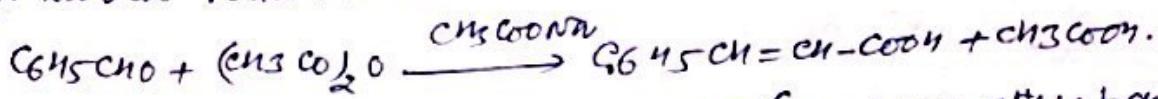


(19) Perkin Reaction V. Grp. III Addn. to C-Hetero bonds H-2008

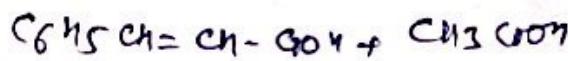
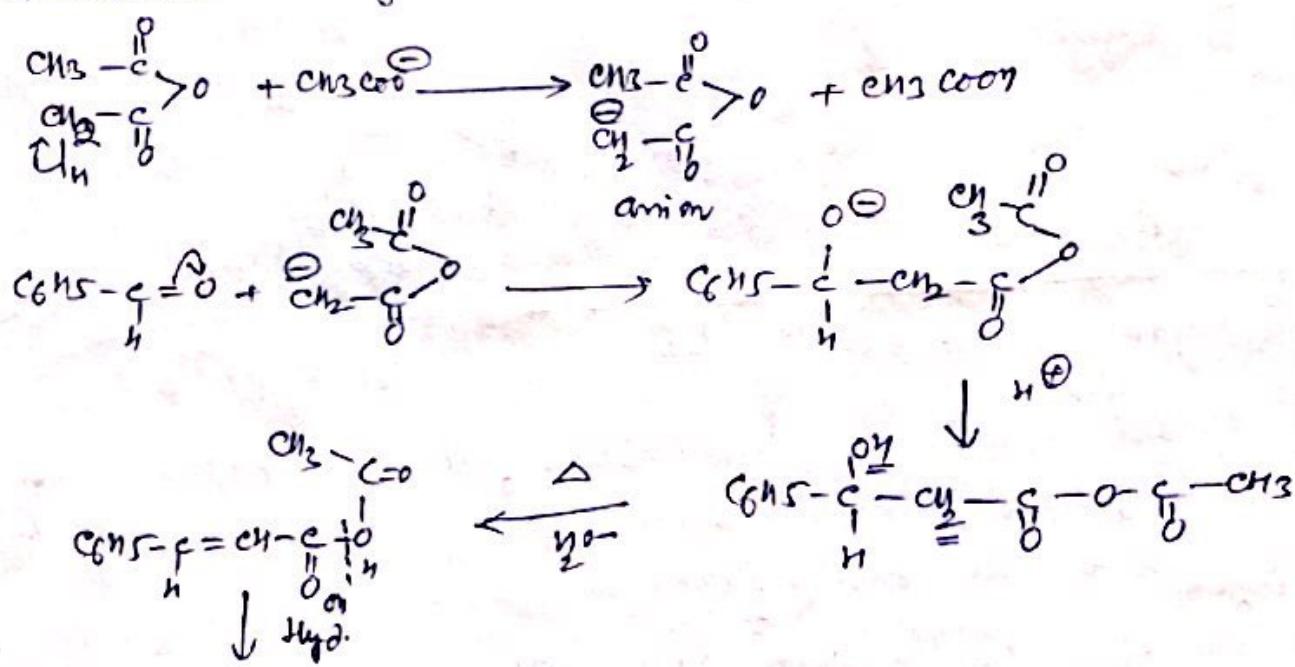
by P. K. Sharma.

Reaction of an aromatic aldehyde with an aliphatic acid anhydride in presence of Na or K salt of the acid corresponding to anhydride 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.

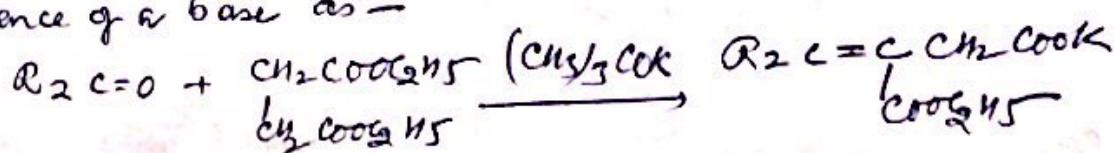
Protonation of the anion followed by removal of water, produces an unsaturated anhydride which is finally hydrolysed to get the acid



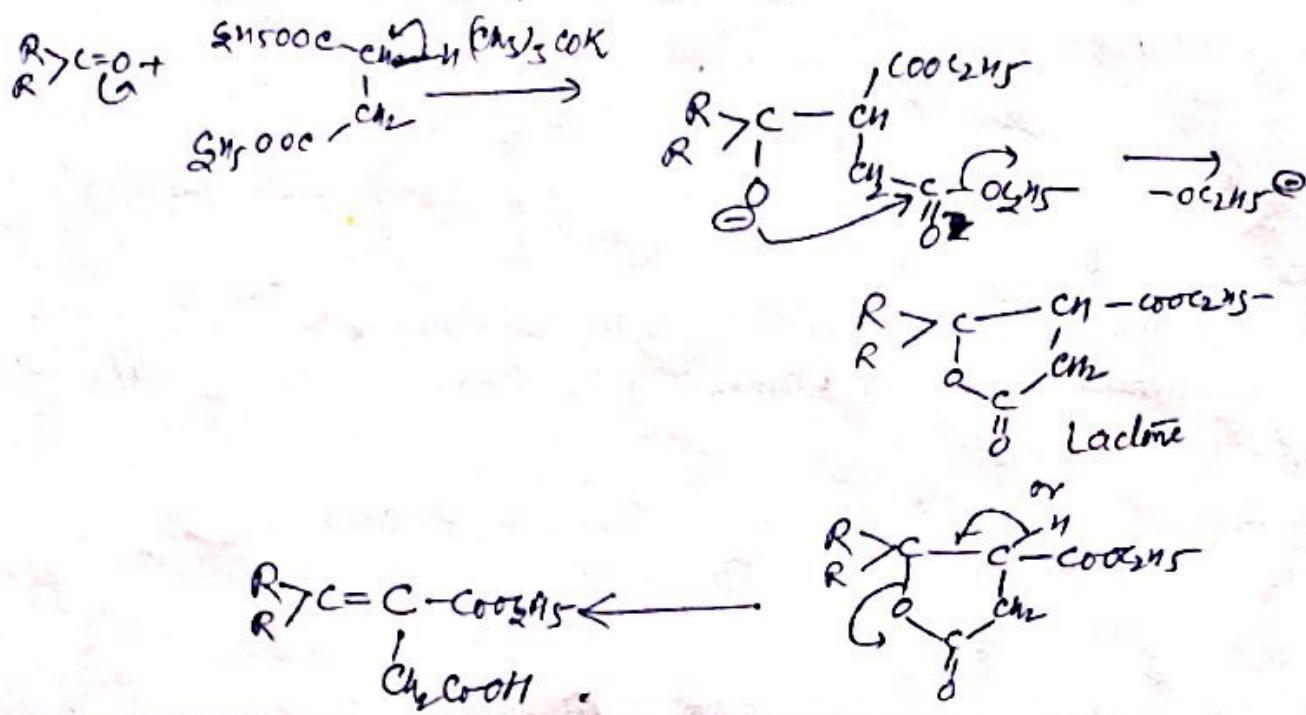
α, β Unsat. acid

(7) Stobbe Condensation

This is a condensation between dialkyl succinates and aldehydes or ketones in presence of base like NaH , Pb. tet. butoxide or Sodium ethoxide to form salts of α, β unsaturated half esters. Benzaldehyde condenses with diethyl succinate in presence of a base as -

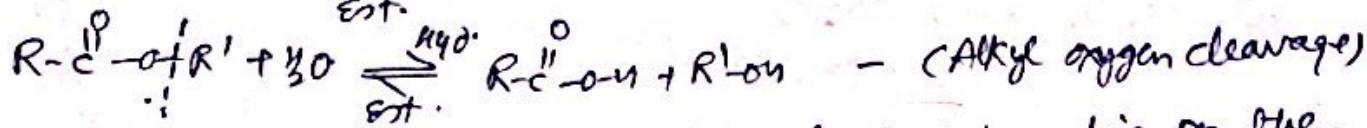
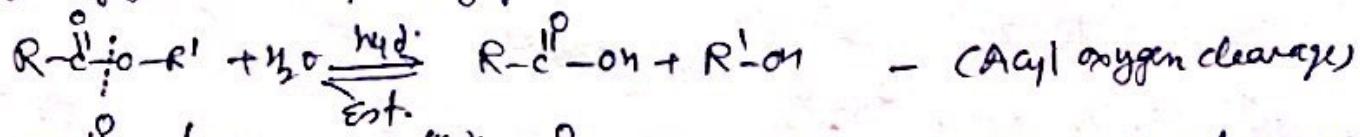


Plech. The enolate from di ester succinate, attacks the carbonyl group followed by cyclization to give lactone intermediate. Lactone then undergoes base catalyzed ring opening to give salt of unsaturated half ester. One of the ester groups is hydrolyzed in the course of the reaction.



Ester Hydrolysis and Esterification

The conversion of an ester into its acid and alcohol species is termed Ester hydrolysis. This conversion can involve cleavage either at acyl oxygen or alkyl oxygen bond.



A variety of mechanisms may be involved depending on the nature of R and R' and the conditions of the reaction.

Since esterification in basic medium is not possible because of the conversion of carboxylic acid to a resonance stabilized carboxylate anion. There are four possible mechanisms by which esterification may proceed. In these mechanisms A or B refers to acidic or basic medium, acyl oxygen or alkyl oxygen is represented by AC or AL and molecularity-

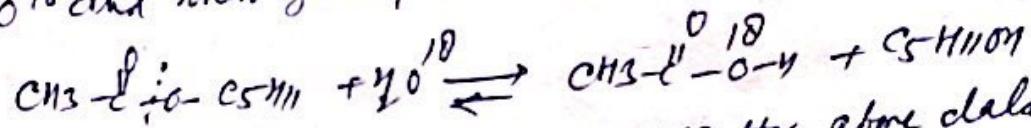
(21)

If the reagent is indicated by usual numbers 1 or 2. Thus
by a BAC_2 hydrolysis we mean Base catalyzed Bimolecular
hydrolysis by acyl oxygen bond cleavage.

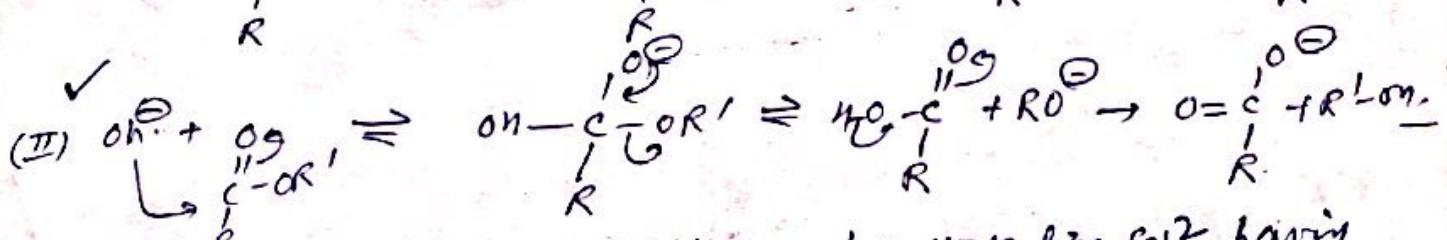
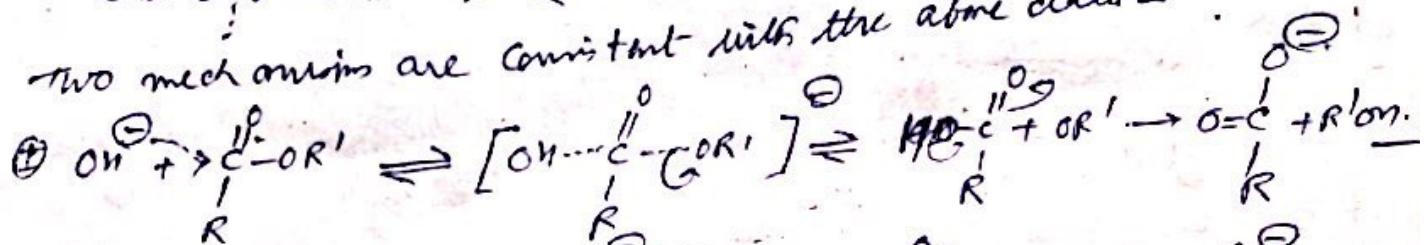
① BAC^2 Mechanism (Base catalyzed Bimolecular hydrolysis
with Acyl oxygen cleavage)

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 without O^{18} .



Two mechanisms are consistent with the above data -

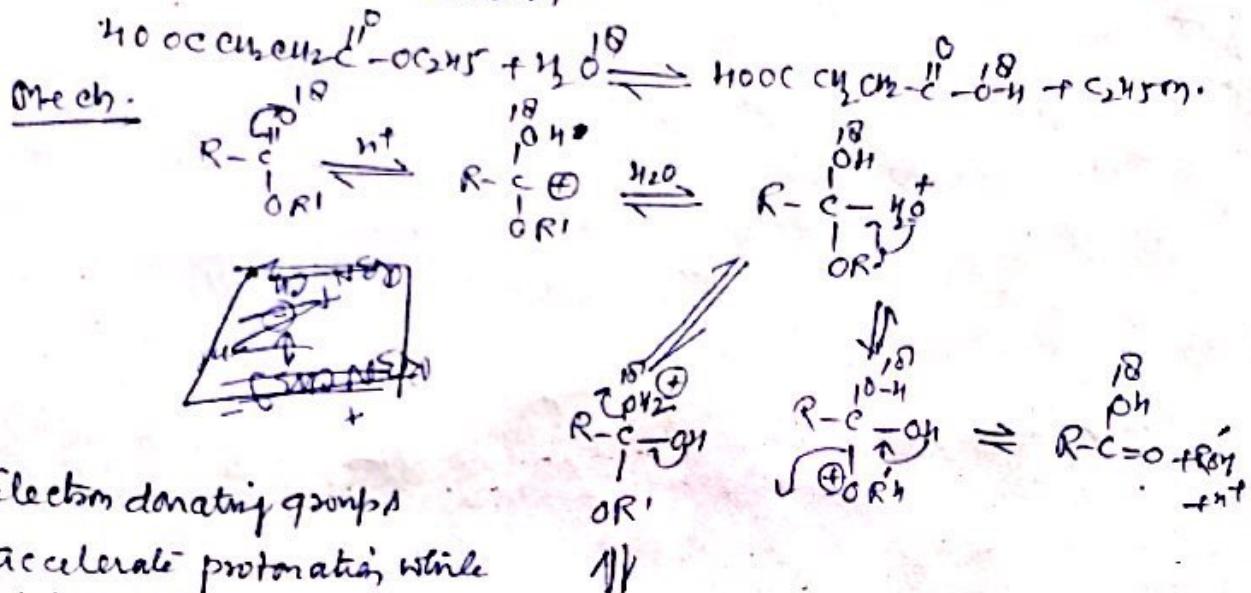


In the first mech. there is transition state like SN^2 having
max. energy whereas in the second mechanism a true inter-
mediate with minimum energy is obtained. Therefore mech. II
is preferred. Labelling experiments confirm BAC^2
mechanism. The effect of substituents again confirms the
above mech. It was observed that substituents Cl, Br
and NO₂ groups accelerate the reaction whereas, CH₃, OCH₃ and
F groups retard it (because they decrease the charge on carbon).

② AAC² mechanism (Acid Catalyzed Bimolecular hydrolysis
with Acyl oxygen fission (cleavage)).

This is most common acid catalyzed 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 catalyzed hydrolysis of esters 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. This is an $A\text{Ac}^2$ 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 catalyzed 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 solvolysis of t-butyl benzoate which on treating with methanol and acid gives t-butyl methyl ether and benzene and rather than t-butyl alcohol and methyl benzoate, the products of normal solvolysis