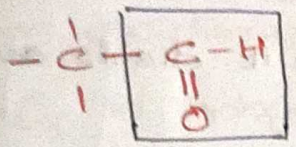
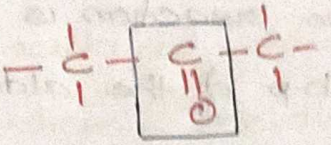
CHEMISTRY OF FUNCTIONAL GROUPS - II

ALDEHYDES AND KETONES



Aldehyde

$R-\underset{\underset{O}{\|}}{C}-H$

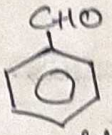


Ketone

$R-\underset{\underset{O}{\|}}{C}-R'$

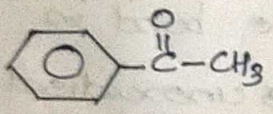
$H-CHO$
formaldehyde
(Methanal)

CH_3-CHO
Acetaldehyde
(Ethanal)

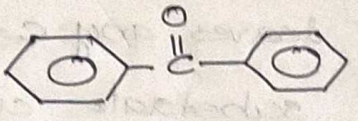


Benzaldehyde

$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$
Acetone
(propanone)



Acetophenone



Benzophenone

PREPARATION OF ALDEHYDES AND KETONES FROM ALCOHOLS

(A) Preparation of aldehydes

① By oxidation of 1° alcohols

→ 1° alcohol is oxidized to corresponding aldehyde, when treated with strong oxidising agent like acidified $KMnO_4$ or $K_2Cr_2O_7$ or salt CrO_3 in an anhydrous medium.

$$R-CH_2-OH + [O] \xrightarrow[\text{or } CrO_3]{KMnO_4/H^+ \text{ or } K_2C_2O_7/H^+} R-CHO + H_2O$$

Eg : $CH_3CH_2OH + [O] \xrightarrow[\text{or } CrO_3]{KMnO_4/H^+ \text{ or } K_2Cr_2O_7/H^+} CH_3\text{-}CHO + H_2O$

Ethanal

$CH_3CH_2CH_2OH + [O] \xrightarrow[\text{or } CrO_3]{KMnO_4/H^+ \text{ or } K_2Cr_2O_7/H^+} CH_3CH_2CHO + H_2O$

propanal

* Inorder to prevent the further oxidation of aldehyde to carboxylic acid, the reaction is carried out at a temperature slightly above the b.p of the aldehyde, so it distills out

② → 1° alcohols are oxidised to aldehyde by (PCC) pyridinium chlorochromate. (complex of Py, HCl & CrO_3) in CH_2Cl_2 / $CHCl_3$

$CH_3CH_2CH_2CH_2OH \xrightarrow[CH_2Cl_2]{PCC} CH_3CH_2CH_2\text{-}CHO$ 1-Butanal

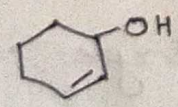
* Advantage of PCC — Unlike acid $KMnO_4$ / $K_2Cr_2O_7$, it leaves any C-C multiple bond in substrate uncleaved & unoxidised

$CH_2=CH-CH_2-OH \xrightarrow[CH_2Cl_2]{PCC} CH_2=CH-CHO$

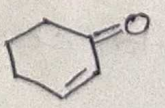
propenal

$CH_3CH=CH-\underset{CH_3}{\underset{|}{CH}}-CH_2OH \xrightarrow[CH_2Cl_2]{PCC} CH_3-CH=CH-\underset{CH_3}{\underset{|}{CH}}-CHO$

2-methyl-3-pentenal



2-cyclohexen-1-ol

$\xrightarrow[CH_2Cl_2]{PCC}$ 

③ By dehydrogenation of 1° alcohols

→ Vapours of 1° alcohol are passed over heated Cu / Ag at 573 K

$R-CH_2-OH \xrightarrow{Cu/573K} R-CHO + H_2$

$CH_3CH_2OH \xrightarrow{Cu\ /\ 573K} CH_3CHO + H_2$

Ethanal

→ Method is suitable for dehydrogenation of volatile alcohol

(B) PREPARATION OF KETONES

① By oxidation of 2° alcohols

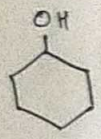
→ Strong oxidising agents such as acidified $KMnO_4/K_2Cr_2O_4$ or CrO_3 in anhydrous medium, oxidises 2° alcohol to corresponding ketone.

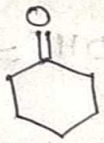
$$R-\underset{OH}{\underset{|}{CH}}-R' + [O] \xrightarrow[\text{or } CrO_3]{KMnO_4/H^+ \text{ or } K_2Cr_2O_4/H^+} R-\overset{O}{\overset{||}{C}}-R' + H_2O$$

Ketone

Eg $CH_3-\underset{OH}{\underset{|}{CH}}-CH_3 + [O] \xrightarrow[\text{or } CrO_3]{KMnO_4/H^+ \text{ or } K_2Cr_2O_4/H^+} CH_3-\overset{O}{\overset{||}{C}}-CH_3 + H_2O$

Acetone / propanone



$+ [O] \xrightarrow[\text{or } CrO_3]{KMnO_4/H^+ \text{ or } K_2Cr_2O_4/H^+}$  $+ H_2O$

Cyclohexanone

② Dehydrogenation

→ Vapours of 2° alcohol passed over heated Cu / Ag at 573 K

$$R-\underset{OH}{\underset{|}{CH}}-R' \xrightarrow{Cu\ /\ 573K} R-\overset{O}{\overset{||}{C}}-R' + H_2$$

Eg $CH_3CH_2-\underset{OH}{\underset{|}{CH}}-CH_3 \xrightarrow{Cu\ /\ 573K} CH_3CH_2-\overset{O}{\overset{||}{C}}-CH_3 + H_2$

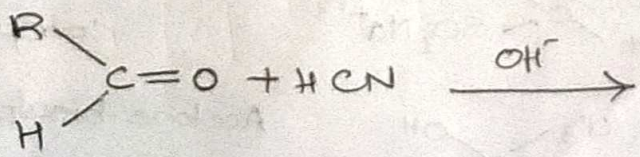
2-Butanone

NUCLEOPHILIC ADDITION REACTIONS OF ALDEHYDE AND KETONES

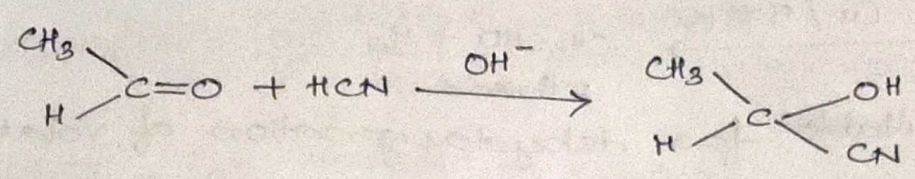
→ Bcz carbonyl grp is polar & C atom is e^- deficient so nucleophile attack

① Addition of HCN

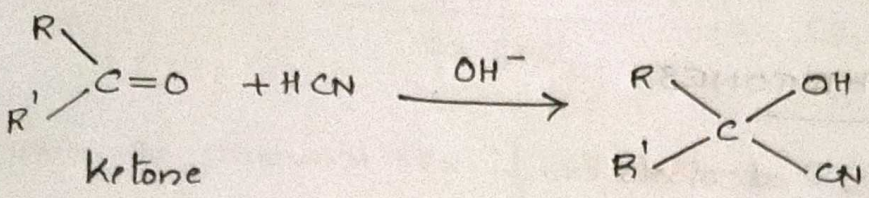
→ Aldehyde & Ketone with HCN in presence of base to form Cyanohydrin



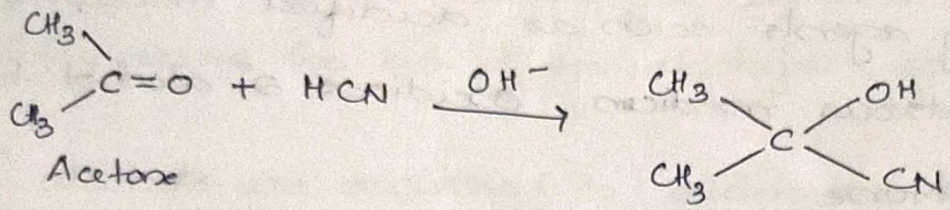
Aldehyde Cyanohydrin

Eg: 

Acetaldehyde - cyanohydrin



Ketone Cyanohydrin

Eg: 

→ The reaction takes place slowly with pure HCN but faster in presence of base which easily generates CN^- (better nucleophile than HCN)

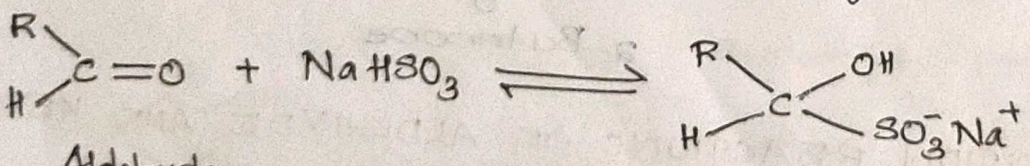
$$HCN + OH^- \rightleftharpoons CN^- + H_2O$$

② Addition of Sodium bisulphite

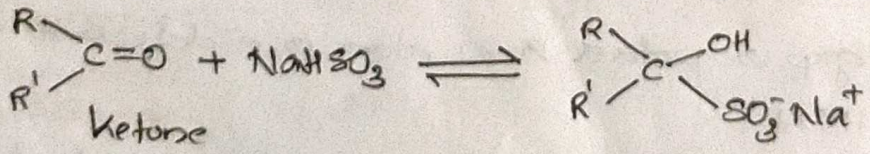
→ With sodium bisulphite they give crystalline addition product

→ Addition compound is water soluble & can be converted back to original compound by treating with dil. acid/alkali

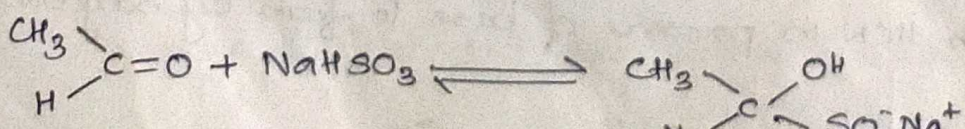
→ Helps in separation & purification of aldehydes



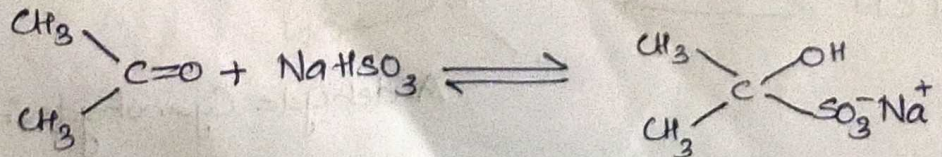
Aldehyde bisulphite compound



Ketone bisulphite compound



Acetaldehyde bisulphite compound



Acetone-bisulphite compound

Comparison of rate of nucleophilic addition for aliphatic aldehyde and ketones

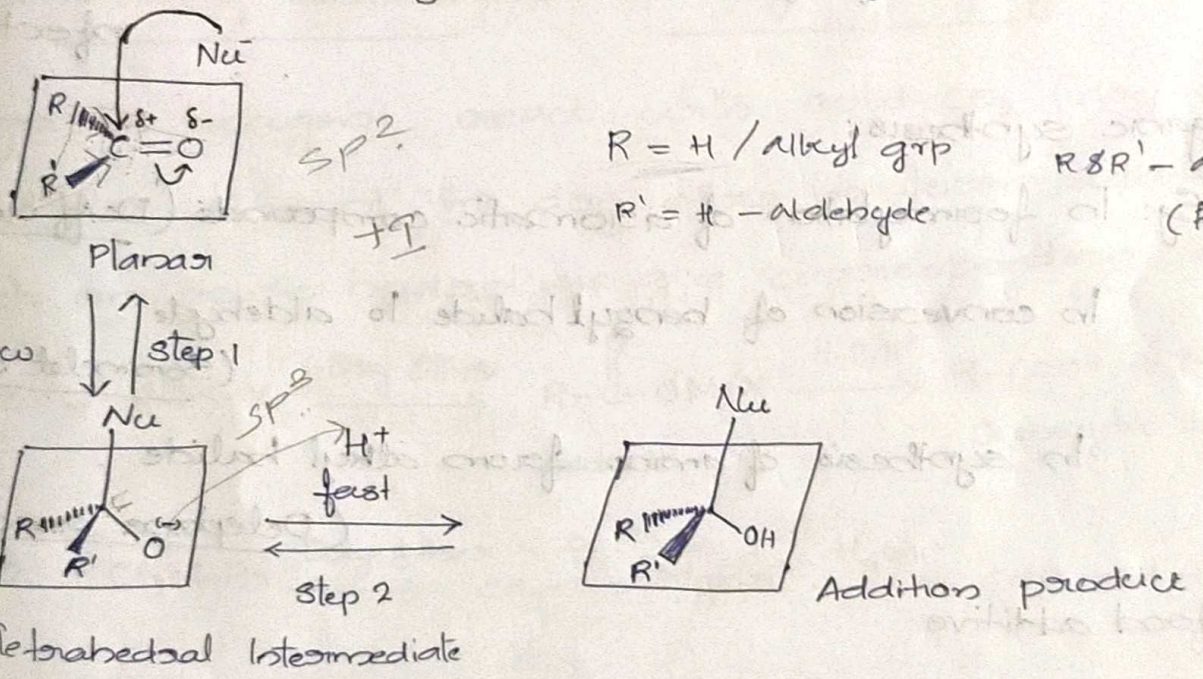
Mechanism can be depicted as:

step 1: Nucleophile attack 'c' atom approximately in a direction perpendicular to the plane of sp^2 hybrid orbitals of the carbonyl carbon.

Hybridisation of carbon changes from sp^2 to sp^3

Tetrahedral alkoxide intermediate is formed.

step 2: Intermediate captures a proton from the reaction medium to give the electrically neutral product.



R = H / alkyl grp

R' = H – aldehyde

R & R' – alkyl groups (Ketones)

Tetrahedral Intermediate

Addition product

→ Ketones are less reactive than aldehydes in nucleophilic addition reaction due to steric and electronic reasons.

As a result.

(i) Approach of nucleophile to carbonyl carbon is sterically hindered more in ketone than in aldehydes and

(ii) due to the electron-releasing (+I) nature of each alkyl groups the electrophilicity of carbonyl group is more decreased in ketone than in aldehydes. ∴ Nucleophile attack is easier on aldehyde than on ketones

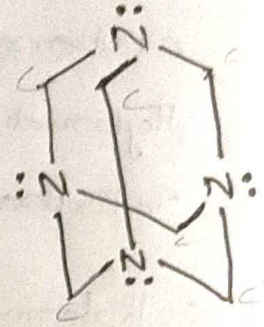
Urotropine (Hexamethylene tetramine) $(CH_2)_6N_4$

Preparation:

→ Formaldehyde react with NH_3 in gas phase to give the white crystalline compound urotropine

$$6\,H\text{-}CHO + 4\,NH_3 \longrightarrow (CH_2)_6N_4 + 6\,H_2O$$

Urotropine
(Hexamethylene tetramine)



Uses:

① In medicine: Drug for the treatment of urinary tract infection

② In organic synthesis:

Eg: In formylation of aromatic compounds (Duff reaction)

In conversion of benzyl halide to aldehyde (Sommelet rxn)

In synthesis of amine from alkyl halide (Delephine reaction)

③ As a food additive

④ As solid fuel:

Together with 1,3,5-trioxane, urotropine is a component of hexamine fuel tablets used by campers and military personnel. This fuel burns smokelessly with a high calorific value without leaving any ash

CARBOXYLIC ACIDS

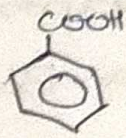
→ Compound containing (-COOH) group $R-\overset{O}{\overset{\|}{C}}-OH$

→ classified as mono-, di-, tri- or polycarboxylic acids depending upon the no. of carboxyl group.

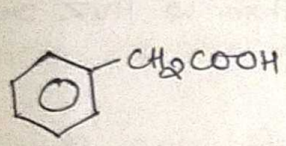
Eg: $H-COOH$ — formic acid (Methanoic acid)

CH_3CH_2COOH — propanoic acid

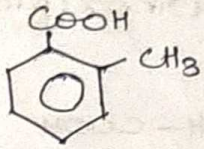
$CH_3-\underset{CH_3}{CH}-COOH$ — 2-methyl propanoic acid



Benzoic acid



2-phenyl ethanoic acid



2-methyl benzoic acid

Preparation of carboxylic acid — from grignard reagent

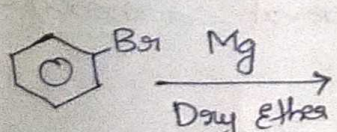
Grignard reagent react with solid CO_2 (dry ice) in equimolar amount in dry ether to form addition product which on acidic hydrolysis give corresponding acid.

$$O=C=O + R-Mg-X \xrightarrow{\text{Dry Ether}} R-\overset{O}{\overset{\|}{C}}-O^{-}Mg^{+}X \xrightarrow{H_2O/H^+} R-COOH + Mg(OH)X$$

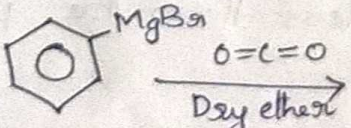
Dry ice — Adduct — Carboxylic acid

$$O=C=O + CH_3MgBr \xrightarrow{\text{Dry Ether}} CH_3-\overset{O}{\overset{\|}{C}}-O^{-}Mg^{+}Br \xrightarrow{H_2O/H^+} CH_3COOH + Mg(OH)Br$$

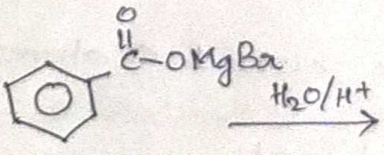
→ Since grignard reagent is prepared from alkyl halide this method is useful for converting alkyl halide into corresponding carboxylic acid having one C atom more than that present in alkyl halides



Bromobenzene



Phenyl magnesium bromide (grignard reagent)



Adduct — Benzoic acid

Some Reactions of Carboxylic acids

① α-Halogenation — Hell-Volhard-Zelinsky reaction / HVZ reaction

→ Carboxylic acid having α-hydrogen is treated with Cl_2 or Br_2 in the presence of small amount of red phosphorus the α-hydrogen is replaced by chlorine or bromine to yield α-halogenated carboxylic acids. This is HVZ reaction.

$$R-CH_2-COOH \xrightarrow[-HX]{X_2/\text{Red P}} R-\underset{\underset{X}{|}}{CH}-COOH \quad (X = Cl \text{ or } Br)$$

Carboxylic acid — α-Halocarboxylic acid

Eg: $CH_3CH_2COOH \xrightarrow[-HBr]{Br_2/\text{red P}} CH_3-\underset{\underset{Br}{|}}{CH}-COOH$

→ On excess of halogen, in HVZ reaction, the α-hydrogens are successively replaced by halogens.

Eg: $CH_3COOH \xrightarrow[-HCl]{Cl_2/\text{red P}} CH_2Cl-COOH \xrightarrow[-HCl]{\text{red P}/Cl_2} CHCl_2-COOH \xrightarrow[-HCl]{\text{red P}/Cl_2} CCl_3-COOH$

Acetic acid — Monochloro acetic acid — Dichloro acetic acid — Trichloro acetic acid

② Decarboxylation

(A) Action of soda lime on sodium carboxylates

→ When the sodium salt of an aliphatic saturated mono carboxylic acid is fused with soda lime (3:1, NaOH & CaO) an alkane with 1 C atom less than the parent carboxylic acid is obtained.

→ Rxn involve the removal of CO_2 from carboxyl group known as decarboxylation

$$R-COONa + NaOH \xrightarrow[\Delta]{CaO} R-H + Na_2CO_3$$

Eg: $CH_3-COONa + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$

(B) Kolbe's electrolytic method

Electrolysis of a concentrated solution of Na or K salt of a carboxylic acid or electrolysis gives an alkane containing even no. of C atoms at the anode

$$2\,R-COONa \xrightarrow[\text{Electrolysis}]{+2H_2O} R-R + 2CO_2 + 2NaOH + H_2$$

Eg: Conc. aqeous solution of sodium acetate is electrolysed ethane is obtained at the anode.

$$2\,CH_3-COONa \xrightarrow[\text{Electrolysis}]{+2H_2O} CH_3-CH_3 + 2CO_2 + 2NaOH + H_2$$