DAY THIRTY TWO

Aldehydes, Ketones and Carboxylic Acids

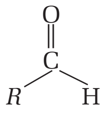
Learning & Revision for the Day

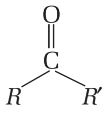
- Aldehydes and Ketones
- Methods of Preparation of Aldehydes and Ketones
- Methods of Preparation of Carboxylic Acids
- Carboxylic Acids
- Carboxylic Acids
- Uses of Carboxylic Acids

The organic compounds containing carbon-oxygen double bond, i.e. $>C=O$ group are called **carbonyl compounds.** These compounds are widely spread both in plant and animal kingdom and they play an important role in biological processes.

Aldehydes and Ketones

- In aldehydes, the carbonyl group is bonded to a carbon and hydrogen, while in the ketones, it is bonded to two carbon atoms.
- Aldehydes and ketones are functional isomers.


Aldehyde


Ketone

Nomenclature

- According to IUPAC nomenclature system, name of aldehyde is obtained by replacing the terminal 'e' of the corresponding alkane by the suffix 'al'.

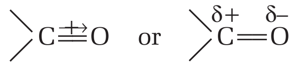
Aldehyde	General name	IUPAC name
HCHO	Formaldehyde	Methanal
CH_3CHO	Acetaldehyde	Ethanal
CH_3CH_2CHO	Propionaldehyde	Propanal

- Name of a ketone is obtained by replacing the terminal '*e*' of the corresponding alkane by the suffix 'one'.

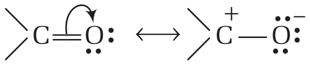
Ketones	General name	IUPAC name
CH_3COCH_3	Acetone	Propanone
$CH_3COCH_2CH_3$	Ethyl methyl ketone	Butanone
$CH_3COCH_2CH_2CH_3$	Methyl *n*-propyl ketone	Pentan-2-one
$CH_3CH_2COCH_2CH_3$	Diethyl ketone	Pentan-3-one

Nature of Carbonyl Group

- In carbonyl group, π-electron cloud is displaced towards more electronegative oxygen atom thus, causing polarisation of the bond so that carbon is partially positive and oxygen is partially negative.



- In resonance terms, electron delocalisation in the carbonyl group is represented by contributions from two principal resonance forms.



Methods of Preparation of Aldehydes and Ketones

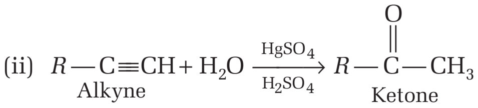
There are several methods from which aldehydes as well as ketones can be synthesised. These methods are as follows:

- **Ozonolysis of alkenes** is carried out by reaction with Zn dust and water to give aldehydes and ketones.

$$CH_2=CH_2 \xrightarrow[\text{(ii) Zn + }H_2O]{\text{(i) }O_3} 2HCHO$$

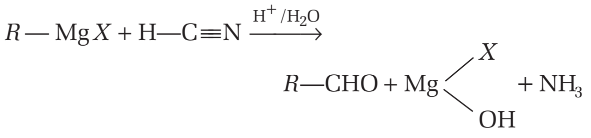
- **Hydration of acetylene** gives acetaldehyde and other alkynes give ketones.

(i) $\underset{\text{Acetylene}}{CH\equiv CH} + H_2O \xrightarrow[H_2SO_4]{HgSO_4} \underset{\text{Acetaldehyde}}{CH_3CHO}$

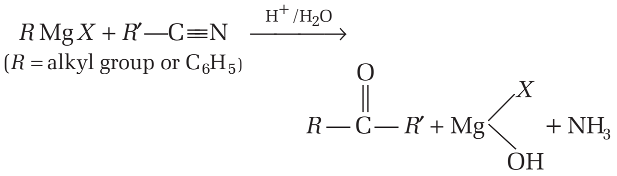


(ii) $\underset{\text{Alkyne}}{R—C\equiv CH} + H_2O \xrightarrow[H_2SO_4]{HgSO_4} \underset{\text{Ketone}}{R—\overset{O}{\overset{\|}{C}}—CH_3}$

- When HCN reacts with Grignard reagent and then subjected to hydrolysis, gives aldehydes while RCN gives ketone.



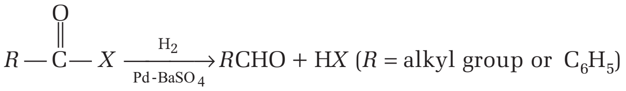
$$R—MgX + H—C\equiv N \xrightarrow{H^+/H_2O} R—CHO + Mg\begin{matrix}X\\OH\end{matrix} + NH_3$$



$$\underset{(R = \text{alkyl group or } C_6H_5)}{RMgX + R'—C\equiv N} \xrightarrow{H^+/H_2O} R—\overset{O}{\overset{\|}{C}}—R' + Mg\begin{matrix}X\\OH\end{matrix} + NH_3$$

The following methods used to synthesise the aldehyde only are given as :

- Acyl chloride is hydrogenated over catalyst, palladium on barium sulphate, to give aldehyde. This reaction is called **Rosenmund reduction**.



$$R—\overset{O}{\overset{\|}{C}}—X \xrightarrow[\text{Pd-BaSO}_4]{H_2} RCHO + HX \ (R = \text{alkyl group or } C_6H_5)$$

NOTE Formaldehyde cannot be obtained by the use of Rosenmund reduction because formyl chloride is unstable at room temperature.

- Nitriles or cyanides are reduced to corresponding imine with stannous chloride in the presence of HCl acid, which on hydrolysis give corresponding aldehyde. This reaction is called **Stephen reaction.**

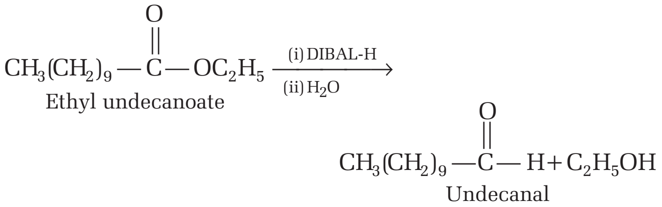
$$R—CN + SnCl_2 + HCl \longrightarrow \underset{\text{Imino chloride}}{RCH=NH} + HCl$$

$$\xrightarrow{H_3O^+} RCHO + NH_4Cl + H_2O$$

- Nitriles are selectively reduced by diisobutylaluminium hydride (DIBAL-H) and gives aldehydes.

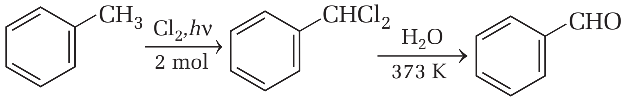
$$CH_3CH=CHCH_2CH_2CN \xrightarrow[\text{(ii) }H_2O]{\text{(i) AlH }(i\text{-Bu})_2} \underset{\text{Hex-4-enal}}{CH_3CH=CHCH_2CH_2CHO}$$

Esters are also reduced to aldehyde with DIBAL-H.



$$\underset{\text{Ethyl undecanoate}}{CH_3(CH_2)_9—\overset{O}{\overset{\|}{C}}—OC_2H_5} \xrightarrow[\text{(ii) }H_2O]{\text{(i) DIBAL-H}} \underset{\text{Undecanal}}{CH_3(CH_2)_9—\overset{O}{\overset{\|}{C}}—H} + C_2H_5OH$$

- **Side chain chlorination** of toluene gives benzal chloride, which on hydrolysis gives benzaldehyde.

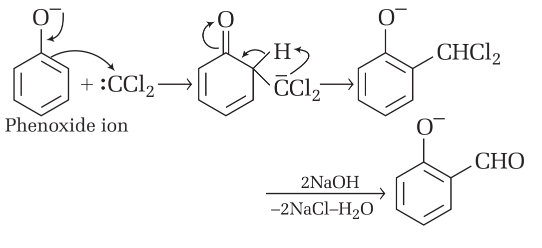


Benzal chloride Benzaldehyde

Treatment of phenol with chloroform in presence of aqueous sodium or potassium hydroxide at 340K followed by hydrolysis of the resulting product gives 2-hydroxybenzaldehyde (salicyldehyde) as major product. This reaction is called **Reimer-Tiemann reaction.** The electrophile involved in this reaction is $:CCl_2$.

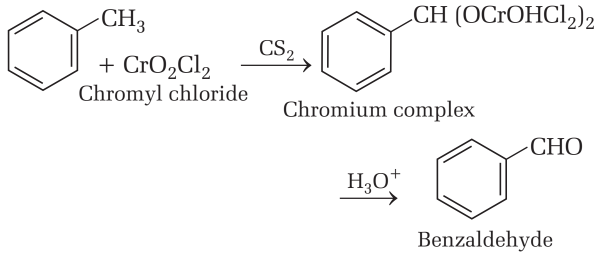
(i) $\bar{O}H + CHCl_3 \rightleftharpoons H_2O + CCl_3^- \longrightarrow :CCl_2 + Cl^-$

(ii)

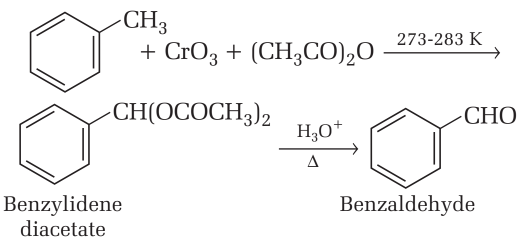


- Chromyl chloride oxidises methyl group to a chromium complex, which on hydrolysis gives corresponding benzaldehyde.

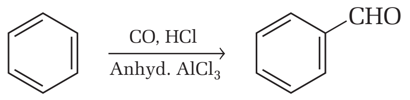
This reaction is called **Etard reaction.**



- Toluene or substituted toluene, on treating **with chromic oxide** in acetic anhydride gives benzylidene diacetate which on hydrolysis gets converted to corresponding benzaldehyde.

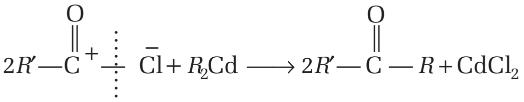


- When benzene or its derivative is treated with carbon monoxide and HCl in the presence of anhy. $AlCl_3$, gives benzaldehyde or substituted benzaldehyde. This reaction is known as **Gattermann–Koch** reaction.



The following methods are used to synthesise the ketones are given as

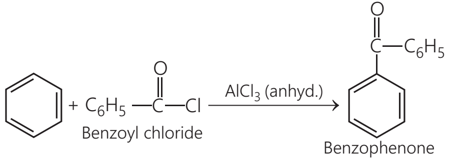
- Treatment of acyl chlorides with dialkylcadmium gives ketones



$$2R'-\overset{\overset{\displaystyle O}{\|}}{C}{}^{+} \vdots \overset{-}{Cl} + R_2Cd \longrightarrow 2R'-\overset{\overset{\displaystyle O}{\|}}{C}-R + CdCl_2$$

- Benzene is treated with acid chloride in the presence of anhy. $AlCl_3$ gives ketone and this reaction is called **Friedel-Craft's acylation.**

NOTE If acylation of benzene is done with benzoyl chloride, benzophenone gets form.



Physical Properties

The physical properties of aldehydes and ketones are following:

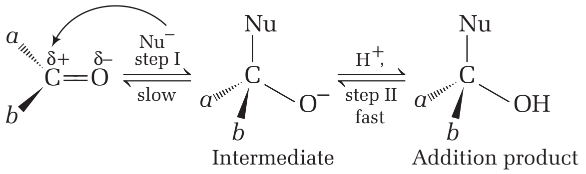
- Aldehydes and ketones are liquid or solid at room temperature. Methanal is a gas at room temperature. Ethanal is a volatile liquid.
- The boiling point of aldehydes and ketones are higher than ethers of comparable molecular masses.
- The lower members of aldehydes and ketones such as methanal, ethanal and propanone are miscible with water in all proportions because they form hydrogen bond with water. However, the solubility of aldehydes and ketones decreases rapidly on increasing the length of alkyl chain.

Chemical Properties

Aldehydes and ketones due to the presence of polar carbonyl group exhibit the following characteristics:

1. Mechanism of Nucleophilic Addition Reaction

- A nucleophile attacks the electrophilic carbon atom of the polar carbonyl group. The hybridisation of carbon changes from sp^2 to sp^3 in this process and a tetrahedral alkoxide intermediate is produced. This intermediate captures a proton from reaction medium to give electrically neutral product.



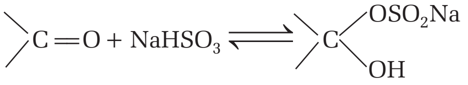
- As the number of carbon atoms increases, **reactivity** decreases due to steric hindrance. Hence, the order of reactivity is

$$HCHO > CH_3CHO > CH_3COCH_3 > C_2H_5COC_2H_5$$

(i) They react with hydrogen cyanide to yield cyanohydrins.

Cyanohydrin

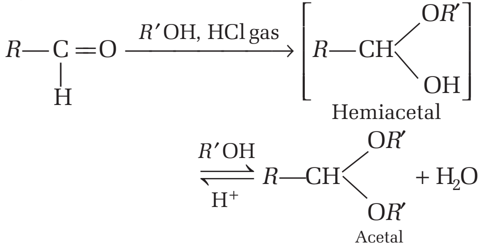
(ii) Sodium hydrogen sulphite adds to aldehydes and ketones to form addition products.

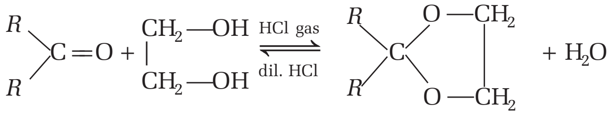


Addition product
(white crystalline solid)

This reaction is used for the separation and purification of aldehydes and ketones. The reason for this is that the hydrogen sulphite addition compound formed, is water soluble and can be converted back to the original carbonyl compound by treating with dilute mineral acid or alkali.

(iii) Aldehydes react **with alcohols** in the presence of dry HCl gas to give *gem*–dialkoxy compounds called acetals, while ketones combine with ethylene glycol to form cyclic ketal.





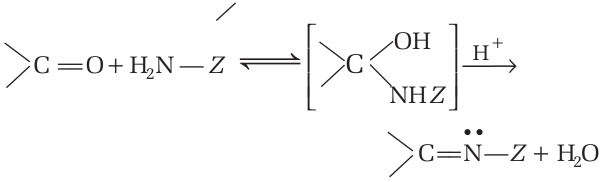
Ethylene glycol ketal

When ketones are treated with excess of alcohol in presence of dry HCl, they form ketal.

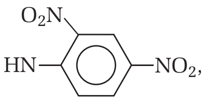
(iv) Aldehydes and ketones with primary amines in presence of a catalytic amount of an acid to form Schiff's bases. e.g.

$$>C=O + \underset{1^\circ\text{-amine}}{H_2NR'} \xrightarrow{H^+,\Delta} \underset{\text{Schiff base}}{>C=NR'} + H_2O$$

(v) Aldehydes and ketones react with ammonia derivatives in weakly acidic medium to form compounds containing carbon–nitrogen double bond. This reaction is reversible and catalysed by acid (pH ≈ 4). The equilibrium favours the product formation due to rapid dehydration of the intermediate to form $>C=N-Z$.



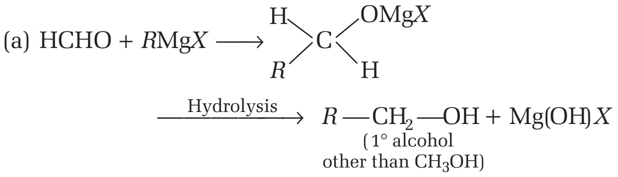
where, Z = alkyl, aryl, —OH, —NH$_2$, —H,



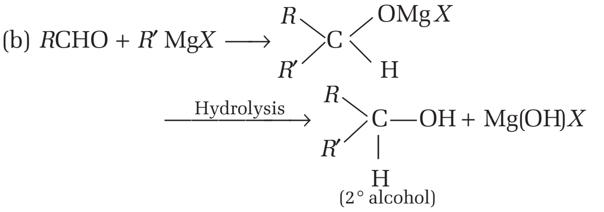
C_6H_5NH—, —NHCONH$_2$, etc.

(vi) These react with **Grignard reagent** to form addition products, which on hydrolysis gives alcohols. Formaldehyde produces primary alcohols, other aldehydes give secondary alcohols, while ketones give tertiary alcohols.

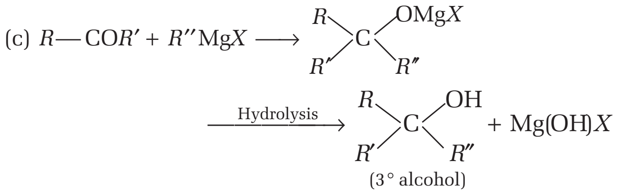
The reactions are as :



(1° alcohol other than CH_3OH)



(2° alcohol)



(3° alcohol)

2. Reduction

Aldehydes and ketones undergo **reduction** to form as follows alkanes.

- The carbonyl group of aldehydes and ketones is reduced to CH_2 group on treatment with zinc-amalgam and conc. HCl. This is called **Clemmensen reduction.**

$$>C=O \xrightarrow[\text{HCl}]{\text{Zn-Hg}} >CH_2 + H_2O$$

- The carbonyl group is reduced to CH_2 group on treatment with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent such as ethylene glycol.

  This is called **Wolff-Kishner reduction.**

$$>C=O \xrightarrow[-H_2O]{NH_2\cdot NH_2} >C=N\cdot NH_2 \xrightarrow[\text{Heat}]{\text{KOH/Ethylene glycol}} >CH_2 + N_2$$

NOTE In presence of Pd-catalyst, selective reduction of α, β-carbonyl group.

3. Oxidation

- Aldehydes are easily oxidised to carboxylic acids on treatment with strong oxidising agents (HNO_3, $K_2Cr_2O_7$, $KMnO_4$, etc). Oxidation of primary alcohols and aldehydes cannot be carried out by alkaline $K_2Cr_2O_7$ because under these conditions, potassium chromate is formed which does not act as an oxidising agent.

  Mild oxidising agents, mainly Tollen's reagent and Fehling's reagent also oxidise aldehydes.

$$\underset{(R = \text{alkyl or } C_6H_5 \text{ group})}{RCHO} + \underset{\text{Tollen's reagent}}{2[Ag(NH_3)_2]^+ + 3OH^-} \longrightarrow RCOO^- + \underset{\text{Silver mirror}}{2\,Ag} + 2\,H_2O + 4\,NH_3$$

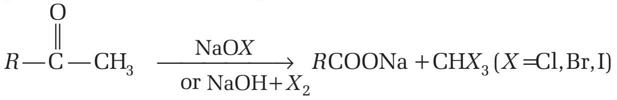
$$R-CHO + \underset{\text{Fehling's reagent}}{2Cu^{2+} + 5OH^-} \longrightarrow RCOO^- + \underset{\text{Red brown ppt.}}{Cu_2O} + 3H_2O$$

This reaction is not given by aromatic aldehydes as well by ketones.

Ketones are oxidised only in the presence of strong oxidising agents and at elevated temperatures. Their oxidation involves carbon-carbon bond cleavage to give a mixture of carboxylic acids having lesser number of carbon atoms than the parent ketone, e.g.

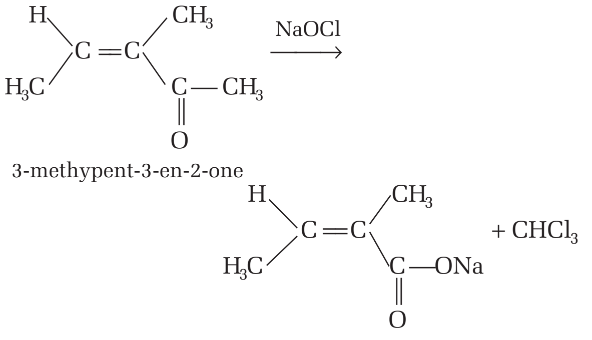
$$R-\underset{\underset{O}{\|}}{C}-R'' \xrightarrow{\text{Alkaline}\cdot KMnO_4} RCOOH + R''COOH$$

Methyl ketones (—$COCH_3$) are also oxidised by **haloform reaction** in which they are treated with halogen in the presence of alkali or hypohalite salt.



$$R-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[\text{or } NaOH+X_2]{NaOX} RCOONa + CHX_3\ (X = Cl, Br, I)$$

This reaction does not affect the carbon-carbon double bond present in molecule.



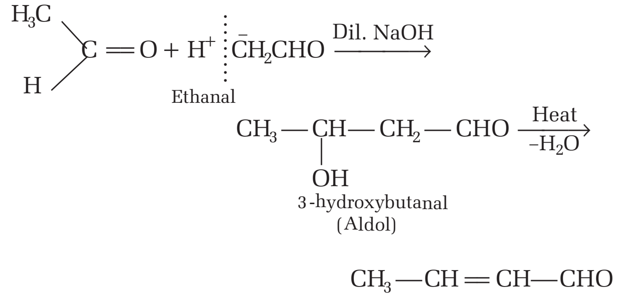
3-methypent-3-en-2-one

Sodium 3-methylpent-3-enoate

—CH_3 group of $COCH_3$ is converted into haloform as it contains acidic hydrogen atoms. Acid salt is obtained corresponding to total number of carbon atoms apart from —CH_3 of $RCOCH_3$.

4. Reactivity of α-Hydrogen in Aldehydes

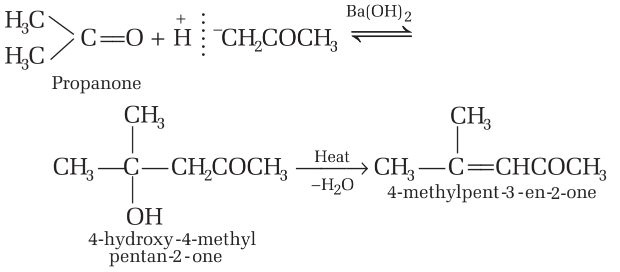
Aldehydes or ketones having atleast one α-hydrogen atom, undergo self condensation in the presence of dilute alkali as catalyst to form β -hydroxy aldehydes (aldol) or β -hydroxy ketones (ketol) respectively. This reaction is called **Aldol condensation**.



3-hydroxybutanal (Aldol)

$CH_3—CH═CH—CHO$

But-2-enal

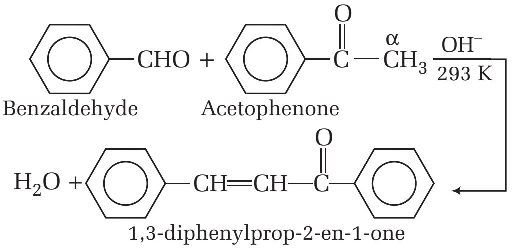


Propanone

4-hydroxy-4-methyl pentan-2-one (Ketol)

4-methylpent-3-en-2-one

When aldol condensation is carried out between two different aldehydes and/or ketones, it is called **cross-aldol condensation**, e.g.



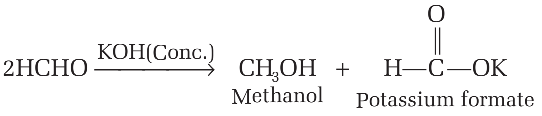
Benzaldehyde

Acetophenone

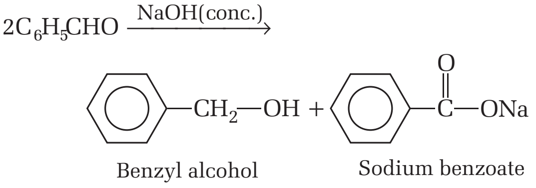
1,3-diphenylprop-2-en-1-one
(Benzalacetophenone)

5. Cannizzaro Reaction

Aldehydes which do not have any α-hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on treatment with concentrated alkali. This reaction is called **Cannizzaro's reaction**.



$$2HCHO \xrightarrow{KOH(Conc.)} \underset{\text{Methanol}}{CH_3OH} + \underset{\text{Potassium formate}}{H—\overset{\overset{\displaystyle O}{\|}}{C}—OK}$$



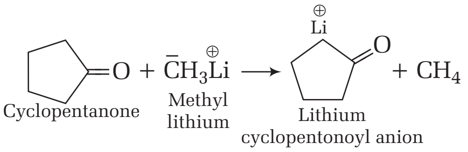
Benzyl alcohol

Sodium benzoate

6. Electrophilic Substitution Reactions

Aromatic aldehydes and ketones undergo **electrophilic substitution reactions**. Carbonyl group shows +*R*-effect, therefore acts as a deactivating and *meta* directing group.

- Benzaldehyde and acetophenone undergo **halogenation reactions** with Cl_2 in presence of $FeCl_3$ to form *m*-chlorobenzaldehyde and *m*-chloroacetophenone respectively. Benzaldehyde and acetophenone undergo **nitration** carried by nitrating mixture of conc. HNO_3 and conc. H_2SO_4 to form *m*-nitrobenzaldehyde and *m*-nitroacetophenone respectively.
- Benzaldehyde and acetophenone undergo sulphonation carried out with conc. H_2SO_4 to form *m*-benzaldehyde sulphonic acid and *m*-acetophenone sulphuric acid.
- Ketones **react with alkyl lithium** and leaves behind an intermediate.



NOTE
- In keto-enol tautomerism, keto form should have α-hydrogens.
- Acetaldehyde due to presence of $\left(CH_3—\overset{\overset{O}{\|}}{C}—\right)$ group, reacts with NaOH and I_2 to give yellow crystals of iodoform while which do not contain this group, does not give the crystals. This is known as iodoform test.

Uses

- In chemical industry, aldehydes and ketones are used as solvents, starting materials and reagents for the synthesis of other products.
- Formaldehyde, under the name formalin (40% solution) is used to preserve biological specimens.
- Formaldehyde is also used to prepare bakelite, urea-formaldehyde glues and other polymeric products.

Carboxylic Acids

Carbon compounds containing a functional group, —COOH are called carboxylic acids. Some higher members of aliphatic carboxylic acids (C_{12}-C_{18}) known as fatty acids, occur in natural fats as esters of glycerol.

Nomenclature According to IUPAC nomenclature system, name of a carboxylic acid is obtained by replacing the terminal 'e' of the corresponding alkane by the suffix 'oic acid'. Their general formula is $C_nH_{2n+1}COOH$.

Carboxylic acid	General name	IUPAC name
HCOOH	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
CH_3CH_2COOH	Propionic acid	Propanoic acid
$CH_3CH_2CH_2COOH$	Butyric acid	Butanoic acid
$(CH_3)_2CHCOOH$	*Iso*-butyric acid	2-methylpropanoic acid

Acidic Nature

- Carboxylic acids are acidic in nature but they are weaker acids than mineral acids but stronger acids than phenols (because the carboxylate ion is more stabilised as compared to phenoxide ion).
- The carboxylic acids form salts with alkalies.
- Strength of acid is indicated by pK_a value. Higher the value of K_a or lower value of pK_a, stronger is the acid.
- Aromatic acids are more acidic than aliphatic acids.

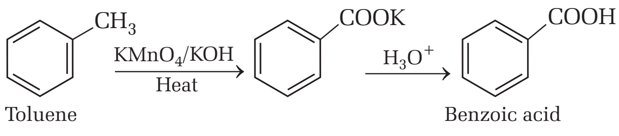
Methods of Preparation of Carboxylic Acids

- All acid derivatives like amides ($RCONH_2$), acid halides ($RCOCl$), esters ($RCOOR'$), acid anhydrides ($RCO—O—COR$) on hydrolysis give carboxylic acids.

$$RCOZ \xrightarrow[\text{Dil. NaOH}]{\text{Dil. HCl} \atop \text{or}} RCOOH$$

$$Z = —NH_2, —X\ (X = Cl, Br, I), OR', RCOO— \textit{ etc.}$$

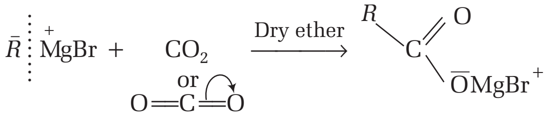
- **Alkyl benzene** when treated with strong oxidising agent like H_2CrO_4(chromic acid), acidic or alkaline $KMnO_4$ gives benzoic acid.



- **Nitriles** are hydrolysed to amides and then to acids in the presence of H^+ or OH^- as catalyst.

$$R—CN \xrightarrow[\Delta]{\text{Dil. HCl}} R—COOH + NH_3$$

- **Grignard reagent** react with CO_2 (dry ice) to form salts of carboxylic acids which on acidification with mineral acid give corresponding carboxylic acids.



(R may be alkyl or aryl group)

$$\xrightarrow[H^+/OH^-]{H_3O^+} RCOOH + Mg(OH)Br$$

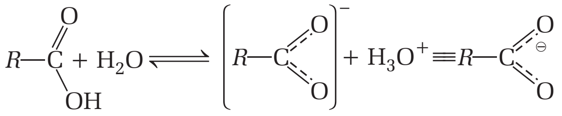
Physical Properties

Carboxylic acid are higher boiling liquids than acetaldehydes, ketones and even alcohols of comparable molecular masses. This is due to extensive association of carboxylic acid molecules through intermolecular hydrogen bonding. Aliphatic carboxylic acid having upto four carbon atoms are miscible in water due to formation of hydrogen bonds with water. But, solubility decreases with increasing number of carbon atoms.

Chemical Properties

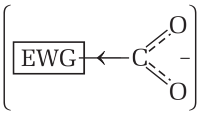
1. Reactions Involving Cleavage of O—H Bond

- Due to the acidic character of carboxylic acids, they react with active metals, alkalies and carbonates, bicarbonates to form their salts with liberation of hydrogen.
  (i) $2RCOOH + 2Na \longrightarrow 2RCOONa + H_2$
  (ii) $RCOOH + NaOH \longrightarrow RCOONa + H_2O$
  (iii) $RCOOH + NaHCO_3 \longrightarrow RCOONa + H_2O + CO_2$
- Carboxylic acids dissociate in water to give resonance stabilised carboxylate anions and hydronium ion.

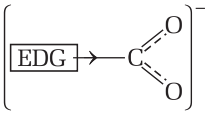


2. Effect of Substituents on the Acidity of Carboxylic Acids

- Electron withdrawing group (EWG) stabilises the carboxylate anion and strengthens the acid.



- Electron donating group (EDG) destabilises the carboxylate anion and weakens the acid. Strong acids have higher value of K_a and lower value of pK_a.



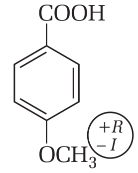
- Following acids are arranged in decreasing order of acidity

$CF_3COOH > CCl_3COOH > CHCl_2COOH$

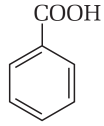
$NO_2CH_2COOH > NC—CH_2COOH$

$C_6H_5COOH > C_6H_5CH_2COOH >$
$CH_3COOH > CH_3CH_2COOH$

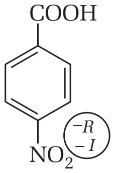
- In case of aromatic carboxylic acids, more the –*R*-effect, more is the acidic nature.



4-methoxy benzoic acid (pK_a = 4.46)



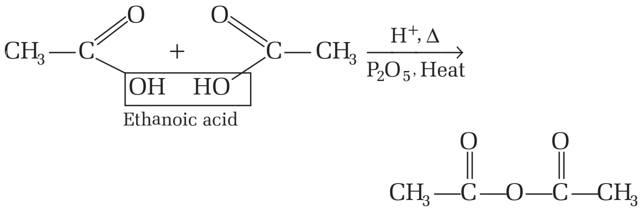
Benzoic acid (pK_a = 4.19)



4-nitrobenzoic acid (pK_a = 3.41)

3. Reactions Involving Cleavage of C — OH Bond

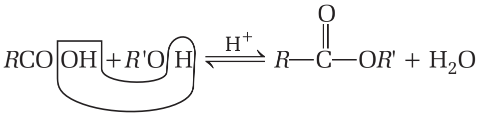
- Carboxylic acids on heating with mineral acids such as H_2SO_4 or with P_2O_5 give corresponding anhydride.



Ethanoic acid

Ethanoic anhydride

- Alcohols or phenols, in the presence of mineral acid such as conc. H_2SO_4 or HCl gas as a catalyst, forms esters. This reaction is called **esterification**.



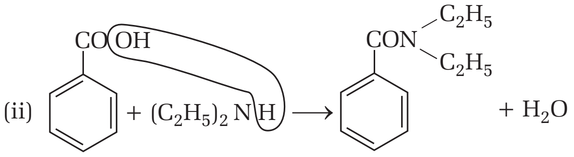
$$RCO\boxed{OH} + R'O\boxed{H} \overset{H^+}{\rightleftharpoons} R-\overset{\overset{O}{\|}}{C}-OR' + H_2O$$

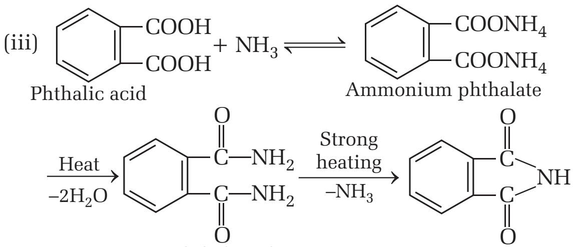
- They react with PCl_5, PCl_3 and $SOCl_2$ to give the following products.

$$RCOOH + PCl_5 \longrightarrow RCOCl + PCl_3 + HCl$$
$$3RCOOH + PCl_3 \longrightarrow 3RCOCl + H_3PO_3$$
$$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2\uparrow + HCl\uparrow$$

- They react with ammonia and its derivatives to give ammonium salts which on further heating at high temperature give amides.

(i) $$CH_3COOH + NH_3 \rightleftharpoons \underset{\text{Ammonium acetate}}{CH_3COONH_4} \xrightarrow{\text{Heat}} \underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow[P_2O_5]{\text{Heat}} CH_3CN + H_2O$$





Phthalic acid

Ammonium phthalate

Phthalamide

Phthalimide

4. Reaction Involving —COOH Group

- Carboxylic acids are reduced to primary alcohols by $LiAlH_4$ or better with B_2H_6. B_2H_6 does not easily reduce functional groups such as esters, nitro, halo, etc. $NaBH_4$ does not reduce the carboxyl group.

$$RCOOH \xrightarrow[\text{(ii)} H_3O^+]{\text{(i) } LiAlH_4/\text{Ether or } B_2H_6} RCH_2OH + H_2O$$

- They lose carbon dioxide to form hydrocarbons when their sodium salt are heated with sodalime. The reaction is known as **decarboxylation.**

$$RCOONa + NaOH \xrightarrow[\text{Heat}]{CaO} RH + Na_2CO_3$$

- Methanoic acid and its sodium salt acts as reducing agent due to —CHO group. It reduces Tollen's reagent, Fehling's reagent, $KMnO_4$ etc. Carboxylic acid (except formic acid) react with chlorine or bromine in presence of small quantities of red phosphorus to give exclusively α-chloro or α-bromo acids. This reaction is called **Hell–Volhard Zelinsky** (HVZ reaction).

$$R—CH_2—COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2, \text{ red P}} \underset{\alpha\text{-halocarboxylic acid}}{R—CHX—COOH}$$

(X = Cl or Br)

Uses

- Methanoic acid is used in rubber, textile, leather and electroplating industries.
- Ethanoic acid is used as solvent and as vinegar in food industry.
- Hexanedioic acid is used in the manufacture of nylon-6,6.
- Sodium benzoate is used as a food preservative.

DAY PRACTICE SESSION 1

FOUNDATION QUESTIONS EXERCISE

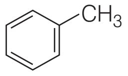
1 Which of the following compounds on heating with aqueous KOH, produces acetaldehyde?

(a) CH_3COCl (b) CH_3CH_2Cl

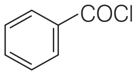
(c) CH_2ClCH_2Cl (d) CH_3CHCl_2

2 Reaction by which, benzaldehyde cannot be prepared?

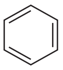
→ NEET 2013

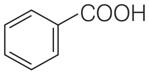
(a) 

+ CrO_2Cl_2 and CS_2 followed by H_3O^+

(b) 

+ H_2 in presence of Pd-$BaSO_4$

(c) 
+ CO + HCl in presence of anhy. $AlCl_3$

(d) 

+ Zn/Hg and conc. HCl

3 When ethanal reacts with CH_3MgBr and C_2H_5OH/dry HCl, the product formed are

(a) ethyl alcohol and 2-propanol

(b) ethane and hemiacetal

(c) 2-propanol and acetal

(d) propane and methyl acetate

4 The product formed by the reaction of an aldehyde with a primary amine is **→ NEET 2016, Phase I**

(a) ketone (b) carboxylic acid

(c) aromatic acid (d) Schiff base

5 An organic compound *X* having molecular formula $C_5H_{10}O$ yields phenyl hydrazone and gives negative response to the iodoform test and Tollen's test. It produces *n*-pentane on reduction. *X* could be

→ CBSE-AIPMT 2015

(a) pentanal (b) 2-pentanone

(c) 3-pentanone (d) *n*-amyl alcohol

6 Self condensation of acetaldehyde in the presence of dilute alkalies gives

(a) an acetal

(b) an aldol

(c) mesitylene

(d) propionaldehyde

7 Which of the following compounds will not undergo aldol condensation?

(a) Methanal

(b) 2-methyl pentanal

(c) Cyclohexanone

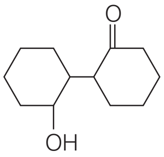
(d) 1-phenyl propanone

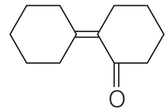
8 Which of the following compounds would be the main product of an aldol condensation of acetaldehyde and acetone?

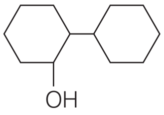
(a) $CH_3CH{=}CH\,CHO$ (b) $CH_3CH{=}CH\,COCH_3$

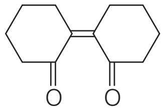
(c) $(CH_3)_2\,C{=}CH\cdot CHO$ (d) $(CH_3)_2\,C{=}CHCOCH_3$

9 Of the following which is the product formed when cyclohexanone undergoes aldol condensation followed by heating? **→ NEET 2017**

(a) 

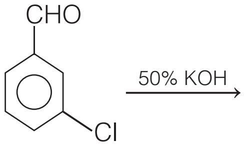
(b) 

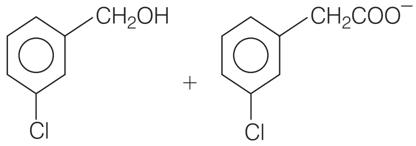
(c) 

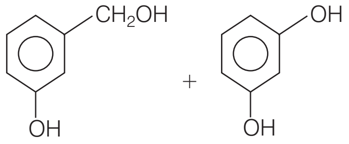
(d) 

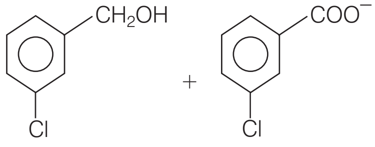
10 Predict the products in the given reaction,

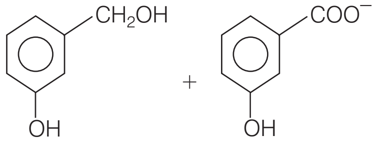
→ CBSE-AIPMT 2012



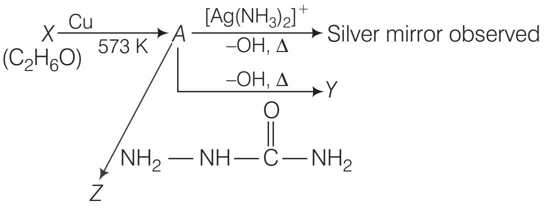
(a) 

(b) 

(c) 

(d) 

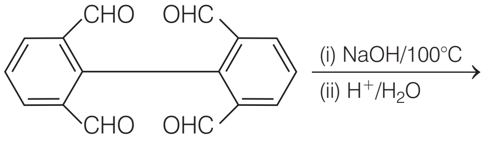
11 Consider the reactions,



Identify A, X, Y and Z. **➞ NEET 2017**

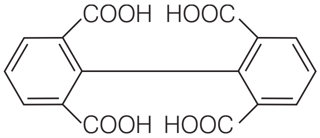
(a) A-methoxymethane, X-ethanoic acid, Y-acetate ion, Z-hydrazine
(b) A-methoxymethane, X-ethanol, Y-ethanoic acid, Z-semicarbazide
(c) A-ethanal, X-ethanol , Y-but-2-enal, Z-semicarbazone
(d) A-ethanol, X-acetaldehyde, Y-butanone, Z-hydrazone

12

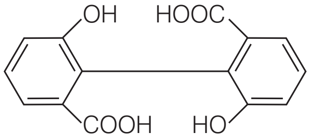


Major product is

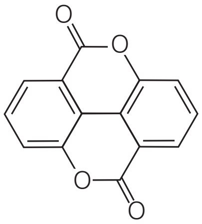
(a)



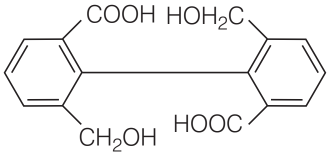
(b)



(c)



(d)



13 In Cannizzaro reaction given below,

$$2PhCHO \xrightarrow{OH^{\ominus}} PhCH_2OH + PhCO_2^{\ominus}$$

the slowest step is

(a) the attack of $OH^{\ominus}$
(b) the transfer of hydride to the carbonyl group
(c) the abstraction of proton from the carboxylic group
(d) the deprotonation of $PhCH_2OH$

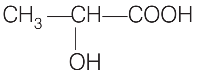
14 Which of the following reactions will not result in the formation of carbon-carbon bonds? **➞ CBSE-AIPMT 2010**

(a) Reimer-Tiemann reaction
(b) Cannizzaro reaction
(c) Wurtz reaction
(d) Friedel-Crafts acylation

15 $CH_3CHO + HCHO \xrightarrow[\Delta]{\text{Dil. NaOH}} A \xrightarrow[H_3O^+]{HCN} B$;

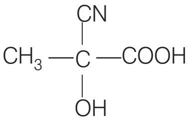
the structure of the compound B is

(a)



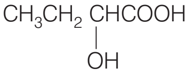
$CH_3—\underset{OH}{\underset{|}{C}H}—COOH$

(b)



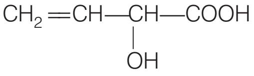
$CH_3—\overset{CN}{\overset{|}{\underset{OH}{\underset{|}{C}}}}—COOH$

(c)



$CH_3CH_2\,\underset{OH}{\underset{|}{C}H}COOH$

(d)

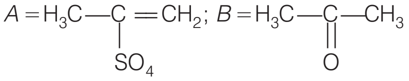


$CH_2=CH—\underset{OH}{\underset{|}{C}H}—COOH$

16 Predict the correct intermediate and product in the following reaction. **➞ NEET 2017**

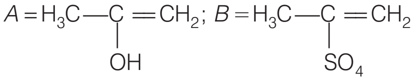
$$H_3C—C\equiv CH \xrightarrow[HgSO_4]{H_2O,\ H_2SO_4} \underset{(A)}{\text{Intermediate}} \longrightarrow \underset{(B)}{\text{Product}}$$

(a)



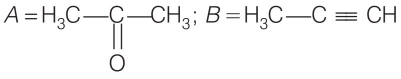
$A = H_3C—\underset{SO_4}{\underset{|}{C}}=CH_2$; $B = H_3C—\underset{O}{\underset{||}{C}}—CH_3$

(b)



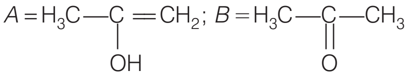
$A = H_3C—\underset{OH}{\underset{|}{C}}=CH_2$; $B = H_3C—\underset{SO_4}{\underset{|}{C}}=CH_2$

(c)



$A = H_3C—\underset{O}{\underset{||}{C}}—CH_3$; $B = H_3C—C\equiv CH$

(d)

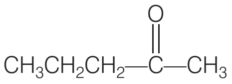


$A = H_3C—\underset{OH}{\underset{|}{C}}=CH_2$; $B = H_3C—\underset{O}{\underset{||}{C}}—CH_3$

17 Acetone is treated with excess of ethanol in the presence of hydrochloric acid. The product obtained is

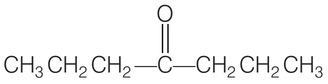
➞ CBSE-AIPMT 2012

(a)



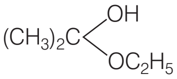
$CH_3CH_2CH_2—\overset{O}{\overset{||}{C}}—CH_3$

(b)



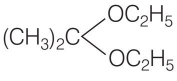
$CH_3CH_2CH_2—\overset{O}{\overset{||}{C}}—CH_2CH_2CH_3$

(c)



$(CH_3)_2C\langle^{OH}_{OC_2H_5}$

(d)



$(CH_3)_2C\langle^{OC_2H_5}_{OC_2H_5}$

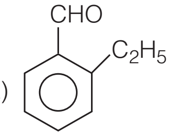
18 Clemmensen reduction of a ketone is carried out in the presence of which of the following? **➞ CBSE-AIPMT 2011**

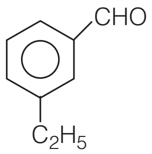
(a) Zn-Hg with HCl	(b) $LiAlH_4$
(c) H_2 and Pt as catalyst	(d) Glycol with KOH

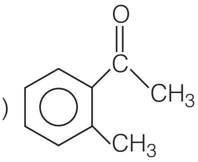
19 An aromatic compound 'X' with molecular formula $C_9H_{10}O$ gives the following chemical tests

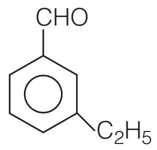
(i) It forms 2,4-DNP derivative.
(ii) It reduces Tollen's reagent.
(iii) It undergoes Cannizzaro reaction.
(iv) On vigorous oxidation, 1,2-benzenedicarboxylic acid is obtained.

Compound X is

(a) 

(b) 

(c) 

(d) 

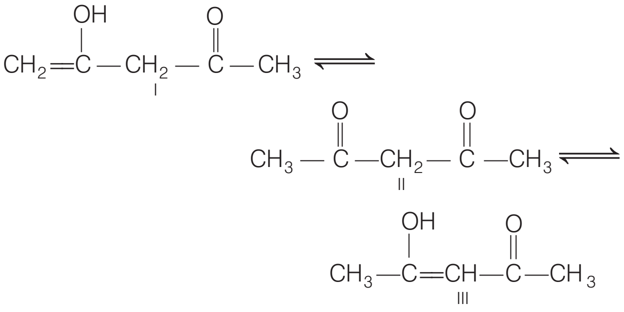
20 Which is not true about acetophenone?

(a) On oxidation with alkaline $KMnO_4$ followed by hydrolysis gives benzoic acid
(b) Reacts with I_2/NaOH to form iodoform
(c) Reacts with Tollen's reagent to form silver mirror
(d) Reacts to form 2,4-dinitrophenyl hydrazine

21 A compound does not react with 2,4-dinitrophenyl hydrazine, compound is

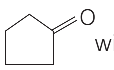
(a) acetone
(b) acetaldehyde
(c) CH_3OH
(d) $CH_3CH_2COCH_3$

22 The correct order of stability of the following tautomeric compounds, is



$$\underset{\text{I}}{CH_2=\overset{OH}{\overset{|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3} \rightleftharpoons \underset{\text{II}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3} \rightleftharpoons \underset{\text{III}}{CH_3-\overset{OH}{\overset{|}{C}}=CH-\overset{O}{\overset{\|}{C}}-CH_3}$$

(a) III > II > I
(b) II > I > III **→ NEET 2013**
(c) II > III > I
(d) I > II > III

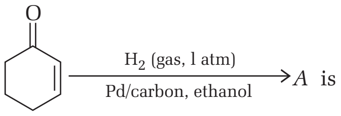
23 Treatment of cyclopentanone,  with methyl lithium gives which of the following species? **→ CBSE-AIPMT 2015**

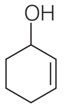
(a) Cyclopentanoyl anion
(b) Cyclopentanoyl cation
(c) Cyclopentanoyl radical
(d) Cyclopentanoyl biradical

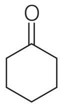
24 The best reagent to convert pent-3-en-2-ol into pent-3-en-2-one is

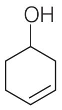
(a) pyridinium chloro chromate
(b) chromic anhydride in glacial acetic acid
(c) acidic dichromate
(d) acidic permanganate

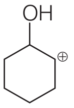
25 The correct structure of the product A formed in the reaction **→ NEET 2016, Phase II**



(a) 

(b) 

(c) 

(d) 

26 Arrange the following compounds in decreasing order of their boiling points

CH_3CHO, CH_3CH_2OH, CH_3OCH_3, $CH_3CH_2CH_3$

(a) $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH$
(b) $CH_3CH_2CH_3 < CH_3CHO < CH_3OCH_3 < CH_3CH_2OH$
(c) $CH_3CH_2CH_3 > CH_3CHO > CH_3OCH_3 > CH_3CH_2OH$
(d) $CH_3CH_2OH > CH_3CHO > CH_3OCH_3 > CH_3CH_2CH_3$

27 Which one of the following undergoes reaction with 50% sodium hydroxide solution to give the corresponding alcohol and acid?

(a) Phenol
(b) Benzoic acid
(c) Butanal
(d) Benzaldehyde

28 Carboxylic acids have higher boiling points than aldehydes, ketones and even alcohols of comparable molecular mass. It is due to their **→ NEET 2018**

(a) more extensive association of carboxylic acid *via* van der Waals' force of attraction
(b) formation of carboxylate ion
(c) formation of intramolecular H-bonding
(d) formation of intermolecular H-bonding

29 A liquid was mixed with ethanol and a drop of concentrated H_2SO_4 was added. A compound with a fruity smell was formed. The liquid was

(a) CH_3OH
(b) HCHO
(c) CH_3COCH_3
(d) CH_3COOH

30 By combining the two calcium salts of carboxylic acids, we are preparing 2-butanone. Find the correct pair from the following

(a) calcium formate + calcium propanoate
(b) calcium acetate + calcium propanoate
(c) calcium acetate + calcium acetate
(d) calcium formate + calcium acetate

31 In the following reaction,

$$CH_3COOH + X \xrightarrow{\text{Conc. } H_2SO_4} Y + CO_2 + N_2$$

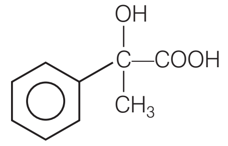
X and Y respectively, are

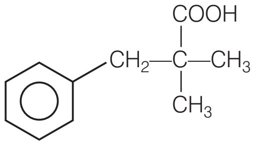
(a) HN_3 and CH_3NH_2 (b) NH_3 and CH_3CONH_2
(c) NH_3 and CH_3NH_2 d) NH_3 and CH_3CONH_2

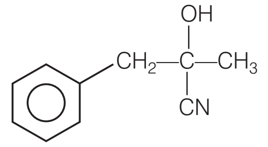
32 In a set of reactions, acetic acid yielded a product D

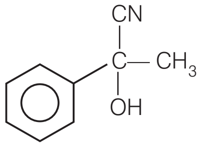
$$CH_3COOH \xrightarrow{SOCl_2} A \xrightarrow[\text{Anhyd. } AlCl_3]{\text{Benzene}} B \xrightarrow{HCN} C \xrightarrow{HOH} D$$

The structure of D would be

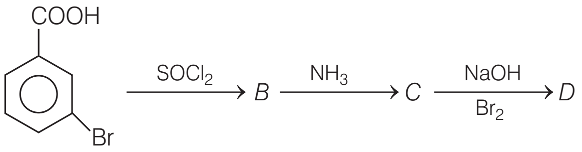
(a) 

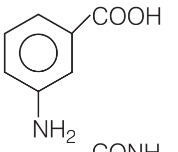
(b) 

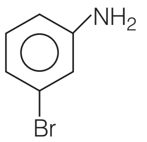
(c) 

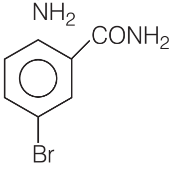
(d) 

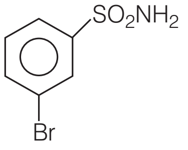
33 In a set of reactions, *m*-bromobenzoic acid gave a product D. Identify the product D. ➞ **CBSE-AIPMT 2011**



(a) 

(b) 

(c) 

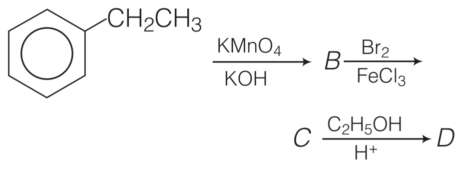
(d) 

34 $CH_3COOH \xrightarrow{LiAlH_4}$

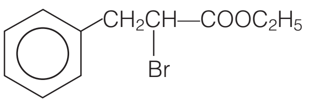
$A + CH_3COOH \xrightarrow{H_3O^+} B + H_2O$ In the above reactions, A and B respectively are

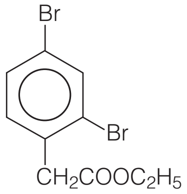
(a) $CH_3COOC_2H_5$, C_2H_5OH (b) CH_3CHO, C_2H_5OH
(c) C_2H_5OH, CH_3CHO (d) C_2H_5OH, $CH_3COOC_2H_5$

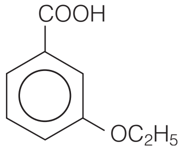
35 In a set of reactions, ethyl benzene yielded a product D. ➞ **CBSE-AIPMT 2010**

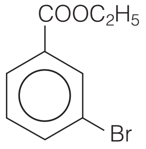


D would be

(a) 

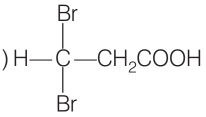
(b) 

(c) 

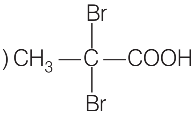
(d) 

36 Propionic acid with Br_2 —P yields a dibromo product. Its structure would be ➞ **CBSE-AIPMT 2009**

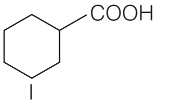
(a) $CH_2Br—CHBr—COOH$

(b) 
$H—\underset{Br}{\overset{Br}{C}}—CH_2COOH$

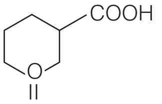
(c) $CH_2Br—CH_2—COBr$

(d) 
$CH_3—\underset{Br}{\overset{Br}{C}}—COOH$

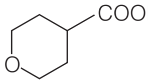
37 The correct order of strengths of the carboxylic acids ➞ **NEET 2016, Phase II**



I



II



III

is

(a) I > II > III (b) II > III >
(c) III > II > I (d) II > I > III

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

(a) $CH_3COOH > BrCH_2COOH > ClCH_2COOH > FCH_2COOH$
(b) $FCH_2COOH > CH_3COOH > BrCH_2COOH > ClCH_2COOH$
(c) $BrCH_2COOH > ClCH_2COOH > FCH_2COOH > CH_3COOH$
(d) $FCH_2COOH > ClCH_2COOH > BrCH_2COOH > CH_3COOH$

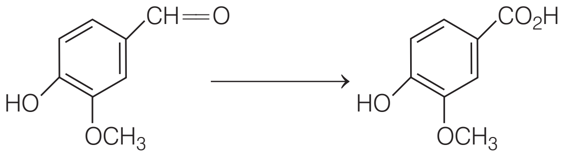
39 Given, cyclohexanol (I), acetic acid (II), 2, 4, 6- trinitrophenol (III) and phenol (IV). In these, the order of decreasing acidic character will be ➞ **CBSE-AIPMT 2010**

(a) III>II>IV>I (b) II>III>I>IV
(c) II>III>IV>I (d) III>IV>II>I

DAY PRACTICE SESSION 2

PROGRESSIVE QUESTIONS EXERCISE

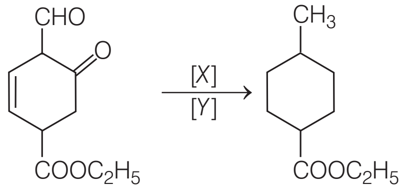
1 Following conversion can be carried out by using



I. $KMnO_4$ in alcohol II. NaClO in a buffer
III. Ag_2O/NaOH, HCl IV. $FeCl_3$ in a buffer

(a) 1, 2 and 3 (b) 1 and 2 (c) 2 and 4 (d) 1 and 3

2

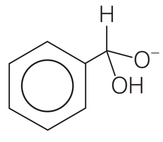


[*X*] and [*Y*] are

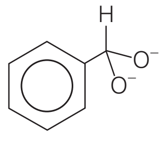
(a) H_2 / Ni and NaOH (b) H_2 / Ni and hydrazine
(c) H_2 / Ni, LAH (d) None of these

3 In a Cannizzaro reaction, the intermediate that will be the best hydride donor is

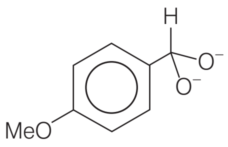
(a)



(b)



(c)



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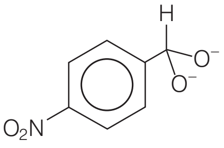
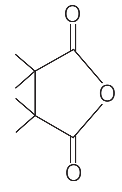


4 A carbonyl compound reacts with hydrogen cyanide to form cyanohydrin which on hydrolysis forms a racemic mixture of α-hydroxy acid. The carbonyl compound is

(a) acetaldehyde (b) acetone
(c) diethyl ketone (d) formaldehyde

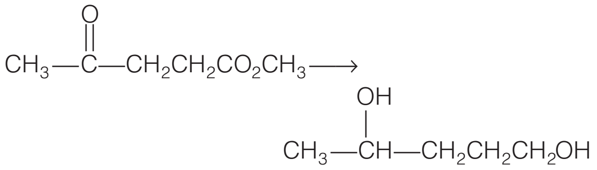
5 The correct set of reagents for the following conversion is

$(CH_3)_2CHCOOH \longrightarrow$



(a) P/I_2, Na, conc. H_2SO_4 (b) P_2O_5, $LiAlH_4$
(c) P_2O_5/Δ, H_2O, P_4/I_2, Na (d) P_4/I_2, Na, P_2O_5/Δ

6



$$CH_3-\overset{\overset{\large O}{\|}}{C}-CH_2CH_2CO_2CH_3 \longrightarrow CH_3-\underset{}{\overset{\overset{\large OH}{|}}{C}H}-CH_2CH_2CH_2OH$$

can be effected using

(a) $LiAlH_4$ and then H^+
(b) $NaBH_4$ and then H^+
(c) H_2 / Pt – C
(d) None of these

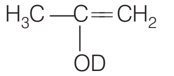
7 With the help of following Grignard synthesis which carboxylic acid is formed?

$$CH_2 = CH\ CH_2\ Br \xrightarrow{\text{Mg/Ether}} \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CO_2} ?$$

(a) $CH_2 = CH\ CH_2\ COOH$ (b) $CH_3\ CH_2\ CH_2\ COOH$
(c) $CH_2 = CHCOOH$ (d) $CH_3CH = CH - COOH$

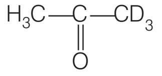
8 The enol-form of acetone after treatment with D_2O, gives

(a)



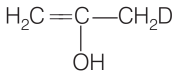
$H_3C-\underset{\underset{\large OD}{|}}{C}=CH_2$

(b)



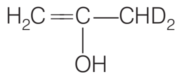
$H_3C-\underset{\underset{\large O}{\|}}{C}-CD_3$

(c)



$H_2C=\underset{\underset{\large OH}{|}}{C}-CH_2D$

(d)

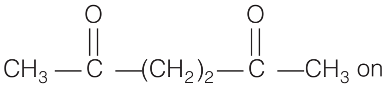


$H_2C=\underset{\underset{\large OH}{|}}{C}-CHD_2$

9 An organic compound *X* on treatment with acidified $K_2Cr_2O_7$ gives compound *Y* which reacts with I_2 and sodium carbonate to form triiodomethane. The compound *X* can be

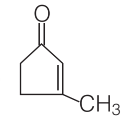
(a) CH_3OH (b) CH_3CHO
(c) CH_3COCH_3 (d) $CH_3CH(OH)CH_3$

10 The diketone



$CH_3-\overset{\overset{\large O}{\|}}{C}-(CH_2)_2-\overset{\overset{\large O}{\|}}{C}-CH_3$ on intramolecular aldol condensation gives the final product.

(a)



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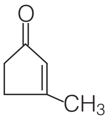

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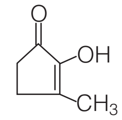

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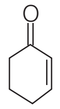

11 Which of the following statements regarding semicarbazone formation from cyclohexanone and benzaldehyde is incorrect?

(a) Both form nearly the same amount of semicarbazone
(b) Semicarbazone of benzaldehyde is more stable
(c) Semicarbazone of cyclohexanone is more stable
(d) Semicarbazone formation from cyclohexanone is more faster