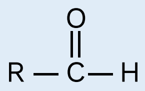
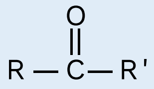
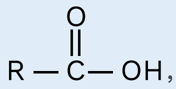
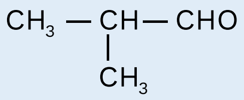
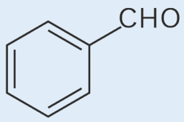
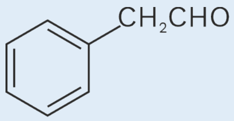
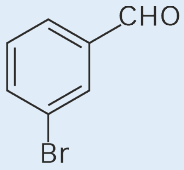
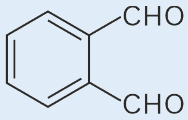
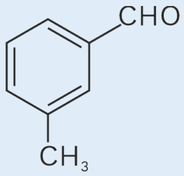
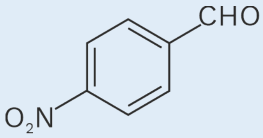
Aldehydes, Ketones and Carboxylic Acid

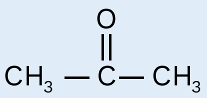
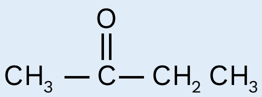
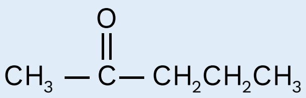
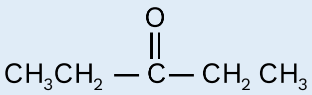
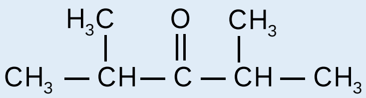
Introduction

Aldehydes	 $R-\overset{\overset{O}{\|}}{C}-H$, where R=H, alkyl or aryl group
Ketones	 $R-\overset{\overset{O}{\|}}{C}-R'$, where R and R' may be same or different alkyl or aryl group
Carboxylic acids	 $R-\overset{\overset{O}{\|}}{C}-OH$, where R=H or any alkyl or aryl group.

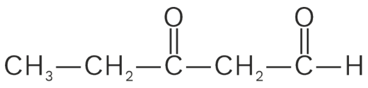
Examples

Aliphatic Aldehydes	IUPAC Name	Common Name
HCHO	Methanal	Formaldehyde
CH_3CHO	Ethanal	Acetaldehyde
CH_3CH_2CHO	Propanal	Propionaldehyde
$CH_3CH_2CH_2CHO$	Butanal	Butyraldehyde
 $CH_3-\underset{\underset{CH_3}{\vert}}{CH}-CHO$	2-Methylpropanal	Isobutyraldehyde
$CH_2=CHCHO$	Prop-2-enal	Acrolein

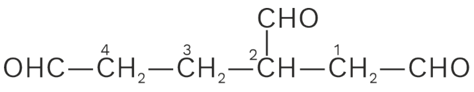
Aromatic Aldehydes	**IUPAC Name**	**Common Name**
	Benzaldehyde or Benzenecarbaldehyde	Benzaldehyde or Benzenecarbaldehyde
	2-Phenylethanal	Phenylacetaldehyde
	3-Bromobenzaldehyde or 3-Bromobenzene-carbaldehyde	m-Bromobenzaldehyde or m-Bromobenzene-carbaldehyde
	Benzene-1, 2-dicarbaldehyde	Phthaldehyde
	m-Methylbenzaldehyde or m-Tolualdehyde	m-Methylbenzaldehyde or m-Tolualdehyde
	p-Nitrobenzenecarbaldehyde	4-Nitrobenzenecarbaldehyde

Aliphatic Ketones	IUPAC Name	Common Name
 $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$	Propanone	Dimethyl ketone or Acetone
 $CH_3-\overset{O}{\overset{\|}{C}}-CH_2\,CH_3$	Butan-2-one or Butanone	Ethyl methyl ketone
 $CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_3$	Pentan-2-one	Methyl n-propyl ketone
 $CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH_2\,CH_3$	Pentan-3-one	Diethyl ketone
 $CH_3-\overset{H_3C}{\overset{\|}{C}H}-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\overset{\|}{C}H}-CH_3$	2, 4-Dimethylpentan-3-one	Di-isopropyl ketone

Q.1 Write down the IUPAC name of the following compound

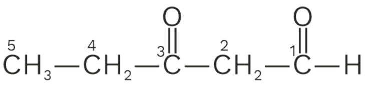
(a) 

$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-H$

(b) 

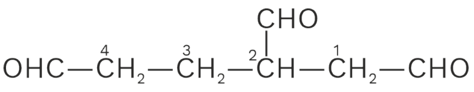
$OHC-\overset{4}{C}H_2-\overset{3}{C}H_2-\overset{2}{\overset{CHO}{\overset{|}{C}H}}-\overset{1}{C}H_2-CHO$

A.1

(a) 

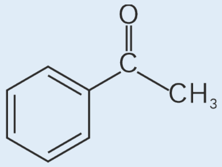
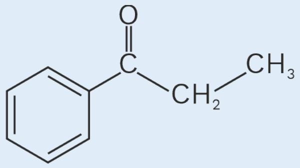
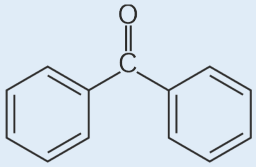
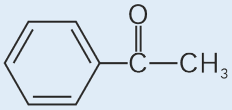
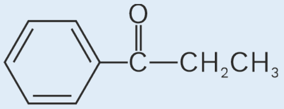
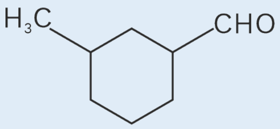
$\overset{5}{C}H_3-\overset{4}{C}H_2-\overset{3}{\overset{O}{\overset{\|}{C}}}-\overset{2}{C}H_2-\overset{1}{\overset{O}{\overset{\|}{C}}}-H$

the IUPAC name is 3-Oxopentanal

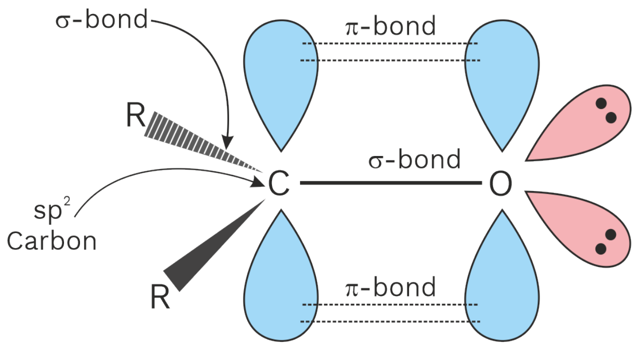
(b) 

$OHC-\overset{4}{C}H_2-\overset{3}{C}H_2-\overset{2}{\overset{CHO}{\overset{|}{C}H}}-\overset{1}{C}H_2-CHO$

the IUPAC name is Butane-1, 2, 4-tricarbaldehyde

Aliphatic Ketones	IUPAC Name	Common Name
	Methyl phenyl ketone or Acetophenone	Methyl phenyl ketone or Acetophenone
	Ethyl phenyl ketone or Propiophenone	Ethyl phenyl ketone or Propiophenone
	Diphenyl ketone or Benzophenone	Diphenyl ketone or Benzophenone
	1-Phenylethan-1-one	Methyl phenyl ketone
	1-Phenylpropan-1-one	Ethyl phenyl ketone
	γ-methylcyclohexane-carbaldehyde	3-methylcyclohexane-carbaldehyde

Orbital Structure of Aldehyde and Ketone



One of the sp²-orbital of carbon overlap with a p-orbital oxygen forming a C—O, sp²-p, σ-bond. The remaining two sp²-orbitals of the carbon atom form two additional σ-bond either by overlappping with 1s-orbital of two H-atom as in formaldehyde, or with 1s-orbital of one hydrogen atom and one sp³-orbital of an alkyl group in aldehyde other than formaldehyde or with two sp³-orbitals of two alkyl groups in ketones. All the three σ-bonds lie in the same plane and are inclined to one another at an angle of 120°.

The two half-filled $2p_z$-orbitals, one each on carbon and oxygen atom, overlap sideways to form a π-bond. The electron cloud of the π-bond lies both above and below the C—O, σ-bond.

Physical properties (Aldehyde and Ketone)

1. Smell

The lower aldehydes pungent unpleasant odour, as the size of the molecule increases, the odour becomes less pungent and more fragrant.

2. Solubility

Aldehydes and ketones upto four carbon atoms eg. ethanal. propanone, propanal, butanal, etc. are soluble in water due to H-bonding. As the size of the R (alkyl group) increases solubility decreases. Solubility of aromatic aldehydes and ketones is lower than that of corresponding aliphatic aldehydes and ketones.

Concept Ladder

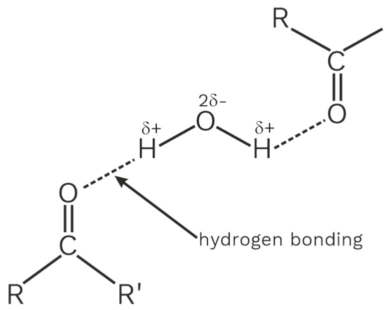
The magnitude of positive charge on the carbonyl carbon is more in aldehydes than in ketones. It is due to smaller +I effect of one alkyl group in aldehydes as compared to larger +I effect of two alkyl groups, as a result, nucleophilic addition reaction occur more readily in aldehydes than in ketones.

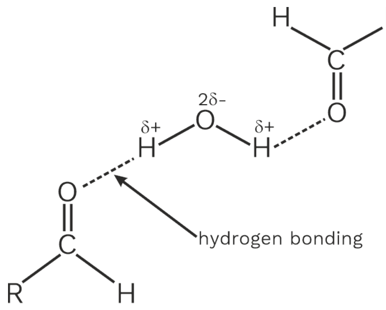
Previous Year's Questions

Carboxylic acids have higher boiling points than aldehydes, ketones and even alcohols of comparable molecular mass. It is due to their

[NEET]

(1) formation of intramolecular H-bonding
(2) formation of carboxylate ion
(3) more extensive association of carboxylic acid via van der Waals' forces of attraction
(4) formation of intermolecular H-bonding





3. **Boiling point**

Aldehydes and ketones has weak intermolecular forces of attraction (dipole-dipole), so have low boiling point. Dipole-dipole intractions are, weaker than intermolecule H-bonding.

CH_3CH_2CHO < CH_3COCH_3 < CH_3COOH < $CH_3CH_2CH_2OH$

Propanal (mol. Mass 58) b.p. 322 K

Propanone (Mol. mass b.p. 329 K

Ethanoic acid (Mol. mass 60) b.p. 391 K

Propan-1-ol (Mol. mass 60) b.p. 370 K

Preparation (Aldehydes and Ketones)

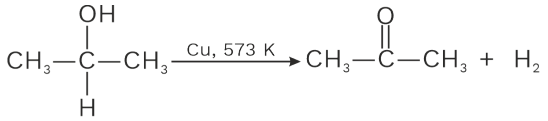
1. **From alcohols**

When the vapours of alcohol are passed over the copper at 300°C:

(a) $R-CH_2OH \xrightarrow{Cu/300°C} R-CHO + H_2$

eg. $\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow{Cu,\ 573K} \underset{\text{Acetaldehyde}}{CH_3CHO} + H_2$

(b) $R_2CHOH \xrightarrow{Cu/300°C} R-CO-R + H_2$



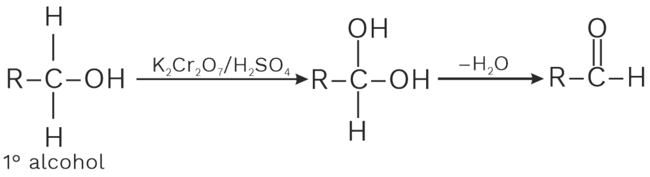
eg. $CH_3-\overset{OH}{\underset{H}{C}}-CH_3 \xrightarrow{Cu,\ 573\ K} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + H_2$

Rack your Brain

There is a large difference in the boiling point of butanal and butan-1-ol?

From oxidation of alcohols

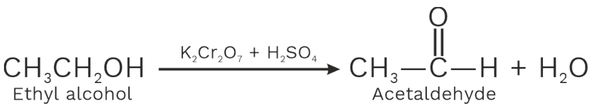
- 1°-Alcohol: A primary alcohol gives aldehyde on oxidation by using acidic $K_2Cr_2O_7$ or pyridinium chlorochromate ($CrO_3.C_5H_5N.HCl$) etc.



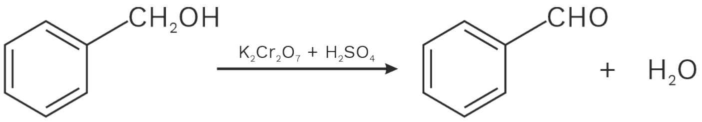
$$\underset{1°\ \text{alcohol}}{R-\overset{H}{\underset{H}{C}}-OH} \xrightarrow{K_2Cr_2O_7/H_2SO_4} R-\overset{OH}{\underset{H}{C}}-OH \xrightarrow{-H_2O} R-\overset{O}{\overset{\|}{C}}-H$$

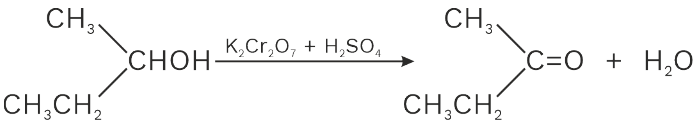
Concept Ladder

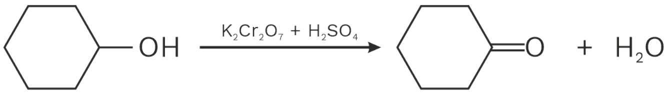
Selective oxidation of 1° alcohol to aldehydes are Collins's reagent ($CrO_3.2C_5H_5N$ in CH_2Cl_2), Sarett reagent ($CrO_3.2C_5H_5N$ in pyrdine), Corey's reagent ($CrO_3.C_5H_5N.HCl$) and Pyridinium dichromate $(C_5H_5NH^+)_2Cr_2O_7^{2-}$.

(a) 

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow{K_2Cr_2O_7\ +\ H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H} + H_2O$$

(b) 

(c) 

(d) 

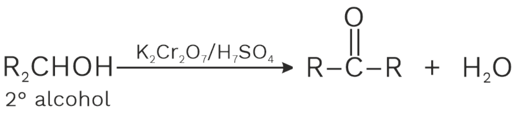
- CrO_3–pyridine/CH_2Cl_2 can also be used instead of $K_2Cr_2O_7$ + H_2SO_4. Here due to absence of H_2O aldehydrate is not formed so for their oxidation is not possible

$$\underset{\text{Ethyl alcohol}}{C_2H_5-OH+[O]} \xrightarrow[CH_2Cl_2,-H_2O]{CrO_3\text{–pyridine}} \underset{\text{Aldehyde(ethanal)}}{H_3C-CHO}$$

$$CH_2=CH-CH_2OH \xrightarrow[CH_2Cl_2]{PCC} CH_2=CH-CHO$$

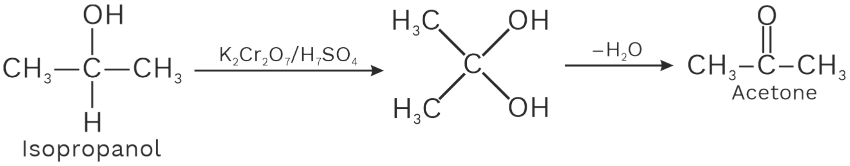
Note : Reaction does not occur at double bond. CrO_3–Pyridine is called **Sarett–Collin's Reagent** or **Sarett's Reagent**.

- 2°-Alcohols: A secondary alcohol gives ketone on oxidation by using acidic $K_2Cr_2O_7$ under extreme conditions.



$$\underset{2^\circ\ \text{alcohol}}{R_2CHOH} \xrightarrow{K_2Cr_2O_7/H_7SO_4} R-\overset{\overset{\displaystyle O}{\|}}{C}-R + H_2O$$

Example



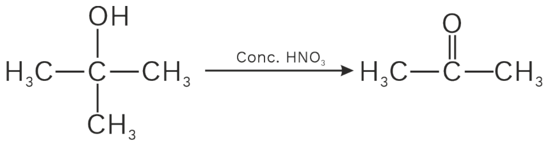
Previous Year's Questions

Ketones [$RCOR_1$] where R = R_1 = alkyl group. It can be obtained in one step by

[NEET]

(1) oxidation of tertiary alcohol
(2) reaction of acid halide with alcohols
(3) hydrolysis of esters
(4) oxidation of primary alcohol

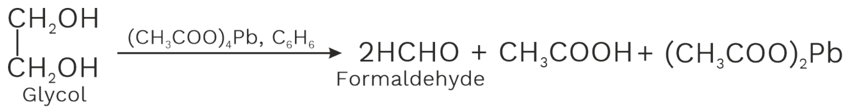
- 3°-Alcohol: A tertiary alcohol gives ketone on oxidation under extreme conditions.



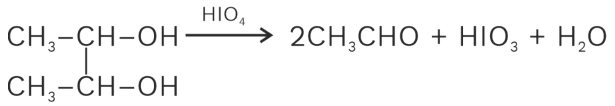
$$\mathrm{H_3C-\underset{CH_3}{\overset{OH}{C}}-CH_3 \xrightarrow{\text{Conc. } HNO_3} H_3C-\overset{O}{\overset{\|}{C}}-CH_3}$$

- 

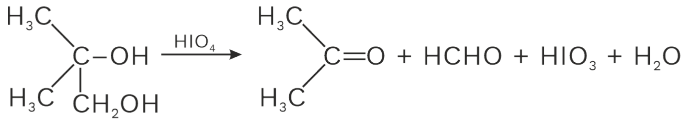
$$\underset{\text{Glycol}}{\begin{matrix}\mathrm{CH_2OH}\\ |\\ \mathrm{CH_2OH}\end{matrix}} \xrightarrow[\text{Periodic acid}]{\mathrm{HIO_4}} \underset{\text{Formaldehyde}}{\mathrm{2HCHO}} + \mathrm{HIO_3} + \mathrm{H_2O}$$



$$\underset{\text{Glycol}}{\begin{matrix}\mathrm{CH_2OH}\\ |\\ \mathrm{CH_2OH}\end{matrix}} \xrightarrow{\mathrm{(CH_3COO)_4Pb,\ C_6H_6}} \underset{\text{Formaldehyde}}{\mathrm{2HCHO}} + \mathrm{CH_3COOH} + \mathrm{(CH_3COO)_2Pb}$$



$$\begin{matrix}\mathrm{CH_3-CH-OH}\\ |\\ \mathrm{CH_3-CH-OH}\end{matrix} \xrightarrow{\mathrm{HIO_4}} \mathrm{2CH_3CHO + HIO_3 + H_2O}$$



2. From amines

$$\mathrm{RCH_2NH_2 \xrightarrow{Alk.\ KMnO_4} R{-}CH{=}NH \xrightarrow{H_2O} RCHO}$$

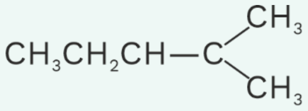
R (alkyl group) may be $-CH_3$, $-C_2H_5$ etc.

3. From hydrocarbons

Ozonolysis of alkenes followed by hydrolysis give aldehydes and ketones.

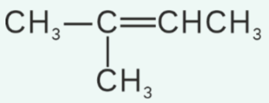
Previous Year's Questions

Which alkene on ozonolysis gives CH_3CH_2CHO and CH_3COCH_3? **[NEET]**

(1) 

(2) $CH_3CH_2CH\bar{C}HCH_2CH_3$

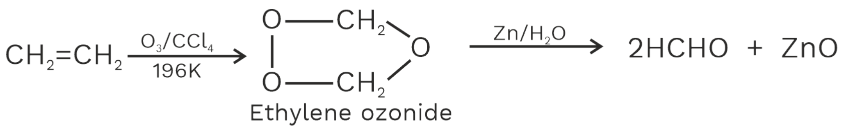
(3) $CH_3CH_2CH\bar{C}HCH_3$

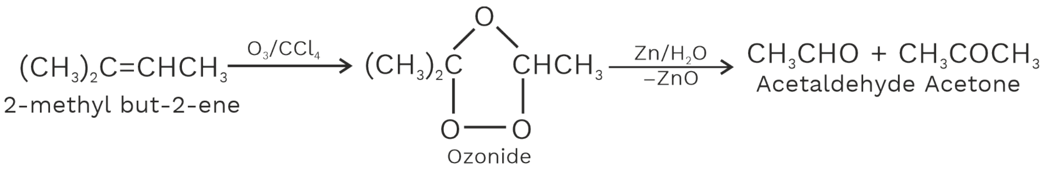
(4) 

$$CH_3-\underset{CH_3}{\underset{|}{C}}=CHCH_3$$

Examples,

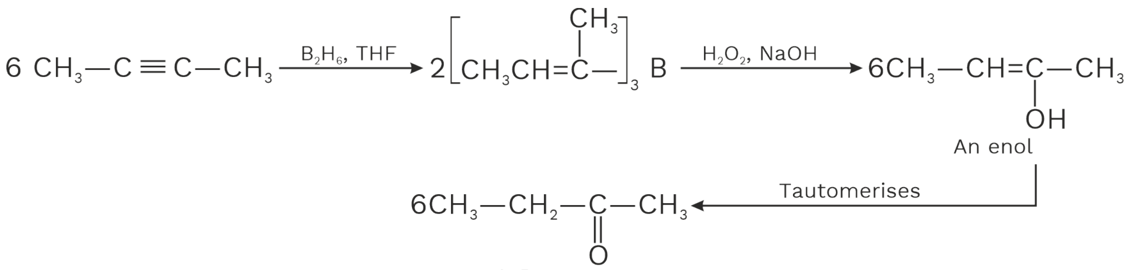
Ozonolysis

(a) 

(b) 

Hydroboration oxidation

(c)



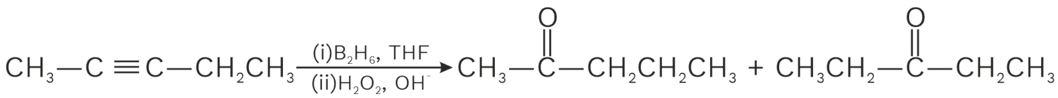
$$6\ CH_3-C\equiv C-CH_3 \xrightarrow{B_2H_6,\ THF} 2\left[CH_3CH=\overset{\displaystyle CH_3}{\overset{|}{C}}-\right]_3 B \xrightarrow{H_2O_2,\ NaOH} 6CH_3-CH=\underset{\underset{\displaystyle OH}{|}}{C}-CH_3$$

An enol

$$6CH_3-CH_2-\underset{\underset{\displaystyle O}{\|}}{C}-CH_3 \xleftarrow{\text{Tautomerises}}$$

2-Butanone

(d)

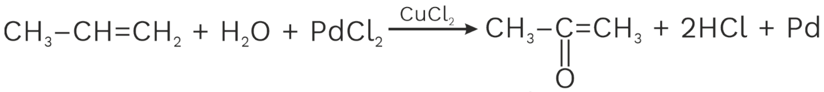


$$CH_3-C\equiv C-CH_2CH_3 \xrightarrow[\text{(ii)}H_2O_2,\ OH^-]{\text{(i)}B_2H_6,\ THF} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2CH_2CH_3 + CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2CH_3$$

2-Pentyne 2-Pentanone (major) 2-Pentanone (minor)

By Wacker method

$$CH_2 = CH_2 + H_2O + PdCl_2 \xrightarrow{CuCl_2} CH_3CHO + 2HCl + Pd$$



$$CH_3-CH=CH_2 + H_2O + PdCl_2 \xrightarrow{CuCl_2} CH_3-\underset{\underset{\displaystyle O}{\|}}{C}=CH_3 + 2HCl + Pd$$

Acetone

By the hydration of alkynes(Kucherov’s Reaction)

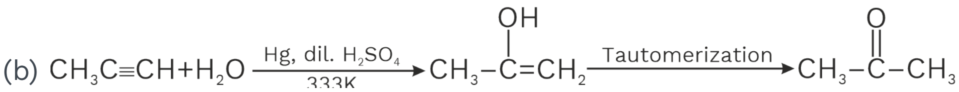
$$RC\equiv CH + H_2O \xrightarrow[333K]{Hg^{2+},\ dil.\ H_2SO_4} RH=CHOH \xrightarrow{\text{Tautomerization}} RCH_2CHO$$

Examples,

(a) $HC\equiv CH+H_2O \xrightarrow[333K]{Hg^{2+},\ dil.\ H_2SO_4} CH_2=CHOH \xrightarrow{\text{Tautomerization}} CH_3CHO$

Acetaldehyde

(b)

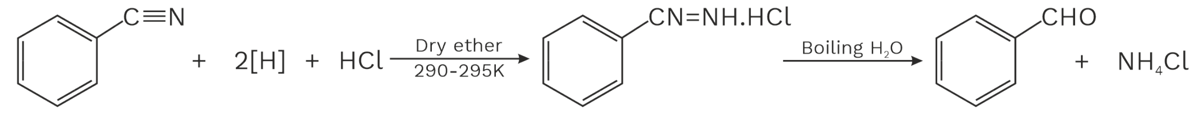


$$CH_3C\equiv CH+H_2O \xrightarrow[333K]{Hg,\ dil.\ H_2SO_4} CH_3-\overset{\overset{\displaystyle OH}{|}}{C}=CH_2 \xrightarrow{\text{Tautomerization}} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

4. From Nitriles and esters

$$CH_3-C\equiv N + 2[H] + KCl \xrightarrow[290-295K]{\text{Dry ether}} CH_3CH=NH.HCl \xrightarrow{\text{Boiling } H_2O} CH_3CHO + NH_4Cl$$

Acetonitrile Acetaldimine hydrochloride Acetaldehyde



Benzonitrile Benzaldimine hydrochloride Benzaldehyde

5. By hydrolysis of gem dihalides

$$RCHX_2 + 2KOH(aq.) \xrightarrow{-2KX} RCH(OH)_2 \xrightarrow{-H_2O} RCHO$$

1, 1-Dihaloalkane

Examples,

(a) $CH_3CHCl_2 + 2KOH(aq) \xrightarrow{-2KCl} [CH_3CH(OH)_2] \xrightarrow{-H_2O} CH_3CHO$

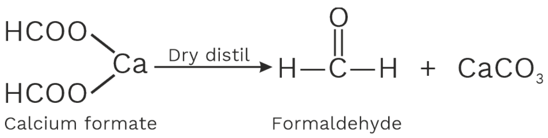
unstable — Acetaldehyde

(b) $(CH_3)_{21}C.Cl_2 + 2KOH\ (aq) \xrightarrow{-2KCl} (CH_3)_2C(OH)_2 \xrightarrow{-H_2O} CH_3{-}CO{-}CH_3$

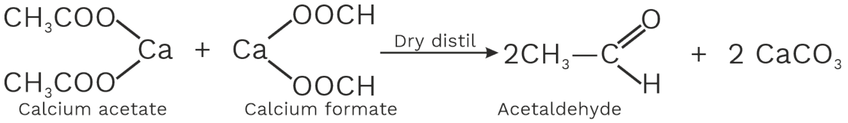
2, 2-Dichloroethane — Acetone

6. By decarboxylation of calcium salts of carboxylic acids

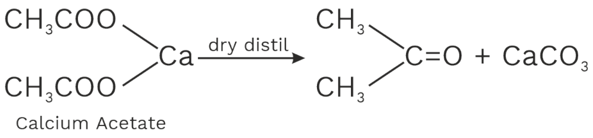
(a)



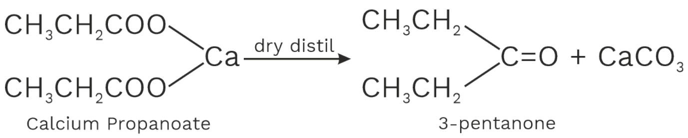
(b)



(c)



(d)



7. By catalytic decomposition of fatty acids:

When vapours of carboxylic acid (fatty acids) are passed over thoria or magnous oxide or heated alumina, carbonyl compounds are formed.

$$RCOOH + HCOOH \xrightarrow[400°C]{Al_2O_3} RCHO + H_2O + CO_2$$

$$CH_3COOH + HCOOH \xrightarrow[400°C]{Al_2O_3} CH_3CHO + H_2O + CO_2$$

$$2CH_3COOH \xrightarrow[500°C]{MnO} CH_3COCH_3 + H_2O + CO_2$$

Acetic acid — Acetone

Previous Year's Questions

In the reaction, $CH_3CN + 2[H] \xrightarrow[Ether]{HCl} X \xrightarrow{Boiling,\ H_2O} Y$; the term Y is

[NEET]

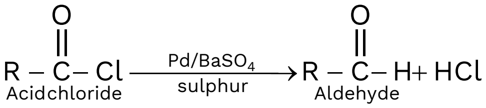
(1) acetaldehyde
(2) ethanamine
(3) acetone
(4) dimethylamine

Preparations for Aldehydes (Aliphatic Aldehyde)

1. **Rosenmund's reaction:**

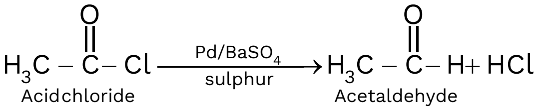
   Aldehydes can be formed by passing H_2 gas through a boiling solution of acid chloride in xylene in the presence Pd/$BaSO_4$.

- Here the catalyst (Pd/$BaSO_4$) is poisoned by sulphur or quinoline to avoid further reduction of aldehydes into alcohols.



$$\underset{\text{Acidchloride}}{R-\overset{\overset{O}{\|}}{C}-Cl} \xrightarrow[\text{sulphur}]{Pd/BaSO_4} \underset{\text{Aldehyde}}{R-\overset{\overset{O}{\|}}{C}-H} + HCl$$

Example,



$$\underset{\text{Acidchloride}}{H_3C-\overset{\overset{O}{\|}}{C}-Cl} \xrightarrow[\text{sulphur}]{Pd/BaSO_4} \underset{\text{Acetaldehyde}}{H_3C-\overset{\overset{O}{\|}}{C}-H} + HCl$$

Lithium tri-tert-butoxyaluminum hydride (LTBA) or S_nH_2 can also be used here.

Previous Year's Questions

A carbonyl compound reacts with hydrogen cyanide to form cyanohydrin which on hydrolysis forms a racemic mixture of α-hydroxy acid. The carbonyl compound is

[NEET]

(1) formaldehyde
(2) acetaldehyde
(3) acetone
(4) diethyl ketone

1. **From Grignard reagent:** RMgX (Grignard reagent) gives aldehyde only with HCN as follows:

$$\underset{\substack{\text{Hydrogen}\\ \text{cyanide}}}{HC\equiv N} + RMgI \xrightarrow{\text{dry ether}} HC=NMgI \xrightarrow{H^+/H_2O} \underset{\text{Aldehyde}}{RCHO} + NH_3 + MgOHI$$

2. **From Nitriles**

$$\underset{\text{Alkane nitrile}}{R-C\equiv N+2[H]} \xrightarrow{Sn/HCl} R-CH=NH \xrightarrow{H^+/H_2O} \underset{\text{Aldehyde}}{RCHO} + NH_3$$

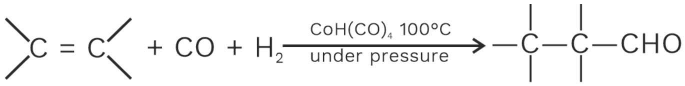
R (alkyl group) may be $-CH_3$, $-C_2H_5$ etc.

The above reaction is also known as Stephen's reduction

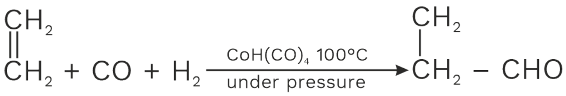
Example,

$$\underset{\text{Ethane nitrile}}{H_3C-C\equiv N+2[H]} \xrightarrow{Sn/HCl} \underset{\text{Imine}}{H_3C-CH=NH} \xrightarrow{H^+/H_2O} \underset{\text{Acetaldehyde}}{CH_3CHO} + NH_3$$

3. From Alkenes by oxo method



e.g.



$$\overset{CH_2}{\underset{CH_2}{\|}} + CO + H_2 \xrightarrow[\text{under pressure}]{CoH(CO)_4,\ 100°C} \overset{\overset{CH_2}{|}}{CH_2} - CHO$$

Previous Year's Questions

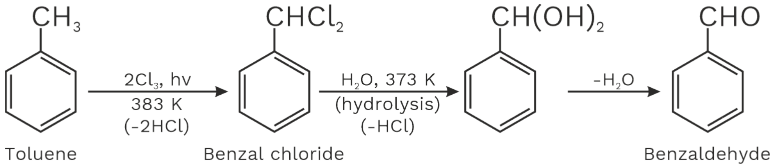
The oxidation of toluene to benzaldehyde by chromyl chloride is called **[NEET]**

(1) Etard reaction
(2) Riemer–Tiemann reaction
(3) Wurtz reaction
(4) Cannizzaro's reaction

Aromatic Aldehyde

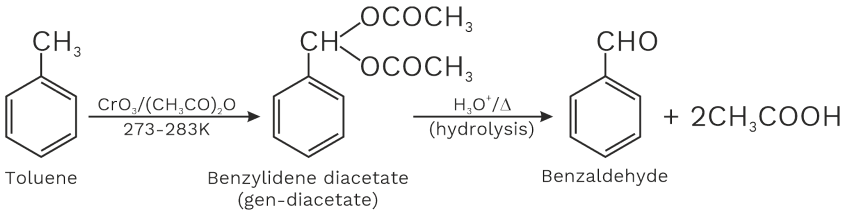
1. From side chain halogenation

(a)



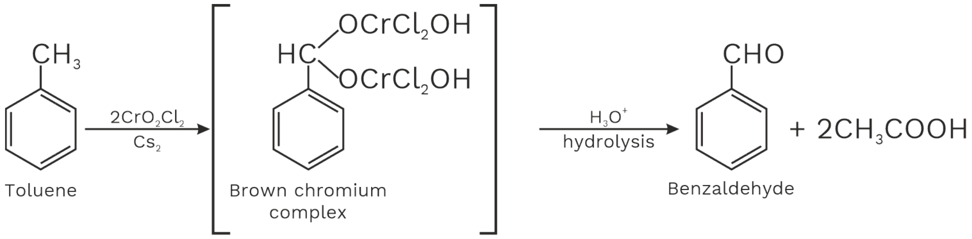
2. From gem-diacetate

(b)



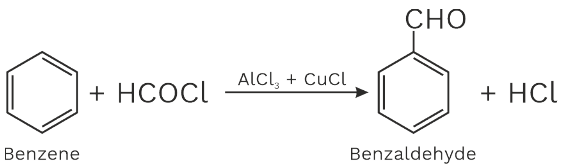
3. From Toluene

(c)



This reaction is also known as Etard reaction.

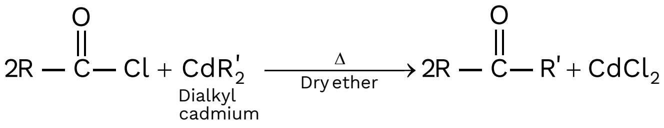
(d)



This reaction is called Gatterminann-Koch formylation.

Preparation for Ketones only

1. From organo metallics



$$2R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl+\underset{\text{Dialkyl cadmium}}{CdR'_2}\xrightarrow[\text{Dry ether}]{\Delta}2R-\overset{\overset{\displaystyle O}{\|}}{C}-R'+CdCl_2$$

R (alkyl group) may be $—CH_3$, $—C_2H_5$ etc.

2. From Grignard reagent:

From Grignard Reagent and Acid Chlorides:

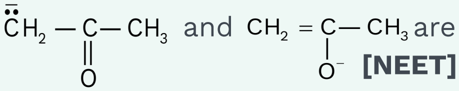
$R-CO-Cl + R'MgX \longrightarrow R-CO-R' + Mg(X)Cl$

R (alkyl group) may be $—CH_3$, $—C_2H_5$ etc.

Example,

$CH_3-CO-Cl + CH_3MgCl \longrightarrow CH_3COCH_3 + MgCl_2$

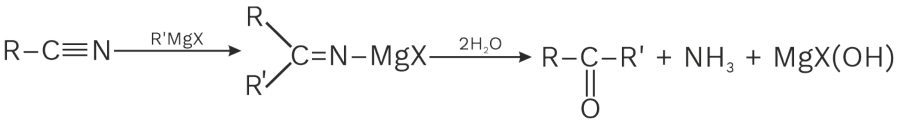
Previous Year's Questions



$\ddot{C}H_2-\underset{\underset{\displaystyle O}{\|}}{C}-CH_3$ and $CH_2=\underset{\underset{\displaystyle O^-}{|}}{C}-CH_3$ are **[NEET]**

(1) resonating structures
(2) tautomers
(3) geometrical isomers
(4) optical isomers

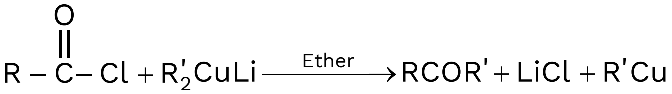
3. From nitriles



$$R-C\equiv N\xrightarrow{R'MgX}\begin{matrix}R\diagdown\\ R'\diagup\end{matrix}C=N-MgX\xrightarrow{2H_2O}R-\underset{\underset{\displaystyle O}{\|}}{C}-R'+NH_3+MgX(OH)$$

R and R' (alkyl group) may be $—CH_3$, $—C_2H_5$ etc.

4. From Dialkyl cuprates



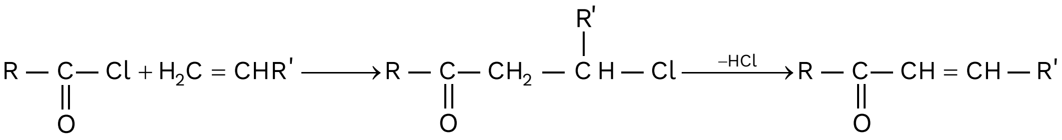
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl+R'_2CuLi\xrightarrow{\text{Ether}}RCOR'+LiCl+R'Cu$$

R and R' (alkyl group) may be $—CH_3$, $—C_2H_5$ etc.

Rack your Brain

Grignard reagent cannot be directly used in the reaction between acid chlorides/ acyl chlorides with dialkylcadmium?

5. From alkenes



$$R-\underset{\underset{\displaystyle O}{\|}}{C}-Cl+H_2C=CHR'\longrightarrow R-\underset{\underset{\displaystyle O}{\|}}{C}-CH_2-\overset{\overset{\displaystyle R'}{|}}{C}H-Cl\xrightarrow{-HCl}R-\underset{\underset{\displaystyle O}{\|}}{C}-CH=CH-R'$$

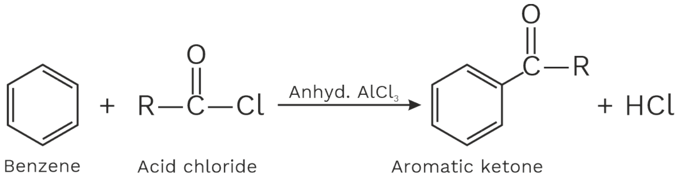
R and R' (alkyl group) may be $—CH_3$, $—C_2H_5$ etc.

Note:

It is the example of Markovnikov's addition initiated by $R-C^+=O$ (acylium cation).

Aromatic Ketones

Friedel-crafts acylation



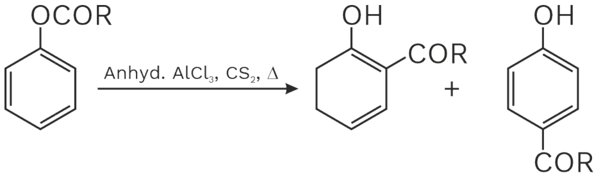
R (alkyl group) may be $—CH_3$, $—C_2H_5$, $—C_6H_5$, —Cl etc.

- This reaction is called Friedel-crafts acylation
- This reaction is the example of electrophilic substitution reaction.

Rack your Brain

Why ethylbenzene not prepared by simple alkylation of benzene?

Fries rearrangement



R (alkyl group) may be $—CH_3$, $—C_2H_5$, $—C_6H_5$ etc.

Chemical Properties

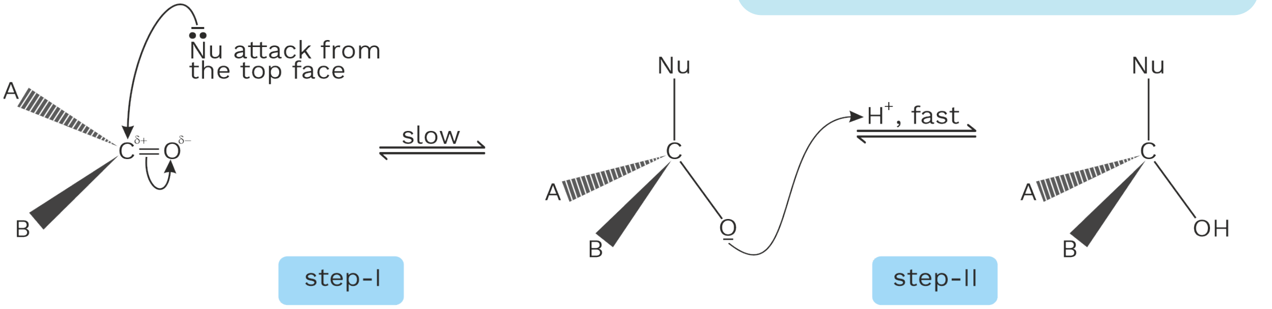
Reactions due to carbonyl group

Nucleophilic addition reactions

Due to the presence of carbonyl group aldehydes and ketones undergo nucleophilic addition reactions.

Concept Ladder

Carbonyl group (in case of aldehydes and ketones) acquires a small positive charge and hence acts as an electrophile (Lewis acid) while the carbonyl oxygen carries a small negative charge and hence behaves as a nucleophile (Lewis base). Thus, the carbonyl group is polar in a nature and that is why aldehyde and ketones have large moment (2.3 –2.8D)



- Reactivity of a carbonyl compound for nucleophilic addition reaction depends upon the magnitude of +ve charge present on the carbon atom of carbonyl group i.e., the reactivity is increased by electron attracting groups like $-NO_2$, $-CX_3$ and decreased by

Rack your Brain

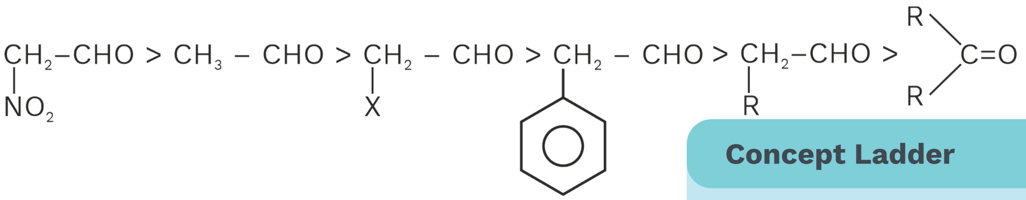
Why aldehydes are more reactive than ketones?

electron releasing groups like methyl, alkoxy groups.

- Reactivity for nucleophilic addition reaction for carbonyl compounds decreases as follows:

(1) $HCHO > CH_3CHO > CH_3CH_2CHO > CH_3COCH_3 > CH_3COC_2H_5 > C_2H_5COC_2H_5 > (CH_3)_3CCOC(CH_3)_3$

(2)



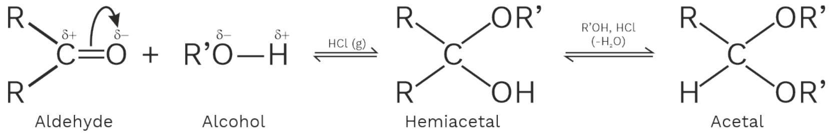
$\underset{NO_2}{CH_2}-CHO > CH_3-CHO > \underset{X}{CH_2}-CHO > \underset{C_6H_5}{CH_2}-CHO > \underset{R}{CH_2}-CHO > R_2C=O$

Concept Ladder

In case of nucleophilic addition reaction, nucleophile readily attacks the electrophilic carbon atom of the polar carbonyl group from a direction approximately perpendicular to the plane of the sp^2-hybridized orbitals of the carbonyl carbon.

1. Acetal and ketal formation

Aldehydes react with one equivalent of a monohydric alcohol in the presence of dry hydrogen chloride gas to yield first alkoxyalcohol intermediates called hemiacetals. These then react with one more molecule of alcohol to give gem-dialkoxy compounds known as acetals.



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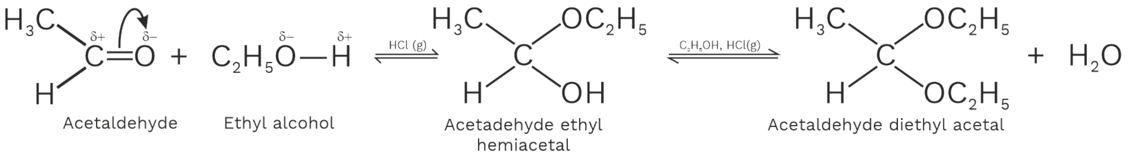
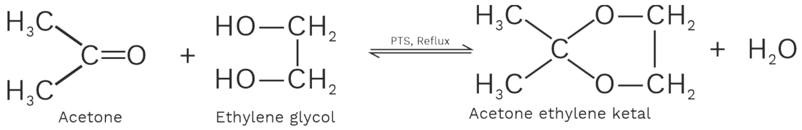
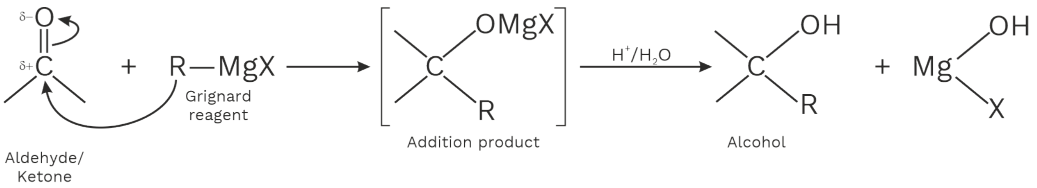
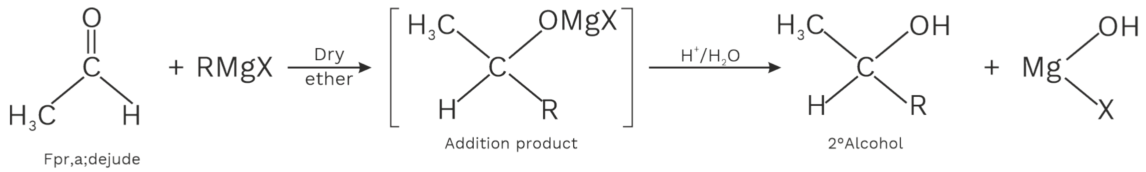
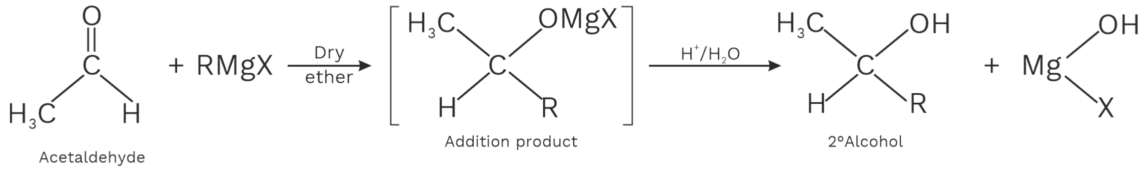




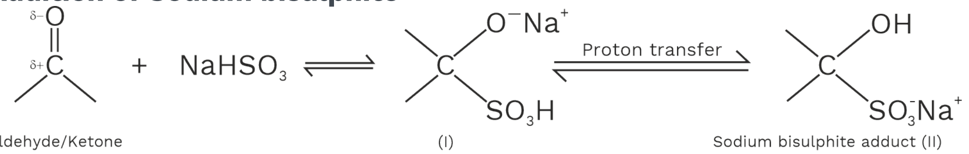
2. Addition of Grignard reagent

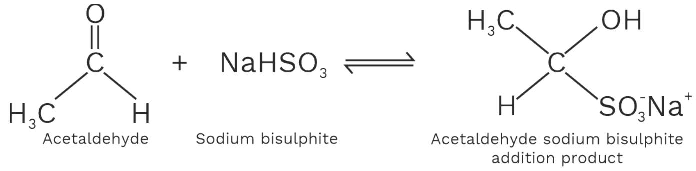


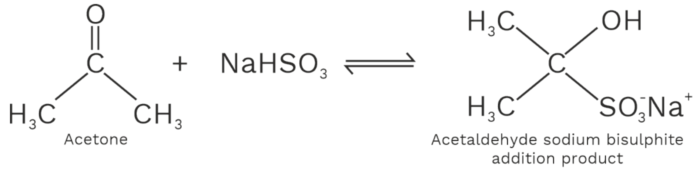




3. Addition of Sodium bisulphite





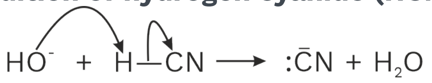


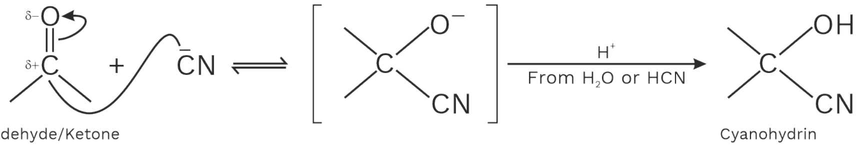
Previous Year's Questions

The product formed by the reaction of an aldehyde with a primary amine is **[NEET]**

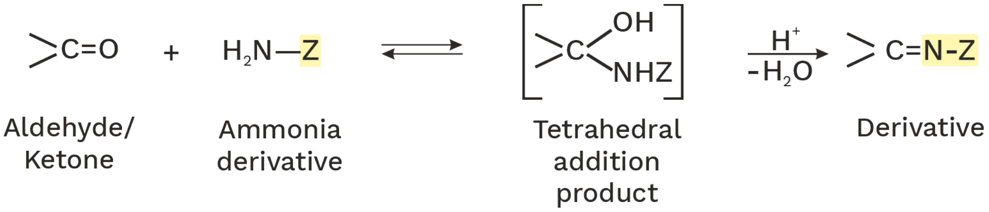
(1) carboxylic acid
(2) aromatic acid
(3) Schiff 's base
(4) ketone.

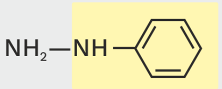
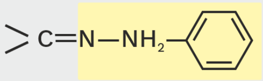
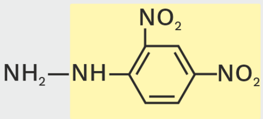
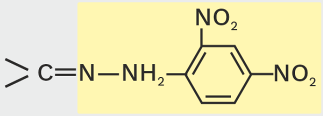
4. Addition of hydrogen cyanide (HCN)

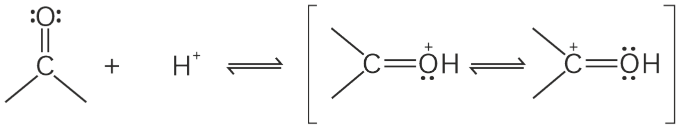


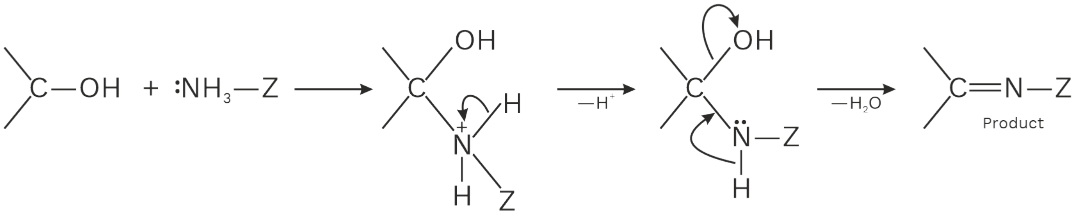


5. Addition of amonia derivatives

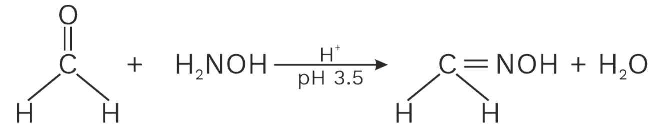


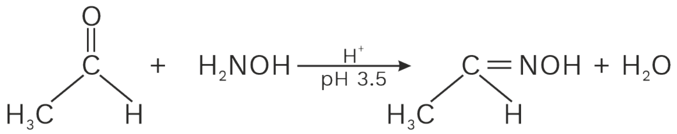
Ammonia (derivative used)		Product obtained	
Structure	**Name**	**Structure**	**Name**
$NH_2—NH_2$	Hydrazine	$>C=N—NH_2$	Hydrazone
$NH_2—OH$	hydroxylamine	$>C=N—OH$	Oxime
	Phenylhydrazine		Phenylhydrazone
$NH_2—CONHNH_2$	Semicarbazide	$>C=NNHCONH_2$	Semicarbazone
	2, 4-dinitro-Phenylhydrazine (DNP) (Brady's reagent)		2, 4-dinitrophenyl-hydrazone (DNP derivative)


Protonated carbonyl group



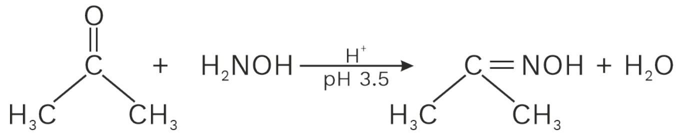
(a) Reaction with hydroxylamine


Methanal Hydroxylamine Methanal oxime


Ethanal Hydroxylamine Ethanal oxime

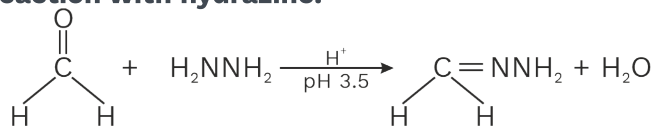
Concept Ladder

Aldehydes and ketones is catalysed by acids. In acidic medium weak nucleophiles like ammonia derivatives readily attack the carbonyl group, if medium is to acidic ammonia derivative being basic in nature will form their respective ammonium salts.

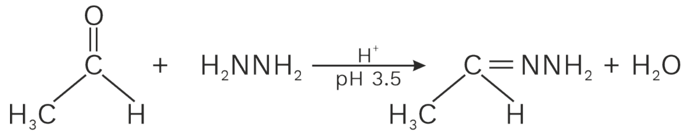


Propanone Hydroxylamine Propanone oxime

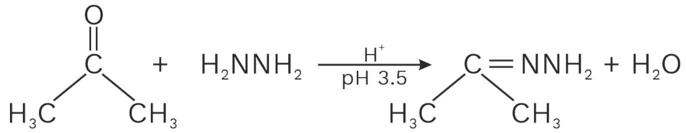
(b) Reaction with hydrazine.



Methanal Hydrazine Methanal hydrazone

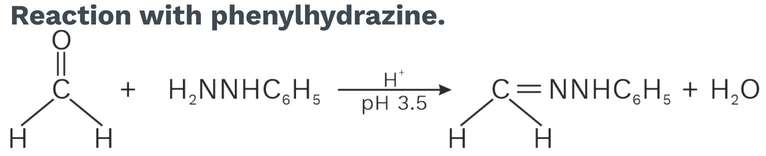


Ethanal Hydrazine Ethanal hydrazone

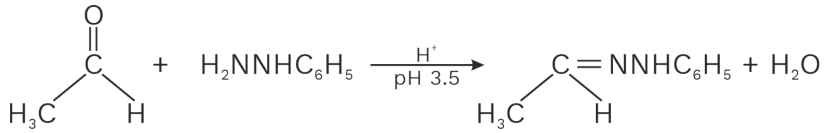


Propanone Hydrazine Propanone hydrazone

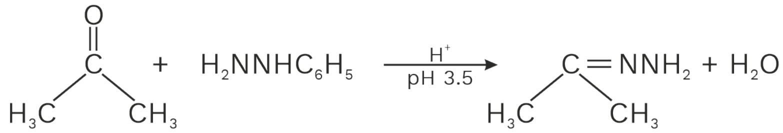
(c) Reaction with phenylhydrazine.



Methanal Phenylhydrazine Methanal phenylhydrazone



Ethanal Phenylhydrazine Ethanal phenylhydrazone



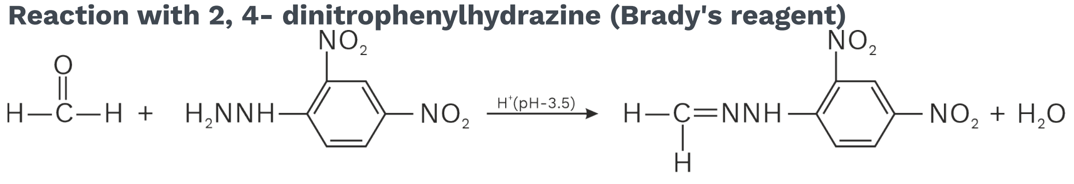
Propanone Phenylhydrazine Propanone phenylhydrazone

Previous Year's Questions

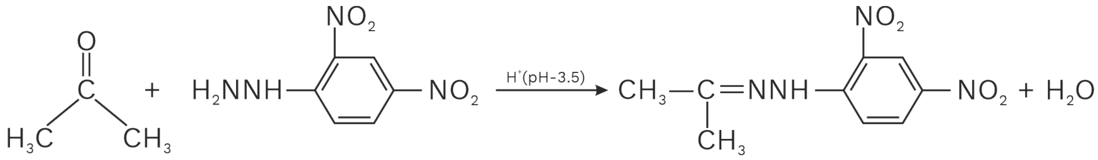
Reaction of a carbonyl compound with one of the following reagents involves nucleophilic addition followed by elimination of water. The reagent is **[NEET]**

(1) hydrazine in presence of feebly acidic solution
(2) hydrocyanic acid
(3) sodium hydrogen sulphite
(4) a Grignard reagent

(d) Reaction with 2, 4- dinitrophenylhydrazine (Brady's reagent)

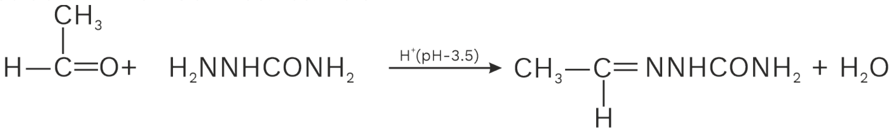


Ethanal 2, 4-dinitrophenylhydrazine Ethanal 2, 4-dinitrophenylhydrazone



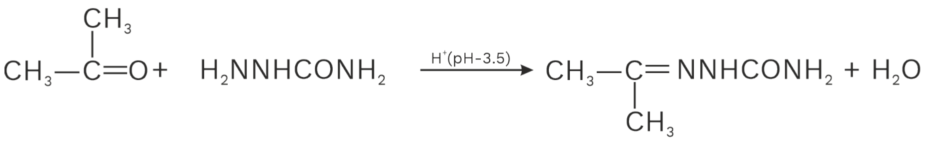
Propanone 2, 4-dinitrophenylhydrazine Propanone 2, 4-dinitrophenylhydrazone

(e) Reaction with semicarbazide



$$H-\underset{}{\overset{CH_3}{\overset{|}{C}}}=O + H_2NNHCONH_2 \xrightarrow{H^+(pH-3.5)} CH_3-\underset{\underset{H}{|}}{C}=NNHCONH_2 + H_2O$$

Ethanal Semicarbazide Ethanal semicarbazone

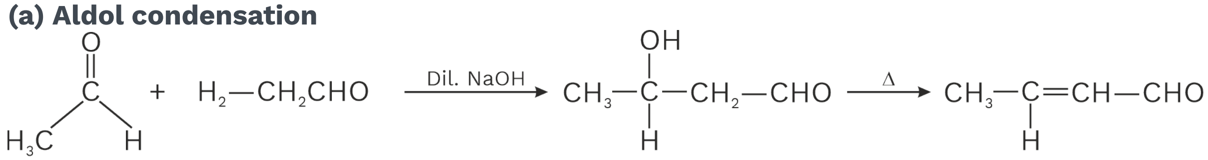


$$CH_3-\overset{CH_3}{\overset{|}{C}}=O + H_2NNHCONH_2 \xrightarrow{H^+(pH-3.5)} CH_3-\underset{\underset{CH_3}{|}}{C}=NNHCONH_2 + H_2O$$

Propanone Semicarbazide Propanone semicarbazone

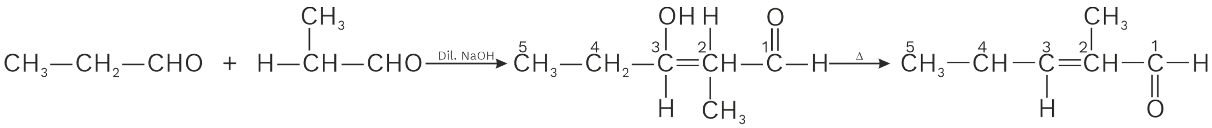
Important naming reactions

1. (a) Aldol condensation



$$CH_3CHO + H_2-CH_2CHO \xrightarrow{\text{Dil. NaOH}} CH_3-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2-CHO \xrightarrow{\Delta} CH_3-\underset{\underset{H}{|}}{C}=CH-CHO$$

Ethanal or Acetaldehyde 3-Hydroxybutanal (Aldol) But-2-enal



$$CH_3-CH_2-CHO + H-\overset{\overset{CH_3}{|}}{C}H-CHO \xrightarrow{\text{Dil. NaOH}} \overset{5}{C}H_3-\overset{4}{C}H_2-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{\overset{3}{C}}}-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{\overset{2}{C}}}-\overset{\overset{O}{\|}}{\overset{1}{C}}-H \xrightarrow{\Delta} \overset{5}{C}H_3-\overset{4}{C}H-\underset{\underset{H}{|}}{\overset{3}{C}}=\overset{\overset{CH_3}{|}}{\overset{2}{C}}H-\underset{\underset{O}{\|}}{\overset{1}{C}}-H$$

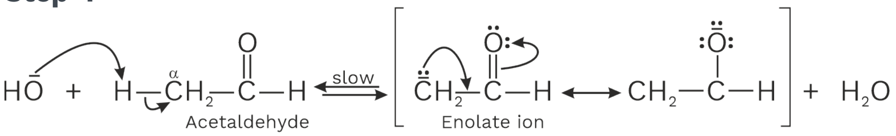
Propanal or Propionaldehyde
(two molecules)

3-Hydroxy-2-methylpentanal (Aldol)

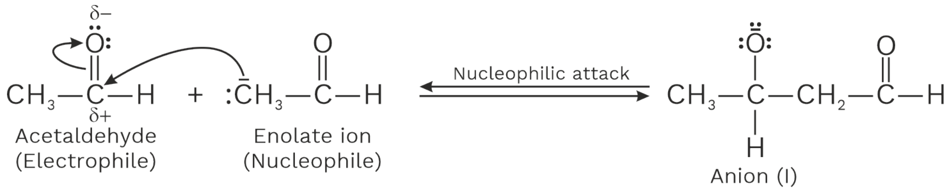
2-methyl pent-3-enal

Mechanism of aldol condensation

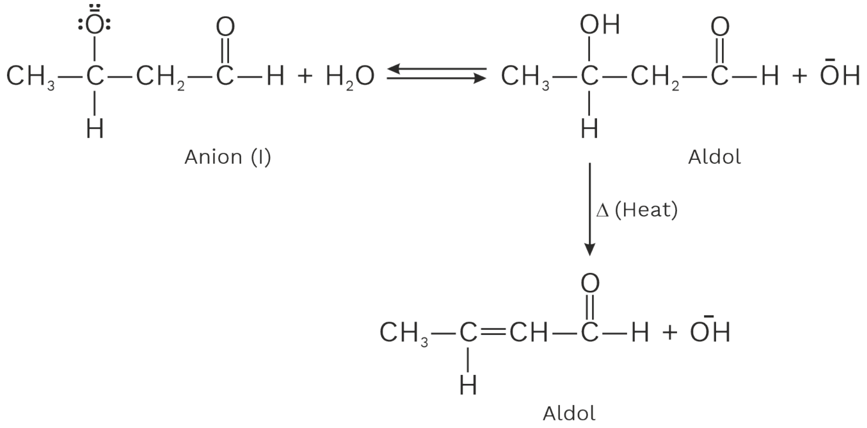
Step-1



Step-2

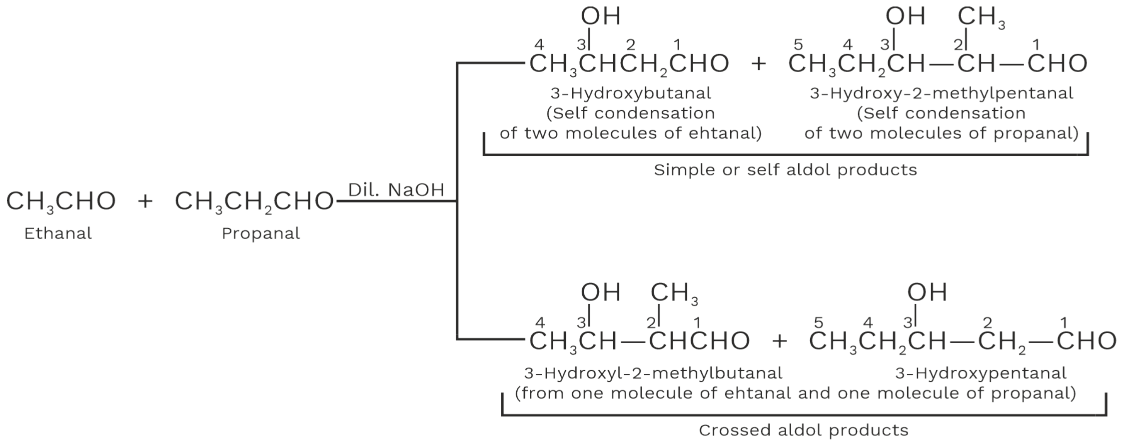


Step-3

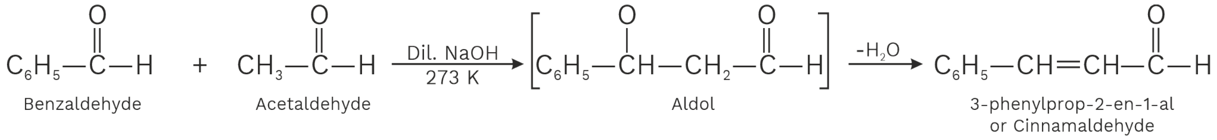


(b) Cross aldol condensation

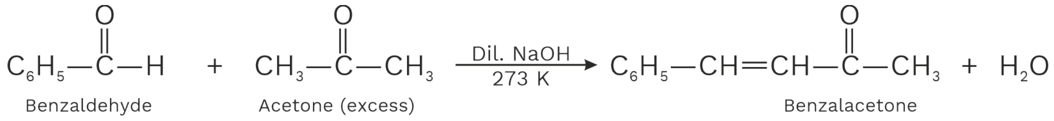
(a)



(b)



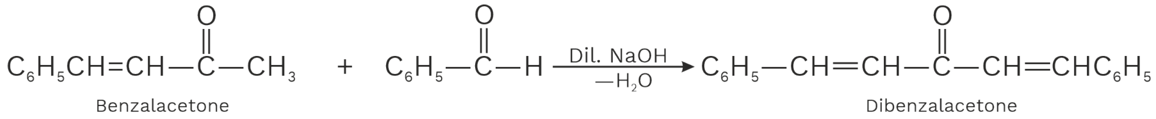
(c)



$$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-H + CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow[273\ K]{Dil.\ NaOH} C_6H_5-CH{=}CH-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + H_2O$$

Benzaldehyde Acetone (excess) Benzalacetone

If benzaldehyde is used in excess, the initially formed benzalacetone further condenses with another molecules of benzaldehyde to form dibenzalacetone. Thus,



$$C_6H_5CH{=}CH-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow[-H_2O]{Dil.\ NaOH} C_6H_5-CH{=}CH-\overset{\overset{\displaystyle O}{\|}}{C}-CH{=}CHC_6H_5$$

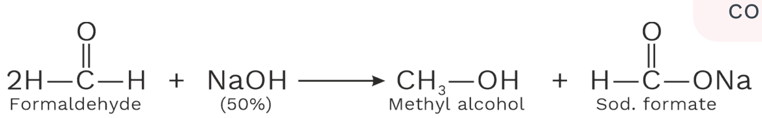
Benzalacetone Dibenzalacetone

Such a base-cotalysed crossed aldol condensation between an aromatic aldehyde and an aliphatic aldehyde or a ketone is called Claisen Schmidt condensation or simply Claisen reaction.

Rack your Brain

What type of aldehydes and ketones undergo aldol condensation?

2. (a) Cannizzaro reaction

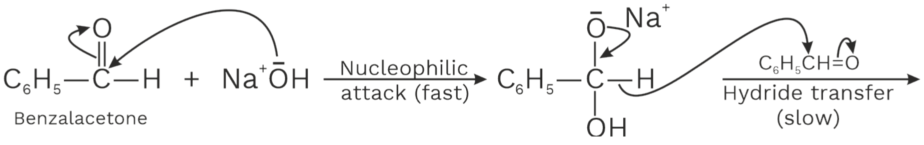


$$2H-\overset{\overset{\displaystyle O}{\|}}{C}-H + NaOH \longrightarrow CH_3-OH + H-\overset{\overset{\displaystyle O}{\|}}{C}-ONa$$

Formaldehyde (50%) Methyl alcohol Sod. formate

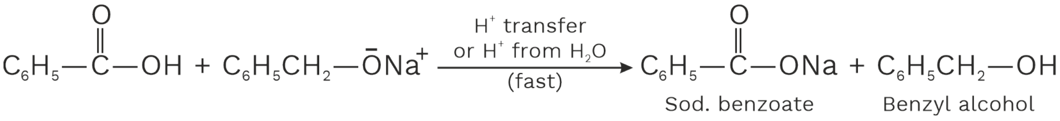
$$\underset{\text{Benzaldehyde}}{2C_6H_5CHO} + \underset{(50\%)}{NaOH} \longrightarrow \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + \underset{\text{Sod. benzoate}}{C_6H_5COONa}$$

Mechanism



$$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-H + Na^+\bar{O}H \xrightarrow[\text{attack (fast)}]{\text{Nucleophilic}} C_6H_5-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle \bar{O}\ Na^+}{|}}{C}}-H \xrightarrow[\text{(slow)}]{\substack{C_6H_5CH{=}O \\ \text{Hydride transfer}}}$$

Benzalacetone

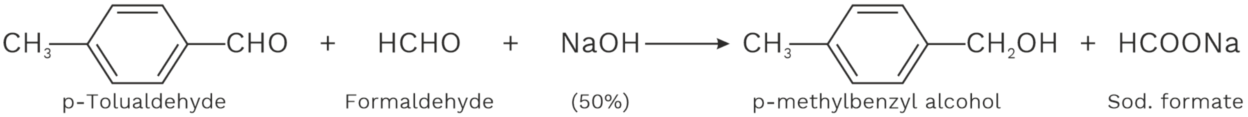


$$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-OH + C_6H_5CH_2-\bar{O}Na^+ \xrightarrow[\text{(fast)}]{\substack{H^+ \text{ transfer} \\ \text{or } H^+ \text{ from } H_2O}} C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-ONa + C_6H_5CH_2-OH$$

Sod. benzoate Benzyl alcohol

(b) Crossed Cannizzaro reaction

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Formaldehyde}}{HCHO} + \underset{(50\%)}{NaOH} \longrightarrow \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + \underset{\text{Sod. formate}}{HCOONa}$$



Note:

All aldehydes (with or without α-hydrogens) can be made to undergo Cannizzaro reaction on treatment with aluminium ethoxide. However, under these conditions, the alcohol and the acid produced as a result of Cannizzaro reaction, combine together to form esters. For example.

$$2CH_3CHO \xrightarrow{Al(OC_2H_5)_3} \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethyl Alcohol}}{CH_3CH_2OH} \xrightarrow{-H_2O} \underset{\text{Ethyl acetate}}{CH_3COOCH_2CH_3}$$

$$\underset{\text{propionaldehyde}}{2CH_3CH_2CHO} \xrightarrow{Al(OC_2H_5)_3} \underset{\text{n-Propyl propionate}}{CH_3CH_2COO—CH_2CH_2CH_3}$$

$$\underset{\text{acrolein}}{CH_2=CH—CHO} \xrightarrow{Al(OC_2H_5)_3} \underset{\text{Allyl acrylate}}{CH_2=CHCOO—CH_2CH=CH_2}$$

Rack your Brain

Formaldehyde and benzaldehyde give cannizzaro reaction but acetaldehyde does not. Explain?

Some important reduction reactions of aldehydes and ketones

Aldehydes and ketones can be reduced to a variety of compounds under different conditions.

1. Reduction to hydrocarbons

The carbonly group in aldehydes and ketones can be reduced to methylene group to form hydrocarbons. The following methods are generally empolyed.

(i) Wolff-Kishner reduction.

In this method, the aldehyde or the ketone is heated with hydrazine and KOH or potassium tert butoxide in a high boiling solvent such as ethylene glycol.

Previous Year's Questions

Reaction between benzaldehyde and acetophenone in presence of dilute NaOH is known as **[NEET]**

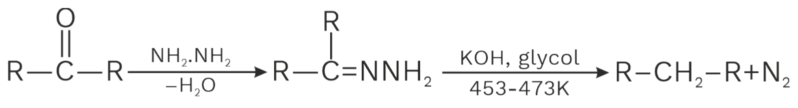
(1) Aldol condensation

(2) Cannizzaro's reaction

(3) Cross Cannizzaro's reaction

(4) Cross Aldol condensation.

$$R-CH=O \xrightarrow[-H_2O]{NH_2.NH_2} \underset{\text{Hydrazone}}{R-CH=NNH_2} \xrightarrow[453-473K]{KOH,glycol} R-CH_3 + N_2$$



$$R—\overset{\overset{\Large O}{||}}{C}—R \xrightarrow[-H_2O]{NH_2.NH_2} R—\overset{\overset{\Large R}{|}}{C}=NNH_2 \xrightarrow[453\text{-}473K]{KOH,\ glycol} R–CH_2–R+N_2$$

(ii) With HI + P (Red.)

On heating an aldehyde or a ketone with hydriodic acid and red phosphorus to 423K (150°C), it is reduced to the corresponding alkane, e.g.,

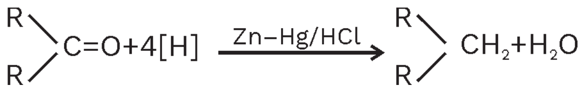
$$\underset{\text{Acetaldehyde}}{CH_3CHO} + 4HI \xrightarrow{\text{Red P, 423K}} \underset{\text{Ethane}}{CH_3-CH_3} + H_2O + 2I_2$$

$$\underset{\text{Acetone}}{CH_3COCH_3} + 4HI \xrightarrow{\text{Red P, 423K}} \underset{\text{Propane}}{CH_3CH_2CH_3} + H_2O + 2I_2$$

(iii) Clemmensen reduction.

This involves the reduction of an aldehyde of a ketone with zinc amalgam and conc. hydrochloric acid. For example,

$$RCHO + 4[H] \xrightarrow{\text{Zn–Hg/HCl}} \underset{\text{Alkane}}{R-CH_3} + H_2O$$

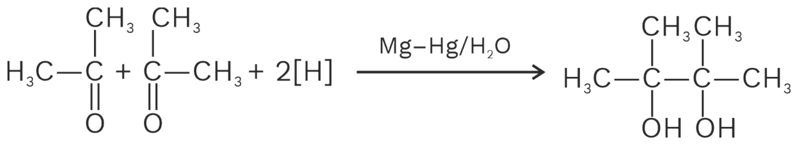


$$R_2C=O + 4[H] \xrightarrow{\text{Zn–Hg/HCl}} R_2CH_2 + H_2O$$

Clemmensen reduction is widely used for the reduction of aldehydes or ketones which are sensitive to alkalies.

2. Reduction to pinacols

Ketones on reduction with magnesium amalgam and water form pinacols.



$$H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{O}{\|}}{C}} + \overset{\overset{CH_3}{|}}{\underset{\underset{O}{\|}}{C}}-CH_3 + 2[H] \xrightarrow{\text{Mg–Hg/}H_2O} H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_3$$

Acetone

2, 3 Dimethylbutane-2, 3-diol (pinacol)

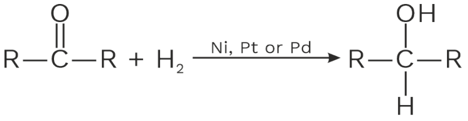
3. Reduction to alcohol

Aldehydes and ketones on reduction give primary and secondary alcohol respectively. Reduction is carried out either catalystically with H_2 in presence of Ni, Pt or Pd or chemically with lithium aluminium hybride ($LiAlH_4$) or simply diborane (B_2H_6).

$$\underset{\text{Aldehyde}}{RCHO} \xrightarrow[\text{or } LiAlH_4 \text{ or } NaBH_4]{H_2\text{+Ni/Pt or Pd}} \underset{1^\circ\text{ Alcohol}}{RCH_2OH}$$

For example,

$$\underset{\text{Formaldehyde}}{HCHO} + H_2 \xrightarrow{\text{Ni, Pt or Pd}} \underset{\text{Methyl alcohol}}{CH_3OH} \quad ; \quad \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[\text{or } NaBH_4]{LiAlH_4} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH}$$



$$R-\overset{\overset{O}{\|}}{C}-R + H_2 \xrightarrow{\text{Ni, Pt or Pd}} R-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-R$$

Previous Year's Questions

Which of the following reactions will not result in the formation of carbon-carbon bonds?

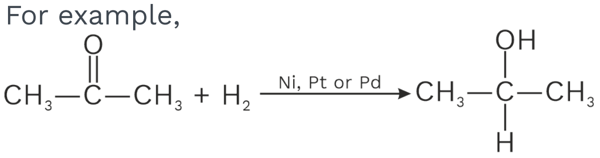
[NEET]

(1) Reimer–Tiemann reaction
(2) Cannizzaro reaction
(3) Wurtz reaction
(4) Friedel–Crafts acylation

Rack your Brain

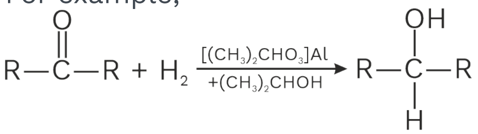
Name one reagent to distinguish between 2-pentaone and 3-pentanone.

For example,



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + H_2 \xrightarrow{\text{Ni, Pt or Pd}} CH_3-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CH_3$$

RCOR (Ketones) can also be reduced to the corresponding secondary alcohols with aluminium isopropoxide in isopropyl alcohol. For example,



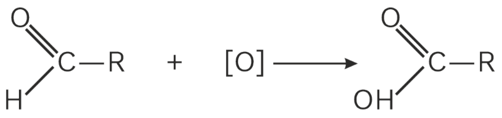
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-R + H_2 \xrightarrow[+(CH_3)_2CHOH]{[(CH_3)_2CHO_3]Al} R-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-R$$

This reaction is called Meerwein-Ponndorf-Verley Reduction. It involves transfer of hydride ion from isopropyl alcohol to the ketone and thus, this reduction can be regarded as reverse of oppenauer oxidation.

Some important oxidation reactions of aldehydes and ketones

1. Oxidation of aldehydes

Aldehydes are easily oxidised to carboxylic acids containing the same number of carbon atom.



Aldehyde Carboxylic acid

Reason: Presence of a hydrogen atom on the carbonyl group which can be converted into —OH group without involving the cleavage of any other bond. Therefore, they are oxidized not only by strong oxidizing agent like HNO_3, $KMnO_4$ and $K_2Cr_2O_7$ but also by weak oxidizing agents like bromine water, Ag^+, Cu^{2+} ions etc. As a result, aldehydes act as strong reducing agent. They reduce

(i) Tollens' reagent to metallic silver (silver mirror) and

(ii) Fehling's solution or Benedict's solution to a red precipitate of cuprous oxide (Cu_2O).

(i) Reduction of Tollen's reagent

When an aldehyde is heated with Tollens' reagent the latter is reduced to metallic silver

Previous Year's Questions

A strong base can abstract an α-hydrogen from

[NEET]

(1) ketone
(2) alkane
(3) alkene
(4) amine

Concept Ladder

Ammoniacal silver nitrate solution is called Tollen's reagent. It is used to test aldehydes. both aliphatic and aromatic aldehydes reduce Tollens' reagent to shining silver mirror. It is also used to distinguish aldehydes from ketones.

Rack your Brain

What is the function of Roschelle salt in Fehling's solution?

which deposits on the walls of the test tube as bright silver mirror. During this reduction, the following reactions occur:

$$AgNO_3 + NH_4OH \longrightarrow NH_4NO_3 + AgOH$$

$$AgOH + 2NH_4OH \longrightarrow \underset{\text{(Tollen's reagent)}}{[Ag(NH_3)_2]^+OH^-} + 2H_2O$$

$$\underset{\text{Aldehyde}}{RCHO} + \underset{\text{(Tollen's reagent)}}{2[Ag(NH_3)_2OH} \longrightarrow \underset{\text{Carboxylic acid}}{RCOOH} + H_2O + 4NH_3 + \underset{\text{silver mirror}}{2Ag\downarrow}$$

or

$$RCHO + Ag_2O \longrightarrow RCOH + 2Ag\downarrow$$

This test also known as silver mirror test.

Note:

Aromatic and aliphatic aldehydes reduce Tollens' reagent.

(ii) Reduction of Fehlling's solution

When an aliphatic aldehyde is heated with Fehling's solution, the latter is reduced to give a red ppt. of cupprous oxide. During this reduction the following reaction occur:

$$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$$

$$Cu(OH)_2 \xrightarrow{\Delta} CuO + H_2O$$

$$\underset{\text{Aldehyde}}{RCHO} + 2CuO \longrightarrow \underset{\substack{\text{Cuprous oxide}\\\text{(Red ppt.)}}}{Cu_2O\downarrow} + \underset{\substack{\text{Carboxylic}\\\text{acid}}}{RCOOH}$$

or

$$RCHO + 2Cu^{+2} + 3OH \longrightarrow RCOO^- + \underset{\text{(Red ppt.)}}{2Cu^+} + H_2O$$

(iii) Reduction of Benedict's solution

Benedict's solution, is the alkaline solution of Cu^{2+} ions complexed with citrate ions.

$$RCHO + 2Cu^{+2} + 3OH^- \xrightarrow{\text{Red ppt.}} RCOO^- + 3H_2O + Cu_2O\downarrow$$

Concept Ladder

Acetaldehyde reduces Tollen's to produce shining silver mirror and produces red ppt. of Cu_2O with Fehling's solution.

Previous Year's Questions

Which of the following is incorrect?

[NEET]

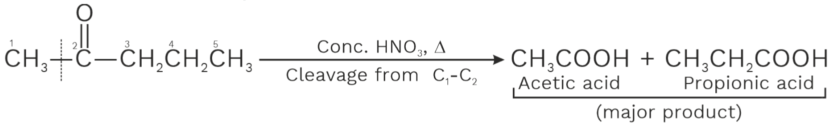
(1) $FeCl_3$ is used in detection of phenol.
(2) Fehling solution is used in detection of glucose
(3) Tollens' reagent is used in detection of unsaturation.
(4) $NaHSO_3$ is used in detection of carbonyl compound.

Concept Ladder

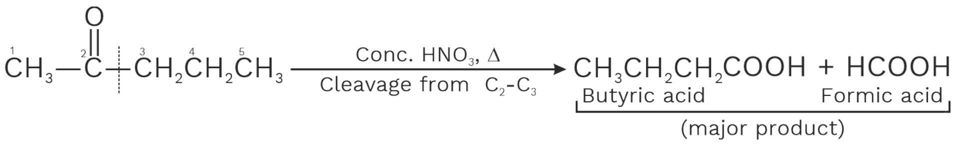
Due to presence of a H-atom on the carbonyl group, aldehydes can be more easily oxidised than ketones. As a result, aldehydes act as reducing agent and thus reduce Tollen's reagent, Fehling's solution etc.

(i) Oxidation with strong oxidising agents.

Strong oxidising agents like conc. HNO_3, $KMnO_4/H_2SO_4$, $K_2Cr_2O_7/H_2SO_4$, etc. oxidises ketones. During these oxidations rupture of the carbon-carbon bond occurs on either side of the keto group giving a mixture of carboxylic acids, each containing lesser number of carbon atoms than the original ketone. For example

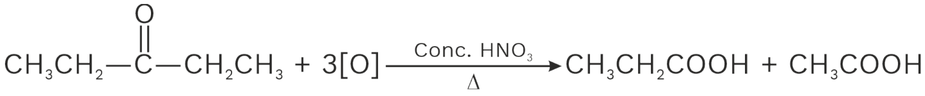


$$\overset{1}{C}H_3 - \overset{O}{\overset{\|}{\overset{2}{C}}} - \overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_3 \xrightarrow[\text{Cleavage from } C_1\text{-}C_2]{\text{Conc. } HNO_3,\ \Delta} \underbrace{\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Propionic acid}}{CH_3CH_2COOH}}_{\text{(major product)}}$$



$$\overset{1}{C}H_3 - \overset{O}{\overset{\|}{\overset{2}{C}}} - \overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_3 \xrightarrow[\text{Cleavage from } C_2\text{-}C_3]{\text{Conc. } HNO_3,\ \Delta} \underbrace{\underset{\text{Butyric acid}}{CH_3CH_2CH_2COOH} + \underset{\text{Formic acid}}{HCOOH}}_{\text{(major product)}}$$

If case of unsymmertical ketones such as butan-2-one, pentan-2-one, etc. the keto group stays perferentially with the smaller alkyl group (Popoff's rule). For example, in case of pentan-2-one, the major mode of cleavage is path 'a' in which the keto group stays with the methyl group.



$$CH_3CH_2 - \overset{O}{\overset{\|}{C}} - CH_2CH_3 + 3[O] \xrightarrow[\Delta]{\text{Conc. } HNO_3} CH_3CH_2COOH + CH_3COOH$$

$$\underset{\text{Acetone}}{CH_3-CO-CH_3} + 3[O] \xrightarrow[+H_2SO_4]{K_2Cr_2O_7} \underset{\text{Acetic Acid}}{CH_3COOH} + \underset{\text{Formic Acid}}{[HCOOH]} \xrightarrow[\Delta]{[O]} \underset{\text{Acetic acid}}{CH_3COOH} + CO_2 + H_2O$$

(ii) Oxidation of methyl ketones with sodium hypohalite (NaOX or X_2 + NaOH)—Halogorm reaction.

Aldehydes and ketones containing CH_3CO— group, on treatment with an excess of halogen in presence of alkali produce a haloform (chloroform, bromoform or iodoform). In this reaction all the three H-atoms of the methyl group are first replaced by halogen atoms to form either a trihaloaldehyde or a trihaloketone which subsequently reacts with alkali to yield a haloform and the salt of a carboxylic acid containing one carbon atom less than the starting aldehyde/ketone, for

Rack your Brain

Benzaldehyde reduces Tollens' reagent but not the Fehling's or the Benedict's solution?

Previous Year's Questions

CH_3CHO and $C_6H_5CH_2CHO$ can be distinguished chemically by

[NEET]

(1) Benedict's test
(2) iodoform test
(3) Tollens' reagent test
(4) Fehling's solution test

example,

(i) $$\underset{\text{Chloral}}{CCl_3CHO} + NaOH \xrightarrow{\text{Hydrolysis}} \underset{\text{Chloroform}}{CHCl_3} + \underset{\text{Sod. formate}}{HCOONa}$$

(ii) $$\begin{tikzcd} CH_3COCH_3 + 3Br_2 \arrow[r, "NaOH", "\text{(Bromination)}"'] & CBr_3COCH_3 + 3HBr \arrow[d, "\text{Hydrolysis}", "NaOH"'] \\ & \underset{\text{Bromoform}}{CHBr_3} + CH_3COONa \end{tikzcd}$$

When this reaction is carried out with sodium hypoiodite, NaOI or NaOH/I_2, yellow precipitate of iodoform is produced. For example,

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + 3I_2 \xrightarrow[\text{(Iodination)}]{NaOH} \underset{\text{Triiodoacetaldehyde}}{Cl_3CHO} + 3\ HI$$

$$CH_3CHO + NaOH \xrightarrow{\text{Hydrolysis}} \underset{\substack{\text{Iodoform}\\\text{(Yellow ppt)}}}{CHI_3\downarrow} + HCOONa$$

Due to the formation of yellow ppt. of iodoform in this reaction, it is known as iodoform test and is used for characterising compounds containing CH_3CO—group or any group such as $CH_3CH(OH)$—which can be easily oxidised to CH_3CO— group by halogens.

Halogenation

Aldehydes and ketones containing α-hydrogen atoms undergo halogenation when treated with halogen in presence of an acid or a base. However, in presence of a base, polyhalogenation occurs (see halogorm reaction) but in presence of acids, the reaction can be stopped at the monohalogenation stage by using one mole of the halogen.

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + Cl_2 \xrightarrow{CH_3COOH} \underset{\alpha\text{-Chloroacetaldehyde}}{ClCH_2CHO} + HCl$$

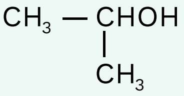
$$\underset{\text{Acetone}}{CH_3COCH_3} + Cl_2 \xrightarrow{CH_3COOH} \underset{\alpha\text{-Chloroacetone}}{ClCH_2COCH_3} + HCl$$

Previous Year's Questions

Following compounds are given

(i) CH_3CH_2OH

(ii) CH_3COCH_3

(iii) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CHOH}}$

(iv) CH_3OH

Which of the above compound(s), on being warmed with iodine solution and NaOH, will give iodoform? **[NEET]**

(1) (i), (iii) and (iv)

(2) Only (ii)

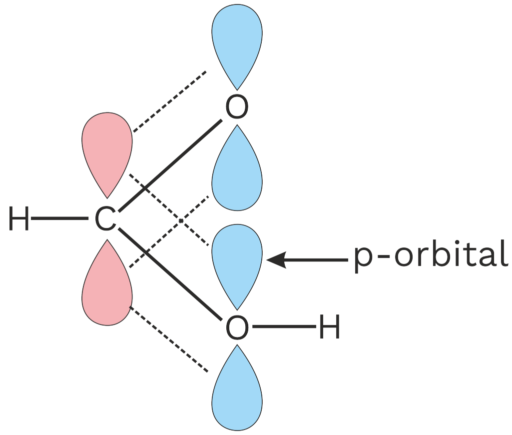
(3) (i), (ii) and (iii)

(4) (i) and (ii)

With excess of halogen, di- and tri-halogen derivatives are formed

Formaldehyde, however, does not undergo this reaction since it does not have α-halogen atoms.

Carboxylic Acids



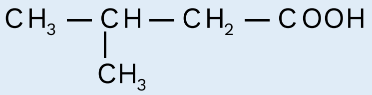
- Organic compounds having carboxylic group —COOH are called carboxylic acids.
- The name carboxyl is derived from carbonyl >C=O and hydroxyl (–OH).
- Monocarboxylic acid (–COOH) of aliphatic series are also known as fatty acids.
- The general formula is $C_nH_{2n}O_2$ or C_nH_{2n+1} COOH.

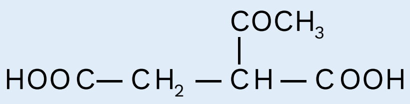
Rack your Brain

What type of ketones undergo iodoform test?

Concept Ladder

Carboxylic acids are much stronger acids (approx. 10^{11}–10^{12} times stronger) than alcohols. This is due to the reason that both carboxylic acid and carboxylate anion are stabilized by resonance but neither the alcohol (ROH) nor their alkoxide ions (RO–) are stabilized by resonance.

Structures	IUPAC Name	Common Name
 $CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-COOH$	3-Methylbutanoic acid	Isovaleric acid
$CH_3-CH=CH-COOH$	But-2-enoic acid	Crotonic acid
$HOOC-CH_2-COOH$	Propane-1, 3-dioic acid	Malonic acid

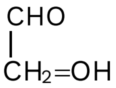
 $HOOC-CH_2-\underset{}{\overset{COCH_3}{\overset{\mid}{C}}}H-COOH$	2-(1-Oxoethyl) butane-1, 4-dioic acid	α-Acetylsuccinic acid

Isomerism Shown by Acids

Carboxylic acids show chain isomerism and functional isomerism with esters, hydroxy carbonyl compounds and hydroxy oxiranes or cyclic ethers. In the case of $C_2H_4O_2$, the various possible arrangements are,

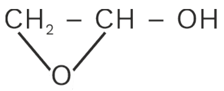
1. CH_3-COOH 2. $HCOOCH_3$

3.



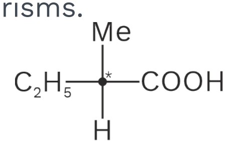
$\overset{CHO}{\underset{\mid}{}}CH_2{=}OH$

4.

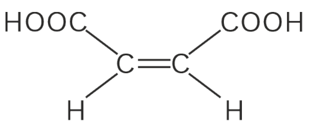


Acids also show optical and geomatrical isomerisms.

e.g.,

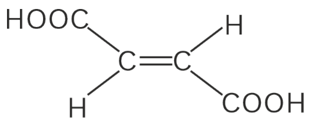


Valeric Acid (optically active)



Maleic acid 'cis'

and



Fumeric acid (trans)

Physical Properties

Physical state:

Carboxylic acids upto C_3 – atoms are colourless liquids and pungent smelling & from C_4 – C_9 are rotten butter smelling colourless liquids.

Solubility:

Due to H-bonding lower acids upto C_4 – atom are completely soluble in H_2O. With the increase of molecular weight the solubility decreases.

Example :

$HCOOH > CH_3COOH > C_2H_5COOH > C_3H_7COOH$

Concept Ladder

Carboxylic acid and carboxylate ion, both are stabilized by resonance but the carboxylate ion is better resonance stabilized because it consists of two equivalent and identical canonical forms. It is character of carboxylic acids.

Rack your Brain

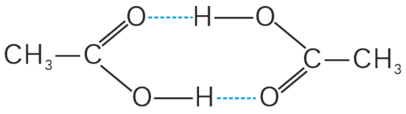
Why are carboxylic acids called fatty acids?

Concept Ladder

Formic acid is a stronger acid than acetic acid Due to +I effect of the alkyl group

Acidic strength $CH_3COOH > CH_3CH_2COOH > (CH_3)_2CHCOOH > (CH_3)_2CCOOH$

- Carboxylic acids get dimerise i.e., exits as cyclic dimmers due to hydrogen bonding



Boiling points

The boiling points of carboxylic acids are more than that of corresponding alcohols, acid derivatives or carbonyl compounds due to higher extent of hydrogen bonding.

- Boiling point of acids $\propto$ Molecular weight

  Example,

  $HCOOH < CH_3COOH < C_2H_5COOH < C_3H_7COOH$

Melting point

The melting point of an acid with even number of carbon atoms is more than the acid having next odd number of carbon atoms.

Example,

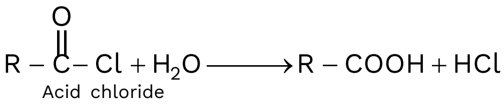
$C_4H_9COOH > C_5H_{11}COOH$

- The —COOH group and R (alkyl group) in acids with even number of carbons, lie on opposite sides and hence provide a closer packing in the lattice and have high melting points.

Preparation

1. By the hydrolysis of acid derivatives

Acid derivatives can be easily hydrolyzed into acids by using dilute acids or dilute alkalines as follows

- 

$$\underset{\text{Acid chloride}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl} + H_2O \longrightarrow R-COOH + HCl$$

$$R-COCl \xrightarrow[-NaCl]{NaOH} R-COONa \xrightarrow{H_2O} R-COOH$$

Concept Ladder

Due to strong H-bonding, the boiling points of carboxylic acids are higher than those of alcohols with comparable molecular masses. Most of the carboxylic acids in the solid, liquid or even in the vapour state exist as cyclic dimers.

Rack your Brain

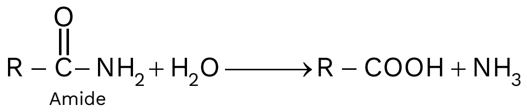
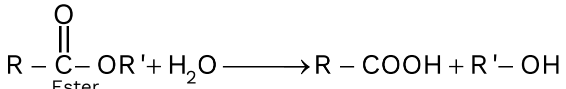
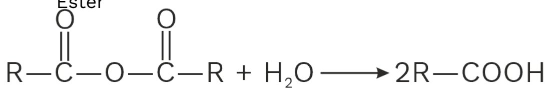
Boiling point of acetic acid is higher than that of n-propanol?

Previous Year's Questions

Which of the following represents the correct order of the acidity in the given compounds?

[NEET]

(1) $FCH_2COOH > CH_3COOH > BrCH_2COOH > ClCH_2COOH$
(2) $BrCH_2COOH > ClCH_2COOH > FCH_2COOH > CH_3COOH$
(3) $FCH_2COOH > ClCH_2COOH > BrCH_2COOH > CH_3COOH$
(4) $CH_3COOH > BrCH_2COOH > ClCH_2COOH > FCH_2COOH$.

- 
$R-\underset{\text{Amide}}{\overset{\overset{O}{\|}}{C}}-NH_2 + H_2O \longrightarrow R-COOH + NH_3$
- 
$R-\underset{\text{Ester}}{\overset{\overset{O}{\|}}{C}}-OR' + H_2O \longrightarrow R-COOH + R'-OH$
- 
$R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R + H_2O \longrightarrow 2R-COOH$

R and R' (alkyl group) may be $-CH_3$, $-C_2H_5$ etc.

2. By the hydrolysis of cyanides (R–CN)

Hydrolysis of cyanides by dilute HCl give acids

$$R-C\equiv N + 2H_2O \longrightarrow R-COOH + NH_3\uparrow$$

Example,

$$CH_3-C\equiv N + 2H_2O \xrightarrow{HCl} CH_3COOH + NH_3\uparrow$$

If hydrolysis is done by H_2O amide is the final product.

Concept Ladder

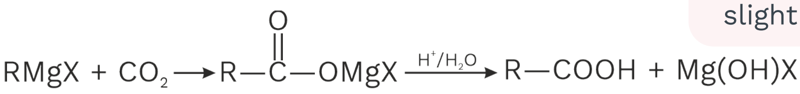
The nature of substituents affects the stability of the carboxylate ion and hence affects the acidity of the carboxylic acids. Electron withdrawing groups (EWG) increase the stability of the carboxylate ion (conjugate base) by dispersing the negative charge and hence increases the acidity.

3. From Grignard reagent and carbon dioxide

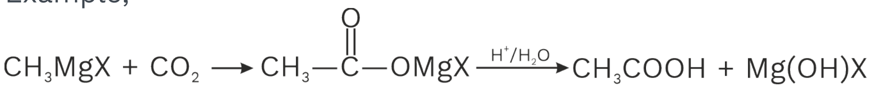
RMgX (Grignard reagent) on reaction with carbon dioxide followed by hydrolysis gives acids as follows:

Rack your Brain

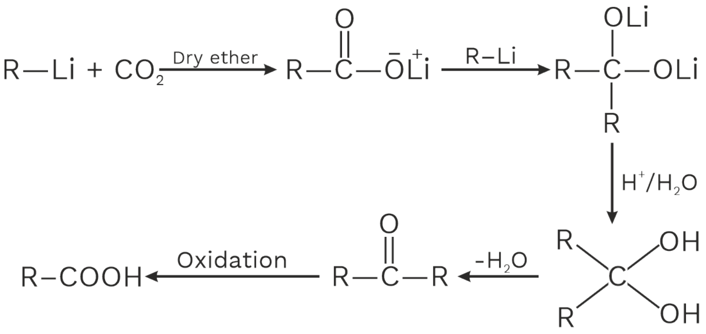
CH_3COOH is highly soluble in water but hexanoic acid is only slightly soluble?


$$RMgX + CO_2 \longrightarrow R-\overset{\overset{O}{\|}}{C}-OMgX \xrightarrow{H^+/H_2O} R-COOH + Mg(OH)X$$

Example,

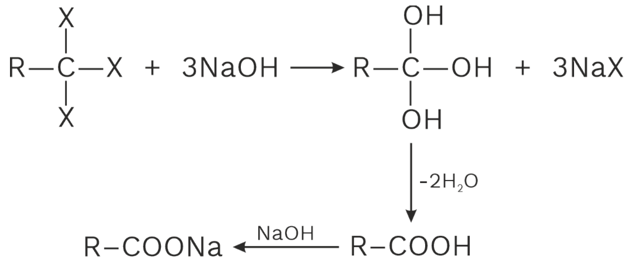

$$CH_3MgX + CO_2 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-OMgX \xrightarrow{H^+/H_2O} CH_3COOH + Mg(OH)X$$

R–Li (R may be $-CH_3$, $-C_2H_5$) also gives R–COOH with CO_2 as follows.



4. From the Hydrolysis of Haloforms

Hydrolysis of haloforms give acids.



Note:

- KOH (strong base) can also be used in place of NaOH (weak base).

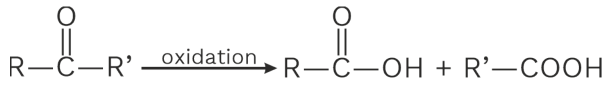
5. By oxidation of carbonyl compounds

By using strong oxidising agent like $K_2Cr_2O_7$ or $KMnO_4$ in acidic medium carbonyl compounds undergo oxidation.

$$R{-}CHO + [O] \longrightarrow R{-}COOH$$

Example,

$$CH_3CHO + [O] \longrightarrow CH_3COOH$$



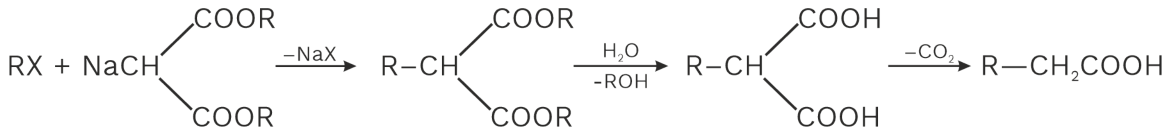
$$R{-}\overset{O}{\overset{\|}{C}}{-}R' \xrightarrow{\text{oxidation}} R{-}\overset{O}{\overset{\|}{C}}{-}OH + R'{-}COOH$$

- During oxidation of ketones the carbonyl group goes with smaller alkyl group according to Popoff 's rule.

  Example,

$$CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH_3 \xrightarrow{\text{oxidation}} 2CH_3{-}\overset{O}{\overset{\|}{C}}{-}OH$$

From dicarboxylic acid or esters



Concept Ladder

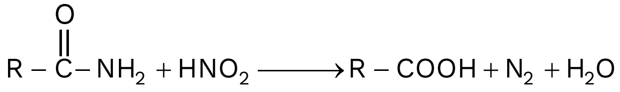
Formic acid contains a H-atom attached to a >C=O group and hence can be regarded as an aldehyde. Therefore, it acts as a reducing agent and hence decolourises pink violet colour of $KMnO_4$ solution. acetic acid, on the other hand, contains an alkyl (i.e., CH_3) group attached to >C=O group. Therefore, it does not act as a reducing agent and hence does not decolourise $KMnO_4$ solution.

Rack your Brain

Formic acid reduces Tollens' reagent but acetic acid does not. Explain?

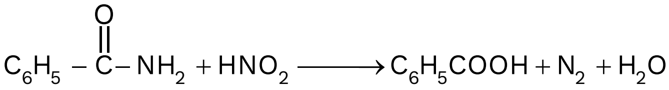
6. **From amide (R–CONH$_2$)**

Amides on reaction with HONO nitrous acid) give acids.



$$R-\overset{\overset{O}{||}}{C}-NH_2 + HNO_2 \longrightarrow R-COOH + N_2 + H_2O$$

Example,



$$C_6H_5-\overset{\overset{O}{||}}{C}-NH_2 + HNO_2 \longrightarrow C_6H_5COOH + N_2 + H_2O$$

7. **From hydrocarbon**

Heating of alkenes with carbon monoxide and water at high temperature and pressure gives acids

$$R-CH=CH_2 + CO + H_2O \xrightarrow[350°C]{H_3PO_4} R-CH_2-CH_2-COOH$$

$$CH_3-CH=CH_2 + CO + H_2O \xrightarrow[350°C]{H_3PO_4} CH_3-CH_2-CH_2-COOH + (CH_3)_2CHCOOH$$

Butanoic acid 2-Methyl propanoic acid

Concept Ladder

Olefins on heating with CO and steam under pressure at 573–673K in presence of H_3PO_4 as catalyst gives monocarboxylic acid.

(a) From higher alkanes

Higher alkanes like C_6H_{14}, C_7H_{16} undergo oxidation to give acids as follows:

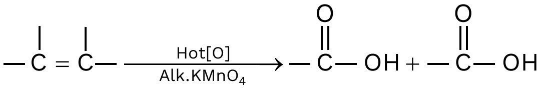
$$2R-CH_3 + 3O_2 \xrightarrow[\text{Mn acetate or stearate}]{\Delta,120°C} 2R-COOH + 2H_2O$$

Example,

$$\underset{\text{Normal heptane}}{2C_6H_{13}-CH_3} + 3O_2 \xrightarrow[\text{Mn acetate or stearate}]{\Delta,120°C} \underset{\text{Heptanoic acid}}{2C_6H_{13}-COOH} + 2H_2O$$

(b) From alkenes

On oxidative cleavage of alkenes by alkaline KMnO$_4$ (hot) gives acids.



$$-\overset{|}{C}=\overset{|}{C}- \xrightarrow[\text{Alk.KMnO}_4]{\text{Hot[O]}} -\overset{\overset{O}{||}}{C}-OH + -\overset{\overset{O}{||}}{C}-OH$$

Example,

$$CH_3-CH=CH-CH_3 \xrightarrow[\text{Alk.KMnO}_4]{\text{Hot[O]}} 2CH_3COOH$$

- If the double bond in alkenes at terminal position formic acid (HCOOH) is formed which further oxidizes into CO$_2$ and H$_2$O.

Rack your Brain

How can you distinguish between an alcohol and a carboxylic acid.

$$CH_3 — CH — CH_2 \xrightarrow[KMnO_4]{Hot} CH_3COOH + HCOOH \xrightarrow{[O]} H_2O + CO_2$$

(c) From alkynes

On ozonolysis alkynes followed by hydrolysis give acids.

$$R — C \equiv C — R' \xrightarrow[2.H_2O]{1.O_3/CCl_4} RCOOH + R'COOH$$

Example,

$$\underset{\text{Pentyne–2}}{CH_3 — C \equiv C — C_2H_5} \xrightarrow[2.H_2O]{1.O_3/CCl_4} CH_3COOH + C_2H_5COOH$$

8. From R–ONa with CO

Sodium alkoxide (RONa) on reaction with CO followed by reaction with HCl gives acids.

$$R — ONa + CO \xrightarrow[NaOH]{\Delta} R — COONa \xrightarrow{HCl} R — COOH$$

Example,

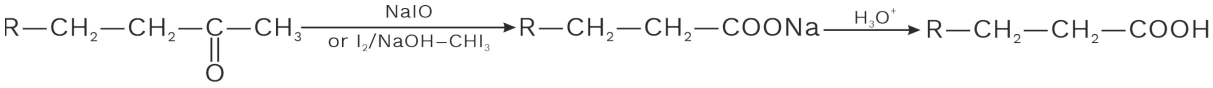
$$\underset{\text{Sod.ethoxide}}{C_2H_5ONa} + CO \xrightarrow[NaOH]{\Delta} C_2H_5COONa \xrightarrow{HCl} C_2H_5COOH$$

Note : For HCOOH preparation CO and NaOH is used.

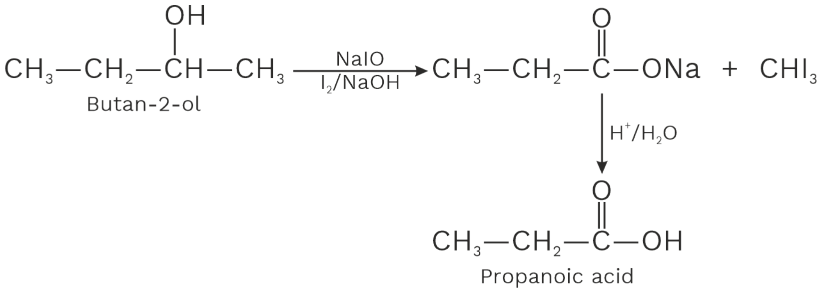
$$CO + NaOH \xrightarrow[473K]{\Delta} HCOONa \xrightarrow[-NaCl]{HCl} HCOOH$$

9. From Ketones

Methyl Ketones on oxidation by NaOX or X_2/NaOH give acids as follows:



$$R—CH_2—CH_2—\underset{\underset{O}{\|}}{C}—CH_3 \xrightarrow[\text{or } I_2/NaOH–CHI_3]{NaIO} R—CH_2—CH_2—COONa \xrightarrow{H_3O^+} R—CH_2—CH_2—COOH$$



$$\underset{\text{Butan-2-ol}}{CH_3—CH_2—\overset{\overset{OH}{|}}{C}H—CH_3} \xrightarrow[I_2/NaOH]{NaIO} CH_3—CH_2—\overset{\overset{O}{\|}}{C}—ONa + CHI_3$$

$$\xrightarrow{H^+/H_2O} \underset{\text{Propanoic acid}}{CH_3—CH_2—\overset{\overset{O}{\|}}{C}—OH}$$

Note:

This reaction is also known as haloform reaction.

Rack your Brain

Why formaldehyde HCHO does not give idoform test?

Chemical Properties

Reactions due to –COOH group

1. **Salt formation**

Acid reacts with Na, NaOH, $NaHCO_3$, Na_2CO_3 to form acid salts.

$$R-COOH \xrightarrow[\substack{NaOH, NaHCO_3 \text{ or} \\ Na_2CO_3}]{Na} R-COONa + H_2$$

Example,

$$CH_3COOH \xrightarrow[NaOH]{Na} CH_3COONa + H_2$$

Here CO_2 evolved is from sodium bicarbonate ($NaHCO_3$) or sodium carbonate (Na_2CO_3) and not of R–COOH.

e.g.,

$$C_6H_5COOH + NaHCO_3 \longrightarrow C_6H_5COONa + CO_2 + H_2O$$

Concept Ladder

Carboxylic acids like alcohols react with active metals like Na, K, Ca, Mg, Zn etc. to form their respective salts liberating H_2 gas.

Reaction with PCl_5 or $SOCl_2$

$$R-COOH + PCl_5 \longrightarrow R-COCl + HCl + POCl_3$$

Example,

$$CH_3COOH + PCl_5 \longrightarrow CH_3COCl + HCl + POCl_3$$

$$R-COOH + SOCl_2 \xrightarrow{\text{Pyridine}} R-COCl + SO_2 + HCl$$

Example,

$$CH_3COOH + SOCl_2 \xrightarrow{\text{Pyridine}} CH_3COCl + SO_2 + HCl$$

Rack your Brain

Esterification of carboxylic acids with alcohols is a nucleophilic acyl substitution reaction. Why?

2. **Ester formation or esterfication**

Acid on reaction with alcohols (ROH) or diazomethane (CH_2N_2) in presence of dilute acid or base gives esters.

$$R-COOH + HOR' \xrightarrow[\text{Acid}]{\text{dil.}} R-COOR' + H_2O$$

Example,

$$CH_3COOH + HOC_2H_5 \xrightarrow[\text{acid}]{\text{dil.}} CH_3COOC_2H_5 + H_2O$$

$$R-COOH + CH_2.N_2 \xrightarrow[\text{HCl}]{\text{dil.}} R-COOCH_3 + NH_3$$

Example,

$$C_2H_5COOH + CH_2N_2 \xrightarrow{\text{dil.HCl}} \underset{\text{Methyl propanoate}}{C_2H_5COOCH_3} + NH_3$$

Concept Ladder

When carboxylic acids are heated with alcohols or phenols in presence of conc. H_2SO_4 or dry HCl gas (Fischer-Speier esterification), esters are formed. The reaction is reversible in nature and is known as esterificiation.

3. Reaction with NH_3

Acid reacts with ammonia (NH_3) to give ammonium salt which on heating gives amide as shown:

$$R-COOH \xrightarrow{NH_3} RCOONH_4 \xrightarrow[-H_2O]{\Delta} R-CONH_2$$

Example,

$$CH_3COOH \xrightarrow{NH_3} CH_3COONH_4 \xrightarrow[-H_2O]{\Delta} \underset{\text{Acetamide}}{CH_3CONH_2}$$

Rack your Brain

What happen when acetic acid is treated with soda-lime?

4. Decarboxylation

Acids undergo decarboxylation with soda lime (CaO + NaOH) to give alkane.

$$R-COOH \xrightarrow[-H_2O]{NaOH} R-COONa \xrightarrow[+NaOH]{CaO,\ \Delta} R-H + Na_2CO_3$$

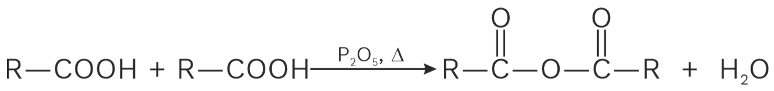
Example,

$$CH_3COOH \xrightarrow[-H_2O]{NaOH} CH_3COONa \xrightarrow[+NaOH]{CaO,\ \Delta} CH_4 + Na_2CO_3$$

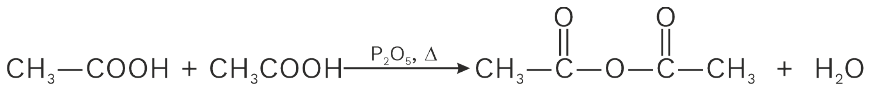
$$HCOONa + NaOH \xrightarrow{CaO, \Delta} Na_2CO_3 + H_2$$

5. Dehydration

Carboxylic acids ndergo dehydration with conc. H_2SO_4 or P_2O_5 to give acid anhydrides.



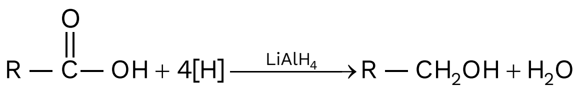
$$R-COOH + R-COOH \xrightarrow{P_2O_5,\ \Delta} R-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-R + H_2O$$



$$CH_3-COOH + CH_3COOH \xrightarrow{P_2O_5,\ \Delta} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + H_2O$$

6. Reduction

with use of $LiAlH_4$ carboxylic acids can be reduced into alcohols.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + 4[H] \xrightarrow{LiAlH_4} R-CH_2OH + H_2O$$

Concept Ladder

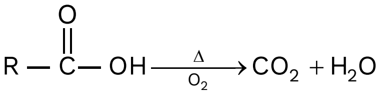
Carboxylic acids containing an electron withdrawing group such as >CO or —COOH or $—NO_2$ at the b-carbon atom w.r.t. the —COOH group readily undergo decarboxylation on heating.

3-Oxobutanoic acid $\xrightarrow{\Delta}$ Propanone

7. Oxidation or burning

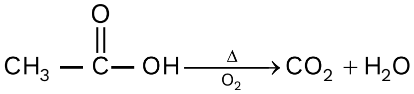
Except HCOOH, all other mono carboxylic acids are resistant to oxidation.

It can be oxidized only by prolong heating using strong oxidizing agents and get converted to CO_2 and H_2O.



$$R-\overset{\overset{\large O}{\|}}{C}-OH \xrightarrow[O_2]{\Delta} CO_2 + H_2O$$

Example,



$$CH_3-\overset{\overset{\large O}{\|}}{C}-OH \xrightarrow[O_2]{\Delta} CO_2 + H_2O$$

8. Reaction with urea

Acid reacts with urea to give amides.

$$R—COOH + NH_2CONH_2 \longrightarrow R—CONH_2 + NH_3 + CO_2$$

Example,

$$CH_3COOH + NH_2CONH_2 \longrightarrow CH_3CONH_2 + NH_3 + CO_2$$

Concept Ladder

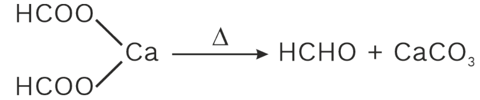
Formic acid may vbe rearded both as an aldehyde as well as a carboxylic acid. Like aldehydes, it can be easily oxidised to carbonic acid which decomposes to give CO_2 and H_2O.

9. Heating effect of acid salts

When calcium salts of carboxylic acids $(RCOO)_2Ca$ are heated, ketones are formed, and when calcium formate is heated an aldehyde is formed.

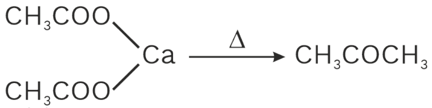
$$(R-COO)_2Ca + (R'COO)_2Ca \xrightarrow{\Delta} R-CO-R + R'-CO-R' + R-COR'$$

Example,



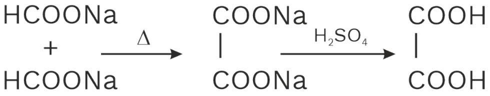
$$(HCOO)_2Ca \xrightarrow{\Delta} HCHO + CaCO_3$$

Calcium formate



$$(CH_3COO)_2Ca \xrightarrow{\Delta} CH_3COCH_3$$

Calcium acetate



$$\begin{array}{c} HCOONa \\ + \\ HCOONa \end{array} \xrightarrow{\Delta} \begin{array}{c} COONa \\ | \\ COONa \end{array} \xrightarrow{H_2SO_4} \begin{array}{c} COOH \\ | \\ COOH \end{array}$$

Oxalic acid

10. Reducing properties of HCOOH

HCOOH shows reducing properties and reduces Fehling's solution, Tollen's reagent, mercuric chloride and $KMnO_4$.

Concept Ladder

Dry distillation of calcium salt of fatty acids gives aldehydes or ketones. For example, dry distillation of calcium formate gives formaldehyde, that of calcium acetate gives acetone while that of a mixture of calcium acetate and calcium formate gives acetaldehyde.

$$HCOOH \xrightarrow[\text{(Tollen reagent)}]{Ag_2O} H_2O + CO_2 + \underset{\text{Silver mirror}}{2Ag\downarrow}$$

$$HCOOH \xrightarrow[\text{(Fehling solution)}]{2CuO} H_2O + CO_2 + \underset{\text{(Red. ppt)}}{Cu_2O\downarrow}$$

$$HCOOH \xrightarrow{2HgCl_2} 2HCl + CO_2 + Hg_2Cl_2\downarrow$$

$$HCOOH \xrightarrow{Hg_2Cl_2} 2HCl + CO_2 + \underset{\text{Black}}{2Hg\downarrow}$$

$$2KMnO_4 + 3H_2SO_4 + 5CH_2O \longrightarrow K_2SO_4 + 3MnSO_4 + 5CO_2 + 8H_2O$$

Rack your Brain

Carboxylic acids are acidic than alcohol or phenols. Why?

11. Reaction with organometallics

Acids react with organo-metallics to give alkanes.

$$R'-CH_2MgX + R-COOH \longrightarrow R'CH_3 + R-COOMgX$$

Example,

$$CH_3CH_2MgX + CH_3COOH \longrightarrow CH_3-CH_3 + CH_3COOMgX$$

$$R-COOH + RLi \longrightarrow R'-H + R-COOLi$$

Example,

$$CH_3COOH + C_2H_5Li \longrightarrow C_2H_6 + CH_3COOLi$$

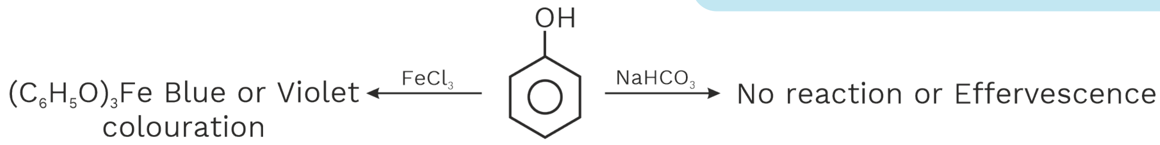
Concept Ladder

Formic acid is used as a coagulating agent for latex in rubber industry, acetic acid is used a solvent in the manufacutre of plastic, rayon and silk and Higher fatty acids are used for the manufacture of soaps and detergents.

Distinction between R–COOH and phenol:

$$\begin{tikzcd}
R\text{–}COOH \arrow[r, "NaHCO_3"] \arrow[d, "FeCl_3"] & R\text{–}COONa + H_2O + CO_2 \\
(R\text{–}COO)_3Fe &
\end{tikzcd}$$

Buff coloured Precipitate



Some Important Naming Reactions

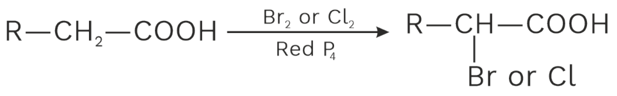
1. **Schmidt reaction:** Acid reacts with hydrazoic acid (N_3H) in presence of conc. H_2SO_4 to give a primary amine.

$$R-COOH + N_3H \xrightarrow[\text{Conc.}H_2SO_4]{\Delta} R-NH_2 + N_2 + CO_2$$

Example,

$$\underset{\text{Hydrazoic acid}}{C_2H_5COOH + N_3H} \xrightarrow[\text{conc.}H_2SO_4]{\Delta} \underset{\text{Ethylamine}}{C_2H_5NH_2} + N_2 + CO_2$$

2. **Hell–Volhard Zelinsky reaction**
   Carboxylic acids having α-H atom react with Cl_2 or Br_2 in presence of catalysts like red P_4, iron to give α-chloro or bromo substituted acids.



$$R-CH_2-COOH \xrightarrow[\text{Red } P_4]{Br_2 \text{ or } Cl_2} R-\underset{\text{Br or Cl}}{\underset{|}{CH}}-COOH$$

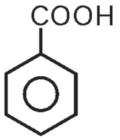
R (alkyl group) may be $-CH_3$, $-C_2H_5$ etc.

Concept Ladder

Chloroacetic acid is stronger than that of acetic acid, Chlorine atom possess –I effect which withdraws electrons from O–H bond. Which results decrease in electron density in the O–H bond and increases the acidity

Some Important Compounds

Benzoic Acid



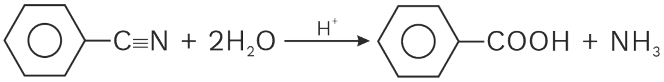
Benzoic acid is present in nature in combined state as esters in Balsam and in the urine of horse as benzoyl glycine (Hippuric acid).

Rack your Brain

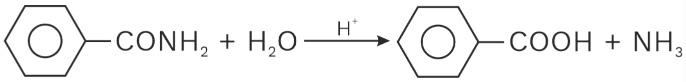
Benzoic acid do not undergo friedel craft reaction?

Preparation

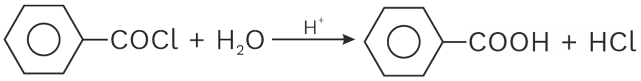
1. **By the hydrolysis of cyanobenzene**



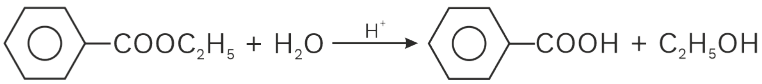
2. **By the hydrolysis of benzamide**



3. **By the hydrolysis of benzoyl chloride**



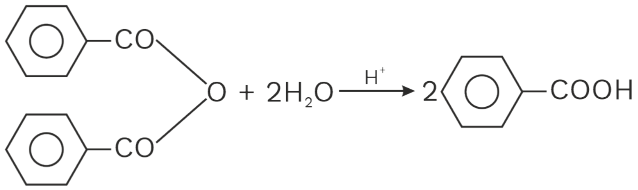
4. **By the hydrolysis of ethyl benzoate**



Concept Ladder

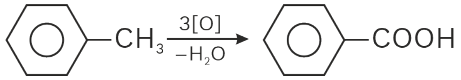
Aromatic acids undergo the electrophilic substitution reactions of the benzene ring such as halogenation, nitration and sulphonation. Since the —COOH group is electron-withdrawing, therefore, it is metal directing.

5. By the hydrolysis of benzoic anhydride

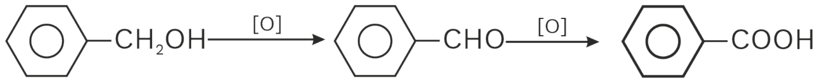


6. By oxidation reactions

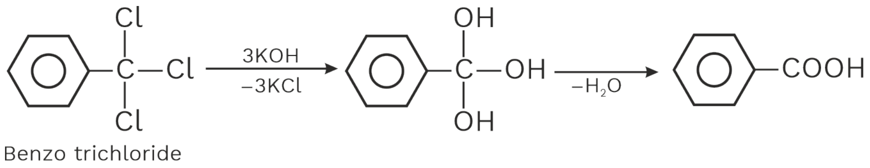
Toluene on oxidation by alkaline $KMnO_4$ or CrO_3 gives benzoic acid.



7. Benzyl alcohol on oxidation by acidic or alkaline $KMnO_4$ gives benzoic acid.

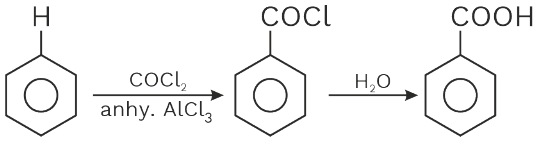


8. By the hydrolysis of benzo trichloride



9. From Grignard Reagent

10. From Benzene



Note:

This reaction is also known as Friedel-craft acylation.

If Benzene is in excess Benzo phenone is formed.

Concept Ladder

Oxidation of alkylbenzenes with alkaline $KMnO_4$ or acidified $K_2Cr_2O_7$ gives benzoic acid. During these oxidation, the aromatic nucleus remains intact but each side chain is oxidised to –COOH group irrespective of its length. The ease of oxidation of alkylbenzenes:

Toluene > Ethylbenzene > Isopropylbenzene > tert-butylbenzene

Rack your Brain

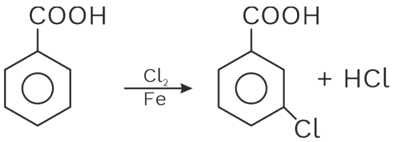
Why does benzoic acid not undergo Friedel-Crafts reaction?

Chemical properties

1. Electrophilic substitution

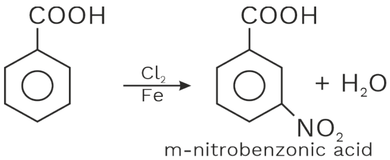
In benzoic acid the –COOH group present on the ring is deactivating and meta directing, so rate of electrophilic substitution will be slower than in benzene.

(a) Halogenation:



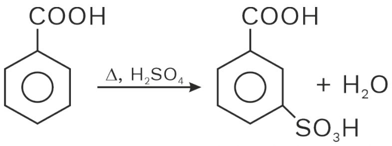
m-chlorobenzonic acid

(b) Nitration:



m-nitrobenzonic acid

(c) Sulphonation:



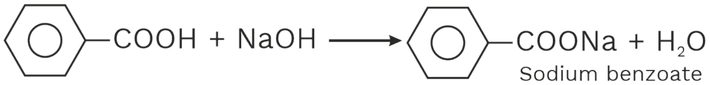
m-sulphonic benzonic acid

Concept Ladder

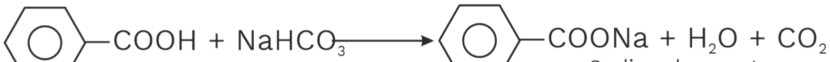
Due to ortho effect, ortho toluic acid is the stronger acid. Further since CH_3 group is electron donating due to hyperconjugation effect, therefore, both m-toluic acid and p-toluic acids are weaker acids than benzoic acid. Since hyperconjugation effect cannot operate at m-position, therefore, m-toluic acid is a stronger acid than p-toluic acid.

2. Reactions due to –COOH groups

(a) Salt formation:

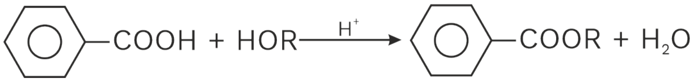


Sodium benzoate

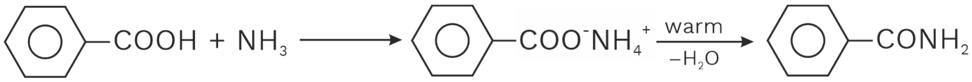


Sodium benzoate

(b) Ester formation:



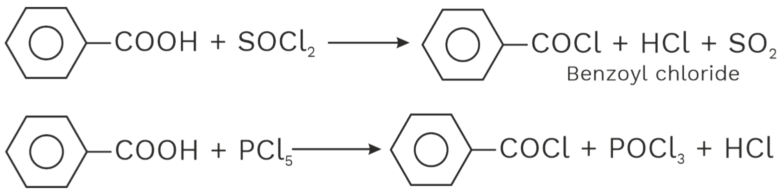
(c) Reaction with NH_3:



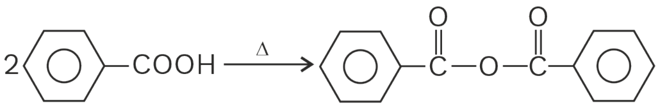
Ammonium benzoate

Benzamide

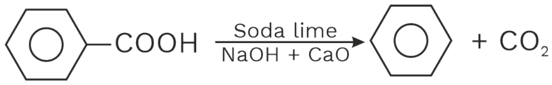
(d) Reaction with $SOCl_2$ or PCl_5:



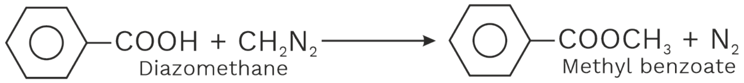
(e) Anhydride formation or dehydration:



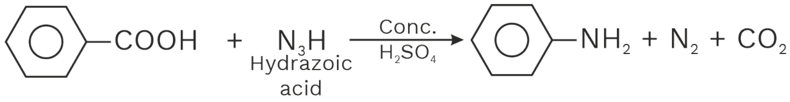
(f) Decarboxylation:



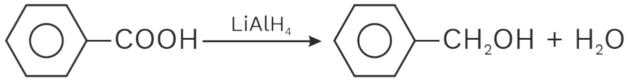
(g) Reaction with diazomethane:



(h) Schmidt reaction:



(i) Reduction:



Dicarboxylic Acid

Dicarboxylic acid have two carboxylic groups with a general formula $C_nH_{2n}(COOH)_2$

Structures	IUPAC Name	Common Name
COOH | COOH	Ethane-1, 2-dioic acid	Oxalic acid
$HOOC—CH_2—COOH$	Propane-1, 3-dioic acid	Malonic acid

CH_2COOH | CH_2COOH	Butane-1, 4-dioic acid	Succinic acid
CH_2CH_2COOH | CH_2CH_2COOH	Hexane-1, 6-dioic acid	Adipic acid

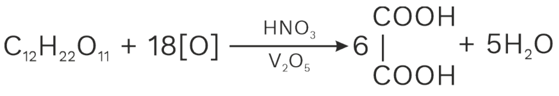
Oxalic Acid

Physical properties

- Oxalic acid is soluble in water and alcohol but insoluble in ether.
- Oxalic acid is a colourless crystalline solid with a melting point of 374.5K in hydrated form and 463K in anhydrous form.

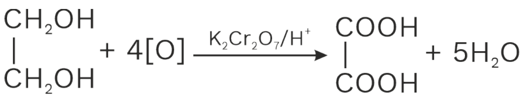
Preparation

(a) When molasses or sucrose is oxidized in presence of V_2O_5 by conc. HNO_3, oxalic acid is formed.



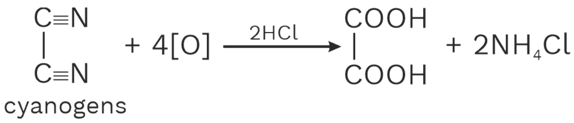
$$C_{12}H_{22}O_{11} + 18[O] \xrightarrow[V_2O_5]{HNO_3} 6\ \begin{array}{c}COOH\\|\\COOH\end{array} + 5H_2O$$

(b) From glycol



$$\begin{array}{c}CH_2OH\\|\\CH_2OH\end{array} + 4[O] \xrightarrow{K_2Cr_2O_7/H^+} \begin{array}{c}COOH\\|\\COOH\end{array} + 5H_2O$$

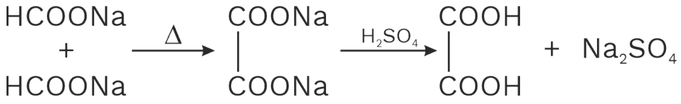
(c) From cyanogen



$$\underset{\text{cyanogens}}{\begin{array}{c}C\equiv N\\|\\C\equiv N\end{array}} + 4[O] \xrightarrow{2HCl} \begin{array}{c}COOH\\|\\COOH\end{array} + 2NH_4Cl$$

(d) Industrial preparation

$$CO + NaOH \xrightarrow[8-10\,atm]{200°C} HCOONa$$



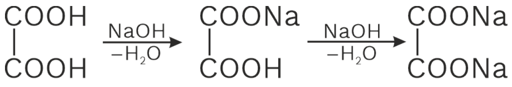
$$\begin{array}{c}HCOONa\\+\\HCOONa\end{array} \xrightarrow{\Delta} \begin{array}{c}COONa\\|\\COONa\end{array} \xrightarrow{H_2SO_4} \begin{array}{c}COOH\\|\\COOH\end{array} + Na_2SO_4$$

Concept Ladder

Water present in $K_2Cr_2O_7$/ H_2SO_4, reacts with the initially formed aldehyde to form aldehyde hydrate. The aldehyde hydrate thus formed then reacts with H_2CrO_7 to form chromate ester which subsequently undergoes oxidation to carboxylic acid.

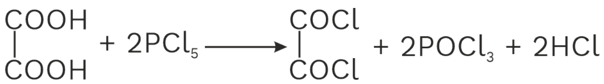
Chemical properties

1. Salt formation



$$\begin{array}{c}\mathrm{COOH}\\|\\\mathrm{COOH}\end{array}\xrightarrow[-H_2O]{NaOH}\begin{array}{c}\mathrm{COONa}\\|\\\mathrm{COOH}\end{array}\xrightarrow[-H_2O]{NaOH}\begin{array}{c}\mathrm{COONa}\\|\\\mathrm{COONa}\end{array}$$

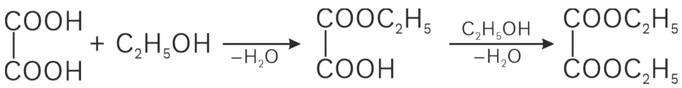
2. Reaction with PCl_5 or $SOCl_2$



$$\begin{array}{c}\mathrm{COOH}\\|\\\mathrm{COOH}\end{array} + 2PCl_5 \longrightarrow \begin{array}{c}\mathrm{COCl}\\|\\\mathrm{COCl}\end{array} + 2POCl_3 + 2HCl$$

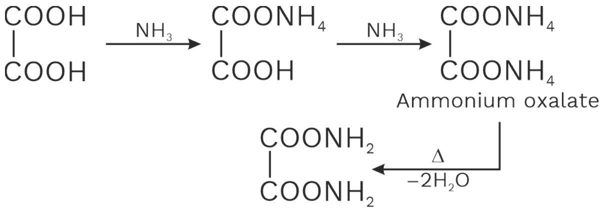
Oxalyl chloride

3. Ester formation



$$\begin{array}{c}\mathrm{COOH}\\|\\\mathrm{COOH}\end{array} + C_2H_5OH \xrightarrow[-H_2O]{} \begin{array}{c}\mathrm{COOC_2H_5}\\|\\\mathrm{COOH}\end{array}\xrightarrow[-H_2O]{C_2H_5OH}\begin{array}{c}\mathrm{COOC_2H_5}\\|\\\mathrm{COOC_2H_5}\end{array}$$

4. Reaction with ammonia



$$\begin{array}{c}\mathrm{COOH}\\|\\\mathrm{COOH}\end{array}\xrightarrow{NH_3}\begin{array}{c}\mathrm{COONH_4}\\|\\\mathrm{COOH}\end{array}\xrightarrow{NH_3}\begin{array}{c}\mathrm{COONH_4}\\|\\\mathrm{COONH_4}\end{array}\xrightarrow[-2H_2O]{\Delta}\begin{array}{c}\mathrm{COONH_2}\\|\\\mathrm{COONH_2}\end{array}$$

Ammonium oxalate

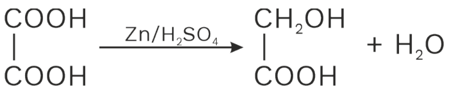
Concept Ladder

Carboxylic acids on heating with alcohols or phenols in presence of conc. H_2SO_4 or dry HCl gas (Fisherspeier esterification), ester are formed. The process is called esterficiation. Ester are also formed when acid chlorides react with alcohols and phenols in presence of pyridine.

5. Oxidation

$$\underset{\text{purple}}{2KMnO_4} + 3H_2SO_4 + 5H_2C_2O_4 \longrightarrow \underset{\text{colourless}}{K_2SO_4} + 2MnSO_4 + 10CO_2 + 8H_2O$$

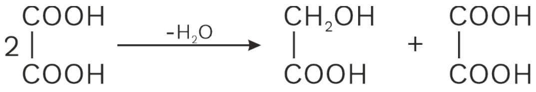
6. Reduction



$$\begin{array}{c}\mathrm{COOH}\\|\\\mathrm{COOH}\end{array}\xrightarrow{Zn/H_2SO_4}\begin{array}{c}\mathrm{CH_2OH}\\|\\\mathrm{COOH}\end{array} + H_2O$$

Glycolic acid

7. Electrolytic reduction

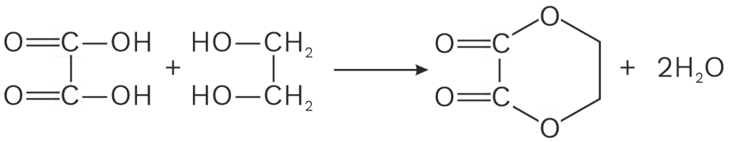


$$2\begin{array}{c}\mathrm{COOH}\\|\\\mathrm{COOH}\end{array}\xrightarrow{-H_2O}\begin{array}{c}\mathrm{CH_2OH}\\|\\\mathrm{COOH}\end{array} + \begin{array}{c}\mathrm{COOH}\\|\\\mathrm{COOH}\end{array}$$

Concept Ladder

Electrolysis of an aqueous solution of sodium or potassium salts of fatty acids gives alkanes.

8. Reaction with glycol



Note:

Test of oxalic acid

$$\text{Oxalic acid} \xrightarrow{NaHCO_3} \text{Efferences of } CO_2$$

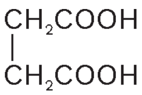
$$\text{Oxalic acid} \xrightarrow{NaHCO_3} \underset{\text{(white ppt)}}{\text{Calcium oxalate}}$$

$$\text{Oxalic acid} \xrightarrow{\text{Hot}\,KMnO_4} \text{decolourize}$$

Concept Ladder

Oxalic acid is widely used as an acid rinse in laundries, very effective in removing rust and ink stains. Oxalic acid converts most insoluble iron compounds into a soluble complex ion.

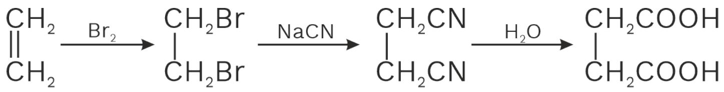
Succinic Acid



$$\begin{array}{l} CH_2COOH \\ | \\ CH_2COOH \end{array}$$

IUPAC Name: Butan-1, 4-dioic acid

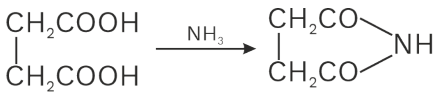
Preparation



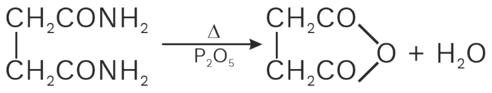
$$\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} \xrightarrow{Br_2} \begin{array}{l} CH_2Br \\ | \\ CH_2Br \end{array} \xrightarrow{NaCN} \begin{array}{l} CH_2CN \\ | \\ CH_2CN \end{array} \xrightarrow{H_2O} \begin{array}{l} CH_2COOH \\ | \\ CH_2COOH \end{array}$$

Chemical Properties

1. **Reaction with ammonia**



2. **Dehydration**



Succinic anhydride

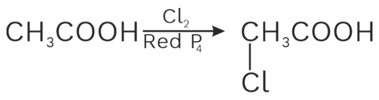
Rack your Brain

Why succinic acid is used in food and beverage industries?

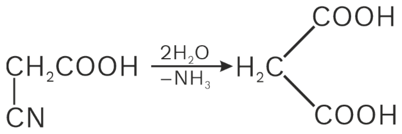
Malonic Acid

$$HOOC—CH_2—COOH$$

Preparation



$$CH_3COOH \xrightarrow[\text{Red } P_4]{Cl_2} \begin{array}{l} CH_2COOH \\ | \\ Cl \end{array}$$



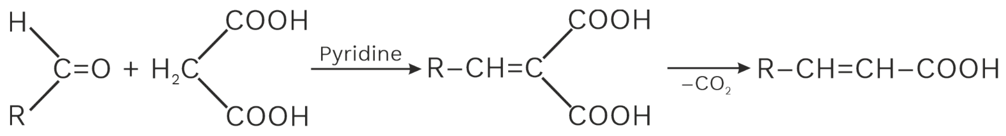
Concept Ladder

Malonic acid is used to synthesis numerous valuable compounds, including the flavor and fragrance compounds.

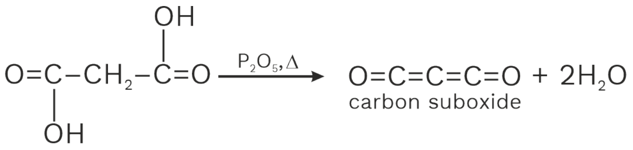
Properties

Reaction with aldehyde

Here an α, β-unsaturated acid is formed.



- When R (alkyl gruop) is $—CH_3$ the acid is crotonic acid and when it is $—C_6H_5$ (phenyl) the corresponding acid is cinnamic acid.



$$O=\underset{OH}{\underset{|}{C}}-CH_2-\overset{OH}{\overset{|}{C}}=O \xrightarrow{P_2O_5,\Delta} O=C=C=C=O + 2H_2O$$

carbon suboxide

Lactic Acid

Lactic acid is a kind of hydroxy acids

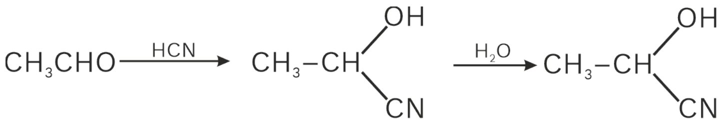
$CH_3.CH.OH-COOH$

2-hydroxy propanoic acid

Concept Ladder

Lactic acid is chiral, consisting of two enantiomers. One is known as l-lactic acid, (S)-lactic acid, or (+)-lactic acid, and the other, its mirror image.

Method of preparation



Properties

Oxidation reactions

$$CH_3.CH.OH-COOH \xrightarrow{KMnO_4} CH_3CHO$$

$$CH_3CH.OH-COOH \xrightarrow{HI} CH_3CH_2COOH$$

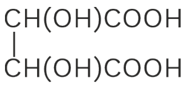
$$CH_3CH.OH-COOH \xrightarrow{dil.H_2SO_4} CH_3CHO + HCOOH$$

$$CH_3CH.OH-COOH \xrightarrow[\text{or } Ag_2O]{Fe^{2+}/H_2O_2} \underset{\text{Pyruvic acid}}{CH.CO.COOH}$$

Concept Ladder

Lactic acid is used in some liquid cleaners as a descaling agent for removing hard water deposits such as calcium carbonate, forming the lactate, Calcium lactate.

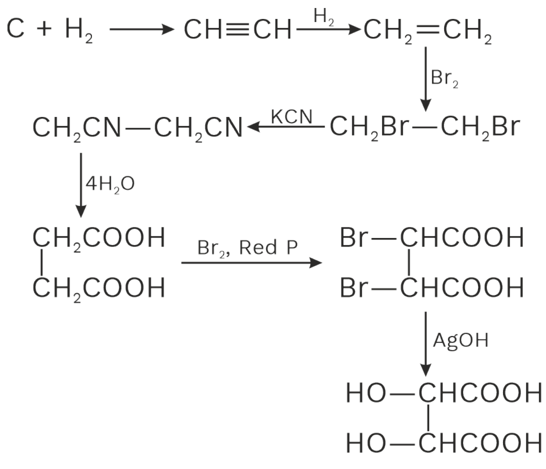
Tartaric Acid



$$\begin{array}{l}CH(OH)COOH\\ |\\ CH(OH)COOH\end{array}$$

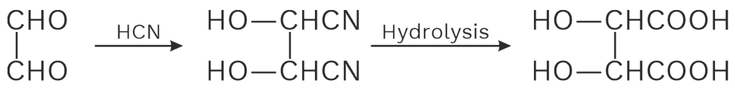
Preparation

1. From Carbon

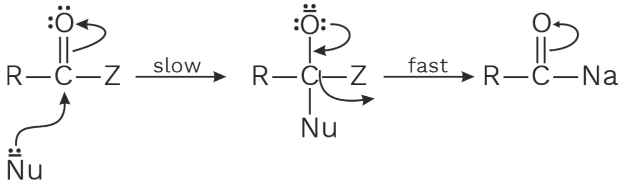


Tartaric acid

2. From glyoxal



Nucleophillic Substitution Reaction



Here Z may be —X, —OCOR, —OR, $—NH_2$ .... etc.

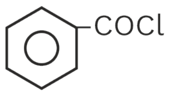
Basicity order of these leaving group as follows :

$$Cl^- < R-COO^- < R-\bar{O}^- < \bar{N}H_2$$

Hence the order of Reactivity is

$R-COCl > (RCO)_2O > R-COOR > R-CONH_2$

R–COCl >



Due to +R effect of Benzene Ring

Concept Ladder

Tartaric acid is a white, crystalline organic acid that occurs naturally in many fruits, most notably in grapes, but also in bananas, tamarinds, and citrus.

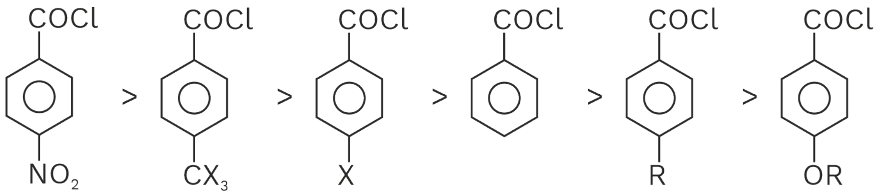
Concept Ladder

Nucleophilic substitution reaction is a class of organic reactions where one nucleophile replaces another. ... The group which takes electron pair and displaced from the carbon is known as “leaving group” and the molecule on which substitution takes place known as “substrate”.

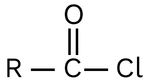
Rack your Brain

What is the role of acid catalyst in nucleophilic addition reaction?

Reactivity ∝ Electron withdrawing groups



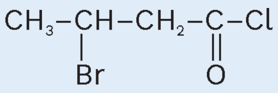
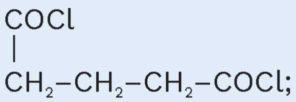
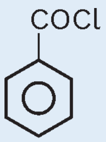
Acid Halides



$R-\overset{\overset{O}{\|}}{C}-Cl$

These are named as alkanoyl chlorides

Example

Structures	**IUPAC Name**
CH_3COCl	Ethanoyl chloride
 $CH_3-\underset{\underset{Br}{\vert}}{CH}-CH_2-\underset{\underset{O}{\Vert}}{C}-Cl$	3-Bromo butanoyl chloride
 $\overset{\overset{COCl}{\vert}}{CH_2}-CH_2-CH_2-COCl;$	Pent-1, 4-dioyl chloride
	Benzoyl chloride

Physical properties

- Acid halides are colourless liquids having pungent smell, e.g., acetyl chloride is a colourless liquid with a pungent smell.
- Acetyl chloride has a boiling point of 51.8°C.
- Acetyl chloride is not soluble in water but soluble in organic solvents like ether, acetone.

Rack your Brain

Why acetyl chloride is insoluble in water?

Preparation

1. **From acids**

   Carboxylic acids on heating with PCl_5 or PCl_3 or $SOCl_2$ give acid chlorides.

$$RCOOH + PCl_5 \xrightarrow{\Delta} RCOCl + POCl_3 + HCl$$

$$3RCOOH + PCl_3 \xrightarrow{\Delta} 3RCOCl + H_3PO_3$$

$$RCOOH + SOCl_2 \xrightarrow{\Delta} RCOCl + SO_2 + HCl$$

Here $SOCl_2$ (thionyl chloride) is the best reagent as the gaseous by products are easily separated by pyridine.

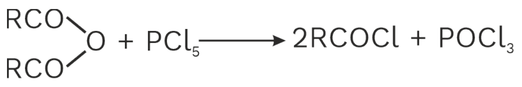
From ester

$$RCOOR' + PCl_5 \longrightarrow RCOCl + POCl_3 + R'Cl$$

Example

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + PCl_5 \longrightarrow CH_3COCl + POCl_3 + C_2H_5Cl$$

From acid anhydride



$$(RCO)_2O + PCl_5 \longrightarrow 2RCOCl + POCl_3$$

2. **Industrial preparation**

$$3RCOONa \xrightarrow[\Delta]{PCl_3} 3RCOCl + Na_2PO_3$$

Example

$$3CH_3COONa \xrightarrow[\Delta]{PCl_3} 3CH_3COCl + Na_3PO_3$$

- $2RCOONa \xrightarrow[\Delta]{PCl_3} 3RCOCl + NaPO_3 + NaCl$

Example

$$2CH_3COONa \xrightarrow[\Delta]{POCl_3} 3CH_3COCl + NaPO_3 + NaCl$$

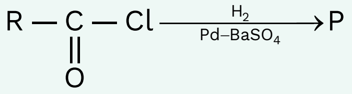
- $(RCOO)_2Ca + SO_2Cl_2 \xrightarrow{\Delta} 2RCOCl + CaSO_4$

Example

$$(CH_3COO)_2Ca + SO_2Cl_2 \xrightarrow{\Delta} 2CH_3COCl + CaSO_4$$

Previous Year's Questions

In the following reaction, product P is



$$R-\underset{\underset{O}{\|}}{C}-Cl \xrightarrow[Pd-BaSO_4]{H_2} P$$

[NEET]

(1) RCH_2OH (2) $RCOOH$

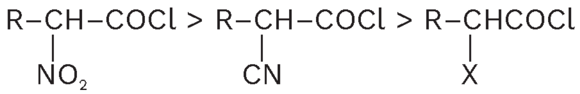
(3) $RCHO$ (4) RCH_3

Concept Ladder

An acid halide (also known as an acyl halide). It derived from an oxoacid by replacing a hydroxyl group with a halide group. If the acid is a carboxylic acid, the compound contains a –COX functional group, which consists of a carbonyl group singly bonded to a halogen atom.

Chemical properties

Acid chlorides are easily attacked by nucleophiles because Cl^- is highly electronegatives, which reduces the electron density from carbon atom, so mostly acid chlorides are reactive in nature.



$$R{-}\underset{NO_2}{\underset{|}{CH}}{-}COCl > R{-}\underset{CN}{\underset{|}{CH}}{-}COCl > R{-}\underset{X}{\underset{|}{CH}}COCl$$

1. **Hydrolysis**

$$RCOCl + H_2O \longrightarrow RCOOH + HCl$$

For example

$$CH_3COCl + H_2O \longrightarrow CH_3COOH + HCl$$

2. **Reaction with Alcohol**

Acid chlorides react with alcohols (R—OH) to form esters. The reaction is called alcoholysis.

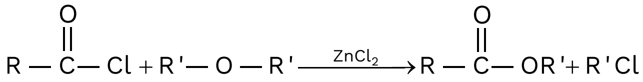
$$RCOCl + HOR' \longrightarrow RCOOR' + HCl$$

Concept Ladder

An acyl halide such as ethanoyl chloride is a colorless, fuming liquid. The strong smell of ethanoyl chloride is a mixture of the smell of vinegar (ethanoic acid) and the acrid smell of hydrogen chloride gas. The smell and the fumes originate from the reactions between ethanoyl chloride and water vapor in the air.

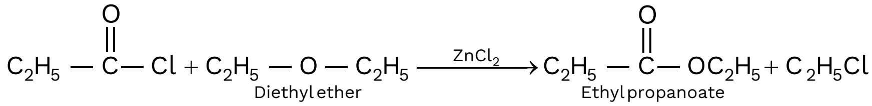
3. **Formation of ester**

Acid chlorides react with ethers (R–O–R) to give esters.



$$R - \overset{O}{\overset{||}{C}} - Cl + R' - O - R' \xrightarrow{ZnCl_2} R - \overset{O}{\overset{||}{C}} - OR' + R'Cl$$

Example,



$$C_2H_5 - \overset{O}{\overset{||}{C}} - Cl + \underset{\text{Diethyl ether}}{C_2H_5 - O - C_2H_5} \xrightarrow{ZnCl_2} \underset{\text{Ethyl propanoate}}{C_2H_5 - \overset{O}{\overset{||}{C}} - OC_2H_5} + C_2H_5Cl$$

4. **Reaction with ammonia**

Acid chlorides react with (NH_3) to form amides.

$$RCOCl + NH_3 \longrightarrow RCONH_2 + HCl$$

Example,

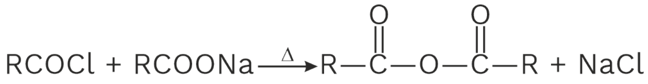
$$CH_3COCl + NH_3 \longrightarrow CH_3CONH_3 + HCl$$

Rack your Brain

Are acid chloride acidic in nature?

5. Formation of acid anhydride or reaction with acid salts

Acid chlorides gives acid anhydrides by the action with acid salts

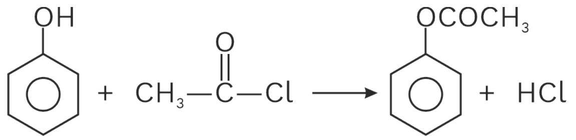


$$RCOCl + RCOONa \xrightarrow{\Delta} R—\overset{O}{\overset{||}{C}}—O—\overset{O}{\overset{||}{C}}—R + NaCl$$

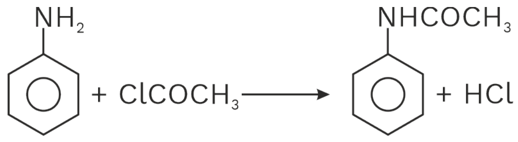
R (alkyl group) may be $—CH_3$, $—C_2H_5$ ..... etc.

6. Acetylation

CH_3COCl is used for the acetylation of – OH group, NH_2 group to find their number and location.

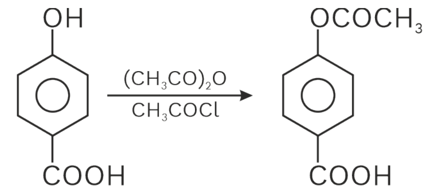


Phenyl acetate



Aniline

Acetanilide



Salicylic acid

Acetyl salicylic acid
Aspirin [Pain killer]

7. Reaction with sodium peroxide (Na_2O_2)

$$2CH_3COCl + Na_2O_2 \longrightarrow (CH_3CO)_2O + 2NaCl$$

8. Reduction reactions

(a) Rosenmund's reduction: Acid chlorides are reduced by Pd/$BaSO_4$ poisoned by sulphur or quinoline to avoid further reduction of carbonyl compounds (aldehyde) into alcohols.

$$RCOCl + 2[H] \xrightarrow{Pd/BaSO_4} RCHO + HCl$$

Concept Ladder

Acid anhydride refers to an acidic oxide, which reacts in water to form an oxyacid or with base to form a salt.

Previous Year's Questions

When aniline reacts with oil of bitter almonds (C_6H_5CHO) condensation takes place and benzal derivative is formed. This is known as **[NEET]**

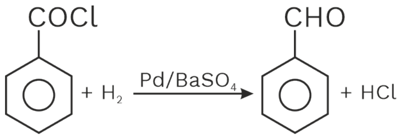
(1) Schiff 's base
(2) Benedict's reagent
(3) Millon's base
(4) Schiff 's reagent

Rack your Brain

Formaldehyde cannot be prepared by Rosenmund reduction. Why?

Example,

$$CH_3COCl \xrightarrow[Pd/BaSO_4]{H_2} CH_3CHO + HCl$$



Note : It is not suitable for HCHO prepration as HCOCl is unstable.

(b) Reaction with LiAlH$_4$

Here alcohols are formed.

$$RCOCl \xrightarrow[LiAlH_4]{4[H]} R - CH_2 - OH$$

Example,

$$CH_3COCl \xrightarrow[LiAlH_4]{4[H]} CH_3 - CH_2 - OH$$

Rack your Brain

LiAlH$_4$ is a much more powerful reducing agent that NaBH$_4$. Why?

(c) Reaction with primary amine

$$RCOCl + RNH_2 \longrightarrow R - CO - NHR + HCl$$

Example,

$$CH_3COCl + CH_3NH_2 \longrightarrow \underset{\text{N–methyl acetamide}}{CH_3 — CO — NHCH_3} + HCl$$

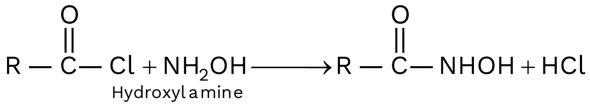
(d) Reaction with secondary amine

$$RCOCl + HNR_2 \longrightarrow R — CO — NR_2 + HCl$$

Example,

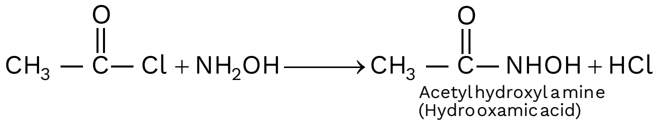
$$CH_3COCl + H.N(CH_3)_2 \longrightarrow \underset{\text{N,N–dimethyl acetamide}}{CH_3 — CO — N(CH_3)_2} + HCl$$

(e) Reaction with hydrazine and hydroxyl amine

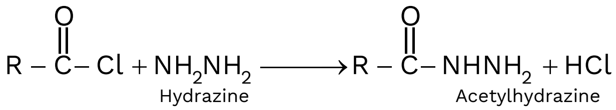


$$R — \overset{\overset{\displaystyle O}{\|}}{C} — Cl + \underset{\text{Hydroxylamine}}{NH_2OH} \longrightarrow R — \overset{\overset{\displaystyle O}{\|}}{C} — NHOH + HCl$$

Example,

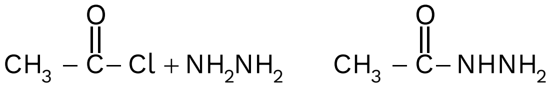


$$CH_3 — \overset{\overset{\displaystyle O}{\|}}{C} — Cl + NH_2OH \longrightarrow \underset{\substack{\text{Acetyl hydroxyl amine} \\ \text{(Hydro oxamic acid)}}}{CH_3 — \overset{\overset{\displaystyle O}{\|}}{C} — NHOH} + HCl$$



$$R - \overset{\overset{\displaystyle O}{\|}}{C} - Cl + \underset{\text{Hydrazine}}{NH_2NH_2} \longrightarrow \underset{\text{Acetylhydrazine}}{R - \overset{\overset{\displaystyle O}{\|}}{C} - NHNH_2} + HCl$$

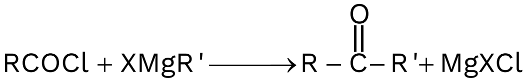
Example,



$$CH_3-\overset{O}{\overset{||}{C}}-Cl+NH_2NH_2 \qquad CH_3-\overset{O}{\overset{||}{C}}-NHNH_2$$

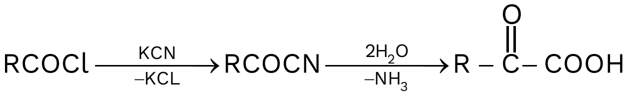
(f) Reaction with Grignard reagent

Acid chlorides react with Grignard reagent (RMgX) to give ketones which further react with Grignard reagent to give 3°-alcohols



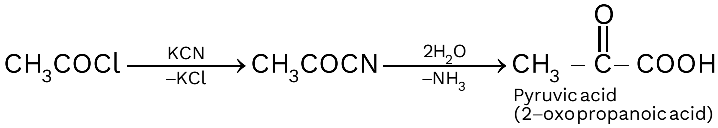
$$RCOCl+XMgR'\longrightarrow R-\overset{O}{\overset{||}{C}}-R'+MgXCl$$

(g) Reaction with KCN



$$RCOCl\xrightarrow[-KCL]{KCN}RCOCN\xrightarrow[-NH_3]{2H_2O}R-\overset{O}{\overset{||}{C}}-COOH$$

Example,

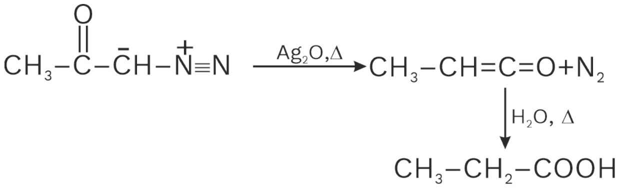


$$CH_3COCl\xrightarrow[-KCl]{KCN}CH_3COCN\xrightarrow[-NH_3]{2H_2O}CH_3-\overset{O}{\overset{||}{C}}-COOH$$

Pyruvic acid
(2–oxopropanoic acid)

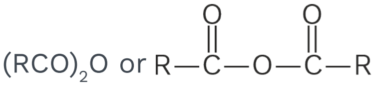
(h) Reaction with diazomethane:

$$CH_3COCl+\underset{\text{Diazo Methane}}{2CH_2N_2}\xrightarrow[\substack{-CH_3Cl\\-N_2}]{}CH_3COCHN_2$$



$$CH_3-\overset{O}{\overset{||}{C}}-\bar{C}H-\overset{+}{N}\equiv N\xrightarrow{Ag_2O,\Delta}CH_3-CH=C=O+N_2\xrightarrow{H_2O,\ \Delta}CH_3-CH_2-COOH$$

Acid Anhydride



$$(RCO)_2O \text{ or } R-\overset{O}{\overset{||}{C}}-O-\overset{O}{\overset{||}{C}}-R$$

R may be $-CH_3$, $-C_2H_5$ etc.

These are named as alkanoic anhydrides.

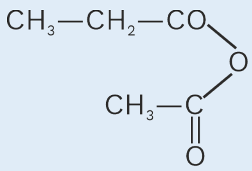
Concept Ladder

Acyl chlorides reacts with Grignard reagents to produce alcohols, while organocuprates (Gilman's) also known as lithium dialkyl cuprates can be used for making ketones from acyl chlorides.

Concept Ladder

Diazomethane (CH_2N_2) is a highly valuable and versatile building block in organic chemistry. It is a potent methylation agent for carboxylic acids, phenols and alcohols.

Example

Structures	IUPAC Name
$(CH_3CO)_2O$	Ethanoic anhydride
$(C_2H_5CO)_2O$	Propanoic anhydride
$C_6H_5CO)_2O$	Benzoic anhydride
	Ethanoic propanoic anhydride

Physical properties

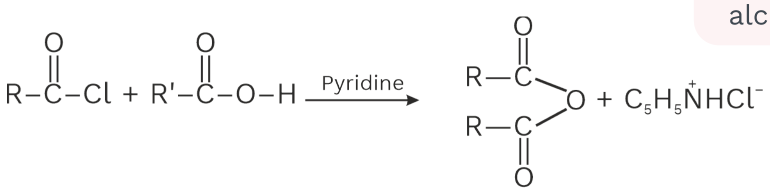
- Acetic anhydride is a colourless liquid having a pungent odour.
- Acetic anhydride has a boiling point of 139.5oC.

Rack your Brain

Acetic anhydride is incomplete soluble in water but readily soluble in solvents like ether, alcohol. Why?

Preparation

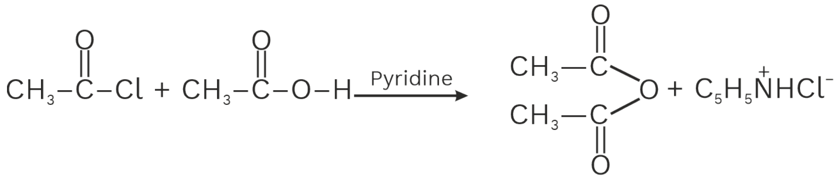
1. **From acid chloride**



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + R'-\overset{\overset{\displaystyle O}{\|}}{C}-O-H \xrightarrow{\text{Pyridine}} \begin{matrix} R-\overset{\overset{\displaystyle O}{\|}}{C} \\ R-\underset{\underset{\displaystyle O}{\|}}{C} \end{matrix}\!\!>O + C_5H_5\overset{+}{N}HCl^-$$

Pyridine hydrogenchloride

Example



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-H \xrightarrow{\text{Pyridine}} \begin{matrix} CH_3-\overset{\overset{\displaystyle O}{\|}}{C} \\ CH_3-\underset{\underset{\displaystyle O}{\|}}{C} \end{matrix}\!\!>O + C_5H_5\overset{+}{N}HCl^-$$

Pyridine hydrogen chloride

2. From acetaldehyde

Acetaldehyde (CH_3CHO) is converted into acetic anhydride by at O_2 at 50–70°C in presence of catalysts like cobalt acetate, copper acetate

$$CH_3CHO \xrightarrow[\text{Catalyst}]{\Delta, O_2} CH_3CO_3H \xrightarrow{CH_3CHO} (CH_3CO)_2O + H_2O$$

3. Reaction with acetone and acetic acid

Ketone reacts with acetone to give acetic anhydride as follows:

$$CH_3COOH \xrightarrow[AlPO_4\,/700°C]{\text{aluminiumphosphate}} \underset{\text{Ketene}}{CH_2 = C = O} + H_2O$$

$$CH_3COCH_3 \xrightarrow{\Delta} CH_2 = C = O + CH_4$$

$$CH_3COOH + CH_2 = C = O \longrightarrow (CH_3CO)_2O$$

From sodium acetate and sulphur dichloride

$$8CH_3COONa + SCl_2 + 2Cl_2 \longrightarrow 4(CH_3CO)_2O + 6NaCl + Na_2SO_4$$

Previous Year's Questions

Acetaldehyde reacts with

[NEET]

(1) electrophiles only
(2) nucleophiles only
(3) free radicals only
(4) both electrophiles and nucleophiles

4. From acetylene

When acetylene (C_2H_2) is passed through glacial acetic acid in presence of mercuric sulphate followed by distillation acetic anhydride is formed.

$$CH{\equiv}CH \xrightarrow[HgSO_4]{2CH_3COOH} CH_3{-}CH(OOCCH_3)_2 \longrightarrow CH_3{-}CHO + (CH_3CO)_2O$$

Chemical properties

1. Hydrolysis

$$(RCO)_2O + R'OH \longrightarrow RCOOR' + RCOOH$$

$$(RCO)_2O + NaOH \longrightarrow RCOOH + RCOONa$$

$$(RCO)_2O \xrightarrow{\text{Dry HCl}} RCOCl + RCOOH$$

2. Reaction with alcohol or alcoholysis

Acid anhydrides on reaction with alcohols (ROH) to give esters.

Concept Ladder

Acetic anhydride is used in the manufacture of cellulose acetate, which is widely used as a base for magnetic tape and in the manufacture of textile fibres. Also, it is heated with salicylic acid to produce acetylsalicylic acid (aspirin).

$$(RCO)_2O + HOR' \xrightarrow{\Delta} R{-}COOR' + R{-}COOH$$

Example,

$$(CH_3CO)_2O + C_2H_5OH \longrightarrow \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + CH_3COOH$$

Reaction with PCl_5

$$(RCO)_2O + PCl_5 \longrightarrow 2RCOCl + POCl_3$$

Example,

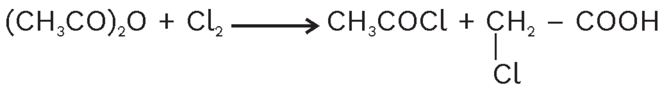
$$(CH_3CO)_2O + PCl_5 \longrightarrow 2CH_3COCl + POCl_3$$

3. Reaction with ammonia

$$(RCO)_2O + NH_3 \longrightarrow 2RCONH_2 + H_2O$$

R (alkyl group) may be $-CH_3$, $-C_2H_5$ etc.

4. Reaction with chlorine



$$(CH_3CO)_2O + Cl_2 \longrightarrow CH_3COCl + \underset{\displaystyle Cl}{\underset{|}{CH_2}} - COOH$$

Chloroacetic acid

5. Reduction:

Acid anhydride gives alcohol on reduction by $LiAlH_4$.

$$(RCO)_2O \xrightarrow{LiAlH_4} 2RCH_2OH + H_2O$$

Example,

$$(CH_3CO)_2O \xrightarrow[\text{Ether}]{LiAlH_4} C_2H_5OH$$

6. Acetylation

Acid anhydride reacts with compounds having active hydrogen atom like aniline, phenol and the active hydrogen atom gets substituted by $CH_3{-}CO{-}$group. It is better to use than $R{-}COCl$ as it reacts less violently.

- This reaction suggests the number of $-OH$ or $-NH_2$ groups. e.g., in glycerol after acetylation glycerol triacetate is formed i.e., glycerol has 3 $-OH$ groups on different carbon atoms.

Concept Ladder

Acid anhydrides are reactive species derived from carboxylic acids and have been used as useful acylating agents in organic synthesis.

Rack your Brain

Why acetic anhydride is banned in some countries?

Previous Year's Questions

The oxidation of toluene with CrO_3 in the presence of $(CH_3CO)_2O$ gives a product A, which on treatment with aqueous NaOH produces **[NEET]**

(1) C_6H_5COONa
(2) 2, 4-diacetyl toluene
(3) C_6H_5CHO
(4) $(C_6H_5CO)_2O$

Examples,

(a) $\underset{\text{Phenol}}{C_6H_5OH} + (CH_3CO)_2O \longrightarrow \underset{\text{Phenyl acetate}}{C_5H_5OCOCH_3} + CH_3COOH$

(b) $\underset{\text{Aniline}}{C_6H_5NH_2} + (CH_3CO)_2O \longrightarrow \underset{\text{Acetanilide}}{C_6H_5NHCOCH_3} + CH_3COOH$

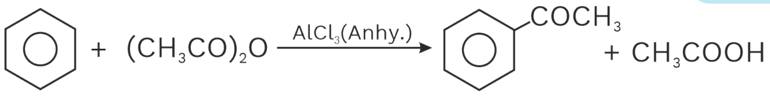
8. Reaction with acetaldehyde

Acetic anhydride reacts with acetaldehyde to give ethylidene diacetat

$(CH_3CO)_2O + CH_3CHO \longrightarrow \underset{\text{Ethylidene diacetate}}{CH_3 - CH.(OOC.CH_3)_2}$

7. Freidal craft reaction

Benzene when treated with acetic anhydride in presence of anhydrous AlCl3 acetophenone is obtained.



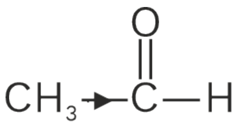
Acetophenone

Concept Ladder

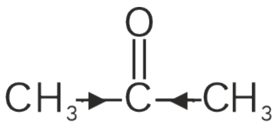
Friedel–Crafts alkylation involves the alkylation of an aromatic ring with an alkyl halide using a strong Lewis acid, such as aluminium chloride, ferric chloride.

Q.2 CH_3CHO is more reactive than CH_3COH_3 towards reaction with HCN? Explain. Or Propanone is less reactive than ethanol towards nucleophilic addition reactions. Give reasons.

A.2 Due to electron-donating inductive effect (+I-effect) of the two CH_3 groups in CH_3COCH_3 as compared to smaller + I-effect of one CH_3 group in CH_3CHO, the magnitude of the +ve charge on the carbon atom of the carbonyl group in CH_3CHO than in CH_3COCH_3.


$$CH_3 \rightarrow \overset{\overset{\displaystyle O}{\|}}{C} - H$$

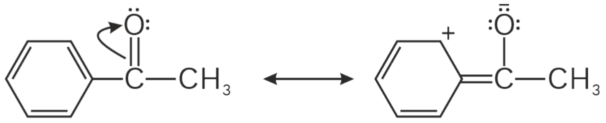
(Smaller +I effect, due to one methyl group)


$$CH_3 \rightarrow \overset{\overset{\displaystyle O}{\|}}{C} \leftarrow CH_3$$

(Stronger +I effect, due to two methyl groups)

Q.3 $C_6H_5COCH_3$ is much less reactive than CH_3COCH_3 towards nucleophilic addition reactions. Explain.

A.3 $C_6H_5COCH_3$, the electron-donating resonance effect (+R-effect) of the benzine ring reduces the +ve charge on the carbon atom of the carbonyl group. Since +R-effect of benzene ring is more pronounced than +I-effect of the CH_3 groups, therefore, magnitude of the +ve charge on the carbon atom of the carbonyl group in $C_6H_5COCH_3$ is reduced to a much greater extent than in CH_3COCH_3. As a result, $C_6H_5COCH_3$ is much less reactive than CH_3COCH_3.



Q.4 Name two reagents which can be used to distinguish acetaldehyde from acetone?

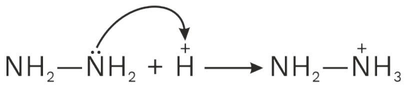
A.4 Acetaldehyde reduces Tollens' reagent to produce shining silver mirror and produces red ppt. of Cu2O with Fehling's solution.

$$\underset{\text{Acetaldeyde}}{CH_3CHO} + \underset{\text{Tollen's reagent}}{2[Ag(NH_3)_2]^+} + 3OH^- \longrightarrow \underset{\text{Acetate ion}}{CH_3COO^-} + \underset{\text{Silver mirror}}{2Ag\downarrow} + 4NH_3 + 2H_2O$$

$$CH_3CHO + 2\underbrace{Cu^{2+} + 5OH^-}_{\text{Fehling's reagent}} \longrightarrow \underset{\text{Acetate ion}}{CH_3COO^-} + \underset{\text{Red ppt.}}{Cu_2O\downarrow} + 3H_2O$$

Q.5 Hydrazones of aldehydes and ketones are not prepared in highly acidic medium. Explain.

A.5 In highly acidic medium, the NH_2 group of hydrazine gets pronated



$$NH_2—\ddot{N}H_2 + \overset{+}{H} \longrightarrow NH_2—\overset{+}{N}H_3$$

Due to strong -I-effect of the   group, the ion pair of electrons on the $-NH_2$ group of protonated hydrazine is not available for nucleophilic attack on the C = 0 group and hence hydrazone formation does not occur.

Q.6 (a)Arrange the following n order of their increasing reactivity towards HCN: CH_3CHO, CH_3COCH_3. $HCHO$,$C_2H_5COCH_3$
(b) HCHO is more reactive than CH_3CHO towards addition of HCN.

A.6 (a) (i) Reactivity increases as the +ve charge on carbonyl carbon increases. Since alkyl groups have +I-effect, therefore, reactivity increases as the number of alkyl groups on the carbonyl carbon decreases.
(ii) Reactivity increases as the number and size of alkyl groups decreases, i.e., steric hindrance decreases. $C_2H_5COCH_3 < CH_3COCH_3 < CH_3CHO < HCHO$.
(b) Due to +I-effect of CH_3 group the +ve charge on the carbonyl carbon of CH_3CHO is less than that on the carbonyl carbon of HCHO. As a result, HCHO is more reactive than CH_3CHO towards addition of HCN.

Q.7 Acetone is highly soluble in water but benzophenone is not. Give reasons.

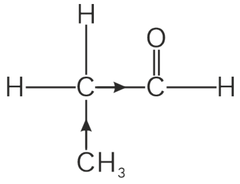
A.7 In acetone, C = 0 group easily forms, H-bonds with water and hence acetone is highly soluble in water. However, in benzophenone, the phenyl groups are bulky and hence C = O group cannot form H-bonds with water due to steric hindrance and hence benzophenone is insoluble in water.

Q.8 Arrange the given compounds in their increasing order of their B.P.: $CH_3CH_2CH_2CHO$, $CH_3CH_2CH_2CH_2OH$, CH_3CH_2COCH, $CH_3CH_2OCH_2CH_3$.

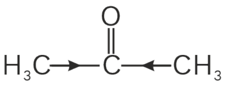
A.8 The four compounds have comparable molecular masses: $CH_3CH_2CH_2CHO$ (72), $CH_3CH_2CH_2OH$ (74), $CH_3CH_2COCH_3$ (72) and $CH_3CH_2OCH_2CH_3$(74). Amongst compounds having comparable molecular masses, alcohols have the highest b.p. due to intermolecular H-bonding, i.e., $CH_3CH_2CH_2CH_2OH$ has the highest boiling point. The boiling points of $CH_3CH_2CH_2CHOCH_2CH_3$ and $CH_3CH_2COCH_3$ depends upon their relative dipole moments. Since dipole moments of these three compounds decreases in the order: ketones > aldehydes > ethers, therefore, their boiling points also decrease in the same order, i.e., b.ps decrease in order: $CH_3CH_2CH_2OH > CH_3COCH_2CH_3 > CH_3CH_2CHO > CH_3CH_2OCH_2CH_3$

Q.9 Alpha carbon of Aldehydes and ketones are acidic in nature.

A.9 Firstly, due to strong–I-effect of the C = O group in aldehydes and ketones, electron density in the bonds decreases and hence α-hydrogen atoms can be abstracted by strong bases such as OH–, OR– etc. As a result, they are weakly acidic.



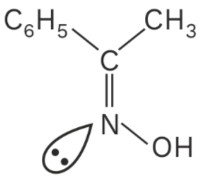
Acetaldehyde



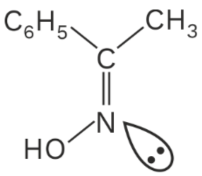
Acetone

Q.10 Acetophenone on reaction with hydroxylamine hydrochloride can produce two isomeric oximes. Write structures of the oximes.

A.10 Like alkenes, oximes also show geometrical isomerism. For example, acetophenone exists in the following two geometrical isomeric forms:



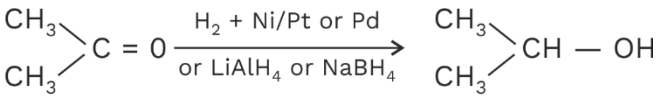
syn-Methyl phenyl ketoxime



anti-Methyl phenyl ketoxime

Q.11 How will you convert propanone to propan-2-ol?

A.11 Propane can be reduced to propan-2-ol by a number of reagents such as catalytic hydrogenation with H_2 in presence of Ni, Pt or Pd, $LiAlH_4$ or $NaBH_4$.



$$(CH_3)_2C=O \xrightarrow[\text{or } LiAlH_4 \text{ or } NaBH_4]{H_2 + Ni/Pt \text{ or } Pd} (CH_3)_2CH-OH$$

Propanone Propan-2-ol

Q.12 What is Fehling's solution?

A.12 Alkaline solution of $CuSO_4$ containing Rochelle salt is called Fehling's solution. It is obtained by adding an alkaline solution of Rochelle salt (sodium potassium tartrate) called Fehling solution 'B' to an aqueous solution of $CuSO_4$ called Fehling solution 'A' until blue ppt. of $Cu(OH)_2$ first formed redissolved to form a deep blue solution.

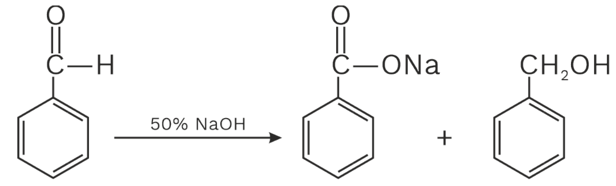
Q.13 What is Tollens' reagent? Write one usefulness of this reagent.

A.13 Ammoniacal silver nitrate solution is called Tollens' reagent. It is used to test aldehydes. Both aromatic and aliphatic aldehydes reduce Tollens's reagent to shining silver mirror. It is also used to distinguish aldehydes from ketones.

$$\underset{\text{Tollens'reagent}}{2[Ag(NH_3)_2]^+} + \underset{\text{Aldehyde}}{RCHO} + 3H^- \xrightarrow{\text{Heat}} \underset{\text{Silver mirror}}{2A\downarrow} + \underset{\text{Carboxylate ion}}{RCOO^-} + 4NH_3 + 2H_2O$$

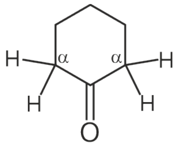
Q.14 Which of the following compounds will undergo Cannizzaro reaction? Benzaldehyde, Cyclohexanone, 2-methylpentanal

A.14 Compounds which do not have -hydrogen/s undergo Cannizzaro reaction. Here, only benzaldehyde does not have α-hydrogen/s and hence undergoes Cannizzaro reaction.

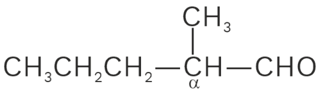


Benzaldehyde Sod. Benzoate Benzyl alcohol

In contrast, cyclohexanone and 2-methylpentanal contain one or more -hydrogen/s and hence do not undergo Cannizzaro reaction.



Cyclohexaone



$$CH_3CH_2CH_2-\underset{\alpha}{\overset{\overset{\textstyle CH_3}{|}}{C}}H-CHO$$

2-Methylpentanal

Q.15 Write method of preparation of urotrophine and give its use.

A.15 Hexamethylene tetramine is called urotropine. It is formed when formaldehyde reacts with ammonia.

$$\underset{\text{Formaldehyde}}{6HCHO} + 4NH_3 \longrightarrow \underset{\text{Urotropine}}{(CH_2)_6N_4} + 6H_2O$$

It is used as antiseptic for urinary tract infections.

Q.16 Why is benzoic acid less soluble in water than acetic acid?

A.16 Due to polar nature of the C = O and O – H parts of COOH group, both CH_3COOH and C_6H_5 COOH for H bonds with water. But due to larger hydrocarbon part the extent of H-bonding is much lower in benzoic acid than in acetic and hence benzoic acid is much less soluble in water than acetic acid.

Q.17 Arrange the given compounds in decreasing order of their boiling point: $CH_3CH_2CH_2CH_2OH$, $CH_3CH_2OCH_2CH_3$, $CH_3CH_2CH_2COOH$.

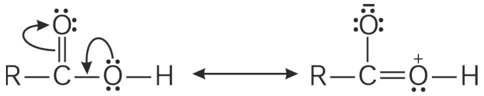
A.17 Due to much stronger H-bonds in carboxylic acids than in alcohols, the boiling points of carboxylic acids are much higher than the boiling points of the corresponding alcohols and carboxylic acids of comparable molecular masses. Thus, the boiling points decrease in the order:
$CH_3CH_2CH_2COOH > CH_3CH_2CH_2CH_2OH > CH_3CH_2OCH_2CH_3$.

Q.18 What makes ethanoic acid a stronger acid than ethanol?

A.18 Ethanoate ion obtained by loss of proton from ethanoic acid is stabilized by resonance but ethoxide ion obtained by loss of a proton from ethanol is not.

Q.19 Why carboxylic acids do not give the characteristics reactions of carbonyl group?

A.19 Due to the presence of lone pairs of electrons on the oxygen atom of the OH group, the carboxylic acids may be regarded as a resonance hybrid of structures (I and II)


I II

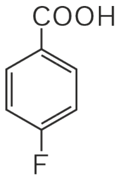
Similarly, a carbonyl group of aldehydes and ketones may be regarded as a resonance hybrid of structures (III and IV):


III IV

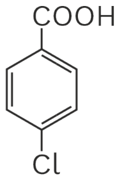
Due to contribution of structure (IV), the carbonyl carbon in aldehydes and ketones is electrophilic. However, due to contribution of structure (II), the electrophilic character of carboxyl carbon is reduced. In other words, carbonyl carbon of carboxyl group is less electrophilic than carbon in aldehydes and ketones and hence nucleophilic addition reaction (such as formation of oximes, hydrazones, phenylhydrazones, 2, 4-dinitrophenylhydrazones and semicarbazones) of aldehydes and ketones do to take place with carboxylic acids.

Q.20 Fluorine is more electronegative thane chlorine even then p-fluorobenzoic acid is a weaker acid than p-chlorobenzoic acid . Explain

A.20 Halogens are more electronegative than that of carbon and also posses lone pairs of electrons, therefore, they exert both –I and +R effects. Now in F, the lone pairs of electrons are present in 2p-orbitals but in Cl, they are present in 3p-orbitals. Since 2p-orbitals of F and C are of almost equal size, therefore, the +R- effect is more pronounced in p-flurobenzoic acid than in p-chlorobenzoic acid



Stronger +R effect



Weaker +R effect

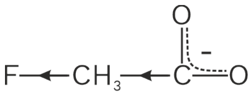
Thus, in p-flurobenzoic acid, +R-effect outweighs the –I-effect but in p-chlorobenzoic acid, it is the -+I-effect which outweighs the +R-effect. Consequently, p-fluorobenzoic acid is a weaker acid than p-chlorobenzoic acid.

Q.21 Why is pKa of FCH_2COOH lower than that of chloroacetic acid?

A.21 pKa of FCH_2 COOH is lower than that of $ClCH_2$ COOH implies that FCH_2 COOH is a stronger acid than $ClCH_2COOH$. This is due to the following two reasons:

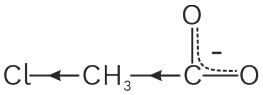
(i) Due to stronger –I-effect of F over Cl, the electron density in the O – H bond in FCH_2COOH is much lower than in $ClCH_2COOH$. As a result, O – H bond in FCH_2COOH is much weaker than in $ClCH_2COOH$ and hence FCH_2COOH loses a proton more easily than $ClCH_2COOH$ i.e., FCH_2COOH is a stronger acid than $ClCH_2COOH$.

(ii) Due to stronger —I-effect of F over Cl, the dispersal of the -ve charge in FCH_2COO^- occurs more effectively than in $ClCH_2COO^-$



$\mathrm{F \leftarrow CH_3 \leftarrow \overset{\overset{O}{\|}}{C} \overset{-}{\cdots} O}$

(Smaller -I effect)



$\mathrm{Cl \leftarrow CH_3 \leftarrow \overset{\overset{O}{\|}}{C} \overset{-}{\cdots} O}$

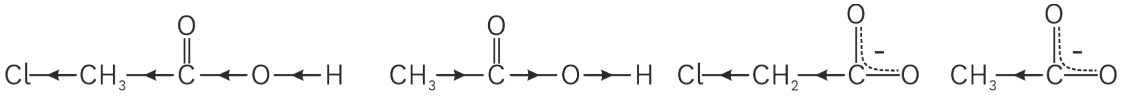
(Weaker -I effect)

In other words, FCH_2COO^- is more stable than $ClCH_2COO^-$ and hence FCH_3COOH is a stronger acid than $ClCH_2COOH$, i.e., FCH_2COOH has lower pKa than $ClCH_2COOH$.

Q.22 pKa of chloroacetic acid is lower than pKa of acetic acid. Explain.

A.22 pKa of chloroacetic acid is lower than pKa of acetic acid. This means, chloroacetic acid is a stronger acid than acetic acid. This may be explained on the basis of the following two reasons:

(i) Due to –I-effect of Cl atom, the electron density in the O–H bond in chloroacetic acid is much lower than due to +I-effect of CH_3 group in acetic acid. As a result, O – H bond in chloroacetic acid is much weaker than in acetic acid and hence loses a proton more easily than acetic acid.

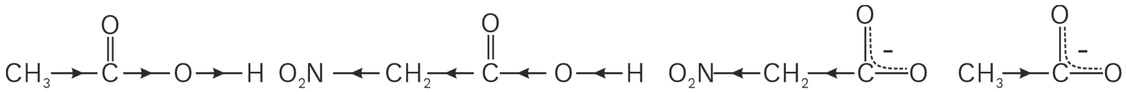


$$Cl \leftarrow CH_3 \leftarrow \overset{\overset{O}{\|}}{C} \leftarrow O \leftarrow H \quad CH_3 \rightarrow \overset{\overset{O}{\|}}{C} \rightarrow O \rightarrow H \quad Cl \leftarrow CH_2 \leftarrow \overset{\overset{O}{\vdots}}{C} \overset{-}{\cdots} O \quad CH_3 \leftarrow \overset{\overset{O}{\vdots}}{C} \overset{-}{\cdots} O$$

(ii) Due to –I-effect of Cl, dispersal of the +-ve charge occurs in chloroacetate ion but due to +I-effect of CH_3 group, intensification of -ve charge occurs in acetate ion. In other words, chloroacetate ion is much more stable than acetate ion.

Q.23 $O_2N–CH_2–COOH$ has lower pKa value than CH_3COOH. Give reasons.

A.23 (i) Due to +I-effect of CH_3 group, electron density increases in the O–H bond of CH_3COOH whereas due to –I-effect of the NO_2 group electron density decreases in O– H bond of NO_2CH_2COOH



$$CH_3 \rightarrow \overset{\overset{O}{\|}}{C} \rightarrow O \rightarrow H \quad O_2N \leftarrow CH_2 \leftarrow \overset{\overset{O}{\|}}{C} \leftarrow O \leftarrow H \quad O_2N \leftarrow CH_2 \leftarrow \overset{\overset{O}{\vdots}}{C} \overset{-}{\cdots} O \quad CH_3 \rightarrow \overset{\overset{O}{\vdots}}{C} \overset{-}{\cdots} O$$

As a result, O – H bond in O_2NH_2COOH is weaker than the O – H bond in CH_3COOH and hence loses a proton more easily than CH_3COOH. In other words, O_2NCH_2COOH has lower pKa value than CH_3COOH.

(ii) Due to –I-effect of NO_2 group dispersal of -ve charge occurs in $O_2NCH_2COOH–$ but due to +I-effect of CH_3 group intensification of -ve charge occurs in $CH_3COOH–$. As a result, O_2NCH_2COOH is stronger acid than CH_3COOH. In other words, O_2NCH_2COOH has lower pKa value than CH_3COOH.

Q.24 Arrange the following in increasing order of acid strength:
$ClCH_2COOH$, CH_3CH_2COOH, $ClCH_2CH_2COOH$, $(CH_3)_2CHCOOH$, CH_3COOH

A.24 +I effect of alkyl groups decreases in order:
$(CH_3)_2CH— > —C_2H_5 > —CH_3$
–I effect decreases with distance, therefore, $ClCH_2CH_2COOH$ is weaker acid than $ClCH_2COOH$. The acid strength increases in the order:
$(CH_3)_2CHCOOH < CH_3CH_2COOH < CH_3COOH < ClCH_2CH_2COOH < ClCH_2COOH$.

Q.25 Why is the ester hydrolysis slow in the beginning and becomes faster after some time?

A.25 An easter on hydrolysis gives an alcohol and an acid.

$$\underset{\text{Easter}}{RCOOR'} + H_2O \xrightarrow{H_2SO_4\ \text{(few drops)}} \underset{\text{Carboxylic acid}}{RCOOH} + \underset{\text{Alcohol}}{R'OH}$$

A small amount of dil. H_2SO_4 is added in the beginning to start the reaction. As the reaction proceeds, a carboxylic acid (RCOOH) is produced. As the amount of carboxylic acid produced increases, the rate of ester hydrolysis also increases.

Chapter Summary

1. HCHO cannot be prepared by Rosenmund reduction since formyl chloride is unstable at room temperature.
2. Formalin is 40% HCHO solution and is used to preserve biological specimens.
3. Aromatic aldehydes do not reduce Fehling's and Benedict's solution.
4. In Cross-Cannizzaro reaction HCHO is always oxidised and other aldehyde is reduced.

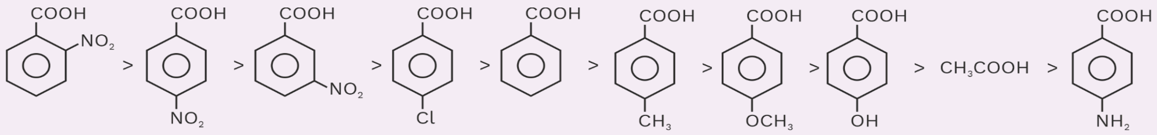
$$HCHO + C_6H_5CHO \xrightarrow{\text{dil. NaOH}} HCOONa + C_6H_5CH_2OH$$

5. 2-methyl propanal has α-H atom but gives both aldol condensation and Cannizzaro reaction.
6. (i) Aldehydes and ketones having α-H atom $\xrightarrow{\text{alkali}}$ Aldol condensation.
   (ii) Aldehydes and with α-H atom $\xrightarrow{\text{aq. alkali}}$ Cannizzaro reaction.
7. Aldol condensation is given by only those aldehydes or ketones which have unsaturated carbon, α-H atom on unsaturated carbon atom cannot be easily removed by base.
8. Glacial acetic acid is pure acetic acid.
9. Quick vinegar process :

$$CH_3CH_2OH + O_2 \xrightarrow{\text{acetobactor acetic}} CH_3COOH + H_2O$$

10. Higher value of Ka or lower value of pKa, stronger is acid.
11. (i) Decarboxylation of sodium format (HCOONa) $\longrightarrow H_2$
    (ii) Decarboxylation of sodium acetate (CH_3COONa) $\longrightarrow CH_4$
12. Formic acid (HCOOH) is strong reducing agent due to presence of —CHO group.
13. Electron withdrawing groups increase the acidity and electron donating groups decrease the acidity.

    The acid strength decreases as :



14. The boiling points of acid derivatives follow the order.

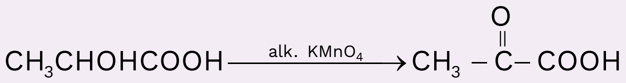
    amide > anhydride > acid > ester > acid chloride
15. The reactivity of acid derivatives towards nucleophilic acyl substitution reaction is as follows.

    $RCOCl > (RCO)_2O > RCOOR' > RCONH_2$

    because the basicity of anhydride leaving group increases i.e.,

    $—Cl < —RCOO < —RO < —NH_2$ (weaker the basic character of leaving group, more will be the ease with which bond can be broken and hence more reactivity).

16. Lactic acid on oxidation gives pyruvic acid.



$$CH_3CHOHCOOH \xrightarrow{alk.\ KMnO_4} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-COOH$$

Lactic acid   Pyruvic acid

17. Urea is salt of weak acid H_2CO_3 and weak base NH_3 so its aqueous solution is neutral.