Chemical properties of aldehydes and ketones.

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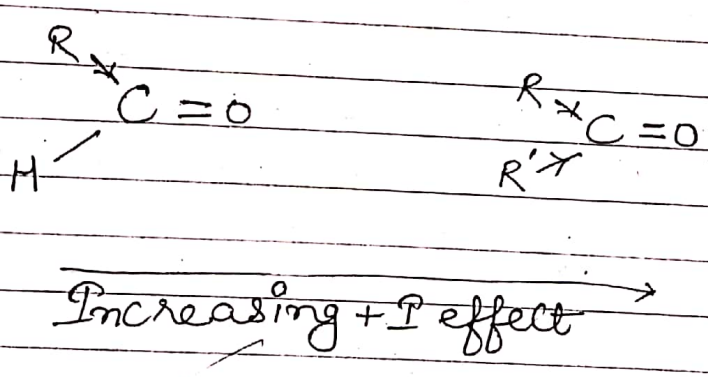
Aldehyde and ketone readily under-go to nucleophillic addition reaction and Condensation reaction.

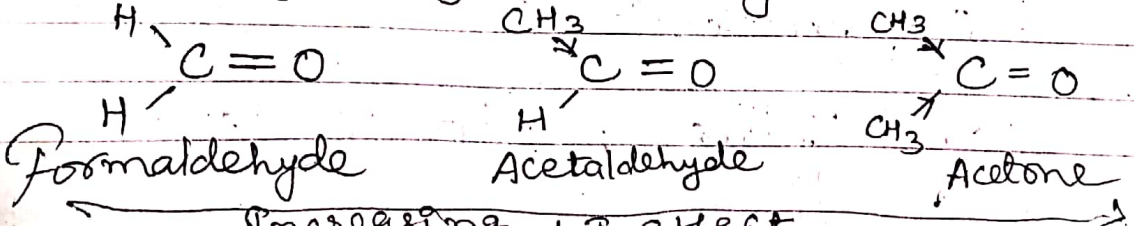
Nucleophillic addition reaction is the characteristic reaction (easily performing) of Carbonyl compounds because Carbonyl group is the unsaturated group in which Carbon atom becomes electron deficient due to high electronegativity of oxygen.

$$>\overset{\delta+}{C}=\overset{\delta-}{O}$$

Aldehydes are more reactive towards nucleophile than ketones because electron deficiency of Carbonyl Carbon of keto-group ~~is Greater~~ is less than aldehyde due to electron pushing tendency of two alkyl groups (increasing +I effect).



Formaldehyde is most reactive towards nucleophile in the aldehyde series because its Carbonyl carbon is most electron deficient. In other aldehydes electron deficiency of Carbonyl group decreases on increasing alkyl chain length.



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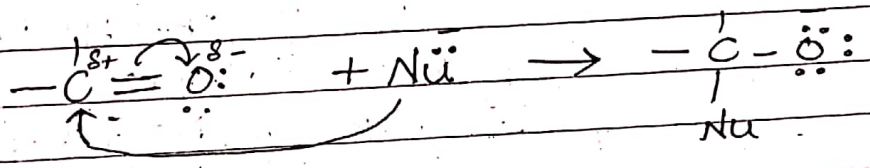
Decreasing reactivity towards nucleophile

* General Mechanism of Nucleophillic Addition Reaction :-

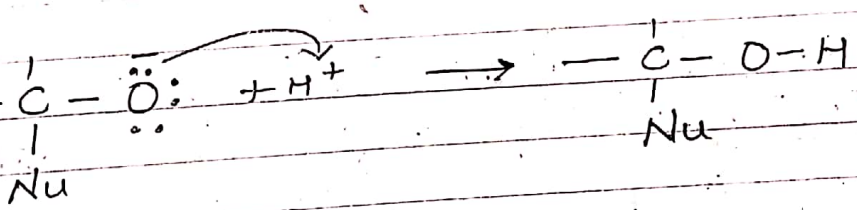
Nucleophillic Addition Reaction is completed in two steps -

$$Nu-H \longrightarrow Nu^{-} + H^{+}$$

Step-1 :-



Step-2 :-



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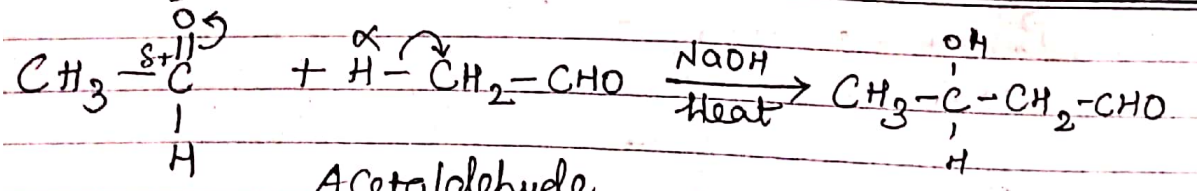
* Aldol Condensation Reaction :-

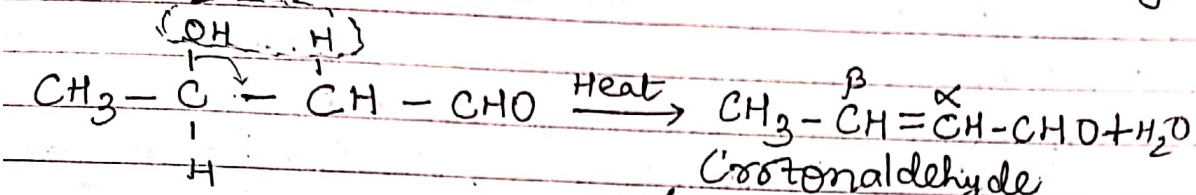
It is base catalysed Condensation reaction of aldehydes and ketones containing α-H atom. Condensation Product of the reaction is called aldol because it contains both an aldehyde and an alcohol functional groups.

In this reaction α-carbon atom of the 1st molecule becomes attached to the carbonyl group of 2nd molecule. Thus, a new carbon-carbon bond is formed.



Acetaldehyde + Acetaldehyde → 3-Hydroxybutanal (An aldol)

On heating, aldol eliminates a water molecule and converts it into an α, β - unsaturated aldehyde.



Crotonaldehyde (An α,β- unsaturated aldehyde)

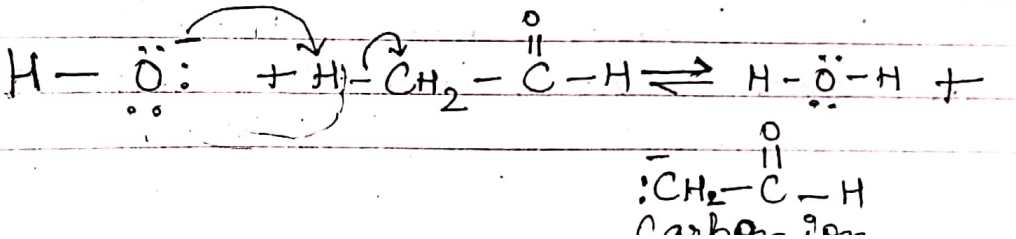
IUPAC → But-2-ene-al

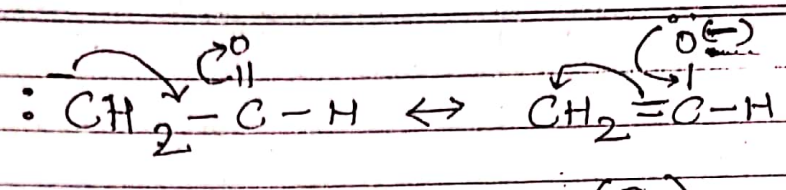
In case of ketones, aldol condensation is reversible and equilibrium mainly shifted towards reactant side.

*Mechanism of the Reaction (Aldol Condensation) :-

Following steps are involved in the aldol formation :-

Step - I :- In this step, the base (^-OH) removes a proton from α- Carbon atom of one molecule of aldehyde to give a resonance stabilised Carbon - anion or enolate ion.





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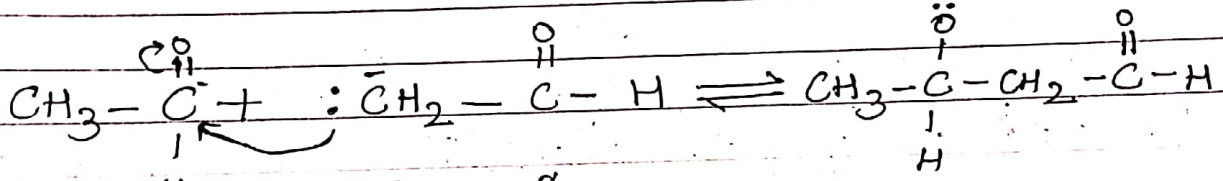
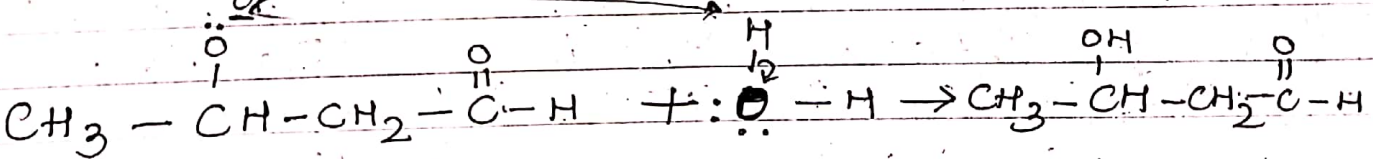
Resonance in the enolate ion.

Step – 2 :- The Enolate ion acts as nucleophile and attacks the carbonyl C-carbon of 2nd molecule of aldehyde. After nucleophillic addition reaction, an alkoxide ion is produced.

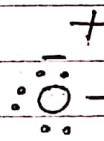


Carbanion Alkoxide ion

Step-3 :- An alkoxide ion is a stronger base than OH^- ion. Therefore, retains a proton from water molecule and converted into aldol.



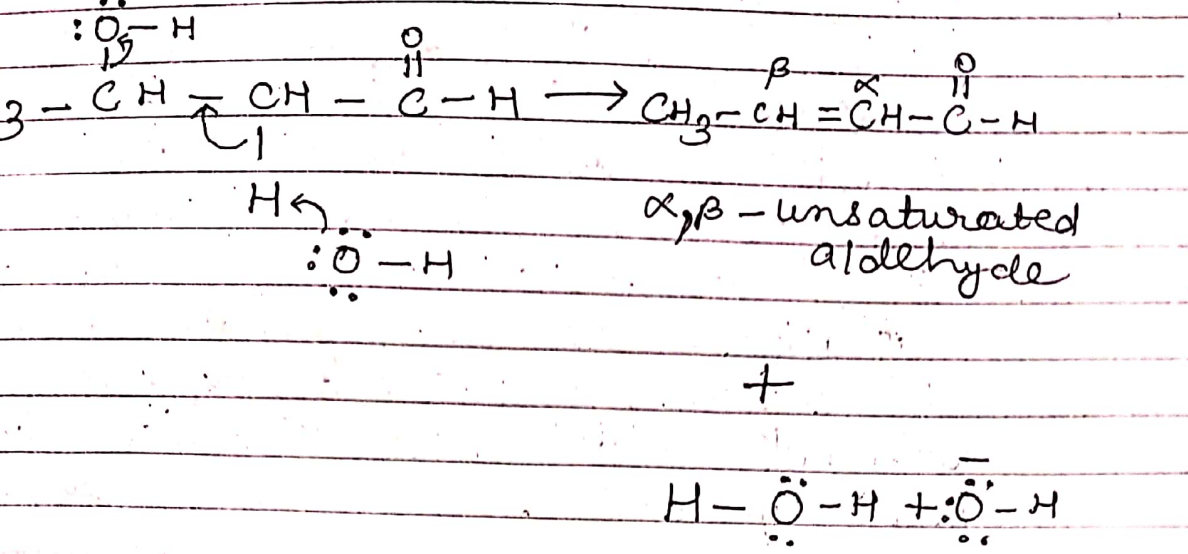
Aldol



* Mechanism of Dehydration :—

Aldol readily undergoes to dehydration due to # acidity of the remaining α-H atom

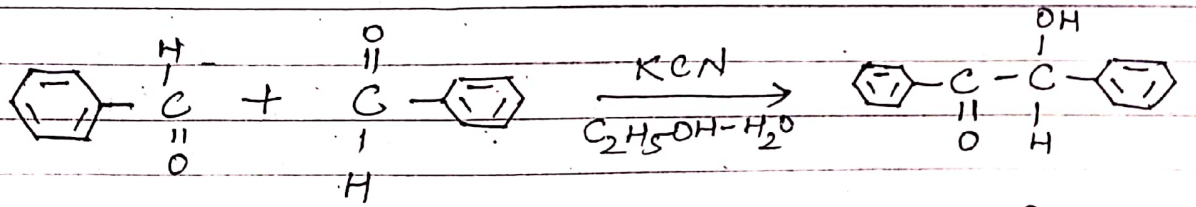
and converted into more stable α,β-unsaturated aldehyde.



* Benzoin Condensation :-

Benzoin Condensation reaction is the condensation of aromatic aldehyde in presence of cyanide ion (CN^-).

On heating Benzaldehyde with aqueous-ethanolic (mixture of H_2O and ethanol) Sodium Cyanide (NaCN) or potassium Cyanide (KCN), it dimerises to form an α-Hydroxyketone known as Benzoin is obtained.



Benzaldehyde Benzaldehyde Benzoin