Date
Page

Class - P.G. Sem II

Subject - chemistry

Paper - C-C - VIII

Dr. Rashmi Sinha, H.D.J.C. Ara

Perkin reaction

condensation of an aromatic aldehyde and aliphatic acid anhydride containing at least two α-hydrogen atoms in the presence of the sodium or potassium salt of the corresponding acid to form α, β-unsaturated acid, is known as perkin reaction or perkin condensation.

$$C_6H_5CHO + (CH_3CO)_2O \xrightarrow{CH_3COONa} C_6H_5CH=CHCOOH + CH_3COOH$$

cinnamic acid

During the condensation only α-hydrogen atoms of the anhydride are involved.

e.g.:-

$$C_6H_5CHO + (\overset{\beta}{CH_3}\cdot\overset{\alpha}{CH_2}\cdot CO)_2O \xrightarrow{CH_3CH_2COONa} C_6H_5CH=\overset{CH_3}{\overset{|}{C}}\cdot COOH$$

α-methylcinnamic acid

Since a weak base is used with a weak acidic reagent, hence high temperature is required

during the perkin reaction. The catalyst may be replaced by other bases such as sodium carbonate, quinoline, Pyridine and triethylamine.

<u>Mechanism!-</u> According to Perkin the anhydride provides the carbanion under the influence of the basic carboxylate ion i.e. the reaction takes place between the aldehyde and anhydride whereas sodium salt of the acid functions as a catalyst. Fitting claimed it quite reverse and according to him anhydride but not the salt acts as a catalyst. But the subsequent researches have shown that Perkin was right. i.e the reaction takes place between the aldehyde and the anhydride represented as below!-

$$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$$

$$CH_3CO\cdot O\cdot COCH_3 + CH_3COO^- \rightleftharpoons \bar{C}H_2CO\cdot O\cdot COCH_3 + CH_3COOH$$

$$C_6H_5-\overset{\overset{\ddot{O}}{\|}}{C}-H + \bar{C}H_2CO\cdot OCOCH_3 \rightleftharpoons C_6H_5-\overset{\overset{O^-}{|}}{C}-H - CH_2CO\cdot OCOCH_3$$

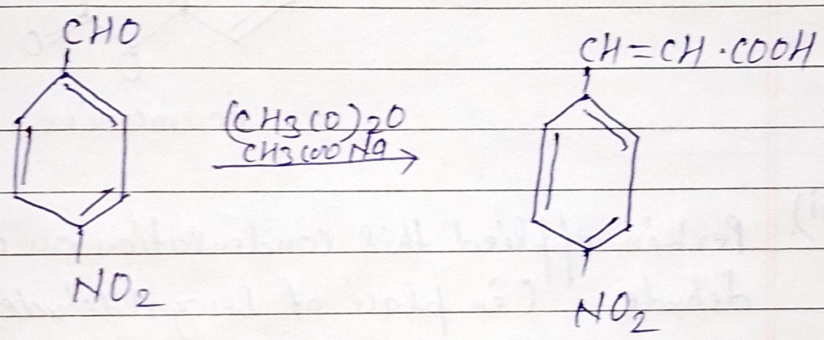
$$\xrightarrow[CH_3COOH]{H^+ \text{ form}} C_6H_5-\overset{\overset{OH}{|}}{C}-H - CH_2CO\cdot O\cdot COCH_3 \xrightarrow{-H_2O}$$

Date
Page

$$C_6H_5CH=CHCO\cdot O\cdot COCH_3 \xrightarrow{H_2O} C_6H_5CH=CH\cdot COOH + CH_3COOH$$

cinnamic acid

Perkin reaction proceeds more easily when the aldehyde contains an electron-attracting gr. on the aromatic ring. e.g -

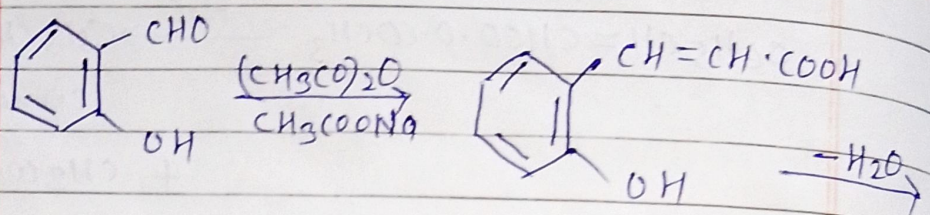


P-nitrocinnamic acid

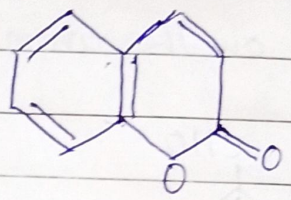
On the other hand, presence of electron-releasing gr. reduces the efficiency of the reaction. e.g :- o-methylbenzaldehyde gives o-methylcinnamic acid only in 15% yield whereas P-di-methylaminobenzaldehyde does not undergo Perkin reaction.

Applications :-

(i) Salicylaldehyde undergoes Perkin reaction and forms trans-o-hydroxycinnamic acid or coumaric acid which on dehydration gives coumarin



coumaric acid



coumarin

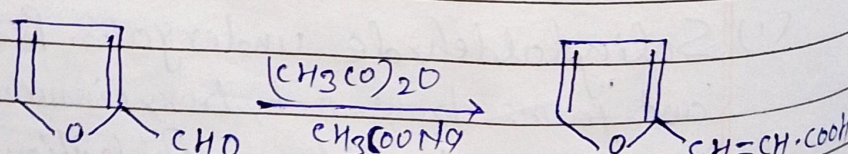
(ii) Perkin applied this condensation on cinnamaldehyde (in place of Benzaldehyde) to form doubly unsaturated acid.

$$C_6H_5 \cdot CH=CH \cdot CHO + (CH_3CO)_2O \xrightarrow{CH_3COONa} C_6H_5 \cdot CH=CH \cdot CH=CHCOOH$$

cinnamylacrylic acid

This principle is used in the synthesis of piperic acid and hence piperine (an alkaloid)

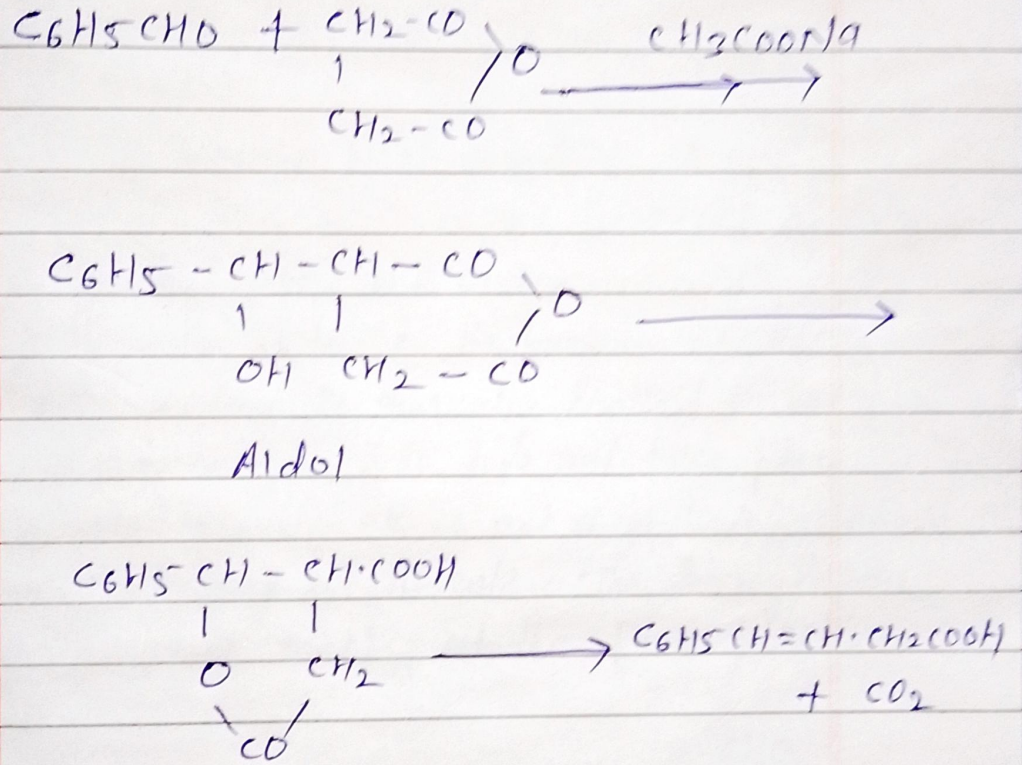
(iii) Furfural may also undergo Perkin reaction to form Furylacrylic acid.



Furfural

Furylacrylic acid

(iv) A valuable modification of Perkin reaction is illustrated and the condensation of Benzaldehyde, Succinic anhydride and Sodium acetate.



(5) A valuable application of the Perkin reaction is Erlenmeyer's azlactone synthesis, in which an acylglycine is condensed with aromatic aldehyde in the presence of acetic anhydride and sodium acetate.