

Study Notes On Perkin Reaction





PERKIN REACTION

The Perkin reaction is similar to Aldol condensation. In this reaction, an aromatic aldehyde is heated with aliphatic acid anhydride (or, alkanoic anhydride) in presence of sodium salt of the same acid (or, alkanoate) which on further hydrolysis yields an α , β unsaturated acid.

General Reaction-

$$C_6H_5CHO + (CH_3CO)_2O \xrightarrow{\Delta} C_6H_5CH = CHCO_2H$$

Or,

Or,

$$\begin{array}{c|c} O \\ H \\ + O \\ \hline \\ O \\ \end{array}$$

$$\begin{array}{c|c} CH_3COONa \\ \end{array}$$

Reaction Mechanism-

- 1. An α -hydrogen is removed from the acid anhydride by carboxylate (anion of corresponding acid of acid anhydride) and a Carbanion is formed.
- 2. The Carbanion so formed, then attacks the aromatic aldehyde and forms Alkoxide ion.
- 3. Then the acetyl group is transferred from carboxyl oxygen to alkoxy oxygen with the formation of cyclic intermediate. It involves the nucleophilic addition of the carbanion to the carbonyl carbon of aldehyde which will result in the formation of a tetrahedral intermediate.
- 4. The removal of α -Hydrogen from this anion gives anion of α , β -unsaturated acid, which on acidification yields α , β -unsaturated acid.



Note:

- 1. This reaction takes place in the presence of alkali salt of acid which acts as a basic catalyst.
- 2. The reaction takes place in the presence of a weak base, usually, a sodium or potassium salt of the acid or triethylamine.
- 3. This reaction is generally applicable only to aromatic aldehydes.
- 4. In this reaction, prolonged heating of about 5 hours is required since a weak base (acetate ion) has to react with a weak acid (anhydride).

Applications-

- 1. This reaction is useful for preparation of substituted Cinnamic acid
- 2. It is used for the synthesis of α - β -unsaturated aromatic acid, used in the pharmaceutical sector.



Example-

When benzaldehyde is heated with acetic anhydride in presence of sodium acetate, the product thus formed on hydrolysis gives cinnamic acid.

$$\begin{array}{c} C_6H_5CH = \underbrace{O+H_1^{\dagger}CHCO}_{\text{Benzaldehyde}} & \underbrace{CH_3CO}_{\text{CH}_3CO} & \underbrace{CH_3COONa, 453 \, K}_{\text{-H}_2O} & \underbrace{CGH_5CH = CHCO}_{\text{CH}_3CO} & \underbrace{CH_3COONa, 453 \, K}_{\text{C}_6H_5CH} & \underbrace{CGH_5CH = CHCO}_{\text{C}_3CO} & \underbrace{CH_3COONa, 453 \, K}_{\text{C}_6H_5CH} & \underbrace{CGH_5CH = CHCOOH}_{\text{C}_6H_5CH} & \underbrace{CGH_5CH}_{\text{C}_6H_5CH} & \underbrace{CGH_5CH}_{\text{C}_6H_$$





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