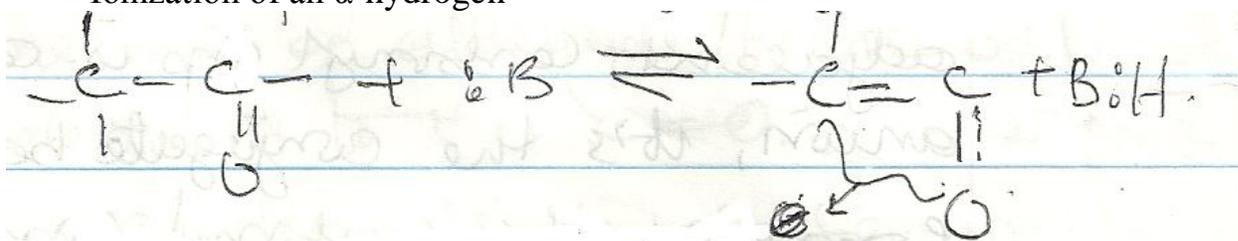


MECHANISM OF ORGANIC REACTIONS

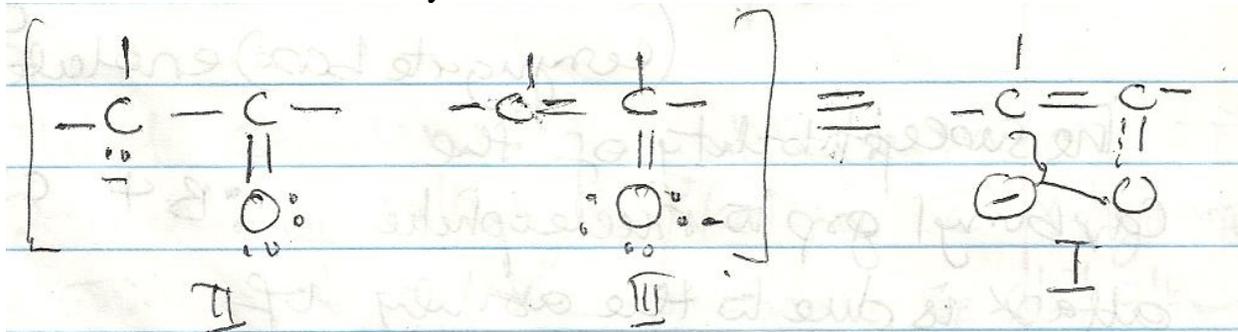
CARBANIONS

The carbonyl can play the role as a functional group as well a substituent. The carbonyl group strengthens the acidity of the hydrogen atoms attached to the α -carbon and by doing this gives rise to a whole set of chemical reactions.

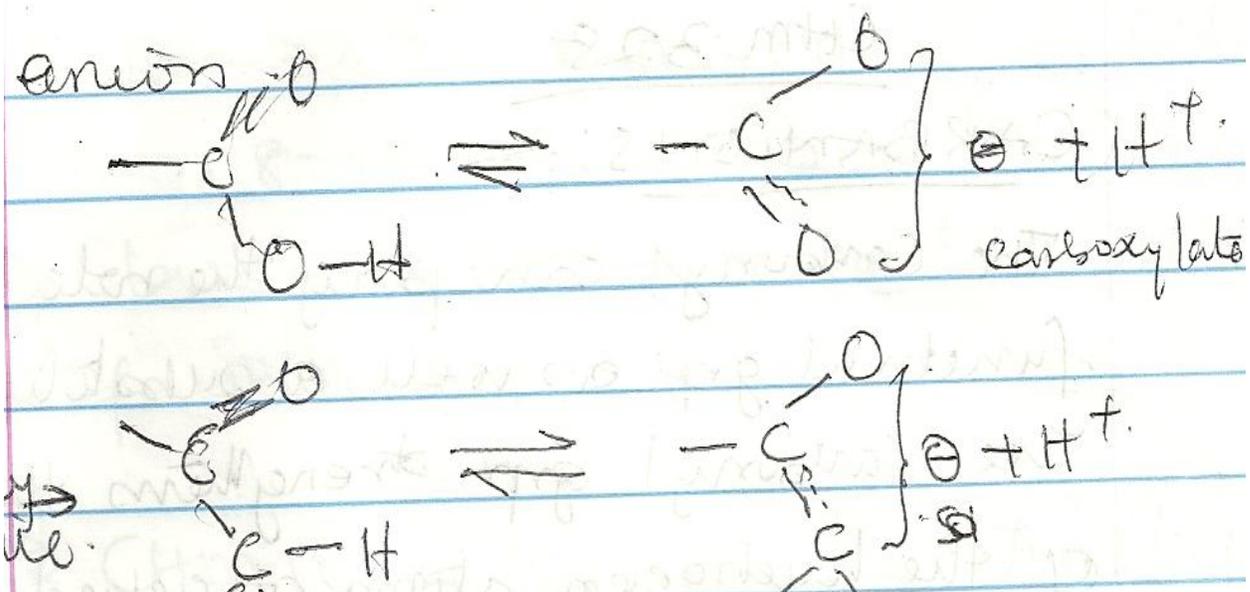
Ionization of an α -hydrogen



[Conjugate base of a carbon acid which loses its proton from carbon
Carbanion I is a resonance hybrid of two structures

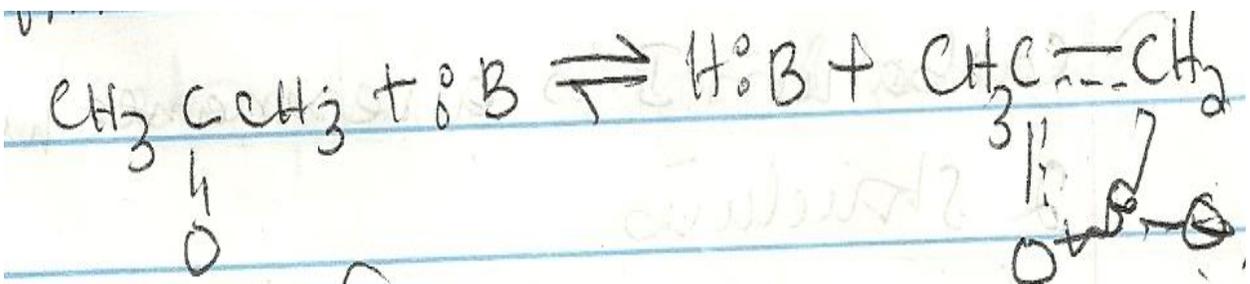


The carbonyl group effects the acidity of α -hydrogen in the same way it affects the acidity of carboxylic acids; by helping to accommodate the negative charge on the anion.

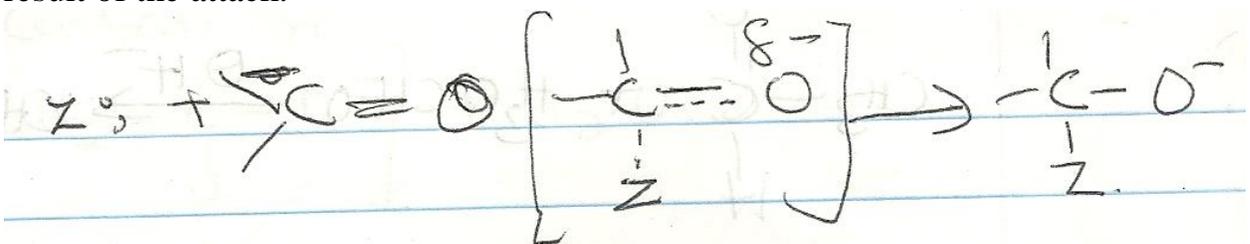


Stability is due to the fact that most of the charge is carried by oxygen and not carbon.

A carbanion which is stabilized by an adjacent carbonyl group is called an enolate anion; it is the conjugate base of the keto form of the carbonyl compound and its enolate form also.



The susceptibility of the carbonyl group to nucleophilic attack is due to the ability of oxygen to accommodate the negative charge that develops as a result of the attack.



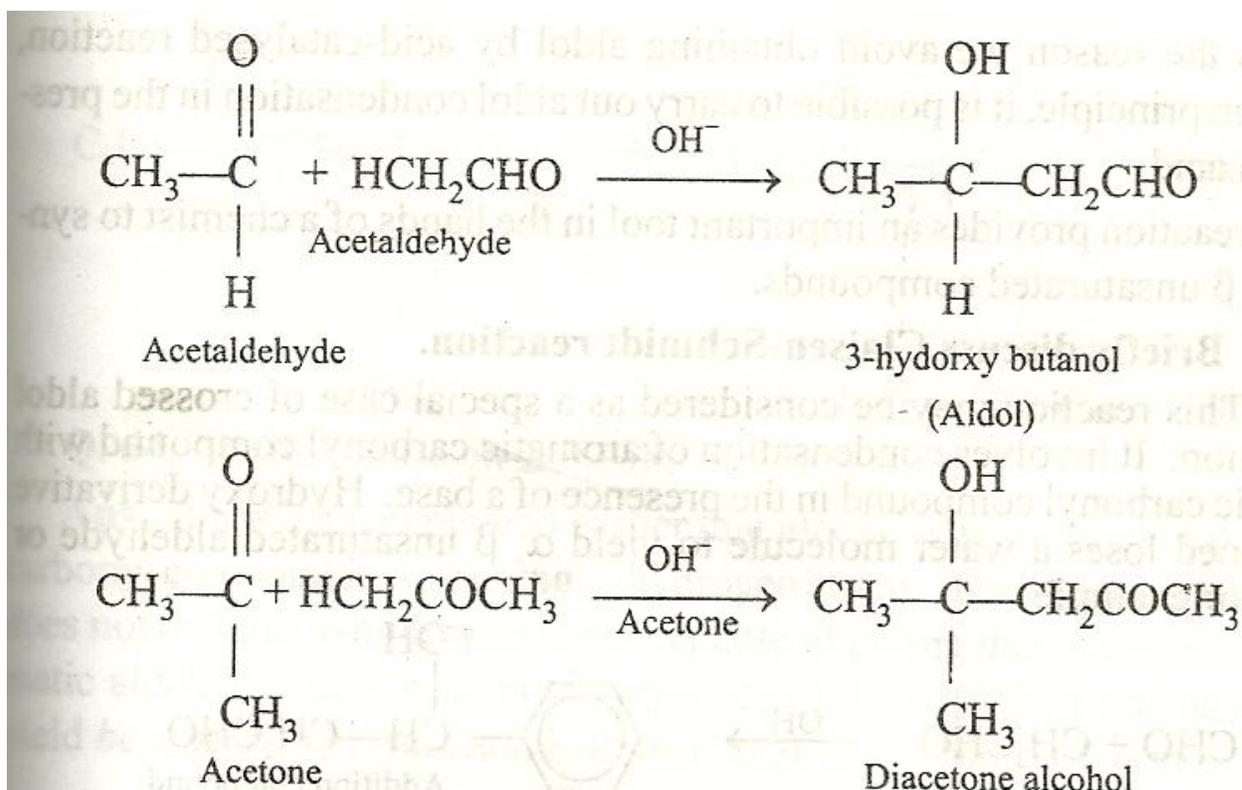
Reactions involving carbanions:

→ Carbanions are highly basic, so they behave as nucleophilic, thus they can attack carbon to form carbon-carbon bonds.

→ Aldol condensation- carbanion generated from one molecule of aldehyde/ ketone add as a nucleophile to the $\text{RC}=\text{O}$ of second molecule of a ketone/aldehyde

Mechanism of Aldol condensation:

→ Two molecules of aldehyde/ ketone with α -hydrogen atoms react in the presence of dilute alkali to form β hydroxyl aldehyde or β hydroxyl ketone.

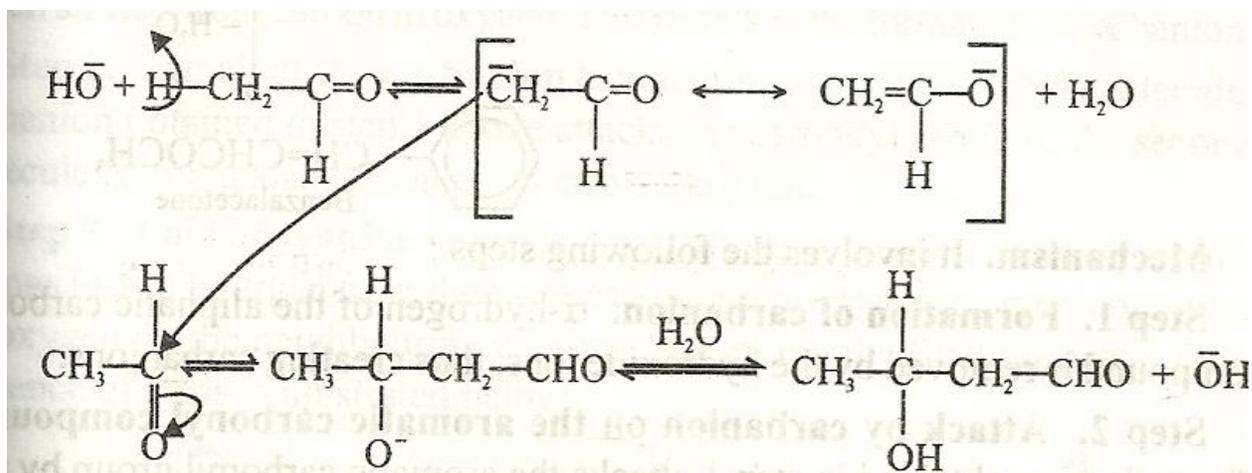


Step 1: Formation of carbanion-hydroxide from a base abstracts a proton from the α -carbon atom to a carbanion which is stabilized by resonance.

Step 2: Attack by the carbanion- the carbanion formed attacks the second molecule by nucleophilic addition mechanism to form an alkoxide ion.

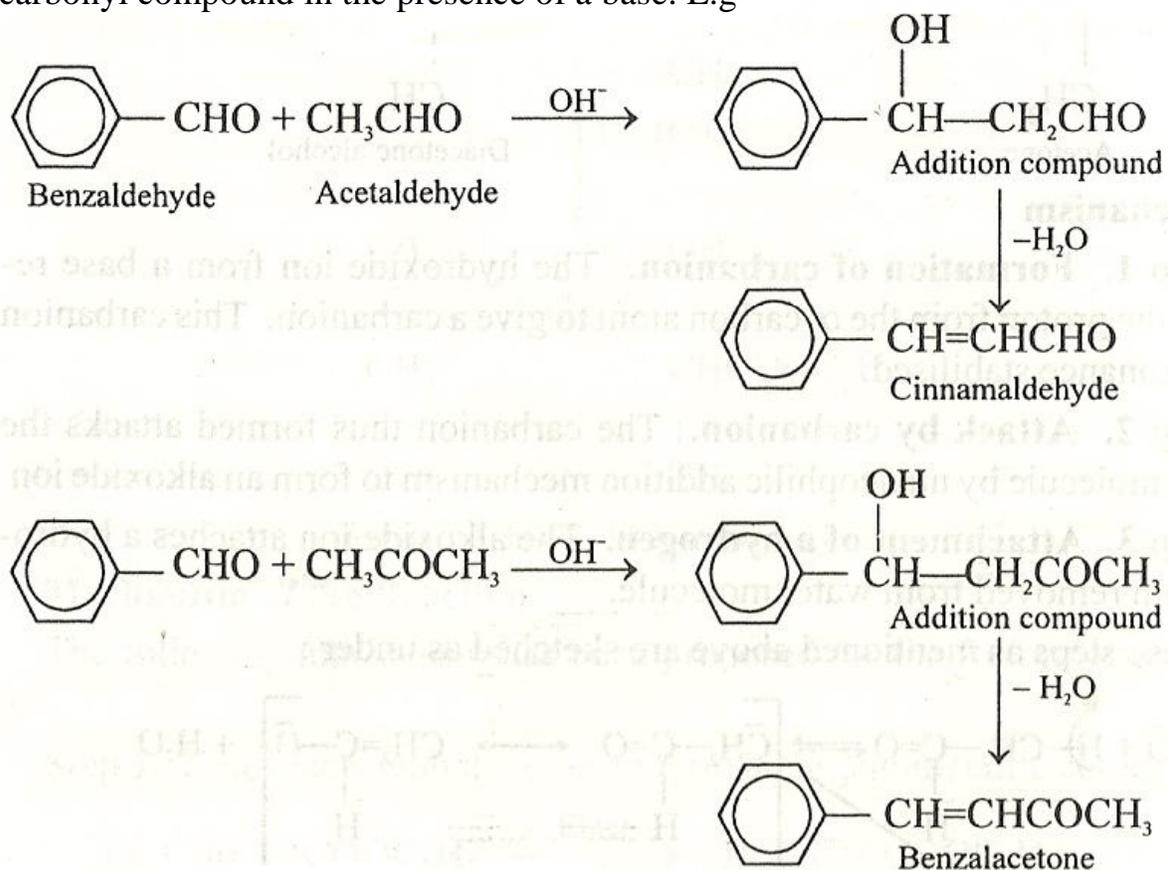
Step 3: Attachment of a hydrogen:- the alkoxide ion attaches a hydrogen atom removed from H_2O molecule.

Equation:-



Claisen- Schmidt reaction

→ a crossed aldol condensation; involving condensation of aromatic carbonyl compound in the presence of a base. E.g



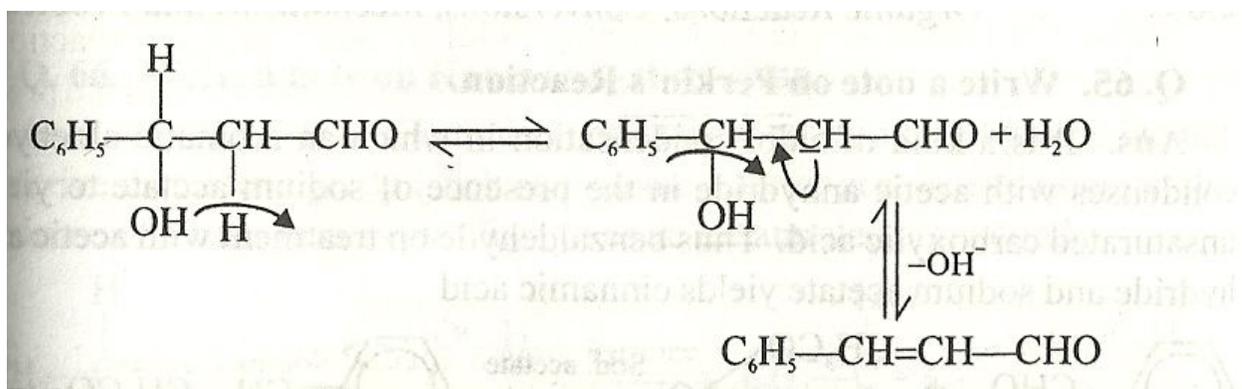
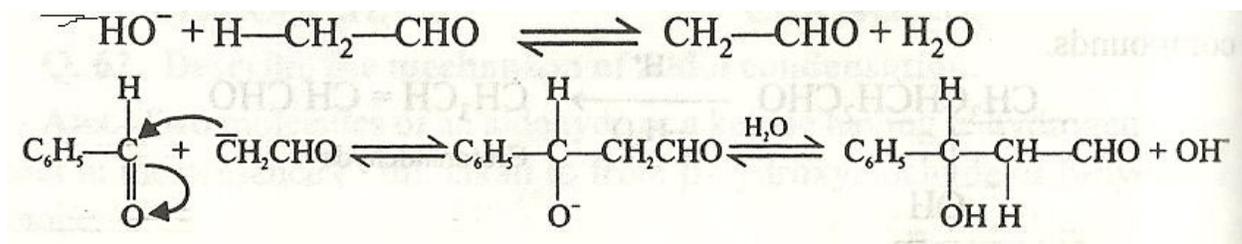
Mechanism:

Step 1: Formation of carbanion

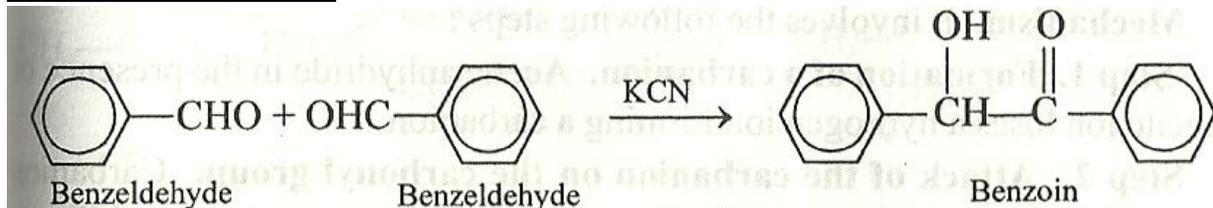
Step 2: Attack by carbanion on the aromatic carbonyl compound to form alkoxide ion.

Step 3: Attachment of a proton

Step 4: α -H atom in the hydroxyl compound is removed by the base, followed by OH group and ultimately H_2O is removed

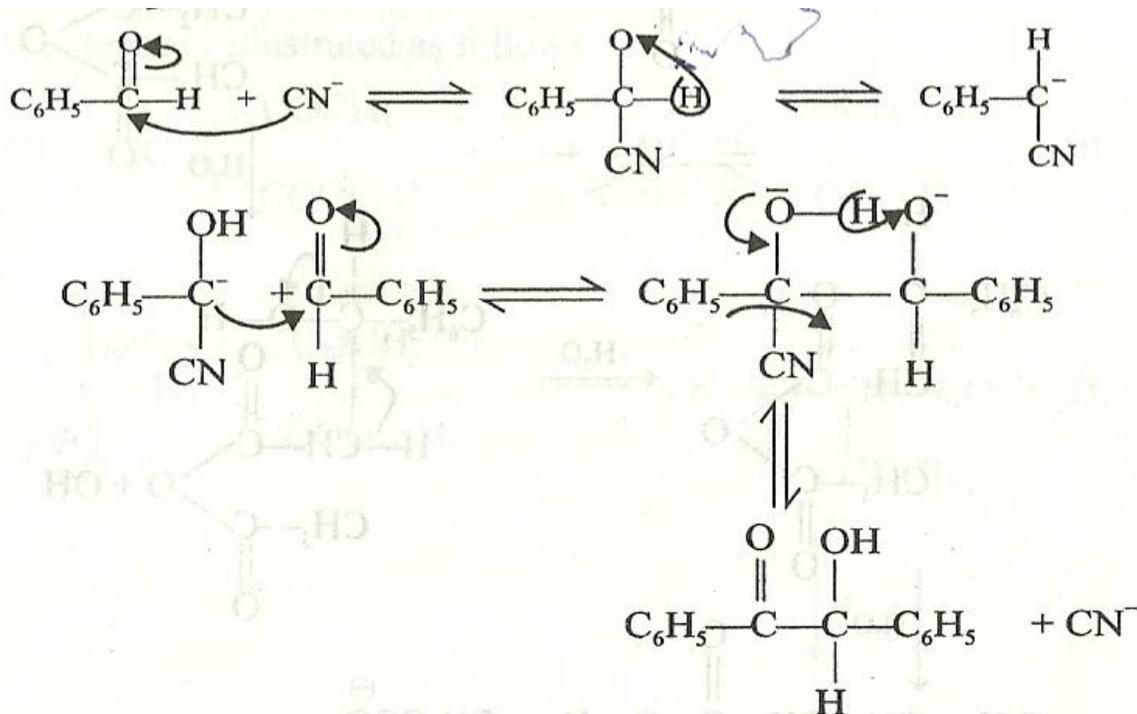


Benzoin condensation



Step 1 and 2 as in other condensation reactions.

Step 3, loss of CN^- ion



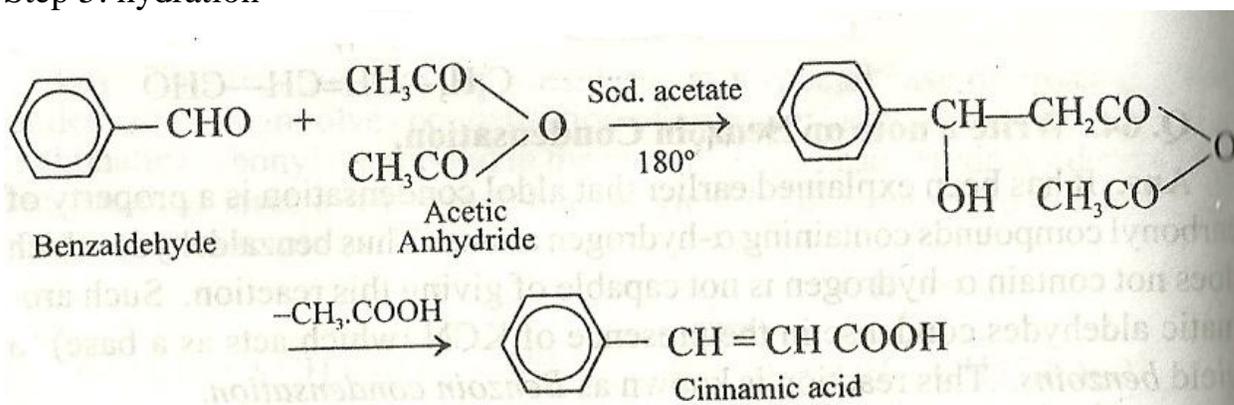
Perkins reaction

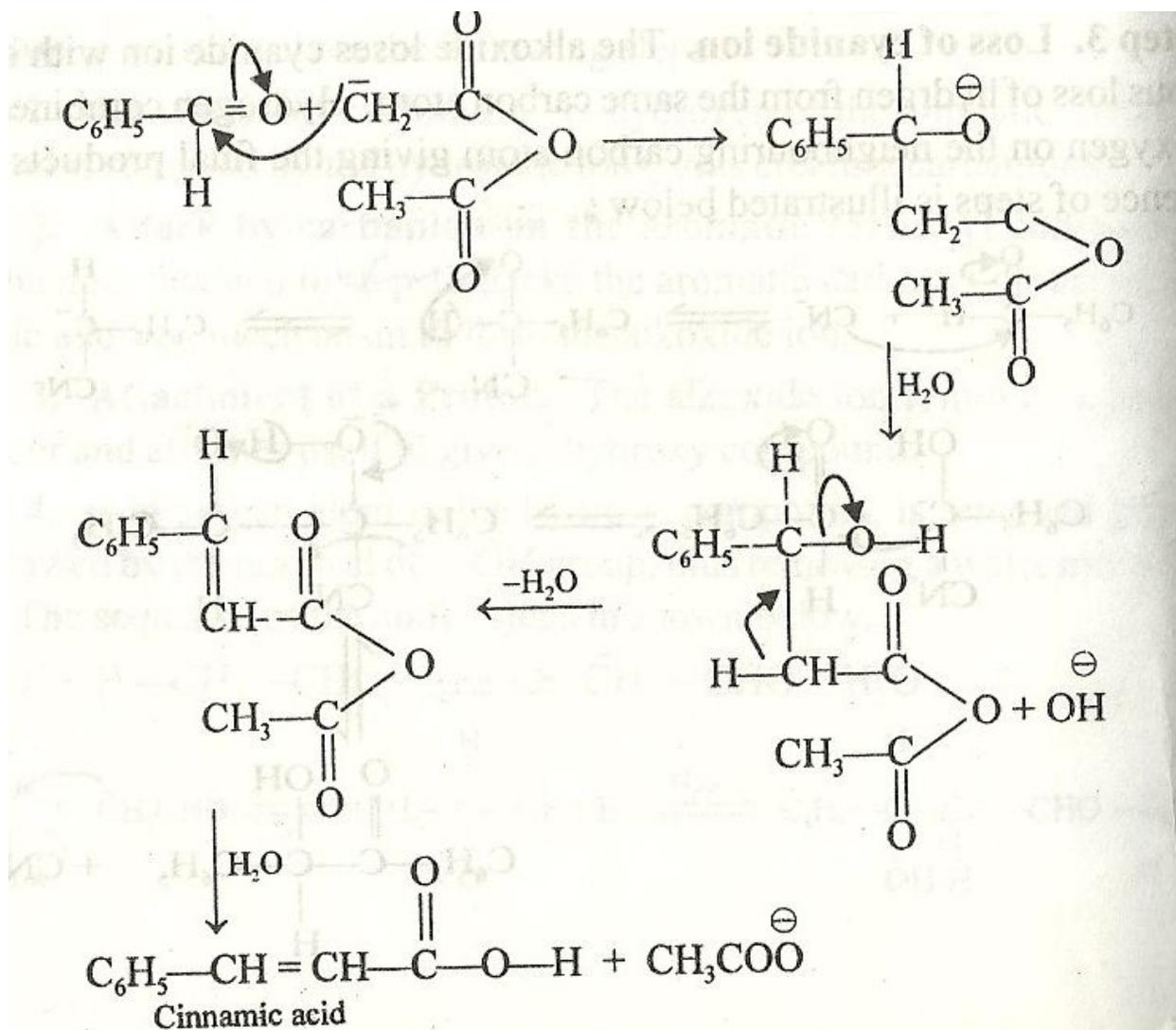
Step 1-2 as in others

Step 3: protonation of the alkoxide ion to form an aldol type compound.

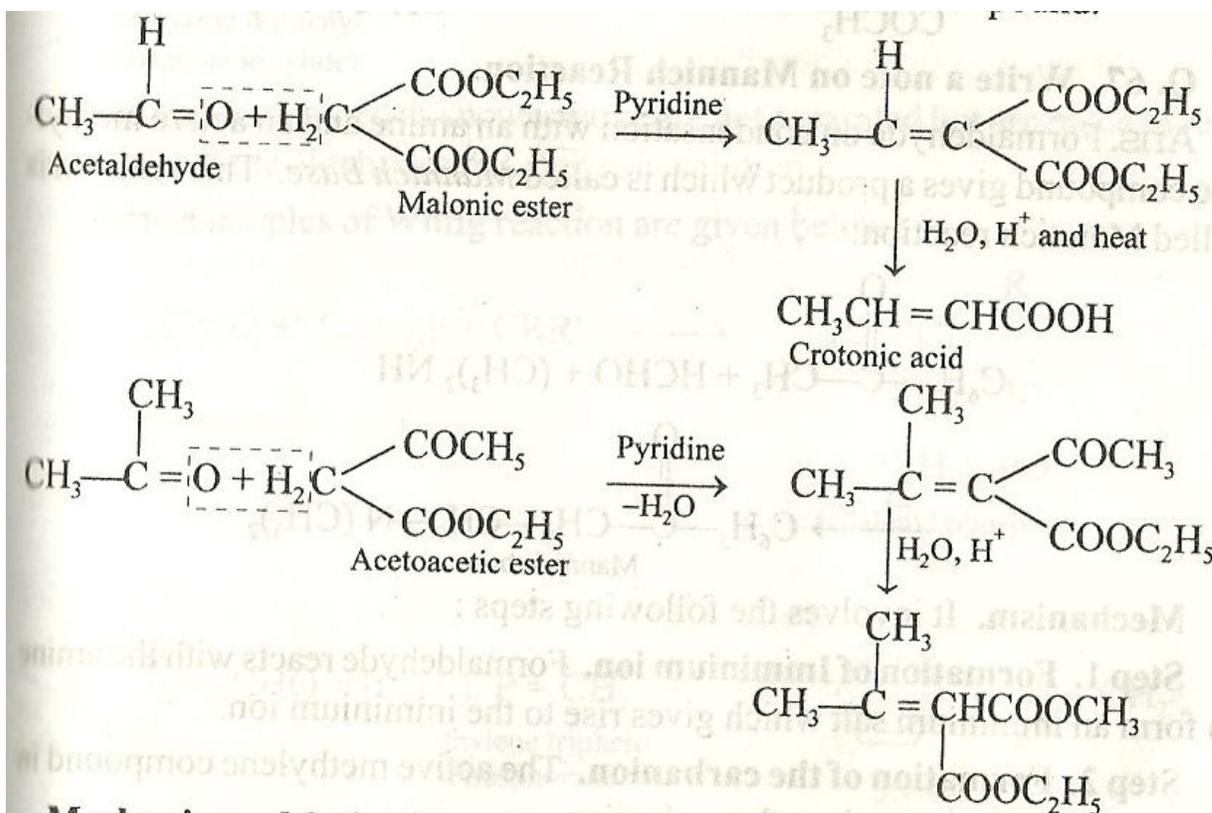
Step 4: dehydration, the hydroxyl group and neighbouring hydrogen are removed as water.

Step 5: hydration





Knoevenagal reaction

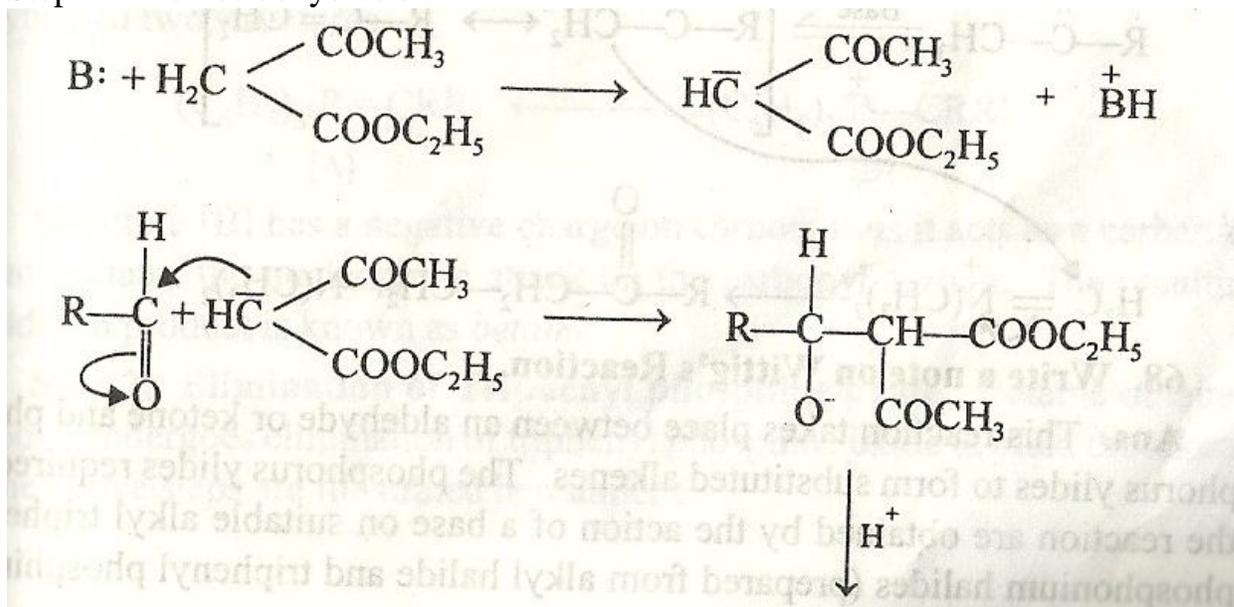


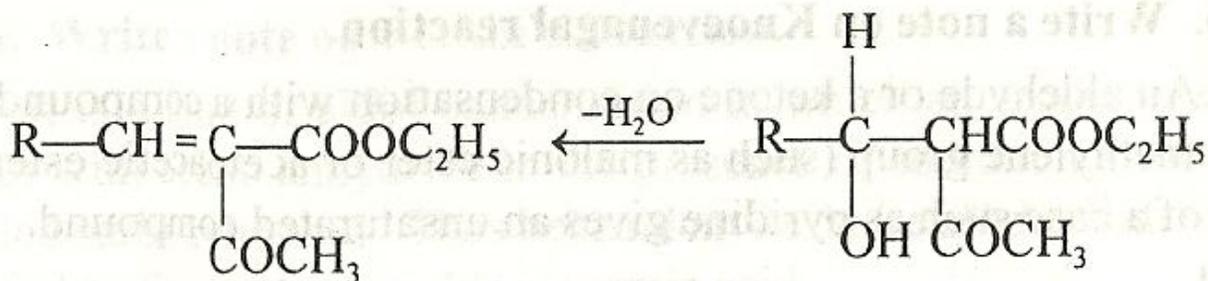
Mechanism

Step 1-2 as explained in other reactions

Step 3: protonation: - alkoxide accepts a proton to form hydroxyl compound.

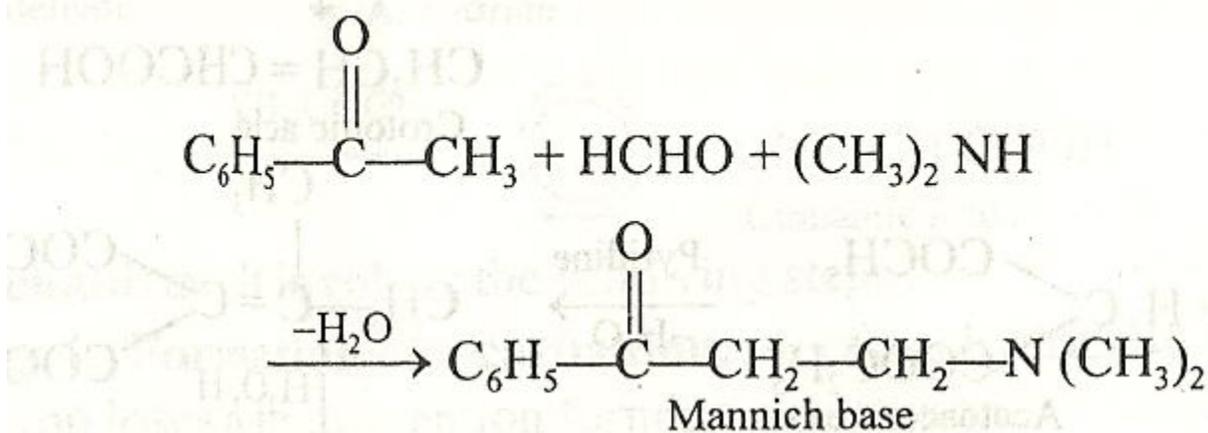
Step 4: involves dehydration





Mannich reaction

Reaction involves condensation of methanol which amine p an active methylene compound to form a Mannich base.

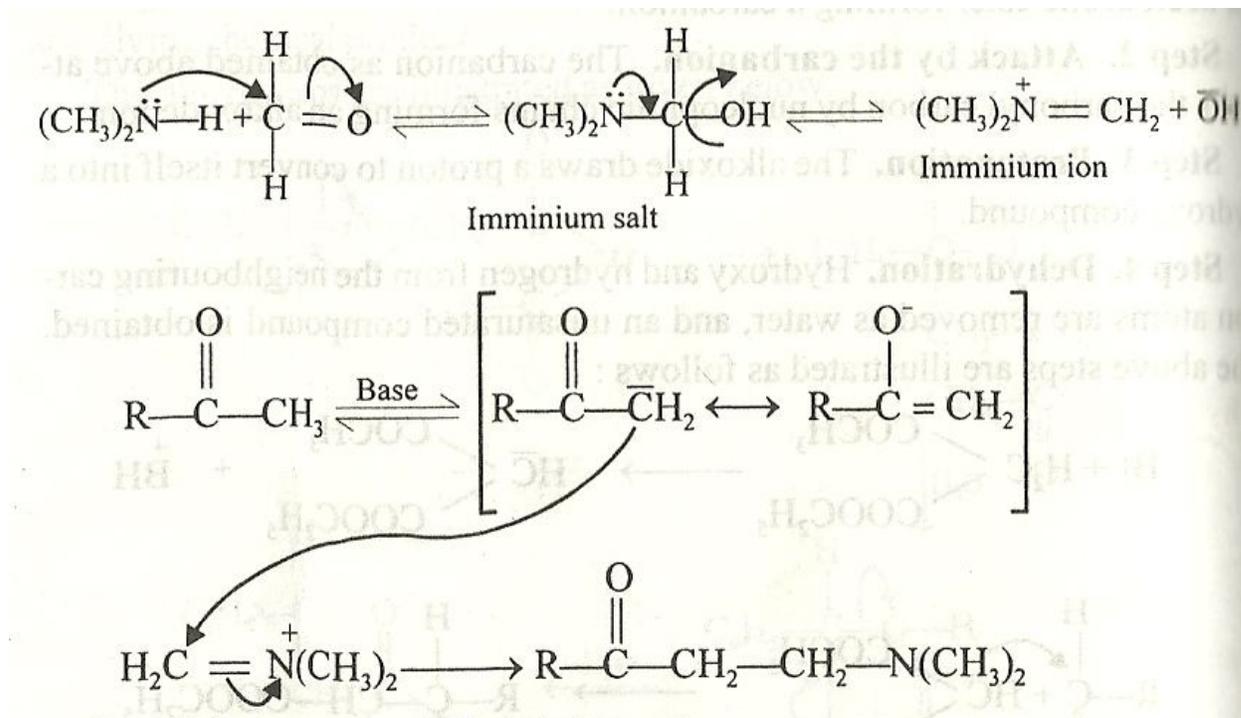


Mechanism:-

Step 1: formation of Imminium ion

Step 2: formation of carbanion

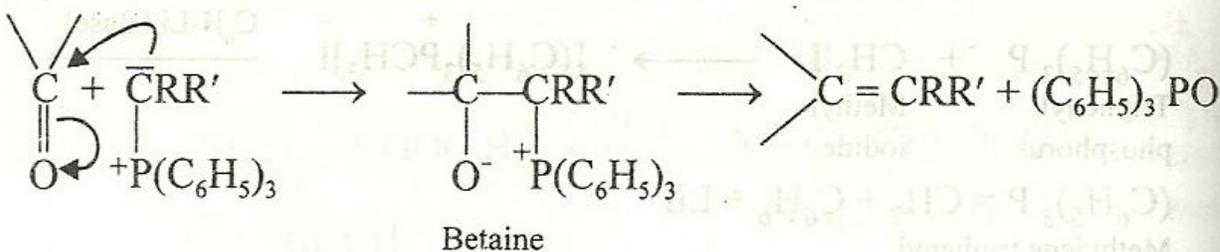
Step 3: attack by carbanion



Witting's reaction

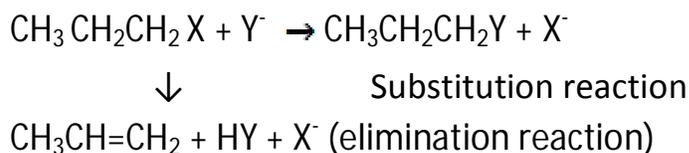
Reaction occurs between an aldehyde/ketone and phosphorous ylides to form substituted alkenes.

Phosphorous ylide is prepared by reacting a base with an alkyl triphenyl phosphonium halide as shown below



Elimination reactions Of Alkyl halides

- In elimination reactions, atoms or groups are removed from a reactant.
- When an alkyl halide undergoes elimination reaction, the halogen X is removed from a carbon and a hydrogen is removed from an adjacent carbon, a double bond is formed below the 2 carbons from which the atoms are removed e.g.
- $\text{CH}_3\text{CHCH}_2\text{CH}_3 + \text{CHO}_3^- \rightarrow \text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3$
- Generally,



Factors affecting elimination reaction

- Structure of the alkyl halide (RX)
- Only secondary and primary alkyl halides undergo E1 reactions. The reaction proceeds through an intermediate of secondary carbocation which rearranges to the more stable tertiary carbocation. Base removes proton from β- carbon.
- Primary, secondary and tertiary alkyl halides undergo E2 reactions. It is a one step mechanism involving bond breaking and bond formation.

Text for further reading

Organic chemistry – Brief course by Robert Atkins and Francis. A.

Carey

Organic reaction mechanism, conversions and problems by R.L

Madan

