2. Introduction

A condensation reaction, also commonly referred to as dehydration synthesis, is a chemical reaction in which two molecules or moieties (functional groups) combine to form a larger molecule, together with the loss of a small molecule. Generally the small molecules lost are water, hydrogen chloride, methanol, or acetic acid but most commonly in a biological reaction it is water.

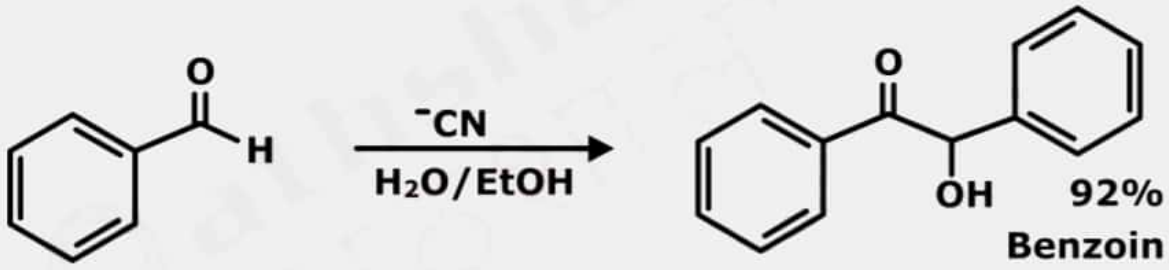
In organic synthesis, by far the most important activating groups are the carbonyl and carboxylic ester groups. Removal of a proton from the α-carbon atom of a carbonyl compound with base produces the corresponding α-carbanion, which are resonance stabilized via enolate anion. These enolate ions are involved in base catalysed reactions of carbonyl compounds.

Amongst these base catalysed reactions, the Stobbe reaction between dialkyl succinate and aldehyde or a ketone is a good method for making carbon-carbon bonds.

Another important reaction for C-C bond formation is Benzoin condensation, in which aromatic aldehydes (with no α- hydrogens) in the presence of CN^- condensed to form

3. Benzoin Condensation

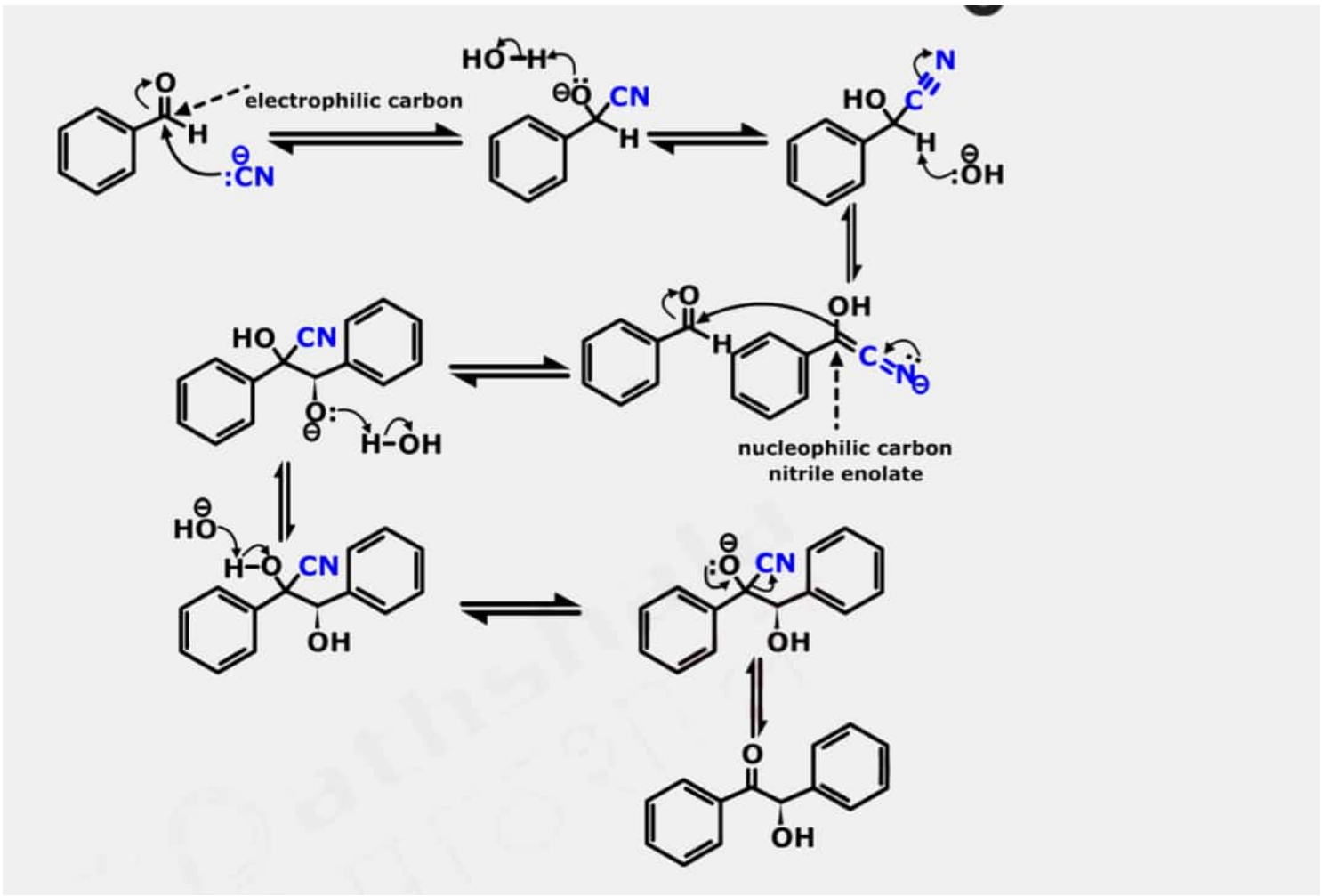
The **benzoin condensation** is a reaction (often called a condensation reaction, for historical reasons) between two aromatic aldehydes, particularly benzaldehyde. The reaction is catalyzed by a nucleophile such as the cyanide anion or an N-heterocyclic carbene. The reaction product is an aromatic acyloin with benzoin as the parent compound.



An early version of the reaction was developed in *1832* by ***Justus von Liebig*** and ***Friedrich Woehler*** during their research on bitter almond oil. The catalytic version of the reaction was developed by ***Nikolay Zinin*** in the late *1830*s, and the reaction mechanism for this organic reaction was proposed in *1903* by ***A. J. Lapworth***.

In the first step, the cyanide anion (as sodium cyanide) attacks the carbonyl carbon of the aldehyde in a nucleophilic addition. Rearrangement of the intermediate results in polarity reversal of the carbonyl group, which then adds to the carbonyl group of the other aromatic aldehyde (instead of H^+ transfer as that of Cannizzaro reaction). Proton transfer and elimination of the cyanide ion results in benzoin as the product.

Mechanism involved:



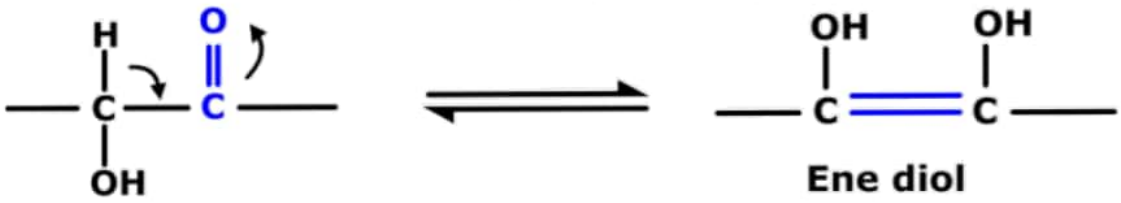
3.2 Characteristics of Benzoin Condensation

- This reaction is completely reversible, the reversibility is indicated by the fact that benzoin is heated with another aromatic aldehyde mixed products are obtained.

- Cyanide ion catalyzes the reaction because:
  (i) It is good nucleophile
  (ii) It is good leaving group
  (iii) It increases the acidity of the C-H bond and stabilizes the carbanion that results from the loss of proton from C.

- The benzoin condensation is in effect a dimerization and not a condensation because a small molecule like water is not released in this reaction. For this reason the reaction is also called a **benzoin addition**.

- In this reaction, the two aldehydes serve different purposes; one aldehyde donates a proton and one aldehyde accepts a proton. In this way it is possible to synthesize mixed benzoins, i.e. products with different groups on each half of the product.
- Rate law of Benzoin condensation, $r = [ArCHO]^2 [CN^-]$
- Benzoin is colorless solid (M.P. 157 C) which assumed to tautomerise to ene diol.



Ene diol

3.3 Reactions of Benzoin

3.3.1. Reduction of Benzoin:

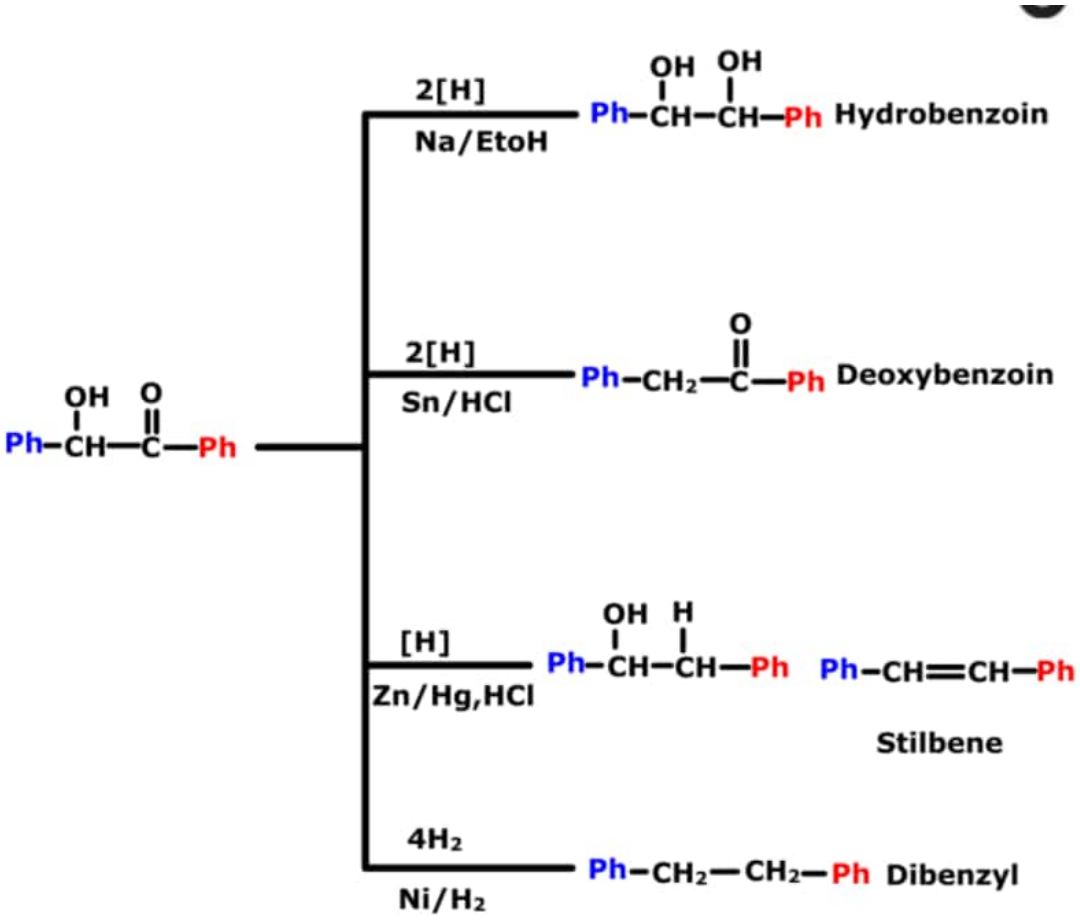
Benzoin is sensitive to reduction and can be reduced to different products using different reaction conditions and catalysts.

(i) Reduction with Na/ EtOH gives hydrobenzoin.

(ii) Reduction with Sn/HCl results in the formation of Deoxybenzoin.

(iii) Clemmensen reduction results in stilbene.

(iv) Complete reduction product dibenzyl is obtained on reducing in the presence of Ni catalyst.



3.3.2. Oxidation of Benzoin:

Benzoin can be easily oxidised using various oxidising agents. One of the most important product of benzoin oxidation is benzil.

(i) Oxidation with CrO_3 results in the formation of an aromatic aldehyde and one benzoin acid derivative.

(ii) Oxidation of benzoin with nitric acid gives benzil.

(iii) And benzoin oxidation