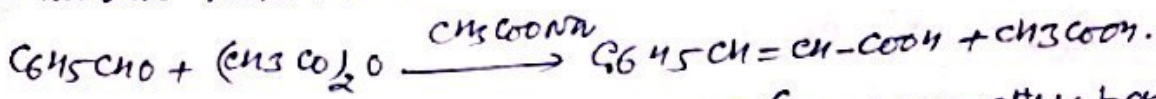


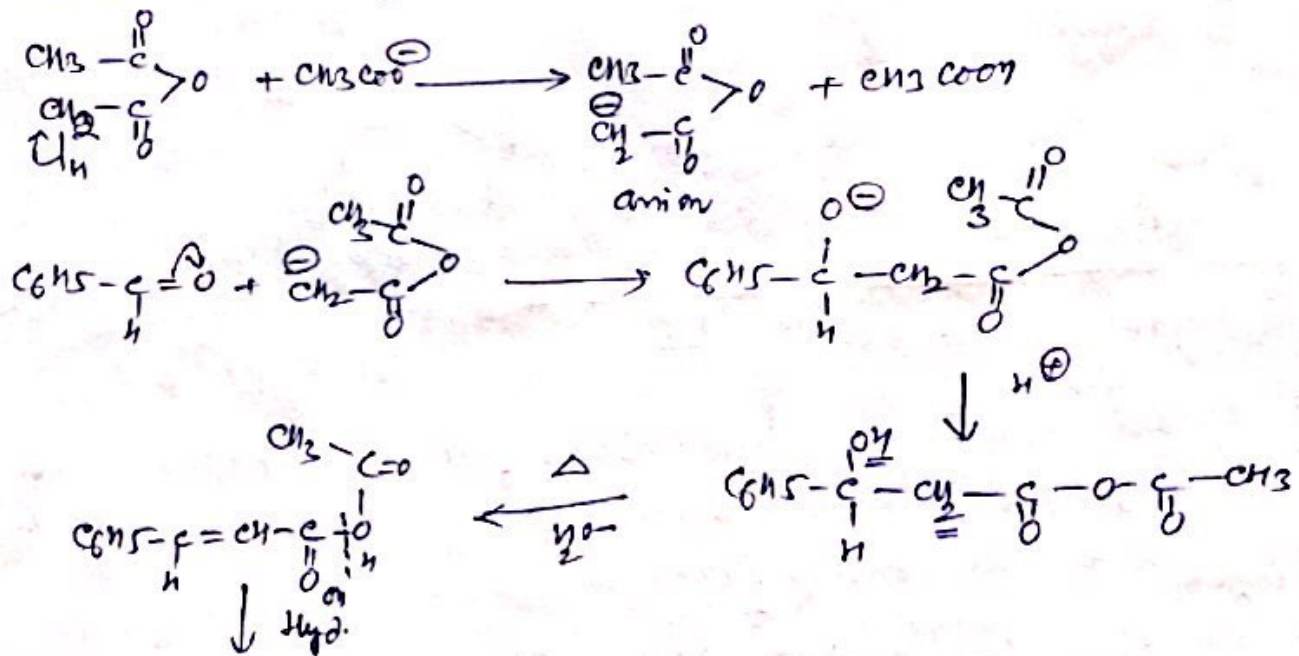
Perkin's Reaction 9mp Subject - Addn-to-c-Hetero bonds H-2008 (19)
 by P.K. Sharma.

Reaction of an aromatic aldehyde with an aliphatic acid anhydride in presence of Na or K salt of the acid corresponding to anhydride to form α, β -unsaturated acid, is known as Perkin Reaction.



Mech. The function of sodium acetate (or of some other base) is to abstract a proton from anhydride to generate a carbanion, which then attacks the carbonyl carbon of the aldehyde.

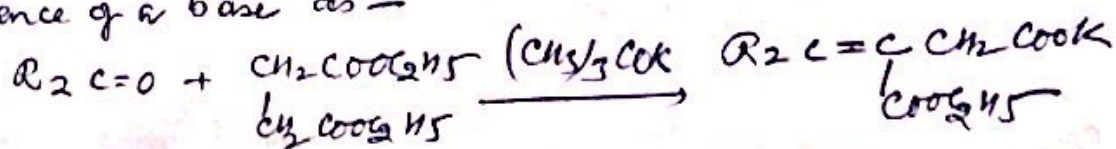
Protonation of the anion followed by removal of water, produces an unsaturated anhydride which is finally hydrolysed to get the acid.



$C_6H_5CH=CH-COOH + CH_3COOH$
 α, β unsaturated acid

(7) Stobbe Condensation

This is a condensation between dialkyl succinate and aldehydes or ketones in presence of base like NaOH, Pot. tert. butoxide or sodium ethoxide to form salts of α, β unsaturated half esters. Benzaldehyde condenses with diethyl succinate in presence of a base as -

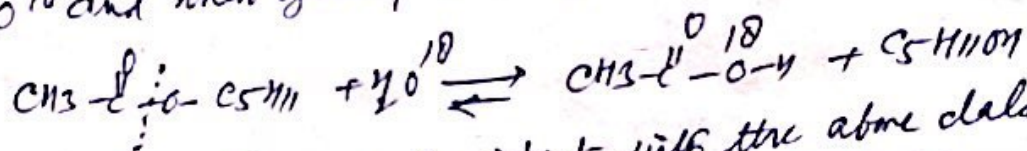


of the reaction is indicated by usual numbers 1 or 2. Thus by a BAC_2 hydrolysis we mean Base Catalysed Bimolecular hydrolysis by acyl oxygen bond cleavage.

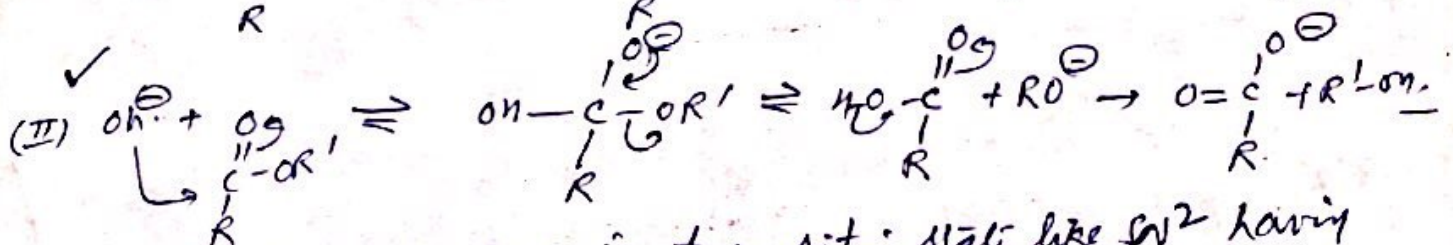
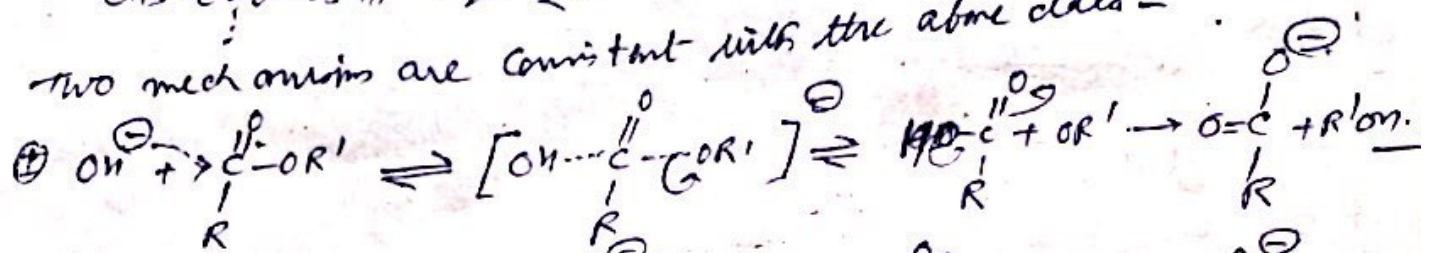
① BAC_2 Mechanism (Base Catalysed Bimolecular hydrolysis with Acyl oxygen cleavage)

This is the most common mechanism and involves nucleophilic attack by base on the ester to give an unstable tetrahedral intermediate, which then decomposes to the product.

The evidence for the acyl oxygen bond fission is provided by carrying out the hydrolysis of *n*-amyl acetate in water enriched in O^{18} and then getting *n*-amyl alcohol with out O^{18} .



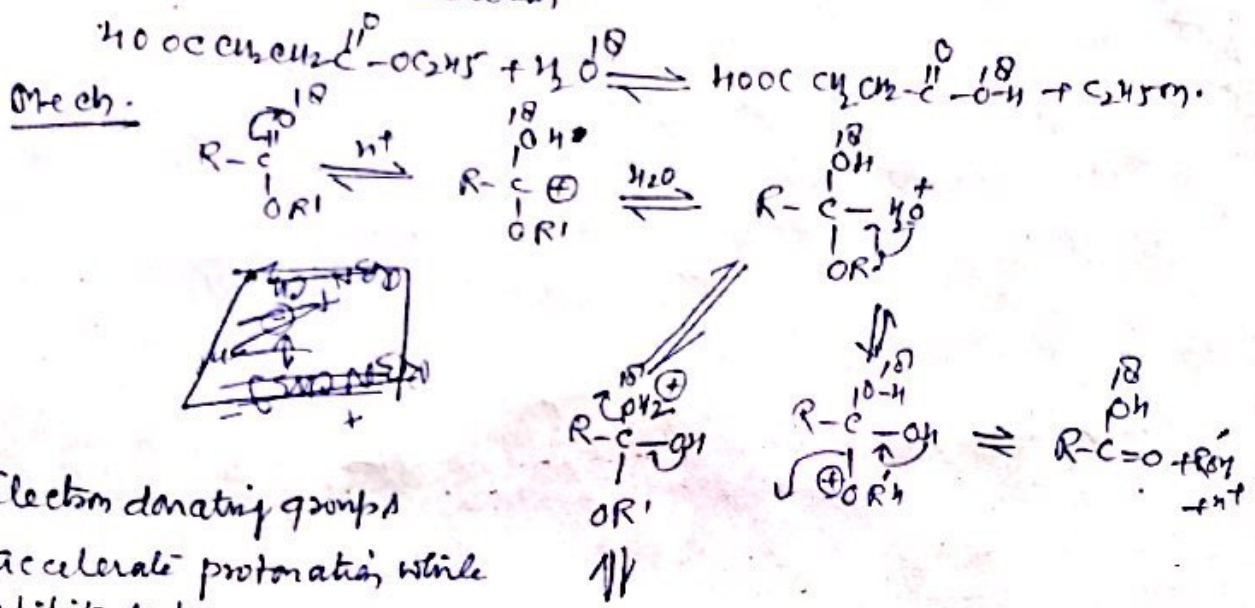
Two mechanisms are consistent with the above data -



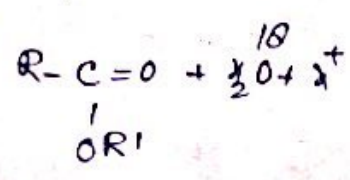
In the first mech. there is transition state like SN_2 having max. energy whereas in the second mechanism a true intermediate with minimum energy is obtained. Therefore mech. (i) is preferred. Labelling experiments confirm BAC_2 mechanism. The effect of substituents again confirms the above mech. It was observed that substituents Cl, Br and NO_2 groups accelerate the reaction whereas, CH_3 , OCH_3 and OH groups retard it (because they decrease free charge on carbon)

② AAC_2 Mechanism (Acid Catalysed Bimolecular hydrolysis with Acyl oxygen functional cleavage).

This is most common acid catalysed hydrolysis mechanism and involves nucleophilic attack by water on the protonated ester to give a tetrahedral intermediate which collapses to protonated acid and alcohol. It is reversible reaction unlike base catalysed one. The rate of acid catalysed hydrolysis of ester is found to be proportional to both H^+ and the ester. When the hydrolysis is carried out in H_2O^{18} , the product alcohol has no O^{18} content. Thus it is an AAC_2 reaction.



Electron donating groups accelerate protonation, while inhibit subsequent attack by nucleophile. On the other hand electron attracting groups inhibit protonation but accelerate the nucleophilic attack.



③ AAL' (Acid catalysed unimolecular hydrolysis with Alkyl oxygen cleavage)

When groups such as *t*-alkyl, benzyl etc. Capable of forming stable carbonium ions are the alkyl moiety in the substrate, hydrolysis and esterification may take place by an alkyl oxygen bond cleavage.

This type of mechanism occurs in the hydrolysis of *t*-butyl benzoate which on treating with methanol and acid gives *t*-butyl methyl ether and benzoic acid rather than *t*-butyl alcohol and methyl benzoate, the products of normal hydrolysis.