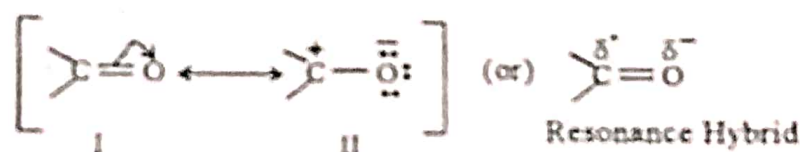
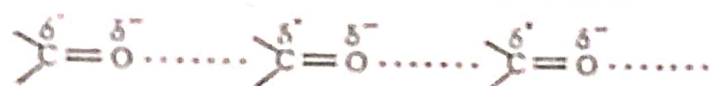


Unit - III

Reactions of Carbonyl Compounds

CARBONYL POLARIZATION

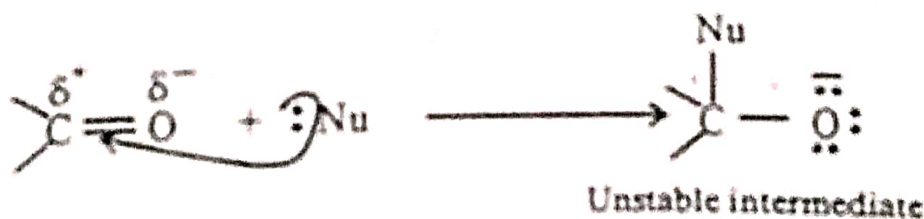
The carbon - oxygen bond in aldehydes and ketones is polar. The greater electronegativity of oxygen than carbon shifts the electrons constituting the π bond partially towards oxygen. Thus carbon becomes slightly positive and oxygen slightly negative. Also, the carbonyl double bond can be represented as a resonance hybrid of the canonical forms I and II.

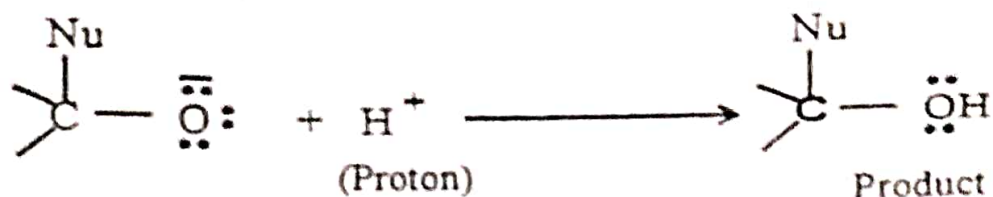


Hence, the carbon - oxygen bond is highly polarised. It implies that the carbon atom of the carbonyl group is electron deficient, while the oxygen atom is electron - rich. This makes the C = O group an extremely reactive function in aldehydes and ketones. The basic principles involved in the general reactions of this class of compounds are discussed below.

I. Nucleophilic addition reactions :

The electron deficient carbon of the carbonyl group is easily attacked by a nucleophile which supplies an electron pair. Thus many addition reactions of the carbonyl compounds are initiated by nucleophiles. A general mechanism of such reactions is given below.



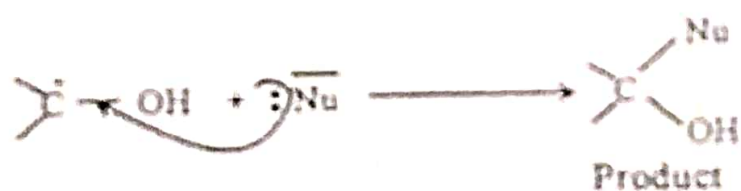


First the nucleophile ($:\bar{\text{Nu}}$) adds to the carbonyl carbon to form an unstable intermediate. The intermediate then yields the final product by abstracting a proton from the solvent or the reacting agent. It is noteworthy that the entire process consisting of the above two steps is frequently reversible under certain conditions when the product is transformed back into the starting carbonyl compound.

The nucleophilic addition reactions of carbonyl group are catalysed by acids or bases.

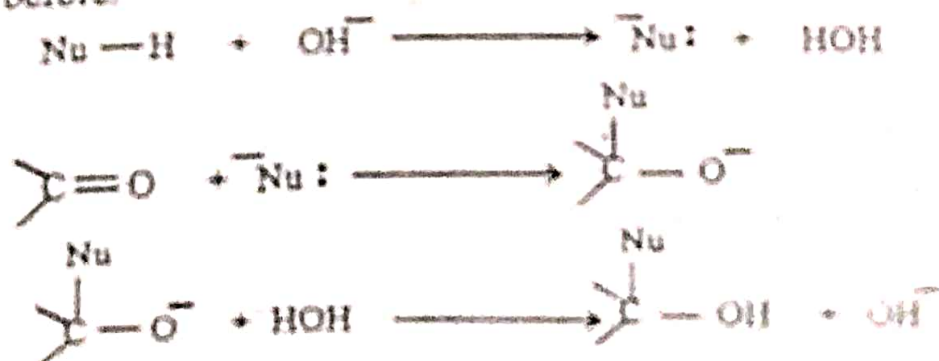
i. Acid catalysed addition :

The proton released by the acid combines with the carbonyl oxygen and thus attenuates the electron deficiency of the carbon atom. In this way the positivity of the carbonyl carbon atom is increased and the attack of the nucleophile enhanced.



ii. Base catalysed addition :

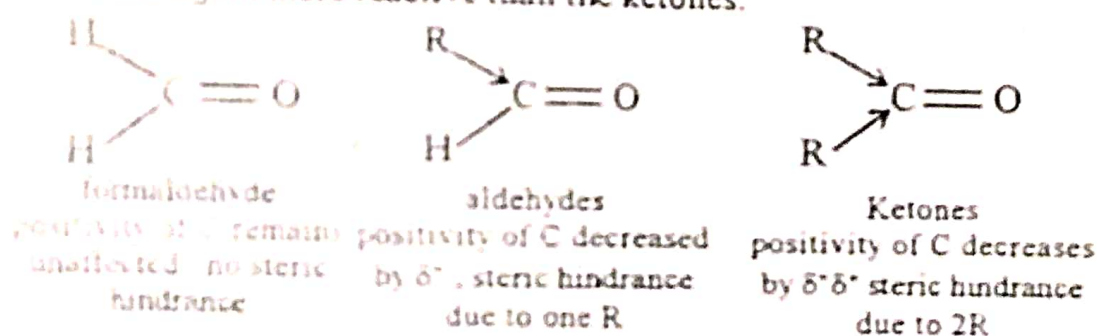
Here the nucleophile ($:\text{Nu}$) is generated from its conjugate and ($\text{Nu} \cdot \text{H}$) in the presence of a base (OH^-) and the addition takes place as described before.



It may be noted that whether the addition is acid - catalysed or base - catalysed, the product obtained is the same. An acid catalyst promotes nucleophilic attack by increasing the nucleophilic character of the carbonyl carbon, while a base does so by increasing the nucleophilicity of the reagent

Relative Reactivities of Aldehydes and Ketones :

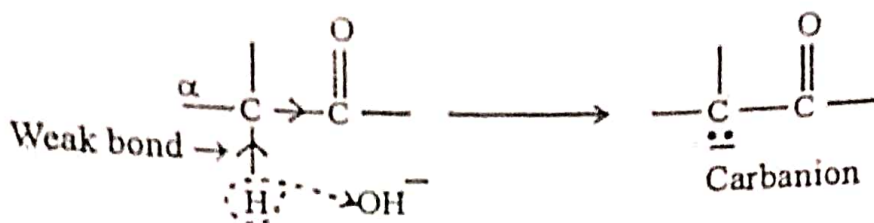
For maximum reactivity towards nucleophiles, the carbonyl carbon atom should be as positive as possible and not sterically hindered by adjacent groups. The ketones have two alkyl groups on the carbonyl carbon while aldehydes have one alkyl group only. Each alkyl group being electron releasing decreases the positivity of the carbon atom and on account of its bulk offers steric hindrance to the approaching reagents. For both these reasons, the nucleophilic attack on the carbonyl carbon is retarded. Thus the carbonyl group in ketones being influenced by two alkyl groups is less reactive than in aldehydes where the carbonyl group is under the influence of one alkyl group only. Formaldehyde having no alkyl group on carbonyl carbon is more reactive than all other aldehydes which are again more reactive than the ketones.



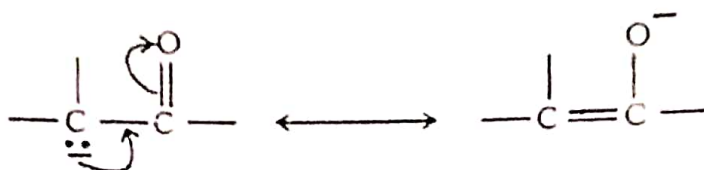
2. Acidity of α - Hydrogen atom :

Another type of reactions of the carbonyl compounds are due to the acidity of the hydrogen atoms on carbon adjacent to carbonyl, or α - carbon atom. The acid character of the α - hydrogen atoms (attached to α - carbon) is explained as follows.

The carbonyl carbon is positive and therefore, attracts the electrons in the single bond shared with α - carbon. The α - carbon in turn pulls towards it the electrons in the next single bond joining hydrogen. The drift of the electrons away from the hydrogen atom weakens the carbon hydrogen bond. Thus there is a tendency for α - hydrogen atom to split off as proton in the presence of strong basic reagents.



The removal of proton leaving an electron pair gives a carbanion or enolate ion which is resonance stabilised. The two contributing forms to the hybrid are

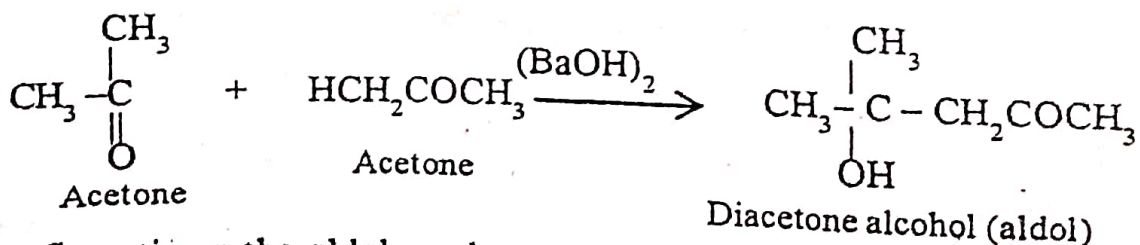
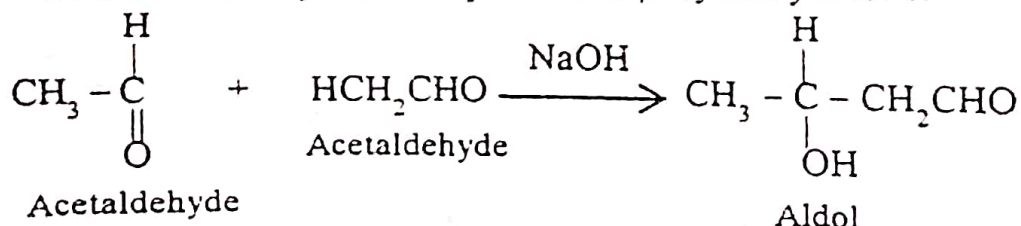


The carbanion thus produced is a good nucleophile and can attack carbonyl group of another molecule. The formation of the carbanion followed by its addition to a carbonyl group is the process involved in all the condensation reactions of aldehydes and ketones.

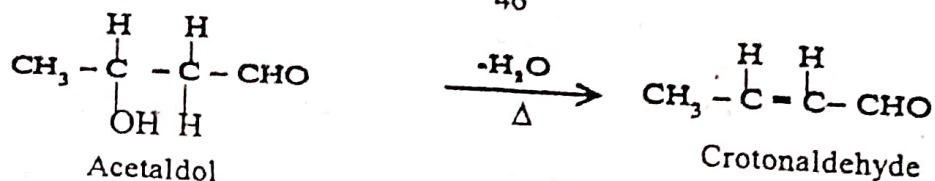
Reactions

1. ALDOL CONDENSATION ✓ *

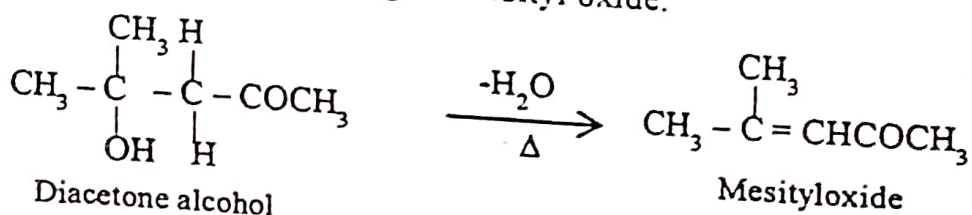
In the presence of a dilute base two molecules of aldehyde combine to form a condensation product containing both an aldehyde group and an alcohol group. This product is β -hydroxy aldehyde called *aldol*. Ketones containing α -hydrogen atom also undergo aldol condensation to a smaller extent than do aldehydes. The product is β -hydroxyketone.



Sometimes the aldol products are stable enough to be isolated. In other cases water may be lost spontaneously to form unsaturated aldehyde or ketone. For example acetaldol may undergo dehydration on warming in presence of an acid to give crotonaldehyde.

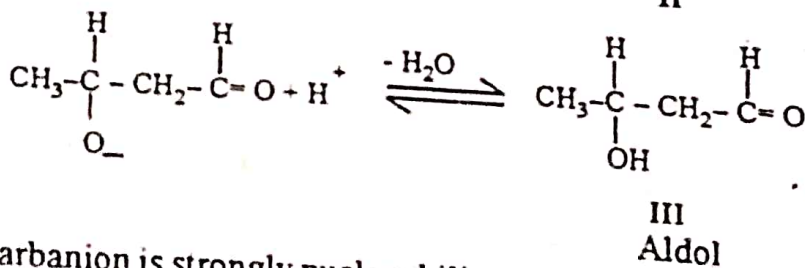
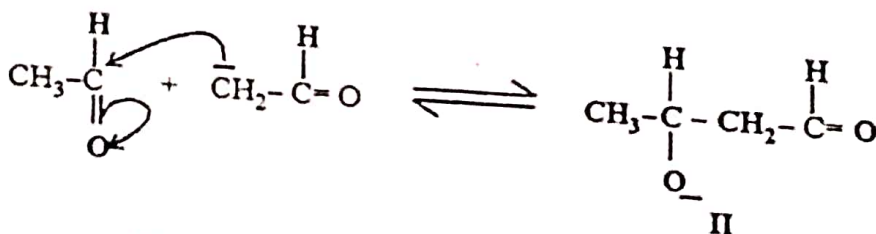
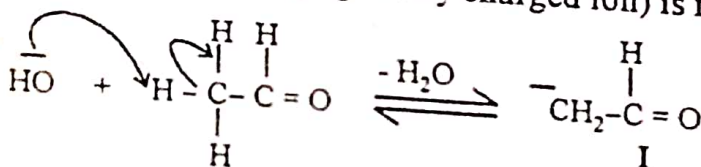


Similarly diacetone alcohol upon heating in the presence of an acid undergoes dehydration to give mesityl oxide.



Mechanism

1. The base ionises to form OH^- ion. It removes a proton (H^+) from α -carbon. Thus a carbanion I (negatively charged ion) is formed.

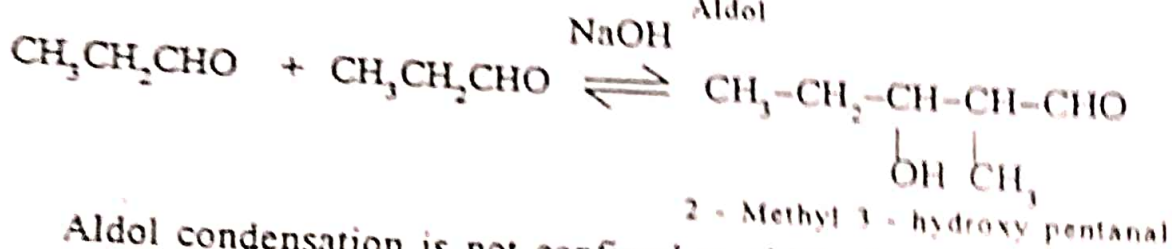
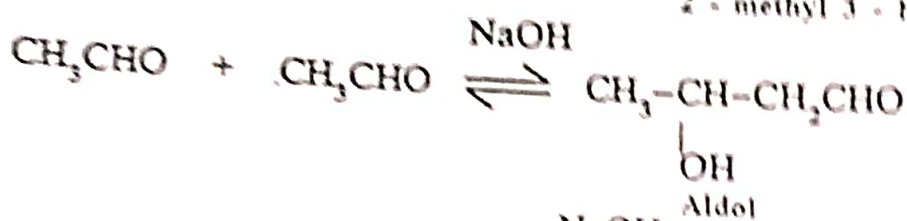
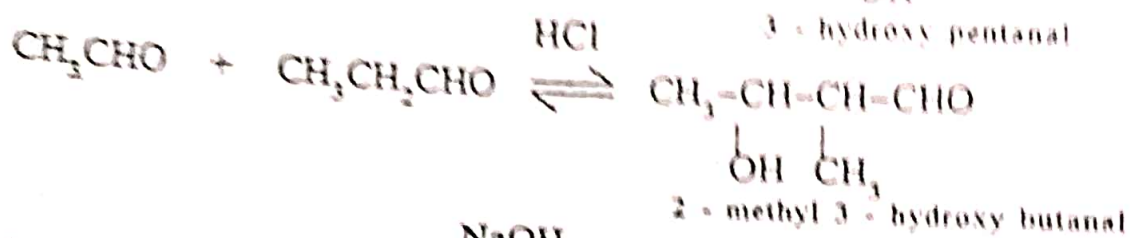
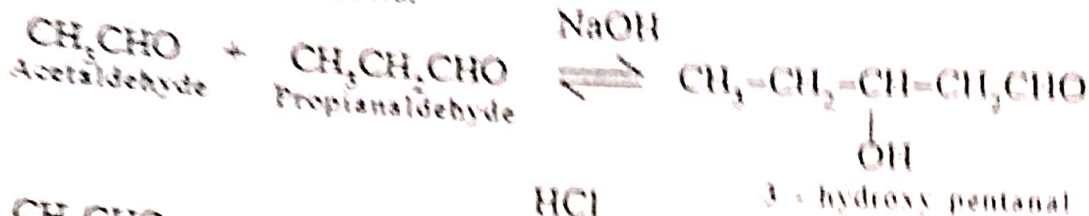


2. The carbanion is strongly nucleophilic and so attacks carbonyl carbon of the second molecule (of aldehyde or ketone). The anion II is formed.

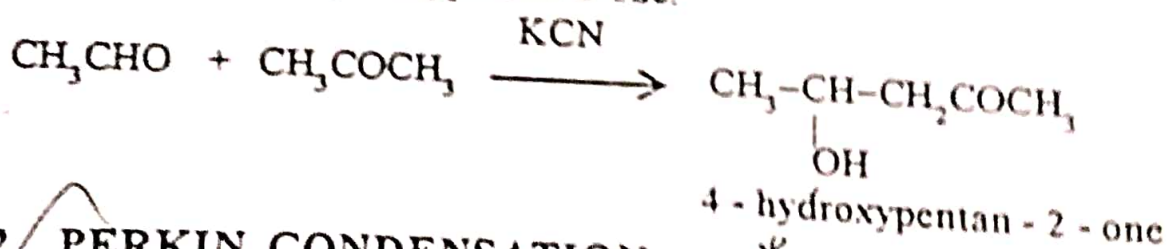
3. The anion picks up a proton from water to form the aldol III.

Two different aldehydes undergo aldol condensation giving all four possible condensation products. But using different catalysts one product may be made to predominate in the mixture.

For example, acetaldehyde and propionaldehyde under an alcohol condensation as follows.



Aldol condensation is not confined to aldehydes alone. It can be between an aldehyde and a ketone. Such a reaction is called *Cross aldol condensation*. Thus acetaldehyde and acetone condense in the presence of KCN to form 4-hydroxypentan-2-one.



2. PERKIN CONDENSATION *

When benzaldehyde (or any other aromatic aldehyde) is heated with an aliphatic acid anhydride containing two α - hydrogen atoms in the presence of the sodium salt of the acid, condensation takes place to form an α - unsaturated acid. *This reaction is known as perkin reaction.*

1. Only aromatic aldehydes are used in Perkin reaction because they do not contain α , β - hydrogen atoms. Aldehydes containing α - hydrogen atoms undergo self condensation in presence of bases and no Perkin condensation takes place.