CHEMISTRY

Live eBook

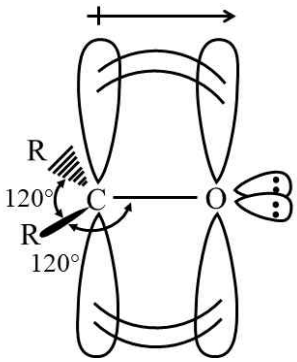
01. Introduction

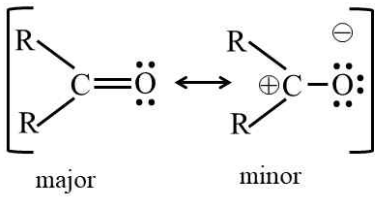
Aldehydes & ketones have general formula $C_nH_{2n}O$ and contains > C = O group. Thus aldehydes (R–CHO) and ketones (R–CO–R) are collectively called as carbonyl compounds. Aldehyde is always at terminal position while ketone is never at terminal position.

Structure and bonding in aldehydes and ketones

The cabronyl carbon atom is sp^2 hybridized. The unhybridized p-orbital overlaps with a p-orbital of oxygen to form a pi bond. The double bond between carbon and oxygen is shorter, stronger, and polarized.

Orbital diagram for the formation of carbonyl group is as follows :



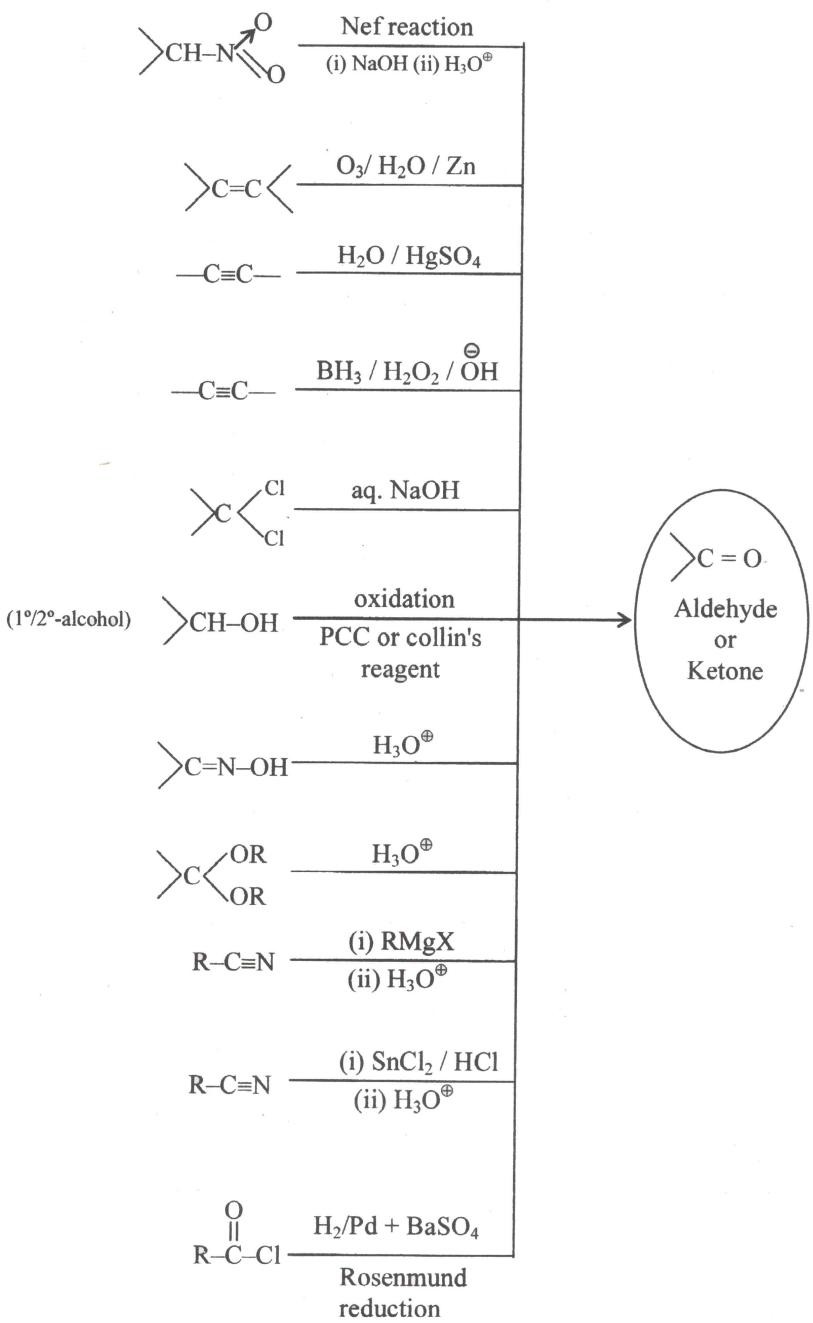


This polarity confirms that there is nucleophilic addition reaction takes place in carbonyl compound. The double bond of the carbonyl group has a large dipole moment because oxygen is more electronegative than carbon.

Carbonyl carbon act as an electrophile (Lewis acid)

Carbonyl oxygen act as a nucleophile (Lewis base)

02. Preparation Methods of Carbonyl Compounds



03. Physical Properties of Aldehydes and Ketones

Methanal – Gas at room temperature. Ethanal – Volatile liquid. Other aldehydes and ketones – Liquid or solid at room temperature.

Boiling points of aldehydes and ketones are higher than those of hydrocarbons and ethers of comparable molecular masses.

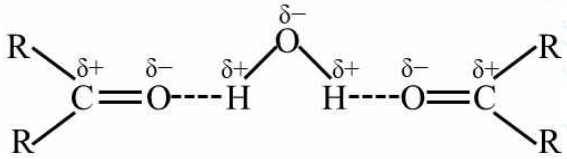
Reason : Weak molecular association in aldehydes and ketones, arising out of the dipole-dipole interactions.

Boiling points of aldehydes and ketones are lower than those of alcohols of similar molecular masses.

Reason : Absence of intermolecular hydrogen bonding.

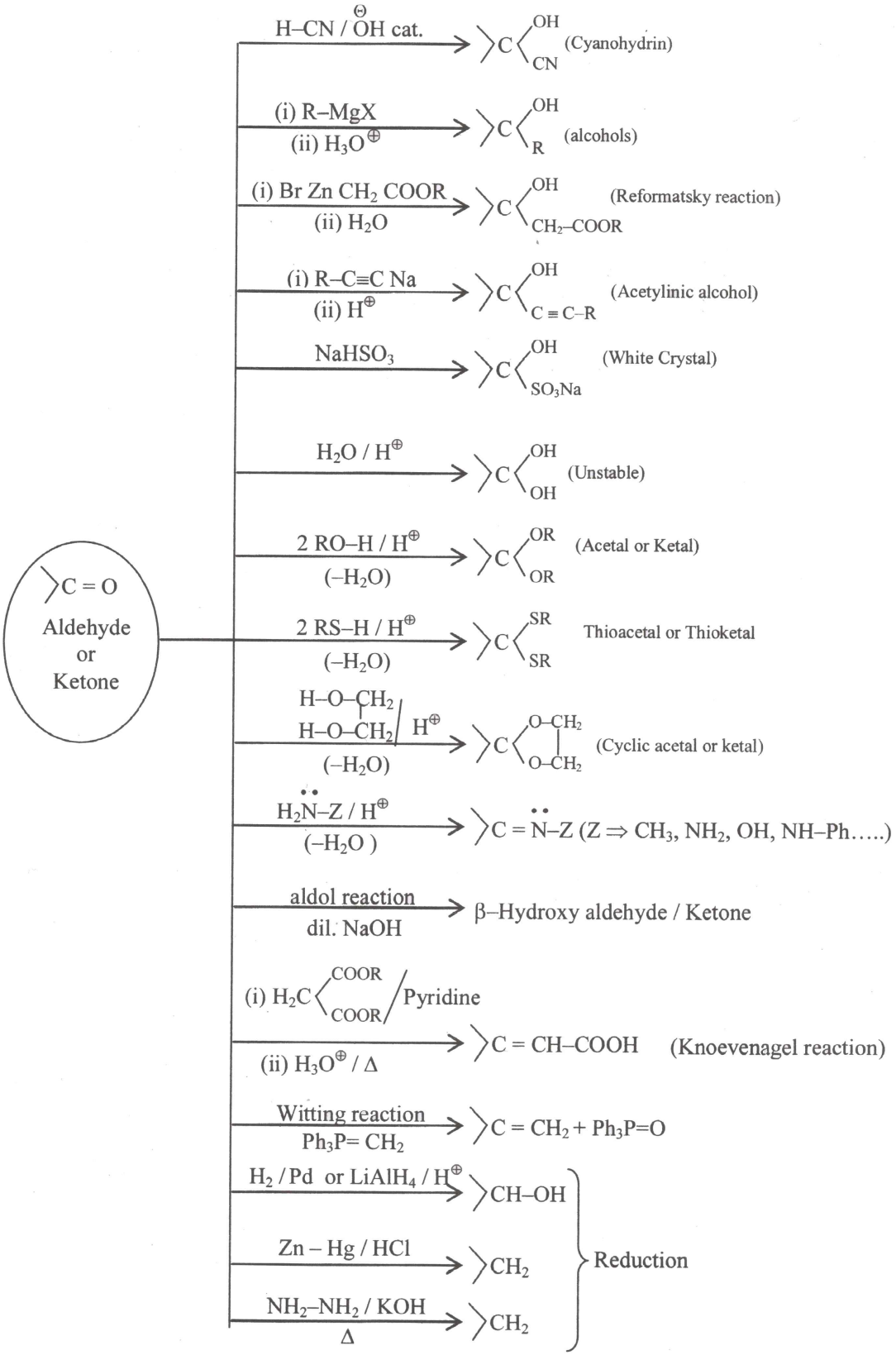
Lower members of aldehydes and ketones are miscible with water in all proportions.

Reason : They form hydrogen bonds with water.



Solubility of aldehydes and ketones decreases rapidly on increasing the length of the alkyl chain. All aldehydes and ketones are fairly soluble in organic solvents such as ether, methanol, etc. Lower aldehydes have sharp pungent odours. As the size of aldehydes increases, the odour becomes less pungent and more fragrant.

04. Chemical Properties of Carbonyl Compounds



05. Some Other Reactions of Aldehyde & Ketone

(i) Cannizzaro Reaction : Only α − H = Zero aldehyde shown this reaction

$$HCHO + HCHO \xrightarrow{50\%\ KOH} HCOOK + CH_3OH$$

$$PhCHO + PhCHO \xrightarrow{50\%\ NaOH} PhCOONa + PhCH_2OH$$

(ii) Tischenko (esterification) Reaction : It is also called modified cannizzaro reaction because all aldehydes show this reaction.

$$CH_3CHO + CH_3CHO \xrightarrow{(C_2H_5O)_3\ Al} CH_3-\overset{\overset{O}{\|}}{C}-O-CH_2CH_3$$

$$HCHO + HCHO \xrightarrow{(C_2H_5O)_3\ Al} H-\overset{\overset{O}{\|}}{C}-O-CH_3$$

(iii) Oxidation by SeO_2 : α − C of aldehyde/ketone is converted into $-\overset{\overset{O}{\|}}{C}-$ group

$$CH_3-\overset{\overset{O}{\|}}{C}-H \xrightarrow{SeO_2} H-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-H + Se + H_2O$$

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{SeO_2} H-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-CH_3 + Se + H_2O$$

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3 \xrightarrow{SeO_2} H-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-CH_2-CH_3 + Se + H_2O$$

(iv) Baeyer-villiger oxidation : Aldehyde is converted into acid but Ketone is converted into ester.

$$CH_3-\overset{\overset{O}{\|}}{C}-H \xrightarrow{CF_3CO_3H} CH_3-\overset{\overset{O}{\|}}{C}-OH + CF_3CO_2H$$

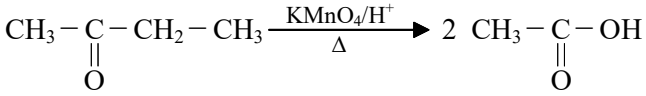
$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{CF_3CO_3H} CH_3-\overset{\overset{O}{\|}}{C}-OCH_3 + CF_3CO_2H$$

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3 \xrightarrow{CF_3CO_3H} CH_3-\overset{\overset{O}{\|}}{C}-O-CH_3-CH_3 + CF_3CO_2H$$

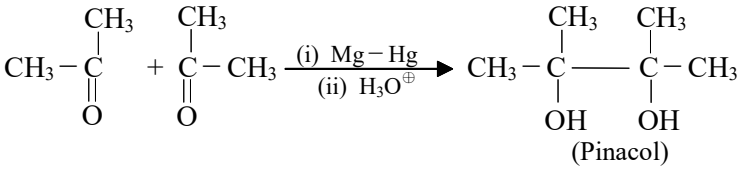
(v) Oxidation by strong oxidants :

$$CH_3-\overset{\overset{O}{\|}}{C}-H \xrightarrow{KMnO_4/H^{\oplus}} CH_3-\overset{\overset{O}{\|}}{C}-OH$$

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[\Delta]{KMnO_4/H^{\oplus}} CH_3-\overset{\overset{O}{\|}}{C}-OH + CO_2\uparrow + H_2O$$

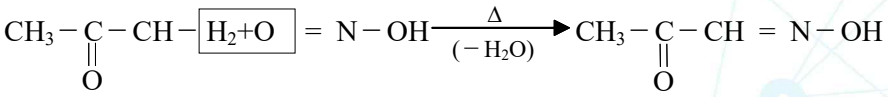


(vi) Bimolecular reduction of acetone :

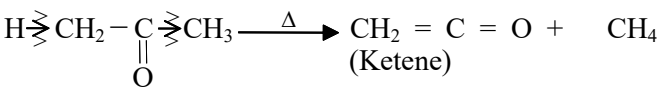


(Pinacol)

(vii) Formation of oximino acetone :



(viii) Pyrolysis :

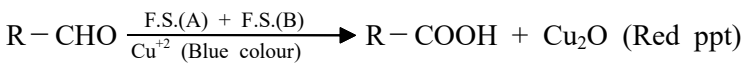


(Ketene)

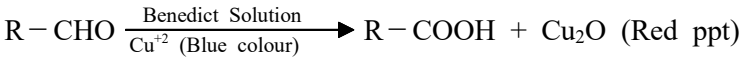
(ix) Reducing property of aldehydes :

(a) **Tollen's reagent :** Ammonical silver nitrate solution $[Ag(NH_3)_2]^{\oplus}\ \overset{\ominus}{O}H$

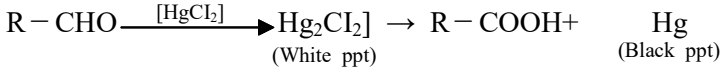
(b) **Fehling's solution :** It is a mixuture of following two solutions.
F.S. (A) → Aqueous solution of $CuSO_4$
F.S. (B) → Alkaline solution of Roschell's salt (sodium potassium tartarate)



(c) **Benedict's solution :** It is a mixture of copper sulphate sodium citrate and sodium carbonate.



(d) Corrosive sublimate ($HgCl_2$) solution :



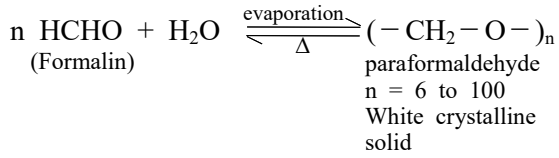
(x) Test of aldehydes with Schiff's Reagent :
aqueous solution of

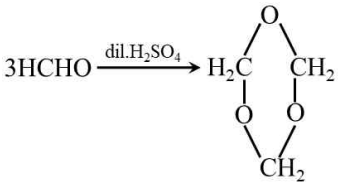
or magenta dye
(pink colour)

(Schiff ' s Reagent)

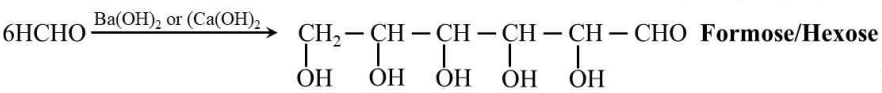
(xi) Aldehyde shows addition polymerization but ketone shown condensation polymerization.

(a)



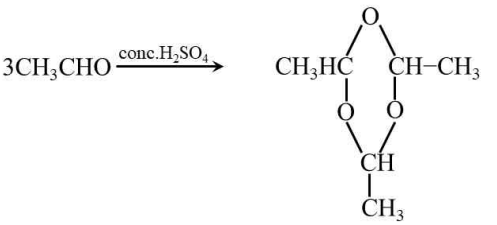


Metaformaldehyde/trioxane

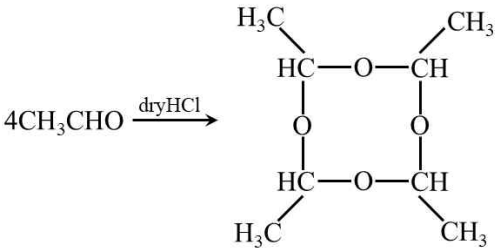


Formose/Hexose

(b)

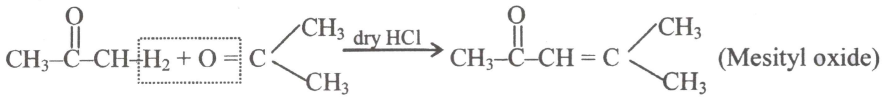


Paraldehyde used as Hypnotic

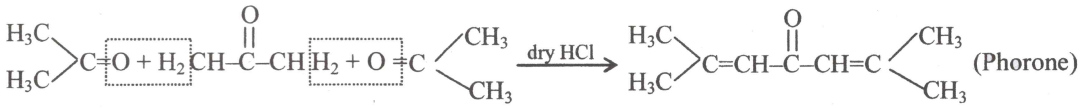


Metaaldehyde used as solid fuel

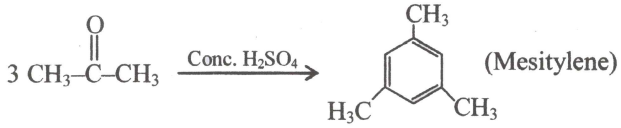
(c)



(Mesityl oxide)

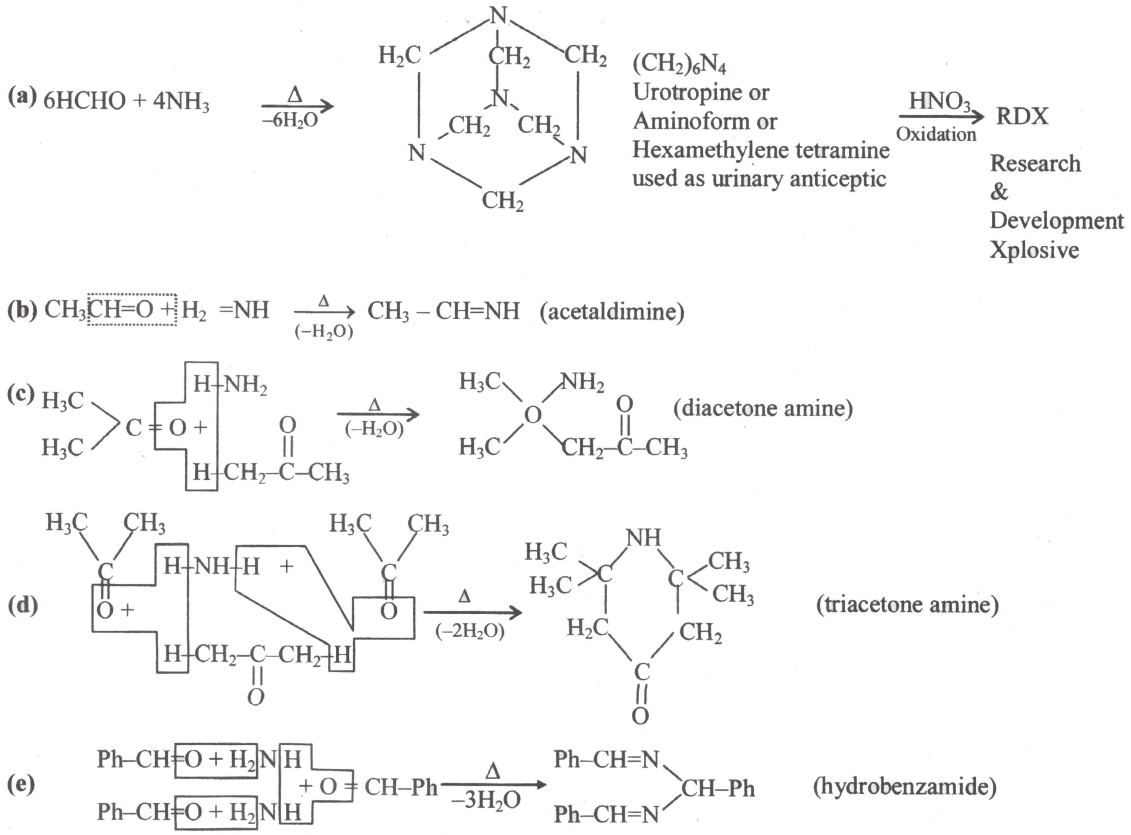


(Phorone)



(Mesitylene)

(Xii) Ammonia gives following types of products with aldehyde and ketone



06. Distinction between formaldehyde, acetaldehyde and acetone (STATE PMT) :

S.No.	Reagent/Test	HCHO	CH_3CHO	CH_3COCH_3
1	Brady reagent / DNP	Coloured crystal	Coloured crystal	Coloured crystal
2	Tollen's reagent	Silver mirror	Silver mirror	×
3	Fehling's solution	Red	Red	×
4	Benedict's solution	Red	Red	×
5	Corrosive sublimate ($HgCl_2$)	Black	Black	×
6	Schiff's reagent	Pink	Pink	×
7	Iodoform test	×	Yellow	Yellow
8	Pyrogallol test	White	×	×
9	Legal test (Sod. nitropruside / NaOH)	×	Red	Red
10	m-dinitrobenzaldehyde test	×	×	Blue