Chemistry Study Materials for Class 12

(NCERT Based Notes of Chapter - 11)

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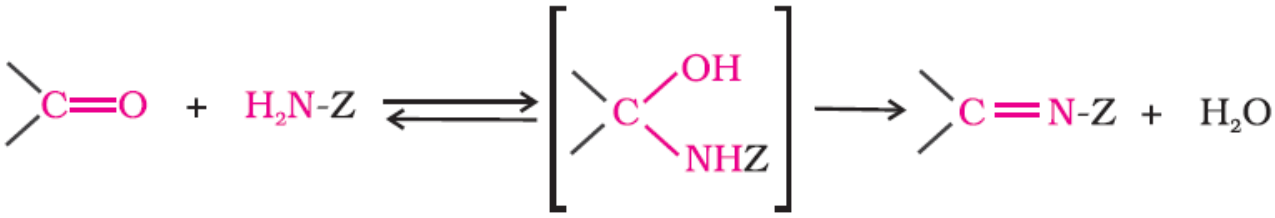
Aldehyde, Ketones and Carboxylic Acid

(e)Addition of ammonia and its derivatives: Nucleophiles like ammonia and its derivatives H_2N-Z are added to the carbonyl group of aldehydes and ketones. The reaction is reversible and catalysed by acid.



(i)Addition of ammonia: Aldehydes and ketones add ammonia followed by elimination of a water molecule to give imines.

$$R\text{-}CHO + NH_3 \rightarrow R\text{-}CH(OH)NH_2 \rightarrow R\text{-}CH{=}NH + H_2O$$

(imines)

$$R_2CO + NH_3 \rightarrow R_2C(OH)NH_2 \rightarrow R_2C{=}NH + H_2O$$

(ii)Addition of Amine: Carbonyl compounds add amines to give substituted imines (Schiff's bases).

$$R\text{-}CHO + R'\text{-}NH_2 \rightarrow R\text{-}CH(OH)NHR' \rightarrow R\text{-}CH{=}NR' + H_2O$$

$$R_2CO + R'\text{-}NH_2 \rightarrow R_2C(OH)NHR' \rightarrow R_2C{=}NR' + H_2O$$

(iii)Addition of hydroxyl amine (NH_2-OH): Carbonyl compounds condensed with hydroxyl amine to give oximes.

$$R\text{-}CHO + NH_2OH \rightarrow R\text{-}CH{=}N\text{-}OH + H_2O$$

(aldoxime)

$$R_2CO + NH_2OH \rightarrow R_2C{=}N\text{-}OH + H_2O$$

(iv)Addition of hydrazine (NH_2-NH_2): Carbonyl compounds condensed with hydrazine to give hydrazone.

$$R\text{-}CHO + NH_2\text{-}NH_2 \rightarrow R\text{-}CH{=}N\text{-}NH_2 + H_2O$$

(hydrazone)

$$R_2CO + NH_2\text{-}NH_2 \rightarrow R_2C{=}N\text{-}NH_2 + H_2O$$

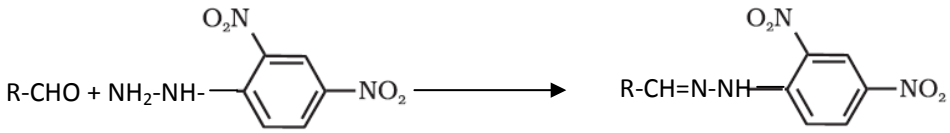
(v)Addition of phenyl hydrazine (NH_2-NH-C_6H_5): Carbonyl compounds condensed with phenyl hydrazine to give phenyl hydrazone.

$$R\text{-}CHO + NH_2\text{-}NH\text{-}C_6H_5 \rightarrow R\text{-}CH{=}N\text{-}NH\text{-}C_6H_5 + H_2O$$

(Phenyl hydrazone)

$$R_2CO + NH_2\text{-}NH\text{-}C_6H_5 \rightarrow R_2C{=}N\text{-}NH\text{-}C_6H_5 + H_2O$$

(vi)Addition of 2,4-dinitrophenyl hydrazine (2,4-DNP): Carbonyl compounds condensed with 2,4-dinitrophenyl hydrazine to give 2,4-dinitrophenyl hydrazone.



2,4-dinitrophenyl hydrazine 2,4-dinitrophenyl hydrazone

2,4-dinitrophenyl hydrazine is also known as Borsches reagent. 2,4-DNP-derivatives are yellow, orange or red solids and hence this reaction is used for the characterisation of aldehydes and ketones.

(vii)Addition of Semicarbazide (NH_2-NH-CO-NH_2): Carbonyl compounds condensed with semicarbazide to yield samicarbazone.

$$R\text{-}CHO + NH_2\text{-}NH\text{-}CO\text{-}NH_2 \rightarrow R\text{-}CH{=}N\text{-}NH\text{-}CO\text{-}NH_2 + H_2O$$

(semicarbazone)

$$R_2CO + NH_2\text{-}NH\text{-}CO\text{-}NH_2 \rightarrow R_2C{=}N\text{-}NH\text{-}CO\text{-}NH_2 + H_2O$$

2.Reduction:

***(i)Reduction to alcohols*:** When reduced using sodium borohydride ($NaBH_4$) or lithium aluminium hydride ($LiAlH_4$) or H_2 in presence of Ni, Pd or Pt catalyst (Catalytic hydrogenation), aldehydes give primary alcohols,

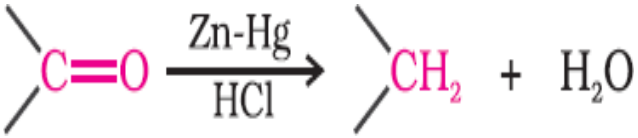
while ketones give secondary alcohols.

$$R\text{-}CHO \xrightarrow{[H]} R\text{-}CH_2OH$$

$$R_2CO \xrightarrow{[H]} R_2CHOH$$

(ii)Reduction to Hydrocarbons: ***Clemmensen reduction*****:**

Aldehydes and ketones can be reduced to alkanes on treatment with zinc amalgam and concentrated hydrochloric acid. During this reaction, the carbonyl group is reduced to CH_2 (methylene) group.



$$CH_3\text{-}CHO + [H] \xrightarrow{Zn/Hg} CH_3\text{-}CH_3$$

$$CH_3\text{-}CO\text{-}CH_3 + [H] \xrightarrow{Zn/Hg} CH_3\text{-}CH_2\text{-}CH_3$$

Wolff-Kishner reduction: Carbonyl group can also be reduced to methylene group, by treating with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent such as ethylene glycol.

3. Oxidation:

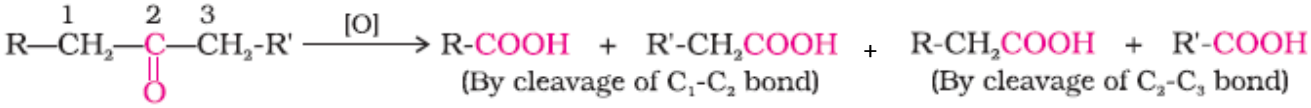
Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents like nitric acid, potassium permanganate, potassium dichromate etc. Mild oxidising agents like CrO_3, Tollens' reagent and Fehlings' reagent can also oxidise aldehydes.

$$R\text{-}CHO \xrightarrow{[O]} R\text{-}COOH$$

$$CH_3\text{-}CHO \xrightarrow{[O]} CH_3\text{-}COOH$$

Ketones when oxidised using strong oxidising agents and at high temperatures, we get a mixture of carboxylic acids having lesser number of carbon atoms.

During this reaction carbon-carbon bond cleavage occurs.

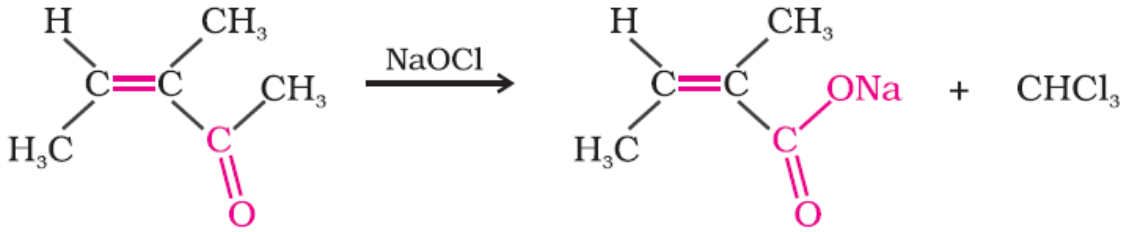


E.g. CH_3-CH_2-CO-CH_2-CH_2-CH_3 $\xrightarrow{[O]}$ 2 CH_3-CH_2-COOH + CH_3-COOH + CH_3-CH_2-CH_2-COOH

4.Haloform Reaction:

Aldehydes or ketones having CH_3-CO- group or CH_3-CHOH- group, when treated with sodium hypohalite or halogen in presence of NaOH, we get a haloform (CHX_3). This reaction is called haloform reaction. During this reaction, the methyl group is converted to haloform. This reaction does not affect a carbon-carbon double bond, if present in the molecule.

R-CO-CH_3 $\xrightarrow{NaOX}$ R-COONa + CHX_3 (where X = Cl, Br or I)



The reaction with sodium hypoiodite gives an yellow precipitate of iodoform and this reaction is used for the detection of CH_3-CO- group or CH_3-CHOH- group in a compound. For example 2-pentanone and 3-pentanone can be distinguished by iodoform reaction. 2-pentanone gives this reaction.

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