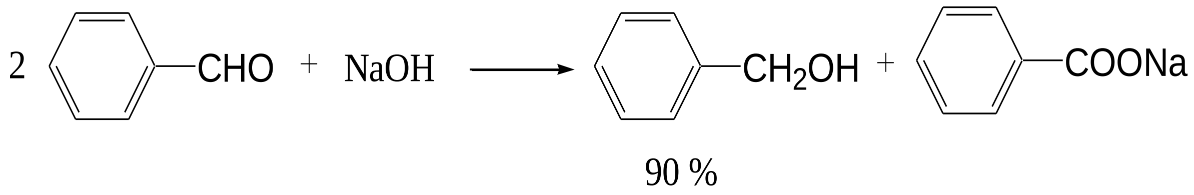
1-By hydrolyzing benzyl chloride with aqueous sodium hydroxide



2-By reducing benzaldehyde with zinc and hydrochloric acid



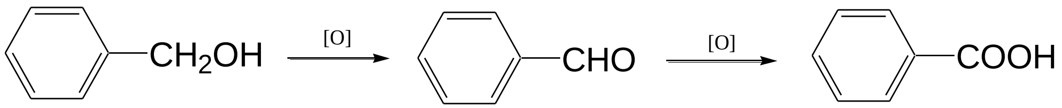
By means of the cannizaro reaction



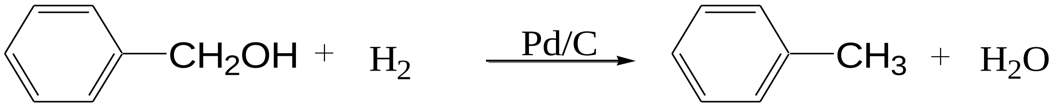
It may also be prepared by means of a crossed Cannizzaro reaction

$$\text{Ar-CHO} + \text{HCHO} \longrightarrow \text{Ar-CH}_2\text{OH}$$

The reactions of benzyl alcohol are similar to those of the primary aliphatic alcohols; e.g., on oxidation, it forms benzaldehyde and finally benzoic acid



Benzyl alcohol may be catalytically (palladium) reduced to toluene:



Aromatic aldehydes

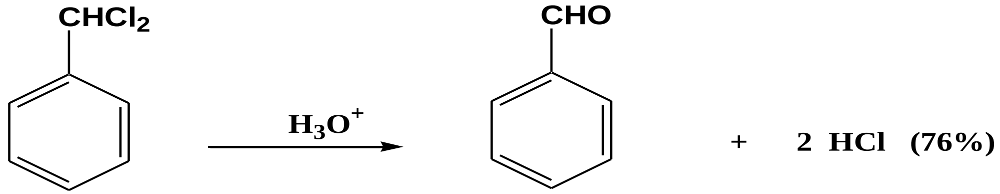
Aromatic aldehydes fall into two groups: those in which the aldehyde group is directly all to the nucleus, and those in which it is attached to the side-chain. The former group comprise the aromatic aldehydes; the latter, which behave as aliphatic aldehydes, are best regarded aryl-substituted aliphatic aldehydes

1- Benzaldehyde (benzenecarbonal)

It is also known as oil of bitter almonds, since it is found in glucoside amygdalin, which occurs in bitter almonds

Preparation

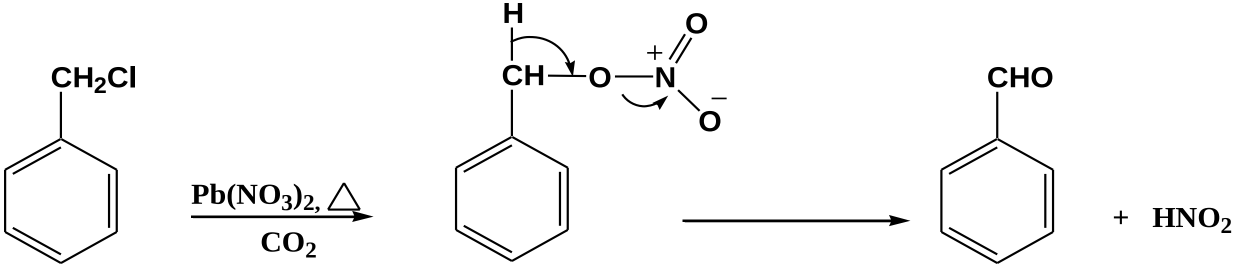
1-



Benzylidene chloride

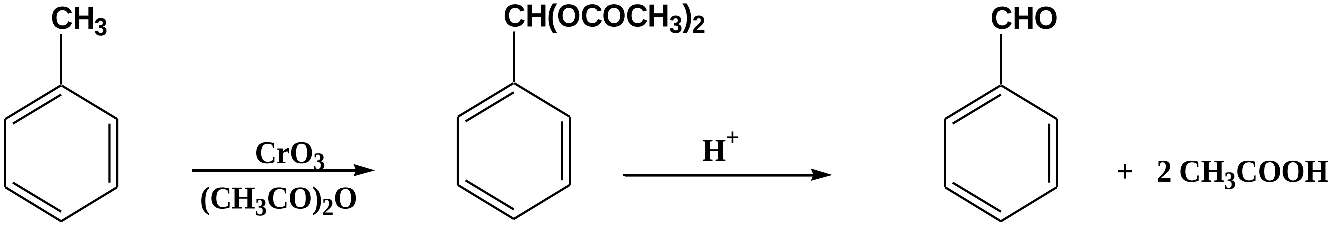
Hydrolysis with aq acid

2-



Benzyl chloride

3-



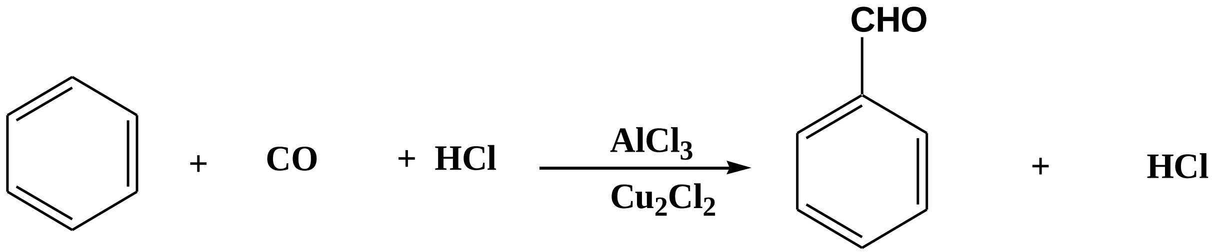
Toluene

Benzylidene acetate

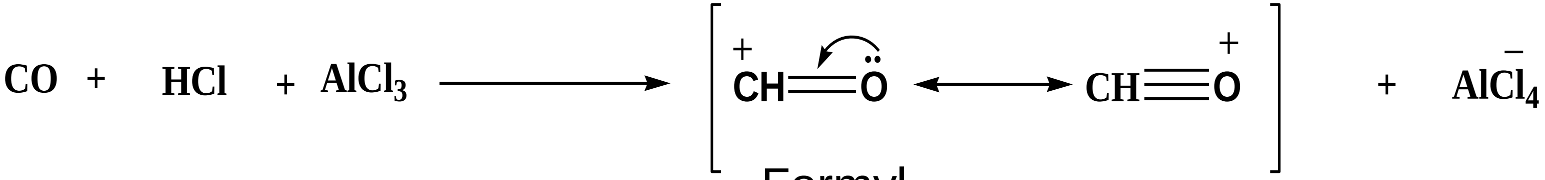
(40-50%)

Hydrolysis with dilute H_2SO_4 or HCl

4- Gattermann-Koch aldehyde synthesis:



Mechanism

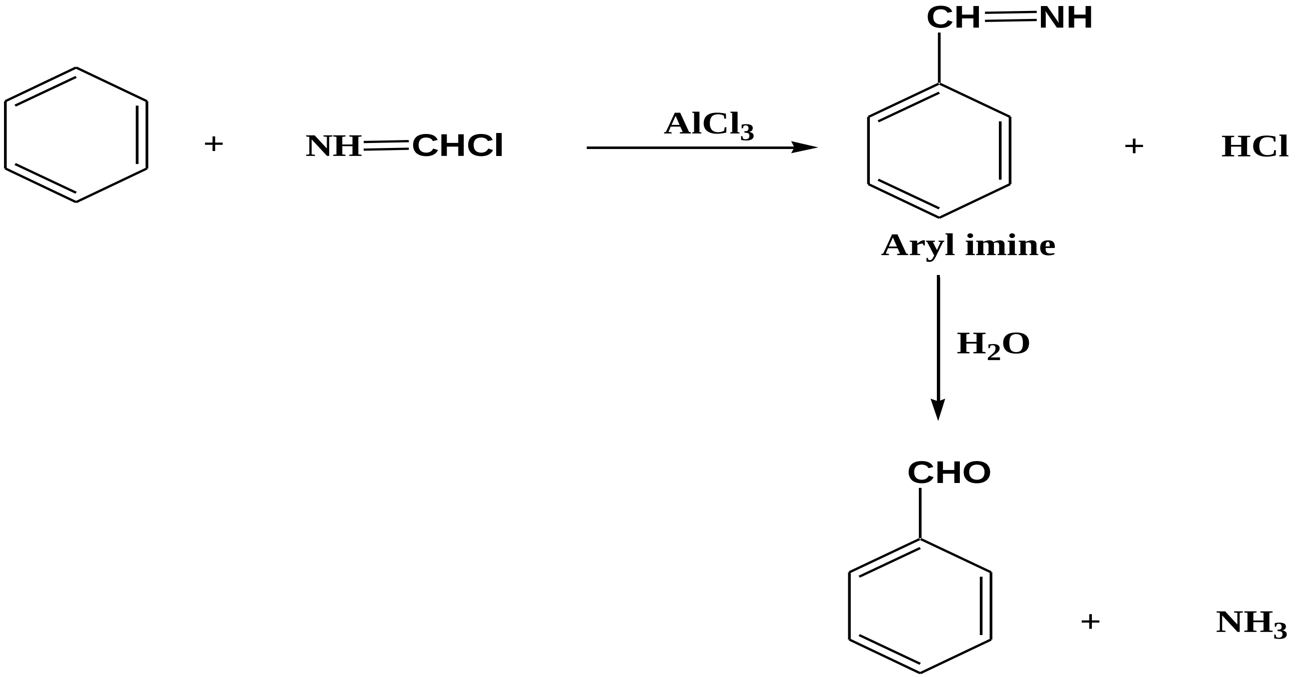


Formyl
cation

5- Gattermann aldehyde synthesis

Mechanism

$$HCl + HCN \xrightarrow{AlCl_3} NH{=}CHCl$$ (imidoformyl chloride)



Benzaldehyde and aromatic aldehydes in general resembles aliphatic aldehydes in the following reactions:

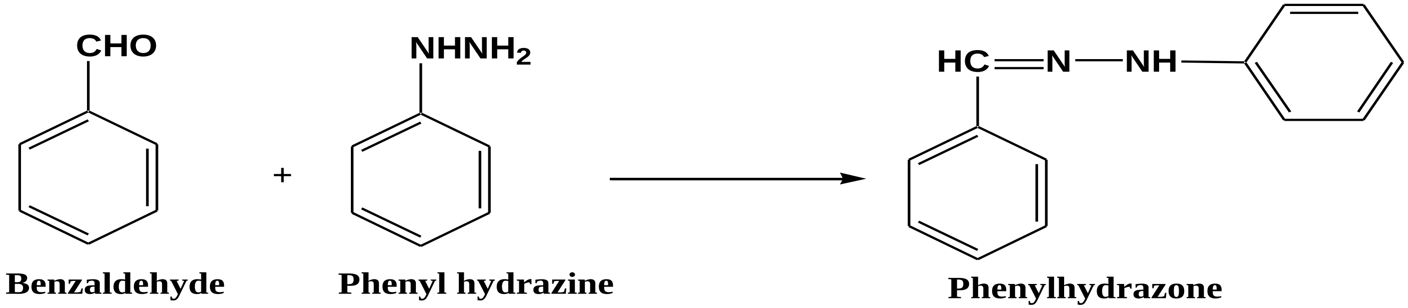
(i) It gives the Schiff's reaction.

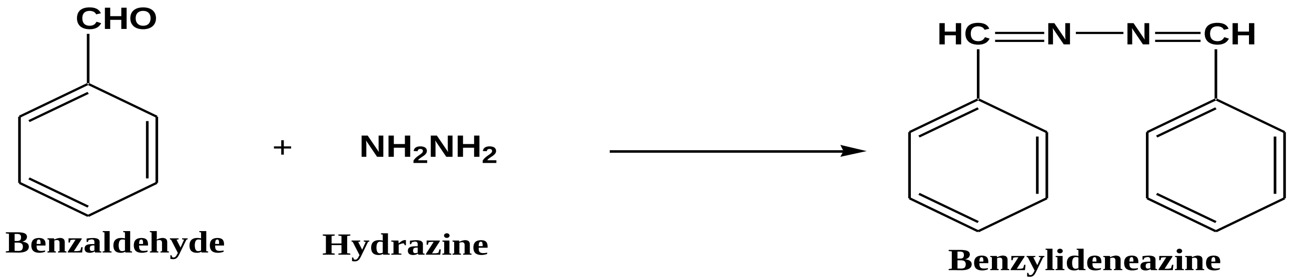
(ii) It is readily oxidised, i.e., it is a strong reducing agent; e.g., it reduces ammoniacal silver nitrate, itself being oxidised to benzoic acid when exposed to air.

(iii) Benzaldehyde forms a bisulphite compound, and may be prepared via this compound:

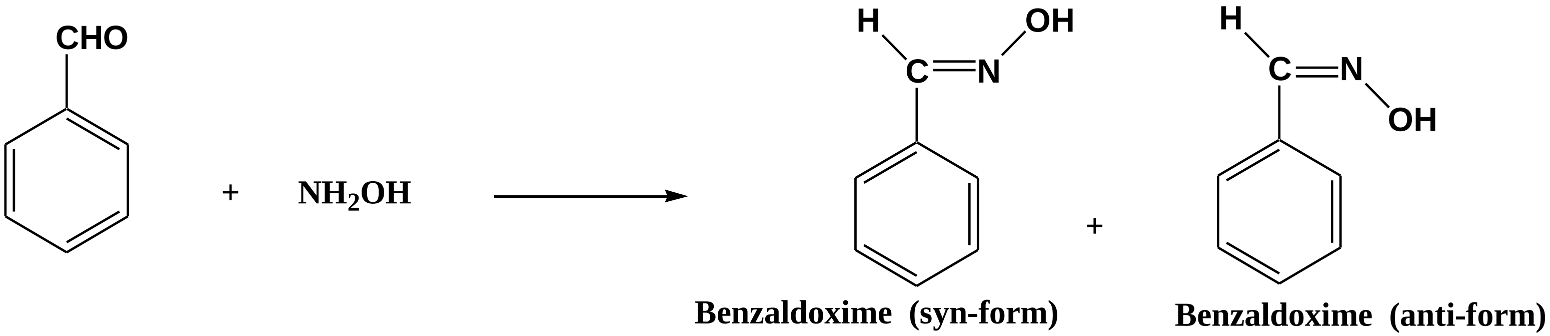
(iv) Benzaldehyde forms a cyanohydrin (mandelonitrile)

Cyanohydrin (mandelonitrile)





Benzaldehyde reacts with hydroxylamine to give benzaldoxime which exists in two geometrical isomeric forms.

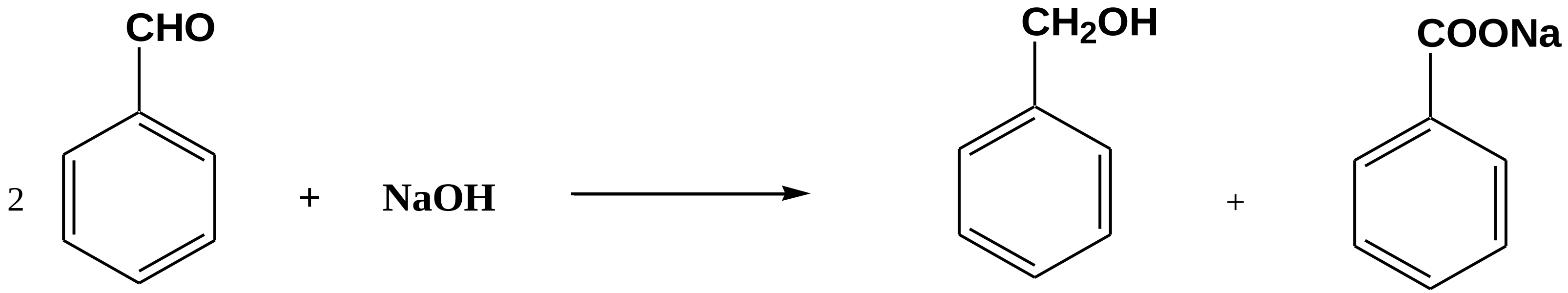


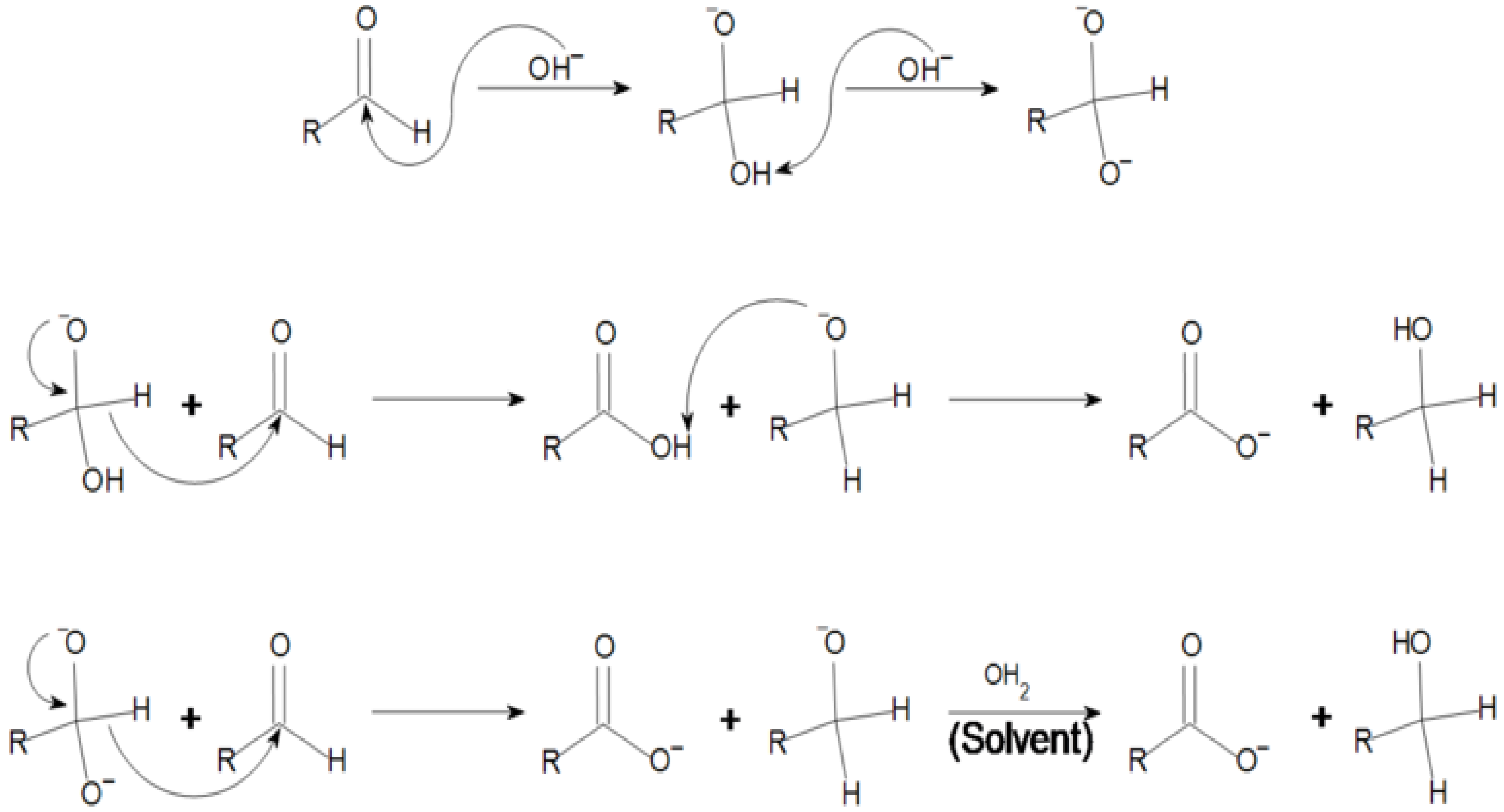
Benzaldehyde and other aromatic aldehydes differs from aliphatic aldehydes in the following ways:

(i) It does not reduce Fehling’s solution.

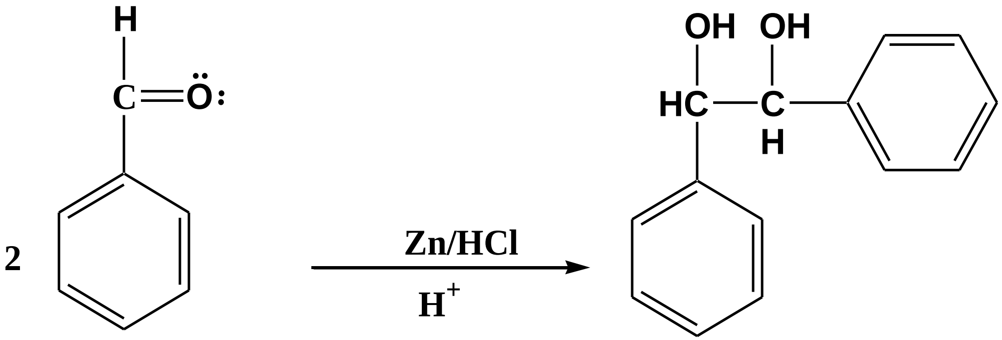
(ii) It does not readily polymerise; e.g., it does not resinify with sodium hydroxide (Aldol reaction no alpha hydrogen),

(iii) but undergoes the Cannizzaro reaction because it is not having an alpha-hydrogen atom (The reaction is limited to aldehydes lacking alpha hydrogen centers. Under ideal conditions the reaction produces only 50% of the alcohol and the carboxylic acid.




O
R
H
OH⁻
⁻O
H
R
OH
OH⁻
⁻O
R
H
O⁻
+
O
R
H
O
R
OH
+
⁻O
R
H
H
O
R
O⁻
+
HO
R
H
H
+
OH₂
(Solvent)

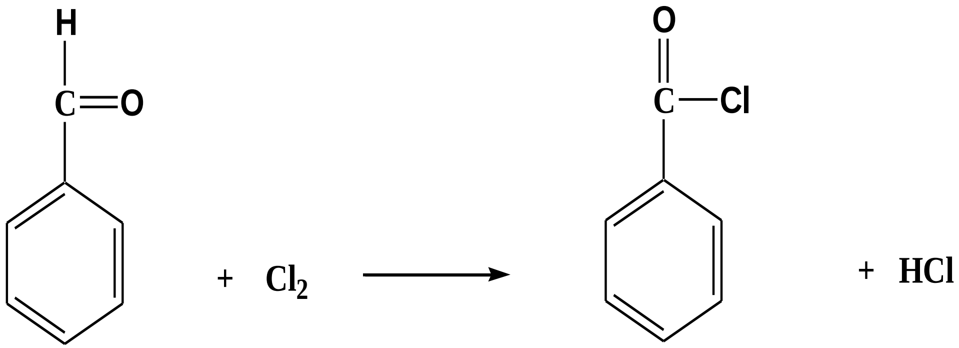
(iii) Reduction of benzaldehyde with zinc/HCl or sodium amalgam gives hydrobenzoin as well as benzyl alcohol.



Hydrobenzoin

With aliphatic aldehydes it gives only the alcohol

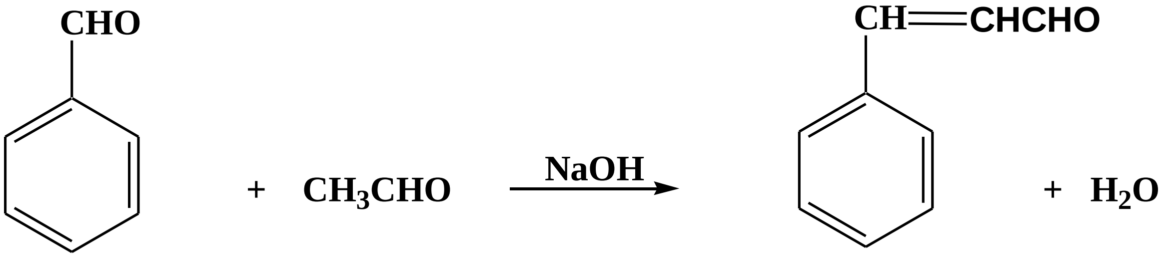
(vi) When benzaldehyde chlorinated , benzoyl chloride is produced (no alpha-hydrogen is present



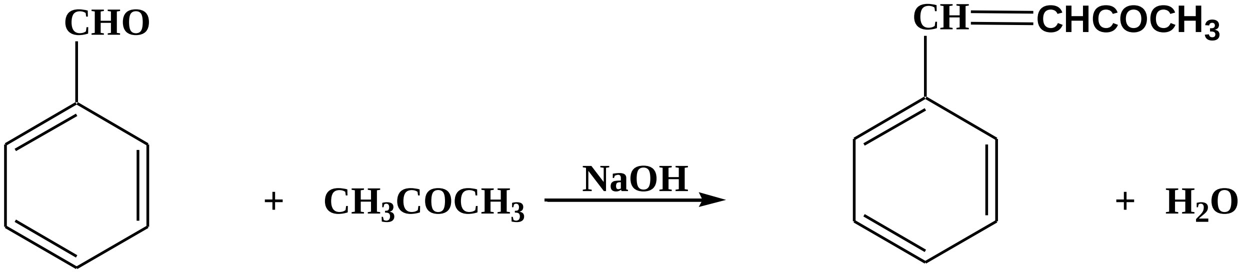
In aliphatic aldehydes, halogenation occur at alpha hydrogen

Condensation reactions of benzaldehyde

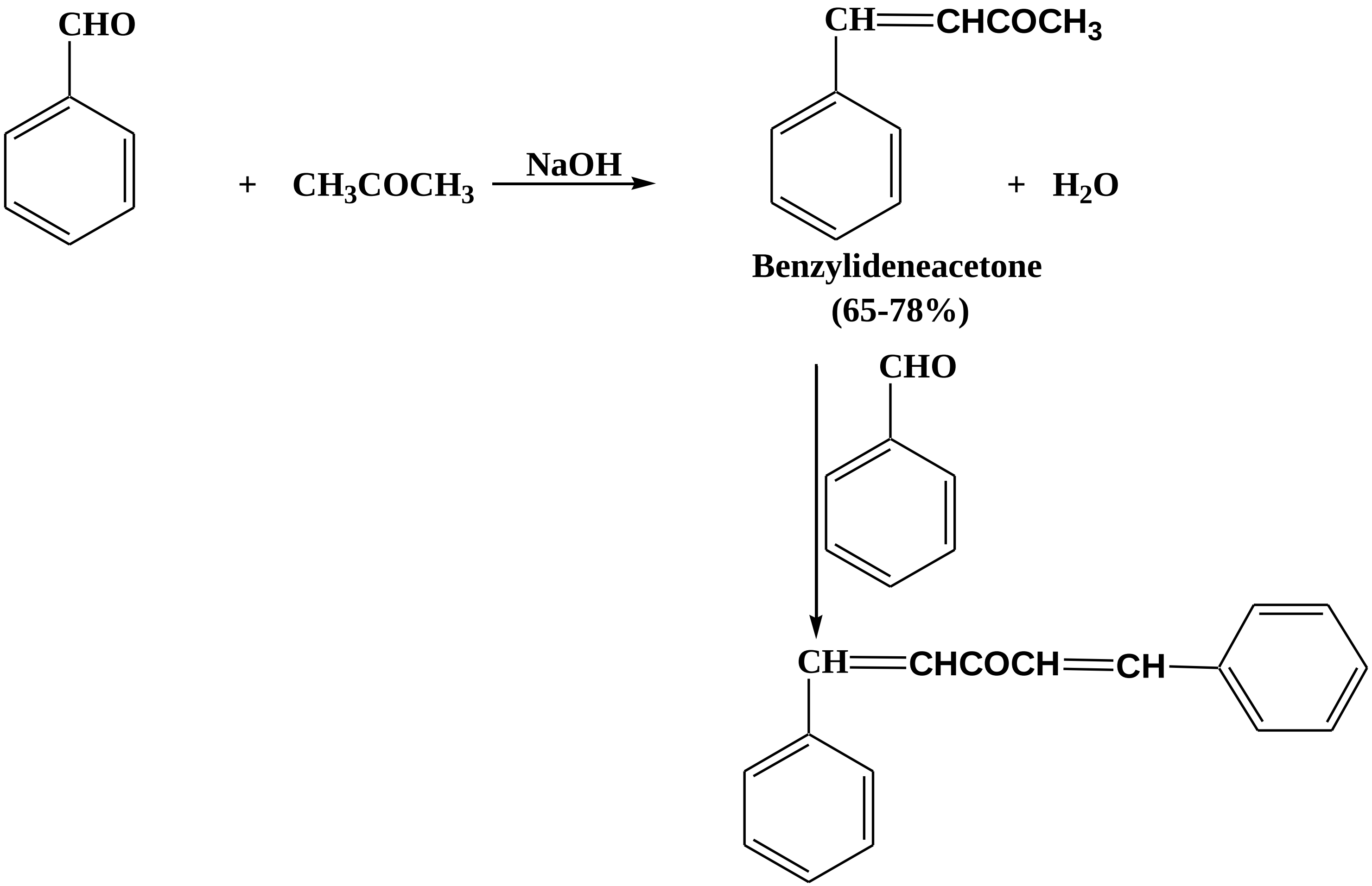
1- <u>Claisen reaction</u> **benzaldehyde, in the presence of dilute alkali, condense with aliphatic aldehydes or ketones containing α-hydrogen**



Cinnamaldehyde

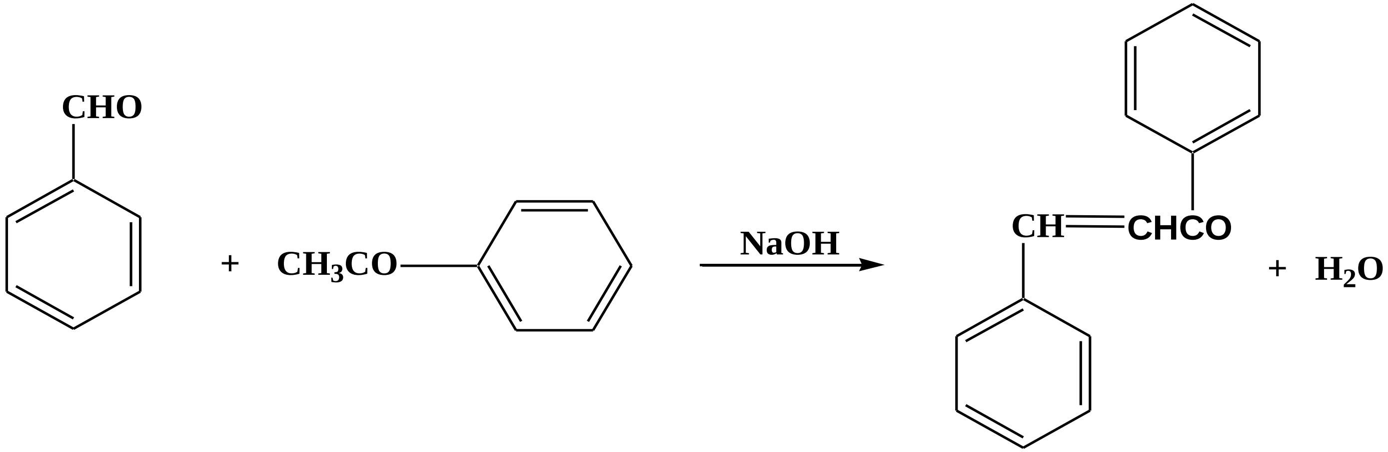


Benzylideneacetone
(65-78%)

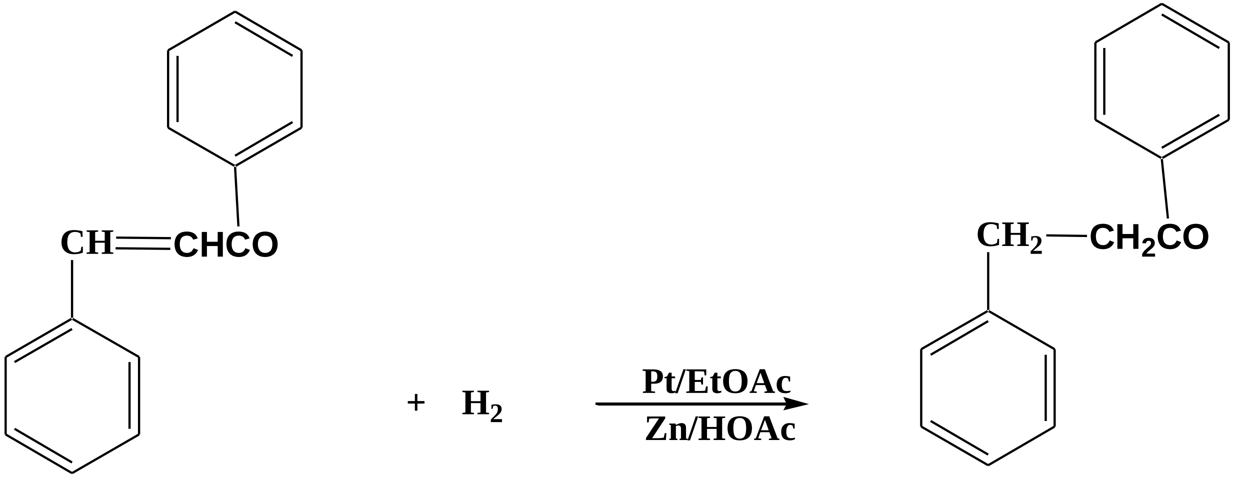


Benzylideneacetone
(65-78%)

Dibenzylideneacetone



(Benzylideneacetophenone, Chalcone)
(phenyl styryl ketone) (85%)

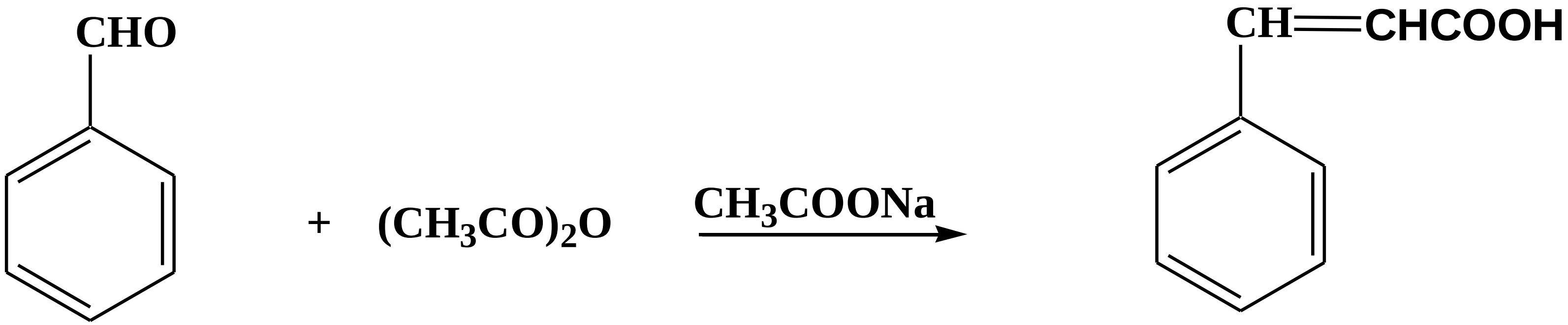


(Benzylideneacetophenone, Chalcone)
(phenyl styryl ketone) (85%)

Benzylacetophenone (81-95%)

2- Perkin reaction

When benzaldehyde (or any other aromatic aldehyde) is heated with the anhydride of an aliphatic acid (containing two α-hydrogen atoms)
in the presence of its salt, condensation takes place to form a β-arylacrylic acid
Perkin reaction does not usually take place with aliphatic aldehydes.

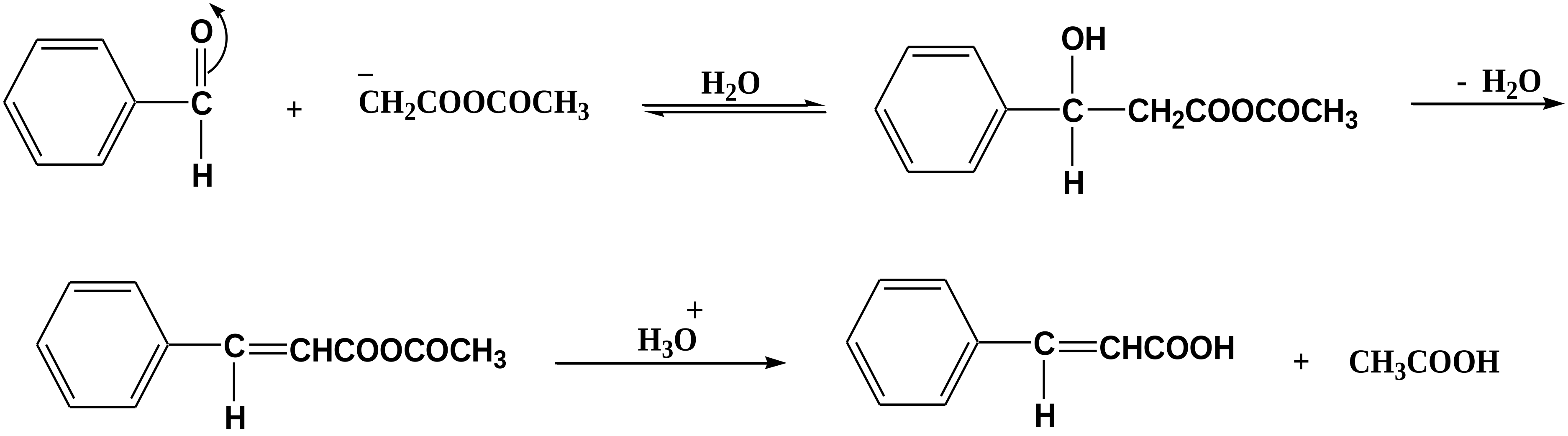


Cinnamic acid

B–arylacrylic acid

Mechanism

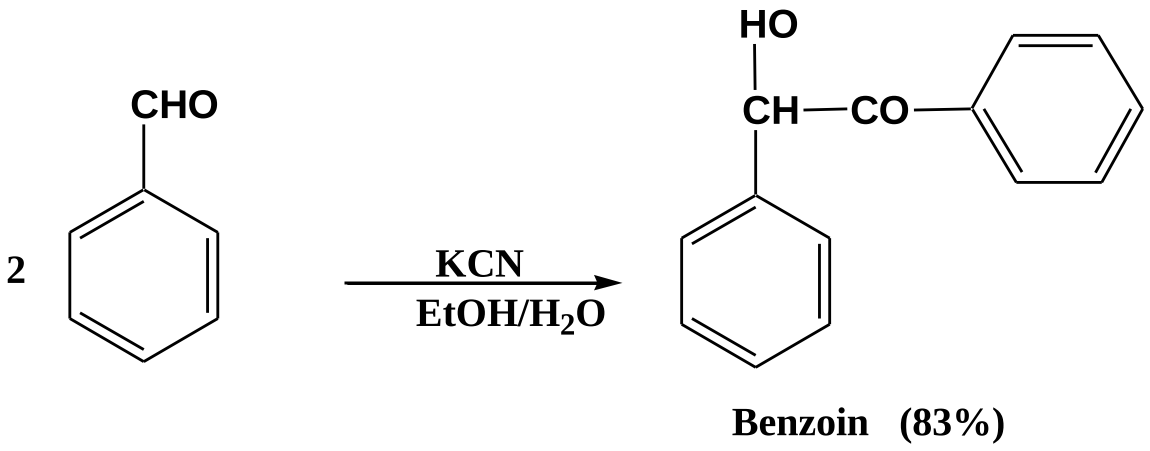
$$CH_3COOCOCH_3 \quad + \quad CH_3COO^- \rightleftharpoons {}^-CH_2COOCOCH_3 \quad + \quad CH_3COOH$$



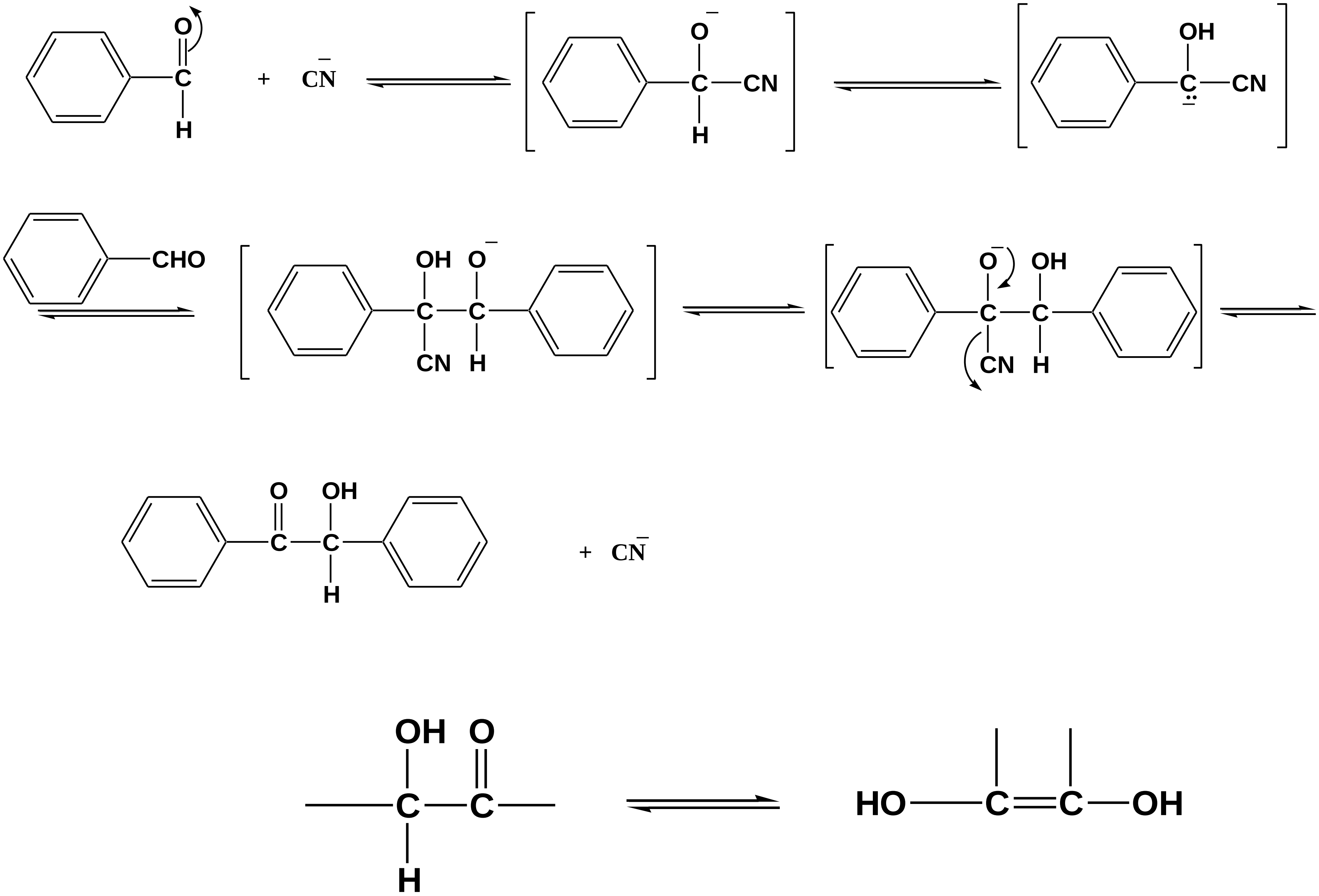
3- Benzoin condensation

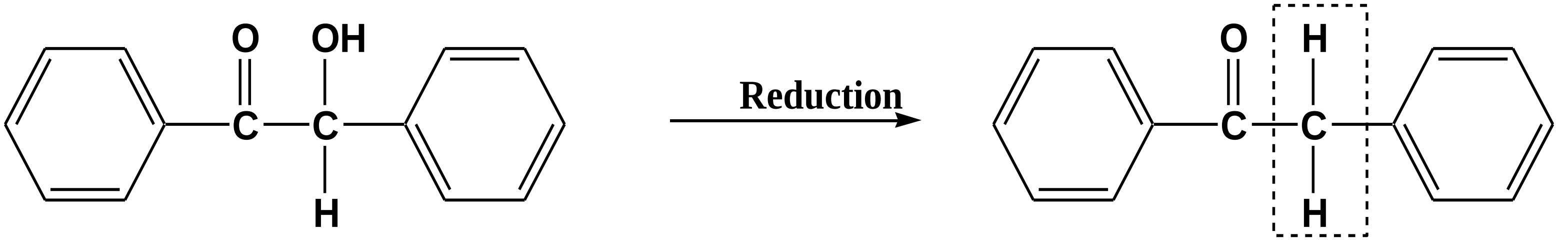
The **benzoin condensation** is a reaction between two aromatic aldehydes, particularly benzaldehyde. The reaction is catalyzed by a nucleophile such as the cyanide anion. The reaction product is benzoin as the parent compound

(aliphatic aldehydes do not undergo the benzoin condensation)



Mechanism


O
C
H
+ CN⁻
O⁻
C
CN
H
OH
C
CN
CHO
OH O⁻
C C
CN H
O⁻ OH
C C
CN H
O OH
C C
H
+ CN⁻
OH O
C C
H
HO C C OH



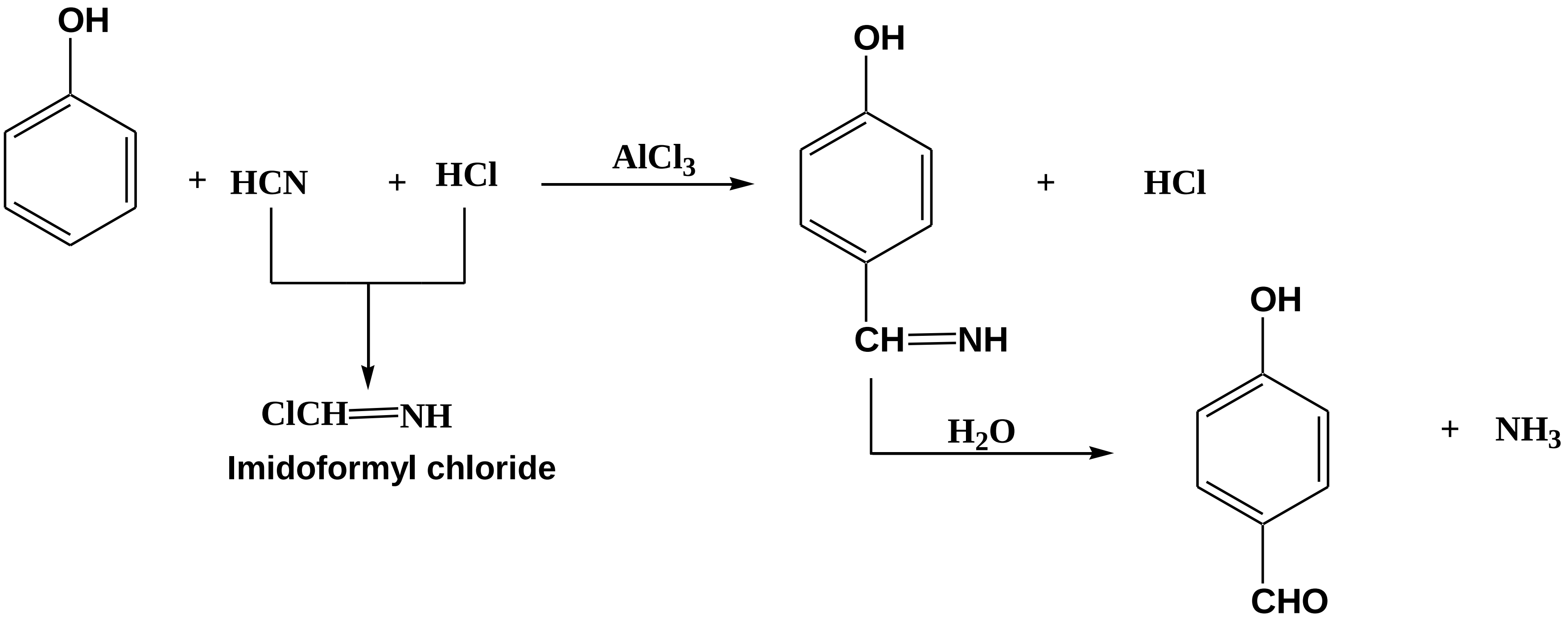
Benzoin

Deoxybenzoin (desoxybenzoin)

Derivatives of Benzaldehyde

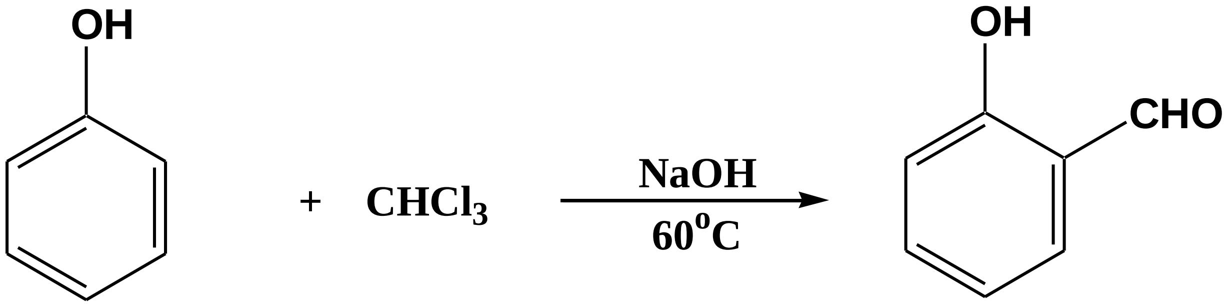
Phenolic aldehydes (Hydroxyaldehydes):

Gattermann's aldehyde synthesis (prep. of ***p*-hydroxybenzaldehyde**



Reimer-Tiemann reaction

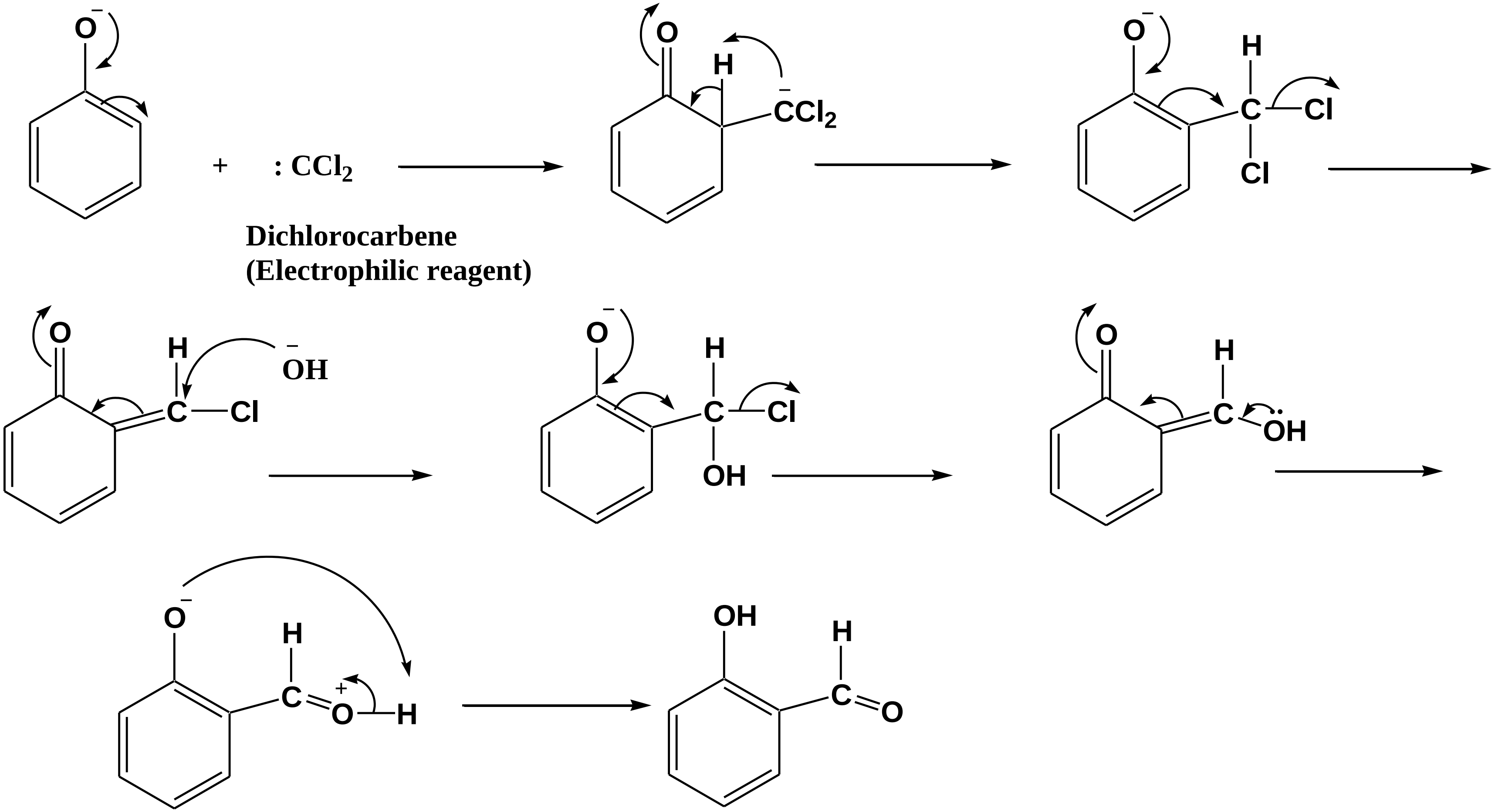
(for prep. of o and p-hydroxybenzaldehyde)



Mechanism

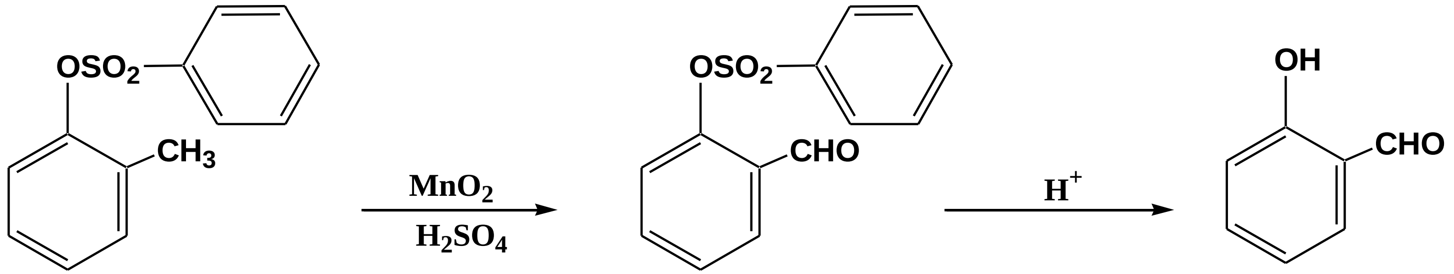
$$CHCl_3 + \overset{-}{OH} \rightleftharpoons H_2O + :\overset{-}{C}Cl_3 \longrightarrow \overset{-}{Cl} + :CCl_2$$

Dichlorocarbene



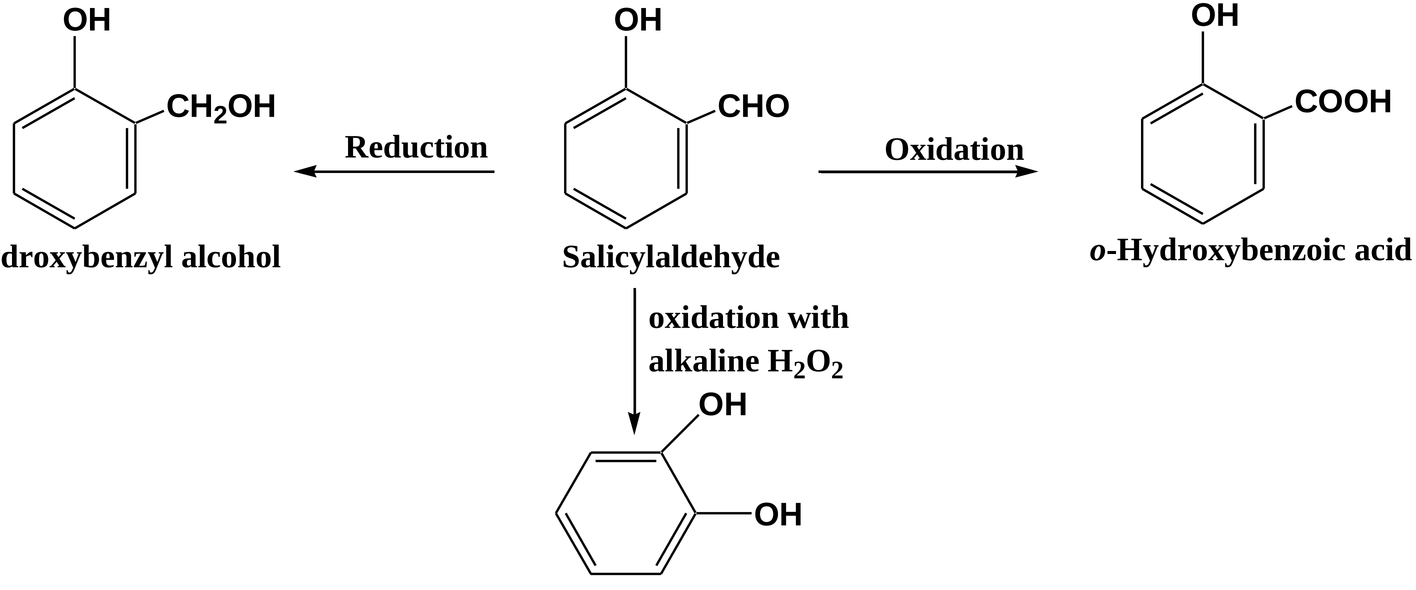
Salicylaldehyde (o-hydroxybenzaldehyde)

<u>Preparation</u>



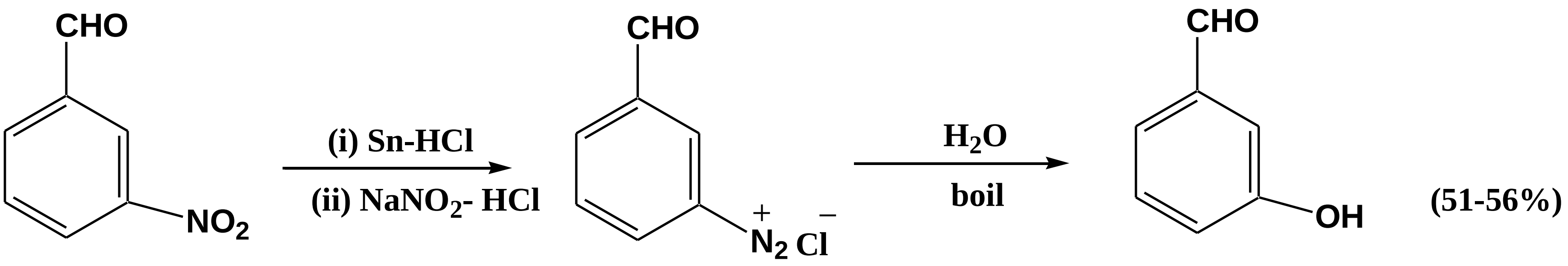
***o*-Methylphenyl benzenesulphonate**

Properties

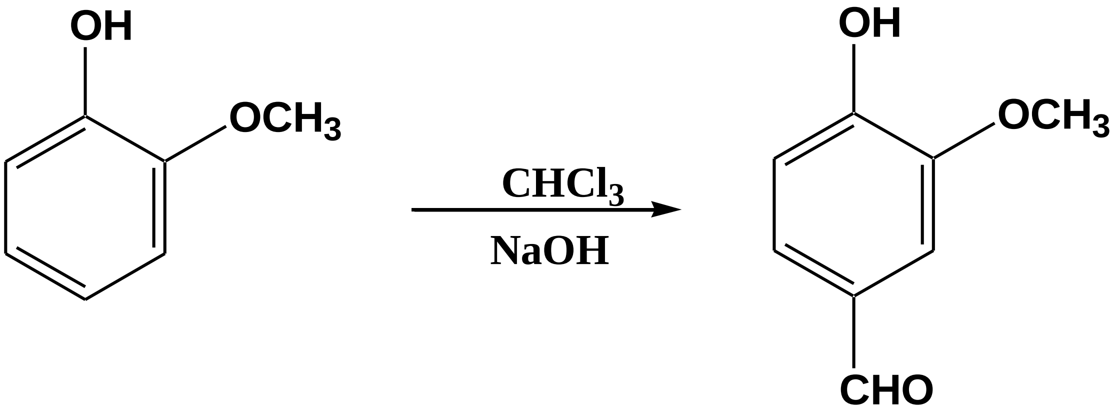


Catechol

m-Hydroxybenzaldehyde



Vanillin



Guaiacol

Vanillin

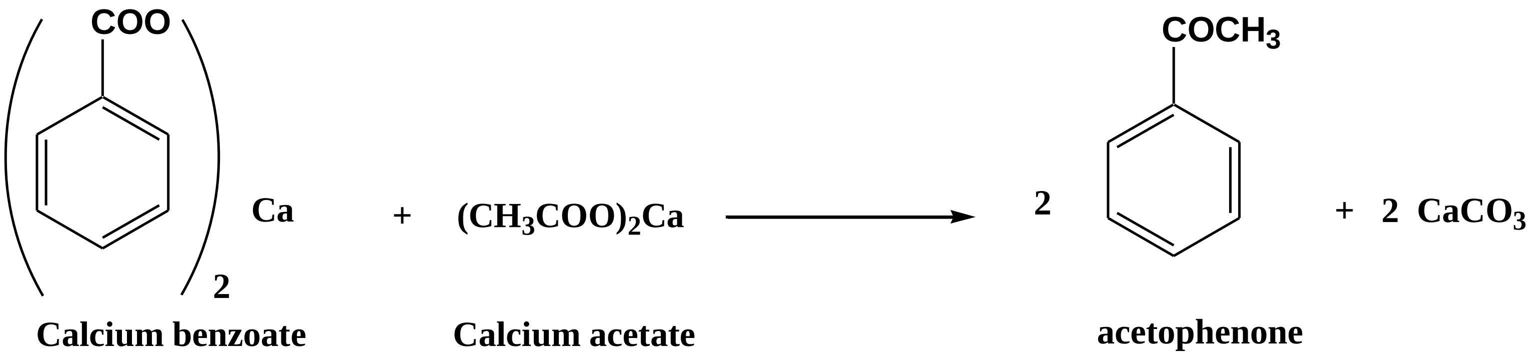
Aromatic Ketones

Aromatic ketones may be either alkaryl ketones or diaryl ketones

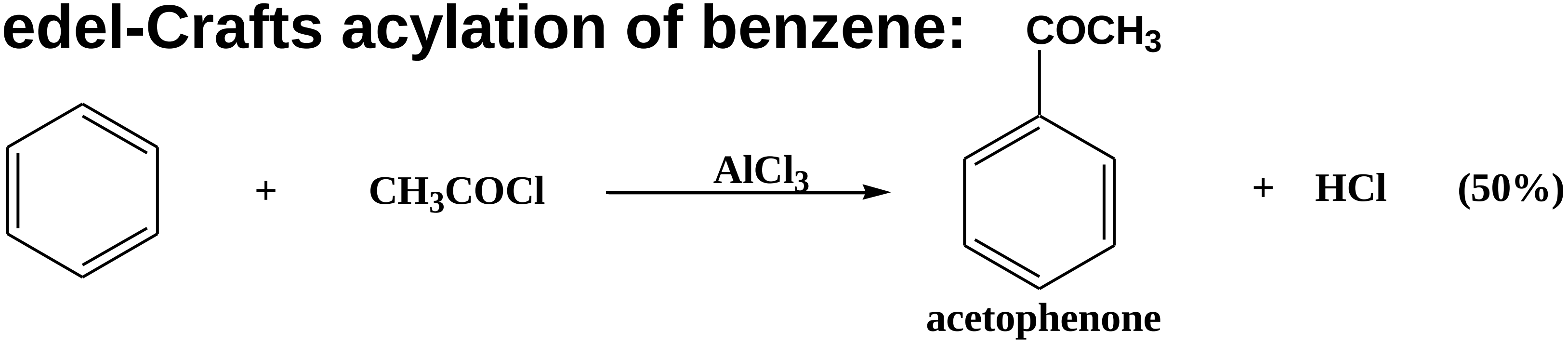
Acetophenone **(methyl phenyl ketone, acetylbenzene)**

Preparation:

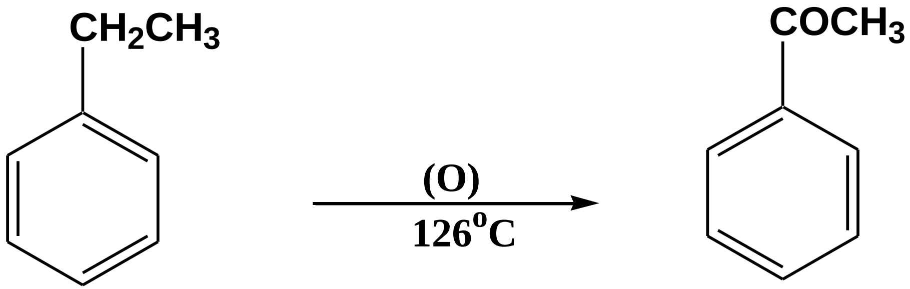
(1) From calcium or iron salt of benzoic acid:



(2) Friedel-Crafts acylation of benzene:



(3) Oxidation of ethylbenzene

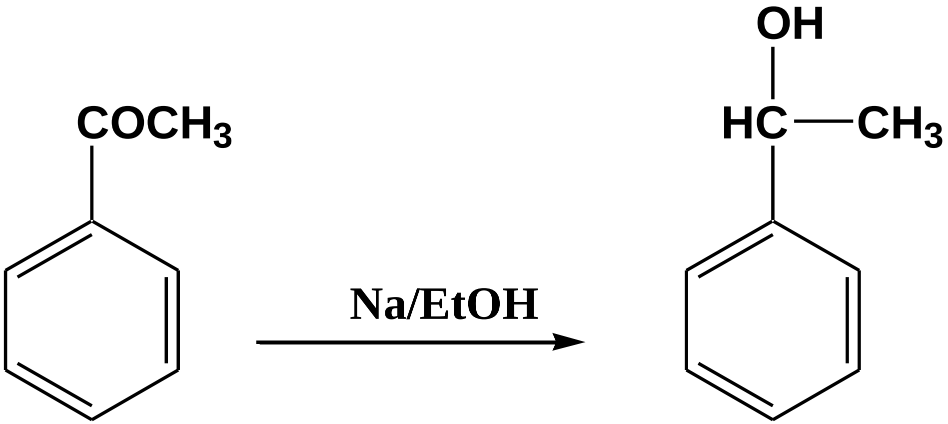


Ethylbenzene

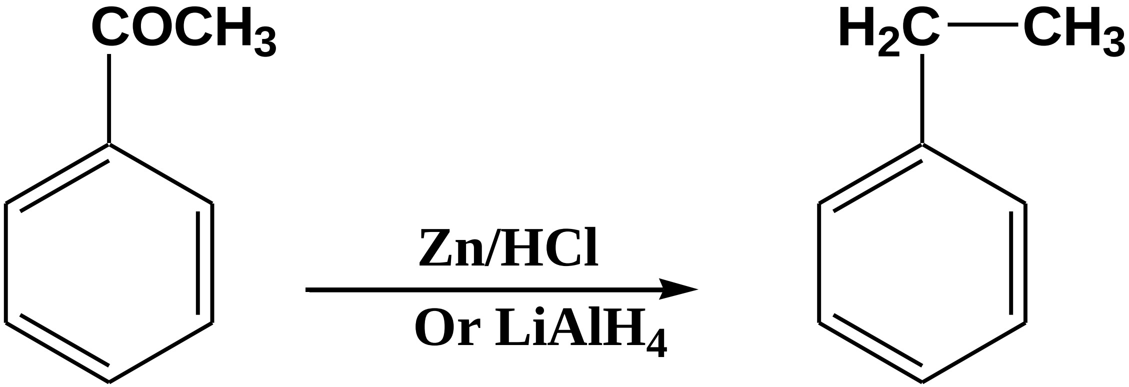
acetophenone

Chemical reactions:-

(1) Reduction:-

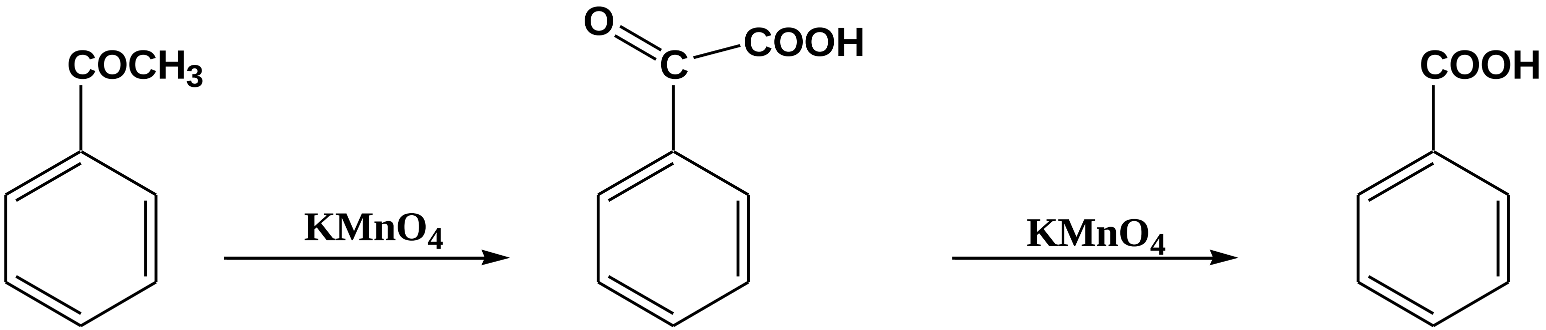


acetophenone Phenylmethylmethanol



acetophenone ethylbenzene

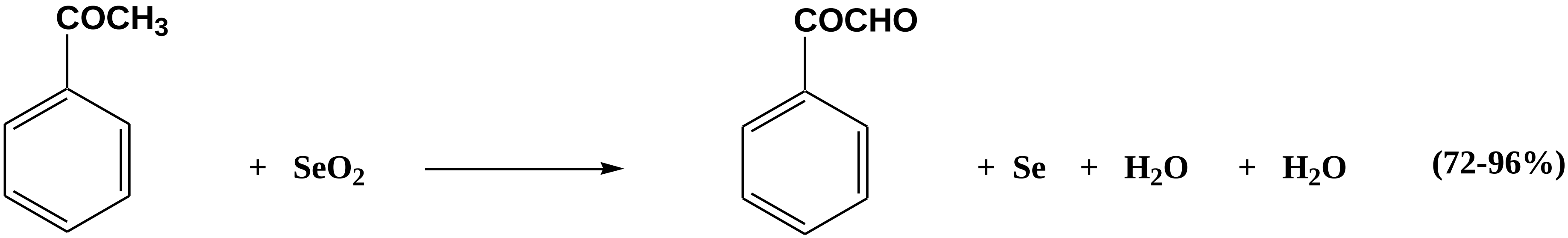
(2) Oxidation:-



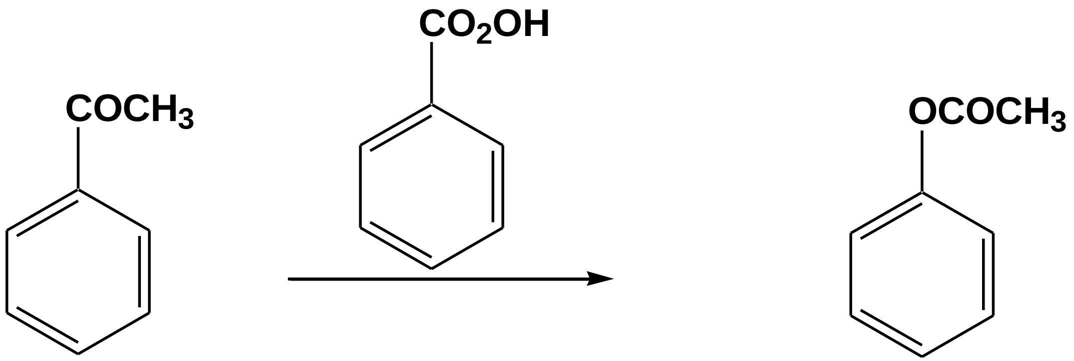
acetophenone

Phenylglyoxylic acid
(benzoyl formic acid)

Benzoic acid



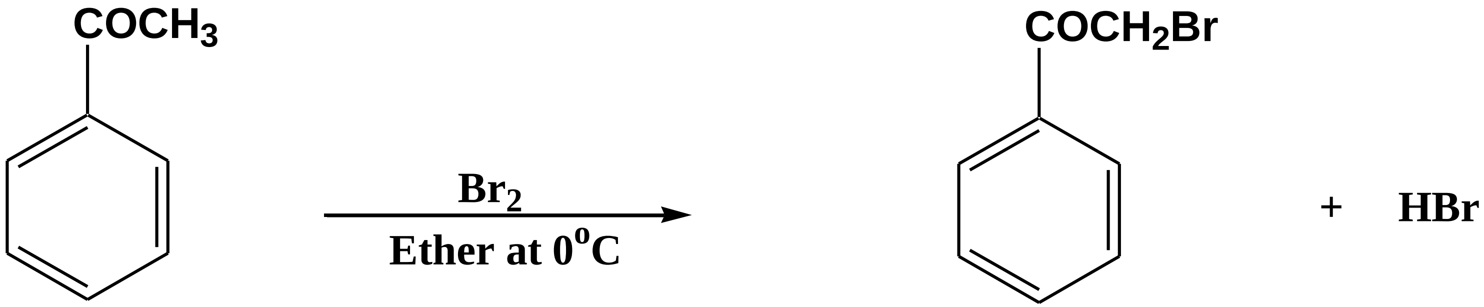
Phenylglyoxal



Phenyl acetate

(63%)

(3) Halogenation



Phenacyl bromide

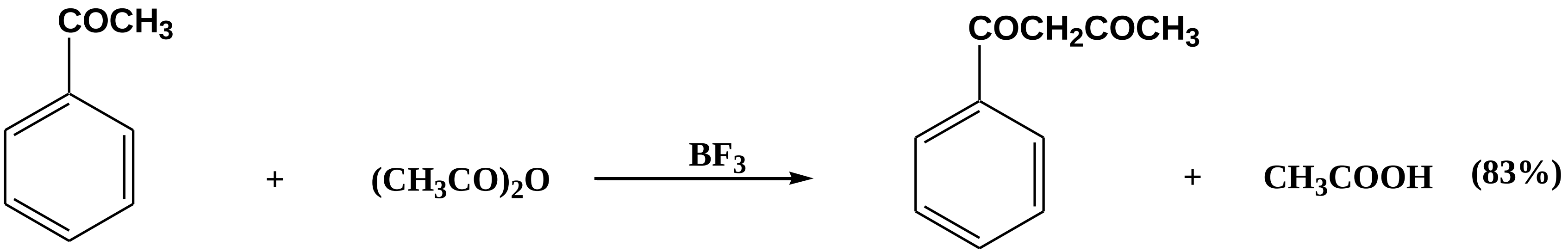
(64-66%)

Acetophenone forms an oxime, phenylhydrazone and cyanohydrin

The acetyl group is *m*-orienting, and so when acetophenone undergoes substitution, the main product is the *m*-derivative.

Condensation reaction of acetophenone

- Acetophenone condenses with acetic anhydride in the presence of BF_3 to form benzoylacetone**.**

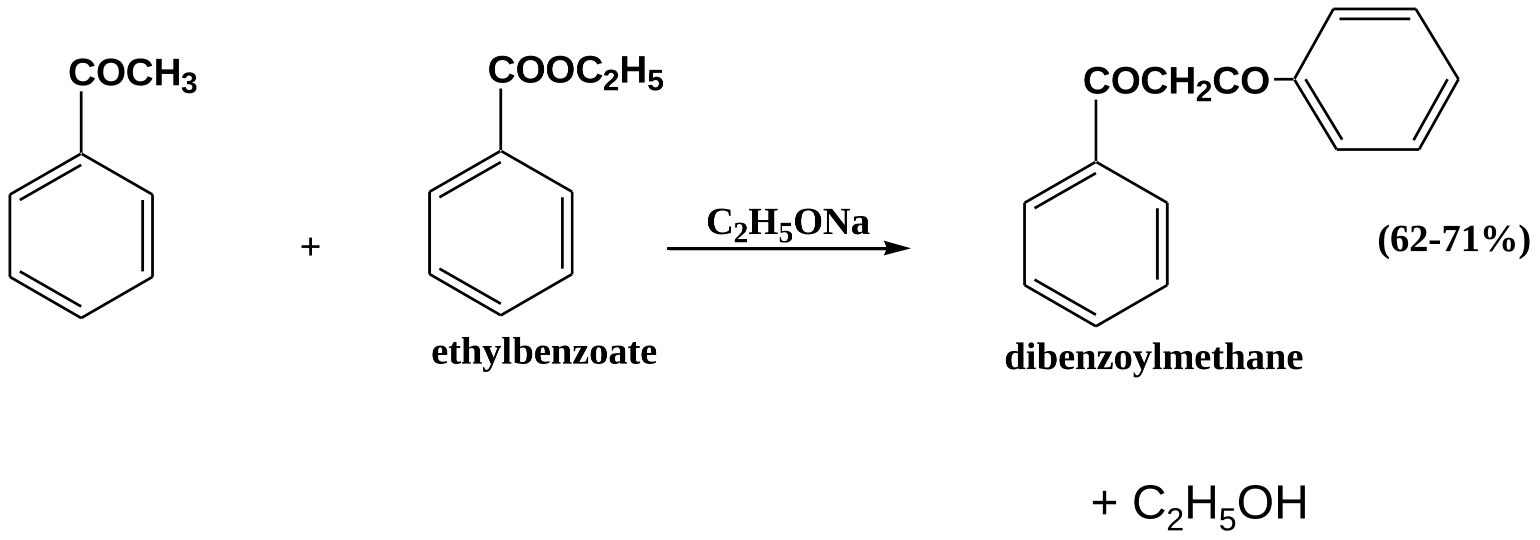


Benzoylacetone

Cinnamic acid

B–arylacrylic acid

Acetophenone condenses with ethyl benzoate in the presence of sodium ethoxide



ethylbenzoate

dibenzoylmethane

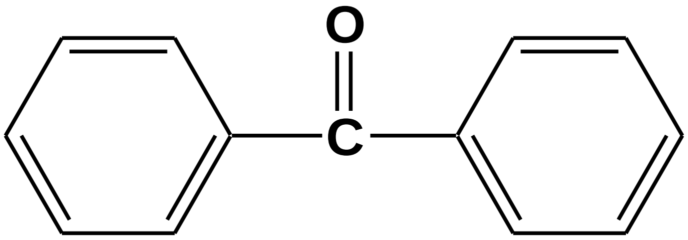
(62-71%)

$+ C_2H_5OH$

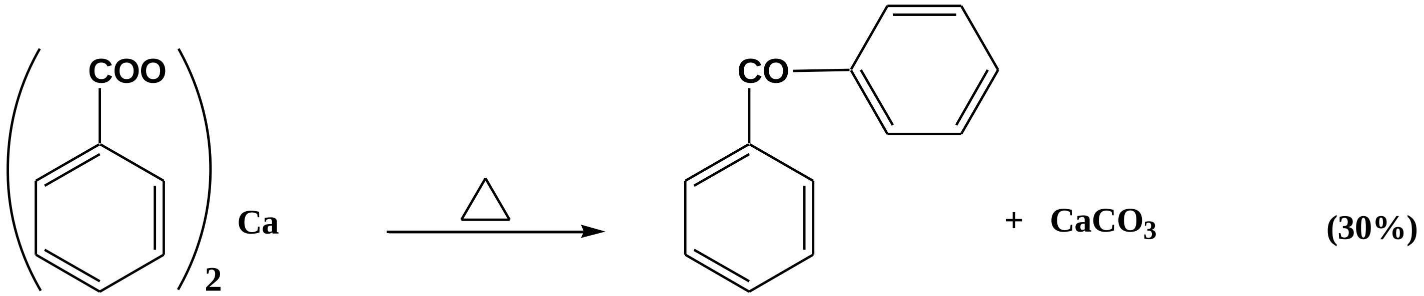
Acetophenone undergoes the Mannich reaction:-

Benzophenone (diphenyl ketone)

Preparation

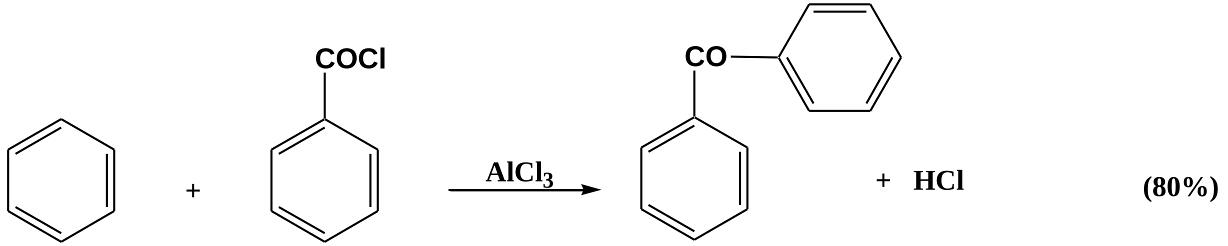


(1) By heating of Calcium benzoate

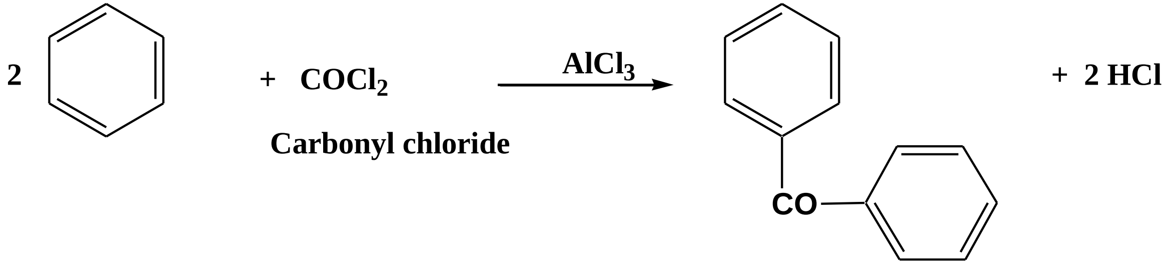


(2) By Friedel-Crafts condensation between benzoyl chloride and benzene

(1)



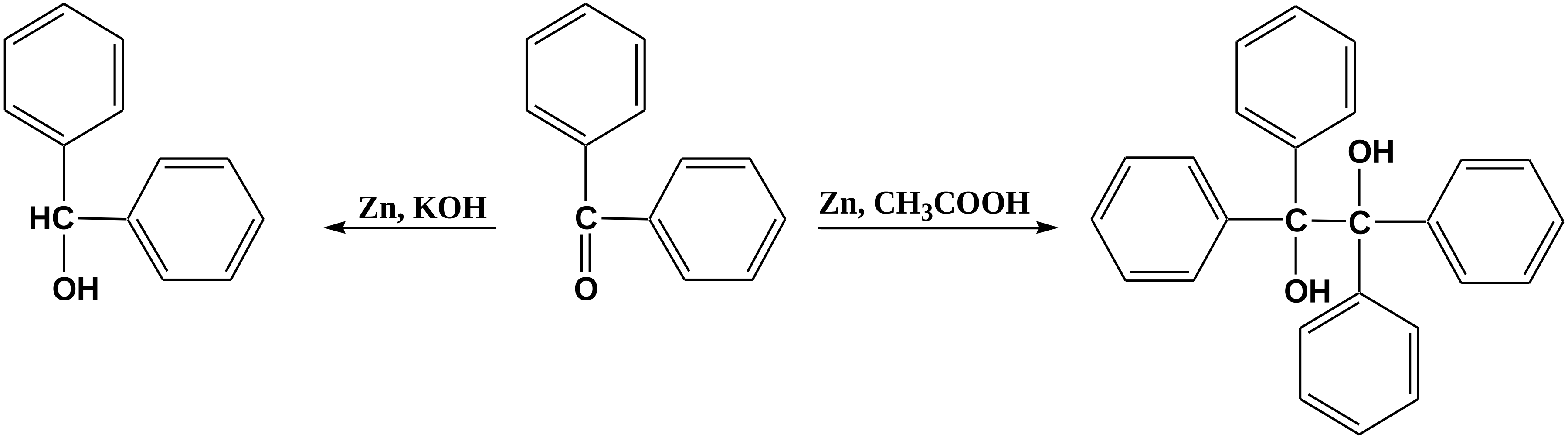
(2)



Chemical reactions

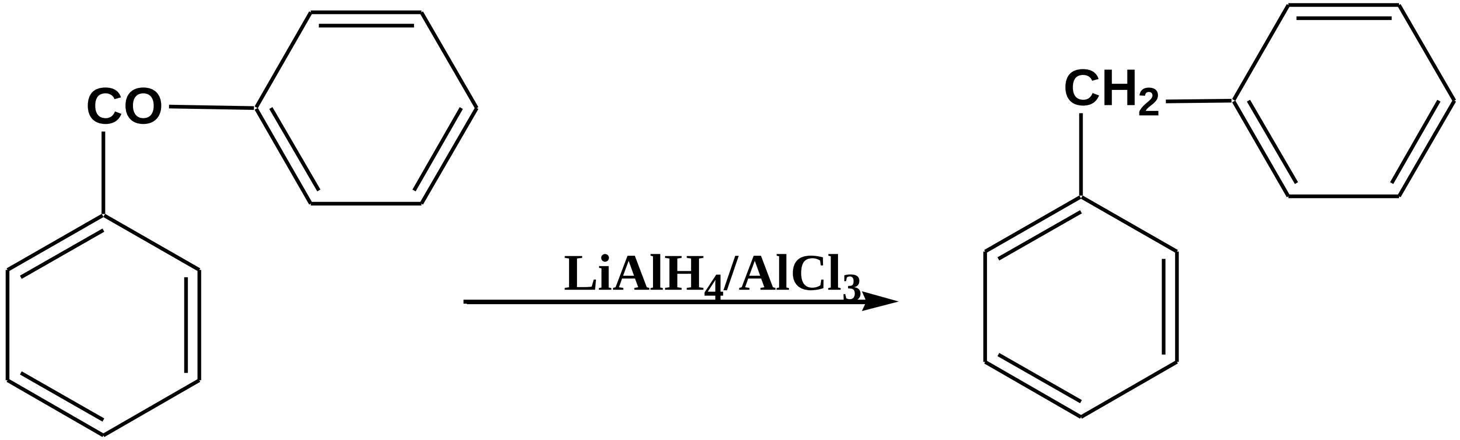
Benzophenone forms an oxime, but does not form a cyanohydrin or bisulphate addition compound

1- Reduction:



Benzhydrol (diphenylcarbinol) (90%)

Benzopinacol (90%)



diphenylmethane

2- Fusion with KOH