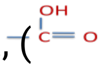
Module 34.5: Carboxylic Acids

Carboxylic acids are organic acids characterized by the presence of a carboxyl group. It has the formula, ( $-\overset{OH}{\overset{|}{C}}=O$) usually written – COOH or – CO_2H . Carboxylic acids are Bronsted – Lowry acids — they are proton donors. Salts and anions of carboxylic acids are called carboxylates. Organic compounds with alcohols are known as esters.

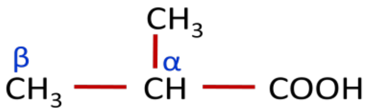
Nomenclature:

The naming of carboxylic acids is done in two ways. They are

a. Common method or trivial method and
b. IUPAC method

a. Common (naming) method:

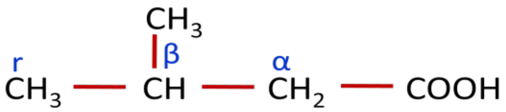
Since carboxylic acids are amongst the earliest organic compounds to be isolated from nature, a large number of them are known by their common names. The common names end with the suffix –ic acid and have been derived from Latin or Greek names of their natural sources. For *e.g.,* formic acid (HCOOH) was first obtained from red ants (formica means ant), acetic acid (CH_3COOH) from vinegar (acetum means vinegar) butyric acid ($CH_3CH_2CH_2COOH$) from rancid butter (butyrum means butter) caproic acid ($CH_3CH_2CH_2CH_2COOH$) from goats (caper means goat). The positions of the substitutes are indicated by Greek letters α, β, γ, δ *etc* the α -carbon being the one directly attached to the carboxyl group, β- the next and so on.



$$\overset{\beta}{CH_3}-\overset{\overset{CH_3}{|\alpha}}{CH}-COOH$$

α -Methylpropionic acid

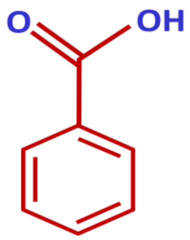
(Isobutyric acid)



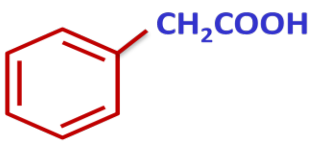
$$\overset{r}{CH_3}-\overset{\overset{CH_3}{|\beta}}{CH}-\overset{\alpha}{CH_2}-COOH$$

β -Methylpropionic acid

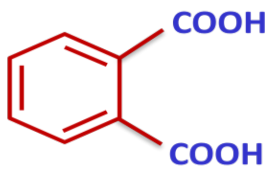
(Isovaleric acid)



Benzoic acid



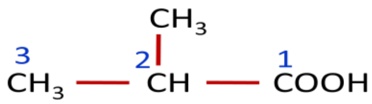
phenylacetic acid



Phthalic acid

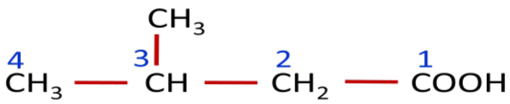
b. IUPAC nomenclature:

In the IUPAC system, the monocarboxylic acids are named as alkanoic acids. The name of the acid is derived by replacing the terminal 'e-' in the name of the corresponding alkane with '-oic acid'. Carboxyl carbon is always given number one while numbering the carbon atoms of the parent chain.



$$\overset{3}{CH_3}-\overset{\overset{CH_3}{2|}}{CH}-\overset{1}{COOH}$$

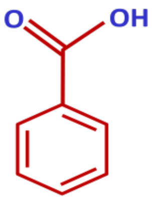
2-Methyl propanoic acid



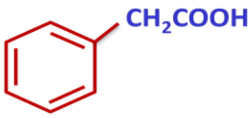
$$\overset{4}{CH_3}-\overset{\overset{CH_3}{3|}}{CH}-\overset{2}{CH_2}-\overset{1}{COOH}$$

3-Methyl butanoic acid

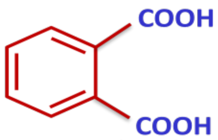
Aromatic carboxylic acids are named by adding the suffix –carboxylic acid in place of ‘e’ of the hydrocarbon name the suffix “-oic acid” can be used.



Benzoic acid



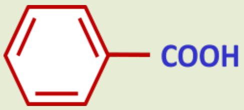
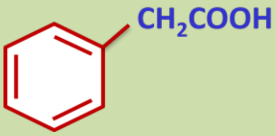
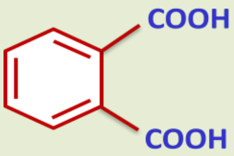
2-phenylethanoic acid



Benzene-1, 2-dicarboxylic acid

Dicarboxylic acids are named as alkanedioic acids in the IUPAC system. Simple dicarboxylic acids having the general formula $HO_2C - (CH_2)_n - CO_2H$ where (n = 0 to 5) are known by the common names: Oxalic (n = 0), Malonic (n = 1), Succinic (n = 2), Glutaric (n = 3), Adipic (n = 4) and Pimelic (n = 5) acids.

Common names such as these can be trouble some to remember, so a catchy phrase, have been devised. For this group of compounds such phrase is "Oh My Such Good Apple Pie".

Structure	Common 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
$(CH_3)_2CHCOOH$	Isobutyric acid	2-Methylpropanoic acid
HOOC – COOH	Oxalic acid	Ethanedioic acid
$HOOC - CH_2 - COOH$	Malonic acid	Propanedioic acid
$HOOC - (CH_2)_2 - COOH$	Succinic acid	Butanedioic acid
$HOOC - (CH_2)_3 - COOH$	Glutaric acid	Pentanedioic acid
$HOOC - (CH_2)_4 - COOH$	Adipic acid	Hexanedioic acid
$HOOC - CH_2 - CH(COOH) - CH_2 - COOH$	---	Propane-1, 2, 3-tricarboxylic acid
	Benzoic acid	Benzenecarboxylic acid (Benzoic acid)
	Phenylacetic acid	2-phenylethanoic acid
	Phthalic acid	Benzene-1, 2-dicarboxylic acid

Methods of Preparation of Carboxylic Acids:

a. From primary alcohols :

Primary alcohols are readily oxidised to carboxylic acids with common oxidising agents such as potassium permanganate ($KMnO_4$) in neutral, acidic or alkaline media.

The acid is first obtained as its potassium salt, which on treatment with a mineral acid gives the carboxylic acid.

$$3RCH_2OH + \underset{\text{(alkaline)}}{4KMnO_4} \longrightarrow 3RCOOK + KOH + 4MnO_2 + 4H_2O$$

$$2RCOOK + H_2SO_4 \longrightarrow 2RCOOH + K_2SO_4$$

Oxidation with $K_2Cr_2O_7$ or CrO_3 in acidic medium often gives some amount of esters. Hence the oxidation by $KMnO_4$ is preferred.

Readily available aldehydes can also be used to obtain carboxylic acids, which may be oxidised even by milder oxidising agents.

b. From nitriles:

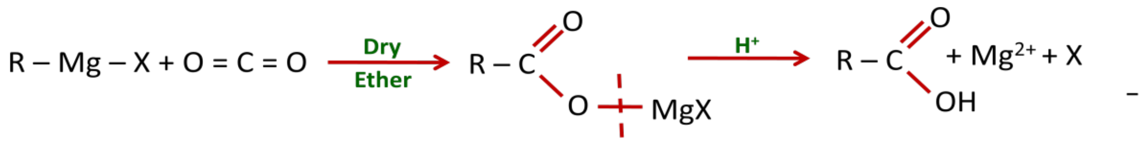
Hydrolysis of nitriles with aqueous acid or alkali gives carboxylic acids.

$$RC \equiv N + 2H_2O + H^+ \longrightarrow RCOOH + NH_4^+$$

$$R - C \equiv N + H_2O + OH^- \longrightarrow RCOO^- + NH_3 \xrightarrow{H^+} RCOOH$$

c. From Grignard reagent:

Grignard reagents react with carbon dioxide to form salts of carboxylic acids which give carboxylic acids on acidification with mineral acids.



Physical properties:

a. Physical state:

1. The first three acids are colourless, pungent-smelling liquids. The acids from butyric to nonanoic are oily liquids. Butyric acid has odour of rancid butter. The acids higher than decanoic acid are odourless

solids.

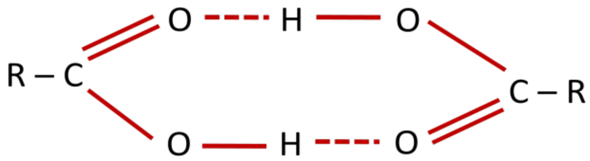
2. **Boiling points:**

Organic acids have high boiling points. It is due to

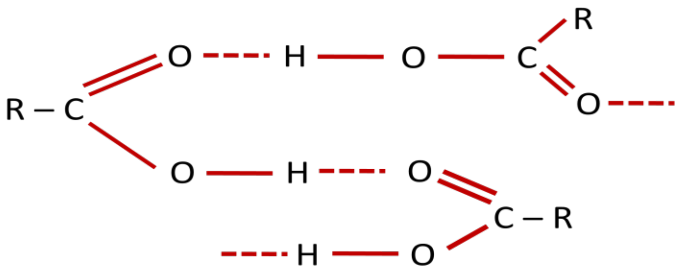
a. Intermolecular hydrogen bondings

b. Strong van der Waals forces due to their polar nature

Lower members exist as
a. Dimers in the aqueous solutions and vapour phase
b. Polymers in the liquid phase



Hydrogen bonding in carboxylic acid molecules

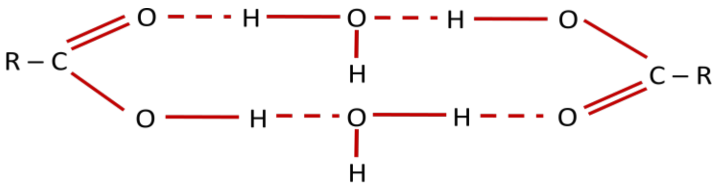


Two polymeric hydrogen bonded structure

Higher boiling points of acids relative to alcohols are due to the higher degree and strength of hydrogen bonding in them (because of the presence of two oxygen atoms)

3. Solubility:

The first few members are highly soluble in water. This solubility is due to the hydrogen bonding between carboxylic acid and water molecules.



Hydrogen bonding between carboxylic acid and water molecules

The solubility decreases with the increase in molecular mass.

Aromatic acids like benzoic acid are less soluble in water due to large number of C-atoms in them. Carboxylic acids are soluble in organic solvents like alcohol, ether and benzene.

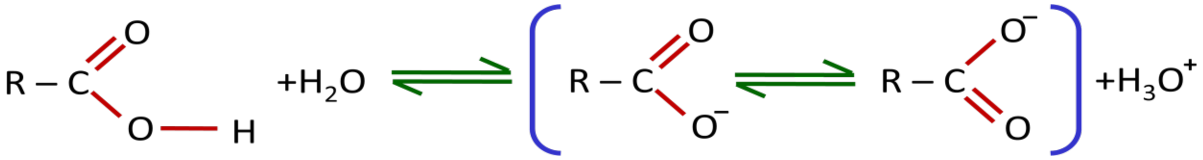
Chemical properties:

The reactions of carboxylic acids are classified as follows

a. Reactions involving cleavage of O – H bonds
b. Reactions involving cleavage of C – OH bonds
c. Reactions involving – COOH groups
d. Substitution reaction in hydrocarbon part

Acidic nature of carboxylic acids :

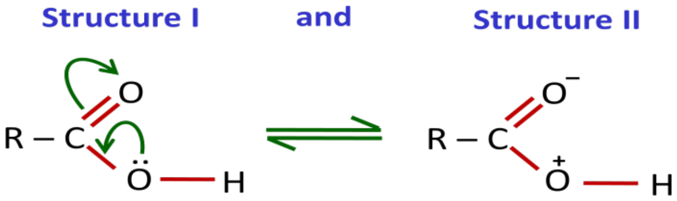
The aqueous solutions of carboxylic acids dissociate as follows:



Since they liberate hydrogen ions in solution, they are acidic. However they are weaker than mineral acids like HCl, HNO_3 *etc.* But stronger acids than alcohols and phenols.

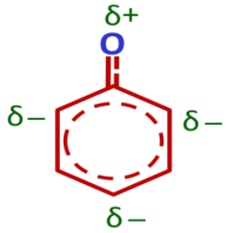
Carboxylic compounds are the most acidic among all the organic compounds. This can be explained as follows:

Carboxylic acids as well as carboxylate ion both are stabilized by resonance. However, carboxylate ion is more stabilized by resonance because its contributing structures are exactly identical. The contributing structures of carboxylic acid involve charge separation.

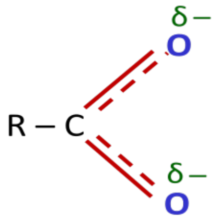


Since carboxylate ion is more stabilized by resonance than carboxylic acid therefore equilibrium in above reaction lies very much in forward direction *i.e.,* in favour of ionized form. Hence carboxylic acids behave as strong acids.

Carboxylic acids are stronger acids than phenols. It can be understood by comparing the hybrid structures of carboxylate ion and phenoxide ions. In carboxylate ion, the negative charge is equally distributed over two electronegative atoms (oxygen atoms) while in phenoxide ion, it is present only on one oxygen atom. Thus, carboxylate ion is more stabilized as compared to phenoxide ion. Hence, carboxylic acids ionize to the greater extent than phenols furnishing higher concentration of H^+ ions. Therefore carboxylic acids behave as stronger acids than phenols.



Phenoxide ion
(Less stable)



Carboxylate ion
(More stable)

a. Reactions involving cleavage of O–H bonds:

All carboxylic acids release proton to form more stable carboxylate ion. These all reactions proves that acidity of carboxylic acids.

1. Carboxylic acids liberate hydrogen with active metals like Mg, Ca, Zn, Fe *etc.,*

$$2RCOOH + Mg \longrightarrow (RCOO)_2Mg + H_2$$

$$2CH_3COOH + Ca \longrightarrow (CH_3COO)_2Ca + H_2$$

2. They also react with metal hydroxides, carbonates and bicarbonates

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

$$2CH_3COOH + Na_2CO_3 \longrightarrow 2CH_3COONa + CO_2 + H_2O$$

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

b. Reactions involving cleavage of C –OH bonds:

1. Formation of anhydride (dehydration):

Carboxylic acids on heating with a phosphorus pentoxide to form acid anhydrides

$$2R-COOH \xrightarrow{P_2O_5,\ \Delta} (RCO)_2O + H_2O$$

$$2CH_3COOH \xrightarrow{P_2O_5,\ \Delta} (CH_3CO)_2O + H_2O$$

2. Esterfication (acid to ester):

Carboxylic acids react with alcohols in the presence of few drops of conc. H_2SO_4 to form esters **(see alcohols unit)**

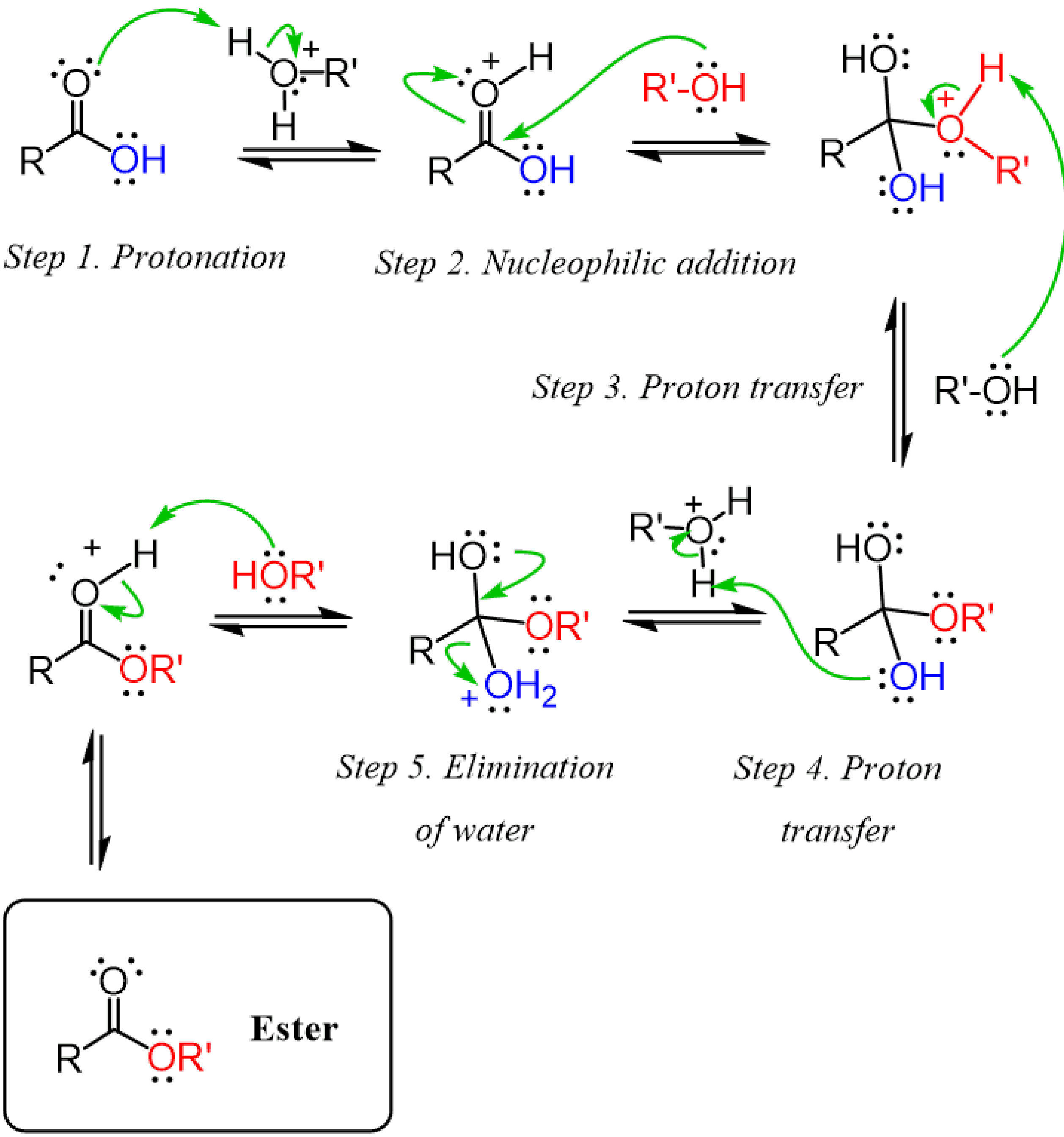
$$RCOOH + R^1OH \xrightarrow{H^+} RCOOR^1 + H_2O$$

$$CH_3COOH + C_2H_5OH \xrightarrow{H_2SO_4} CH_3COOC_2H_5 + H_2O$$

When dry hydrogen chloride is used in this reaction, we called it **Fischer Esterification.**

Mechanism :

Fischer Esterification Mechanism



3. Action with $SOCl_2$:

Carboxylic acids react with $SOCl_2$ to form acid chlorides.

$RCOOH + SOCl_2 \text{-------------}\rightarrow RCOCl + SO_2 + HCl$

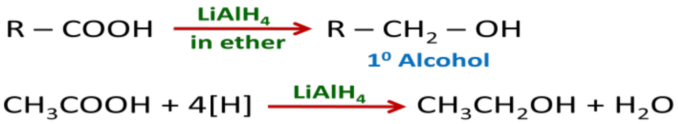
Example :

$CH3COOH + SOCl_2 \text{-------------} > CH_3COCl + SO_2 + HCl$

C, Reaction involving –COOH group:

4. Reduction:

Acids are not easily reduced by catalytic hydrogenation or with sodium and ethanol. Strong reducing agent as lithium aluminium hydride reduces an acid into primary alcohol.

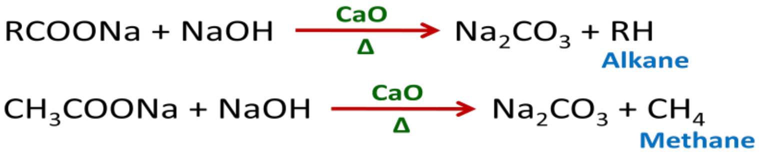


$$R-COOH \xrightarrow[\text{in ether}]{LiAlH_4} \underset{1^0\ \text{Alcohol}}{R-CH_2-OH}$$

$$CH_3COOH + 4[H] \xrightarrow{LiAlH_4} CH_3CH_2OH + H_2O$$

5. Decaboxylation:

Simple monocarboxylic acids do not lose carbon dioxide (decarboxylation) when heated alone. However, when sodium salt of the carboxylic acids are heated with soda lime (NaOH + CaO), they yield hydrocarbons.



$$RCOONa + NaOH \xrightarrow[\Delta]{CaO} Na_2CO_3 + \underset{\text{Alkane}}{RH}$$

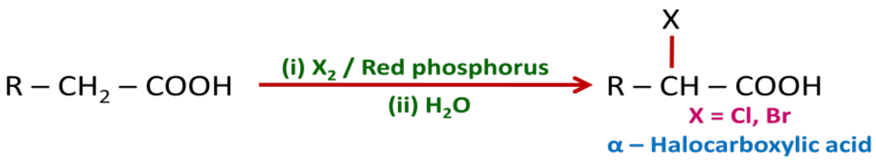
$$CH_3COONa + NaOH \xrightarrow[\Delta]{CaO} Na_2CO_3 + \underset{\text{Methane}}{CH_4}$$

The reaction is known as Kolbe’s electrolysis.

c. Substitution reactions in hydrocarbon part:

1. Halogenations:

When carboxylic acids react with chlorine or bromine in the presence of red phosphorous, the α-hydrogen atoms are replaced by halogen atoms. It is called Hell-Volhard-Zelinsky (HVZ) reaction.

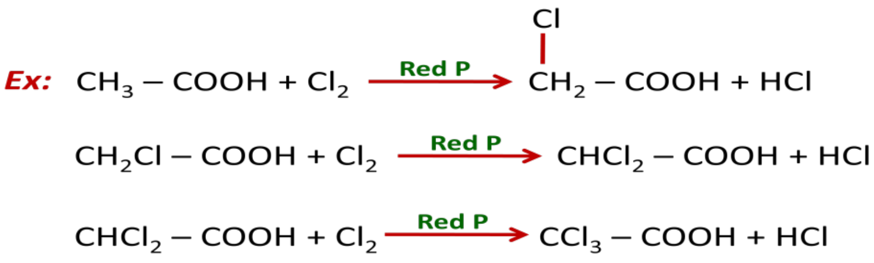


$$R-CH_2-COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2\text{ / Red phosphorus}} R-\overset{\overset{\displaystyle X}{|}}{C}H-COOH$$

X = Cl, Br

α – Halocarboxylic acid

Acetic acid reacts with chlorine in presence of red phosphorus to form chloro acetic acid, dichloro acetic acid or trichloro acetic acid depending on the quantity of chlorine reacting.



Ex:

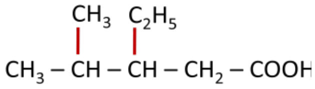
$$CH_3-COOH + Cl_2 \xrightarrow{\text{Red P}} \overset{\overset{\displaystyle Cl}{|}}{C}H_2-COOH + HCl$$

$$CH_2Cl-COOH + Cl_2 \xrightarrow{\text{Red P}} CHCl_2-COOH + HCl$$

$$CHCl_2-COOH + Cl_2 \xrightarrow{\text{Red P}} CCl_3-COOH + HCl$$

Review questions:

Example set:

1. The IUPAC name of  $CH_3-\overset{CH_3}{\overset{|}{C}H}-\overset{C_2H_5}{\overset{|}{C}H}-CH_2-COOH$ is

   a. 3-ethyl-2-methyl pentanoic acid
   b. 2 -ethyl-3-methyl pentanoic acid
   c. 3-ethyl-4-methyl pentanoic acid
   d. 2-methyl-3-ethyl pentanoic acid

Solution: c)

2. When____is treated with Grignard reagent, followed by hydrolysis with an acid, it forms carboxylic acid
   a. $CH_2 = CH_2$
   b. CO_2
   c. $CH_3 - CO - CH_3$
   d. CH_3CHO

Solution: b)

3. Which compound is likely to have the highest boiling point
   a. CH_3CH_3
   b. CH_3OCH_3
   c. CH_3CH_2OH
   d. CH_3COOH

Solution: d)

4. Acetic acid undergoes reduction with $LiAlH_4$ to give finally _
   a. Ethanol
   b. Ethane
   c. Ethanal
   d. Ethyne

Solution: a)

5. Which of the following reagents will convert acetic acid into acetyl chloride
   a. NaCl
   b. Conc. HCl / $ZnCl_2$
   c. $SOCl_2$
   d. HCl

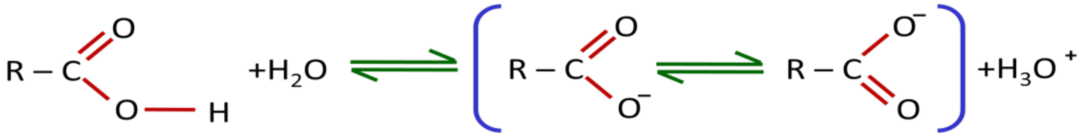
Solution: c)

6. Discuss about acidity of carboxylic acids

Solution:

Acidic nature:

The aqueous solutions of carboxylic acids dissociate as follows:



Since they liberate hydrogen ions in solution, they are acidic. However they are weaker than mineral acids like HCl, HNO_3 *etc.*, But stronger acids than alcohols and phenols.

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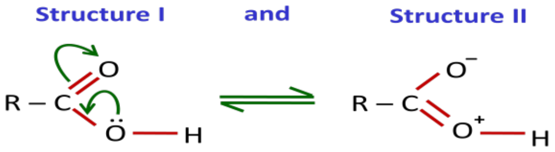

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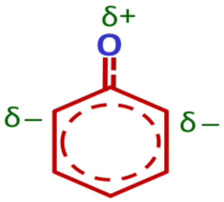
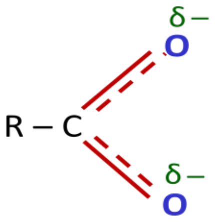


Phenoxide ion
(Less stable)



Carboxylate ion
(More stable)

7. Write any two methods of preparation of carboxylic acids

Solution:

Methods of Preparation of Carboxylic Acids:

1. From primary alcohols and aldehydes:

Primary alcohols are readily oxidised to carboxylic acids with common oxidising agents such as potassium permanganate ($KMnO_4$) in neutral, acidic or alkaline media.

The acid is first obtained as its potassium salt, which on treatment with mineral acid gives the carboxylic acid.

$$3RCH_2OH + \underset{\text{(alkaline)}}{4KMnO_4} \longrightarrow 3RCOOK + KOH + 4MnO_2 + 4H_2O$$

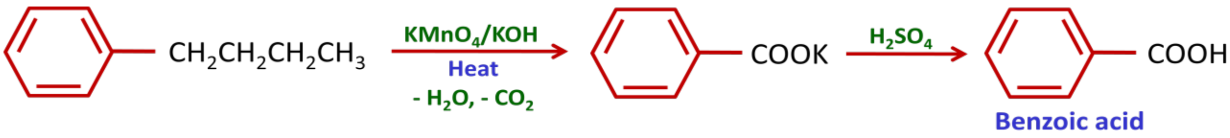
$$2RCOOK + H_2SO_4 \longrightarrow 2RCOOH + K_2SO_4$$

Oxidation with $K_2Cr_2O_7$ or CrO_3 in acidic medium often gives some amount of esters. Hence the oxidation by $KMnO_4$ is preferred.

Readily available aldehydes can also be used to obtain carboxylic acids, which may be oxidised even by milder oxidising agents.

2. From alkyl benzenes and alkenes

Aromatic carboxylic acids can be prepared by vigorous oxidation of alkyl benzenes with chromic acid or acidic or alkaline $KMnO_4$. The –COOH group formed is always attached to the aromatic ring and position of -COOH group indicates the position of original side chain in the starting arene (alkyl benzene).



8. Write the reaction involving cleavage of C – OH bond in carboxylic acids

Solution:

a. Reactions involving cleavage of C –OH bonds:

1. Formation of anhydride (dehydration):

Acid on heating with a phosphorus pentoxide to form acid anhydrides

$$2R-COOH \xrightarrow{P_2O_5,\ \Delta} (RCO)_2O + H_2O$$

$$2CH_3COOH \xrightarrow{P_2O_5,\ \Delta} (CH_3CO)_2O + H_2O$$

2. Esterification (acid to ester):

Carboxylic acids react with alcohols in the presence of few drops of conc. H_2SO_4 to form esters **(see alcohols unit)**

$$RCOOH + R^1OH \xrightarrow{H^+} RCOOR^1 + H_2O$$

$$CH_3COOH + C_2H_5OH \xrightarrow{H_2SO_4} CH_3COOC_2H_5 + H_2O$$

When dry hydrogen chloride is used in this reaction, we called it Fischer Esterification

3. Action with PCl_3, PCl_5 or $SOCl_2$ [acid to acid chloride]:

Carboxylic acids react with PCl_3, PCl_5 or $SOCl_2$ to form acid chlorides

$$3RCOOH + PCl_3 \longrightarrow 3RCOCl + H_3PO_3$$
$$RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$$
$$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$$

Ex:

$$3CH_3COOH + PCl_3 \longrightarrow 3CH_3COCl + H_3PO_3$$
$$CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl$$
$$CH_3COOH + SOCl_2 \longrightarrow CH_3COCl + SO_2 + HCl$$

The byproducts with thionyl chloride are gases whereas with PCl_5 and PCl_3, we have phosphorous oxychloride (volatile liquid) and phosphorous acid (non-volatile) respectively. Thus, if the boiling point of the acid chloride is higher than the boiling point of thionyl chloride, then thionyl chloride is preferred because the resulting acid chloride can be separated easily from the excess of thionyl chloride by distillation.

4. Reaction with ammonia:

Carboxylic acids is heated with ammonia to form amides

$$RCOOH + NH_3 \longrightarrow RCOONH_4 \xrightarrow{\Delta} RCONH_2 + H_2O$$
$$CH_3COOH + NH_3 \longrightarrow CH_3COONH_4 \xrightarrow{\Delta} CH_3CONH_2 + H_2O$$

Problem set:

1. Aliphatic carboxylic acids are isomeric with
   a. Esters
   b. Ethers
   c. Ketones
   d. Acid anhydride

Solution: a)

2. In α-halogenation of aliphatic acids, the catalyst used is
   a. P_4
   b. Zn
   c. $FeCl_3$
   d. Al

Solution: a)

3. When ammonium formate is heated, it gives
   a. Acetaldehyde
   b. Acetic acid
   c. Formamide
   d. Formaldehyde

Solution: c)

4. Acetic acid reacts with methyl alcohol in the presence of an acid catalyst to give
   a. Methyl formate
   b. Ethyl formate
   c. Methyl acetate
   d. Ethyl acetate

Solution: c)

5. Butyric acid reacts with PCl_5 to give
   a. α-chloro butyric acid
   b. Butyryl chloride
   c. 1-chlorobutane
   d. α, α-dichloro butyric acid

Solution: b)

6. How is acetic acid obtained using a
   a. Nitriles
   b. Grignard reagent

Solution:

a. From nitriles:

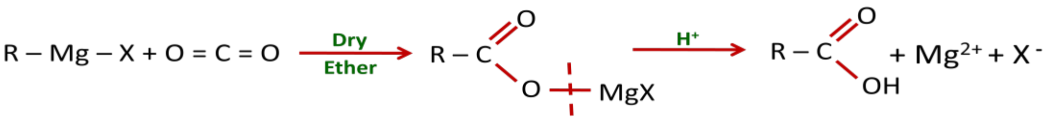
Hydrolysis of nitriles with aqueous acid or alkali gives carboxylic acids.

$$RC \equiv N + 2H_2O + H^+ \longrightarrow RCOOH + NH_4^+$$

$$R - C \equiv N + H_2O + OH^- \longrightarrow RCOO^- + NH_3 \xrightarrow{H^+} RCOOH$$

b. From Grignard's reagent:

Grignards reagents react with carbon dioxide to form salts of carboxylic acids which give carboxylic acids on acidification with mineral acids.



7. Give the major organic product in the following reactions

a. $C_2H_5COOH + PCl_5 \longrightarrow$

b. $CH_3COOH + CH_3OH \xrightarrow{H_2SO_4}$

c. $CH_3CH_2COOH \xrightarrow[\text{in ether}]{LiAlH_4}$

d. $C_2H_5COONa + NaOH \xrightarrow[\Delta]{CaO}$

e. $C_2H_5COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } Cl_2 / \text{Red P}}$

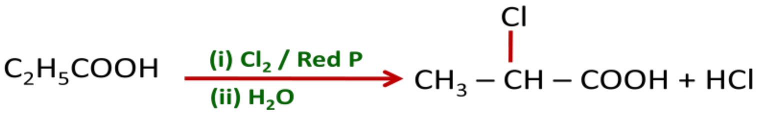
Solution:

a. $C_2H_5COOH + PCl_5 \longrightarrow C_2H_5COCl + POCl_3 + HCl$

b. $CH_3COOH + CH_3OH \xrightarrow{H_2SO_4} CH_3COOCH_3 + H_2O$

c. $CH_3CH_2COOH \xrightarrow[\text{in ether}]{LiAlH_4} CH_3CH_2CH_2OH + H_2O$

d. $C_2H_5COONa + NaOH \xrightarrow[\Delta]{CaO} C_2H_6 + Na_2CO_3$

e. 

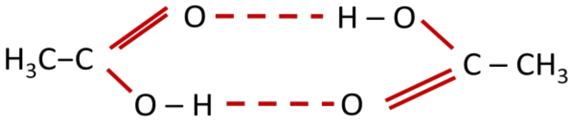
$C_2H_5COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } Cl_2 / \text{Red P}} CH_3-\overset{\displaystyle Cl}{\overset{|}{C}H}-COOH + HCl$

8. Why boiling points of carboxylic acid are higher than those of alcohols or ethers of comparable molecular weights

Solution:

For example, acetic acid, n-propyl alcohol and ethyl methyl ether are having same molecular weights (60)

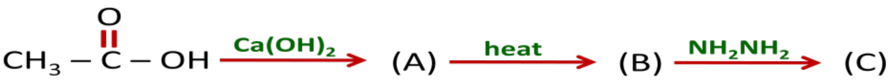
Acetic acid has more boiling point than n-propanol and ethyl methyl ether. It is due to intermolecular hydrogen bonding and also it exists as a dimer in acetic acid.



n-propanol has inter molecular hydrogen bonds only.

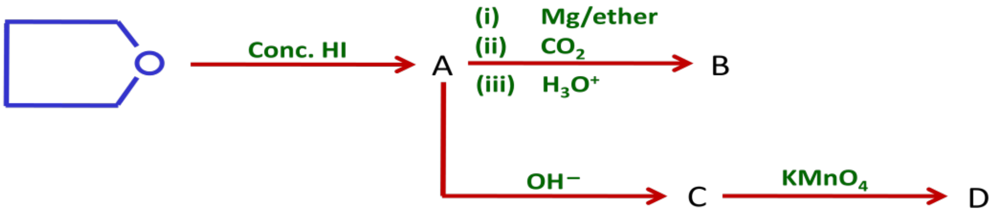
Exercise questions:

1. How will you synthesize acetic acid from acetylene
2. Identify (A), (B) and (C) in the following reaction sequence



$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-OH \xrightarrow{Ca(OH)_2} (A) \xrightarrow{\text{heat}} (B) \xrightarrow{NH_2NH_2} (C)$

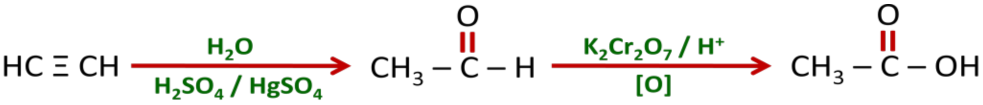
3.



4. How will you synthesise chloroacetic acid from methyl chloride (in 4 steps)
5. Show how each of the following compounds can be converted to benzoic acid
   - a. Ethylbenzene
   - b. Acetophemone
   - c. Phenylethene (styrene)

Solutions to exercise questions:

1. Following steps are involved

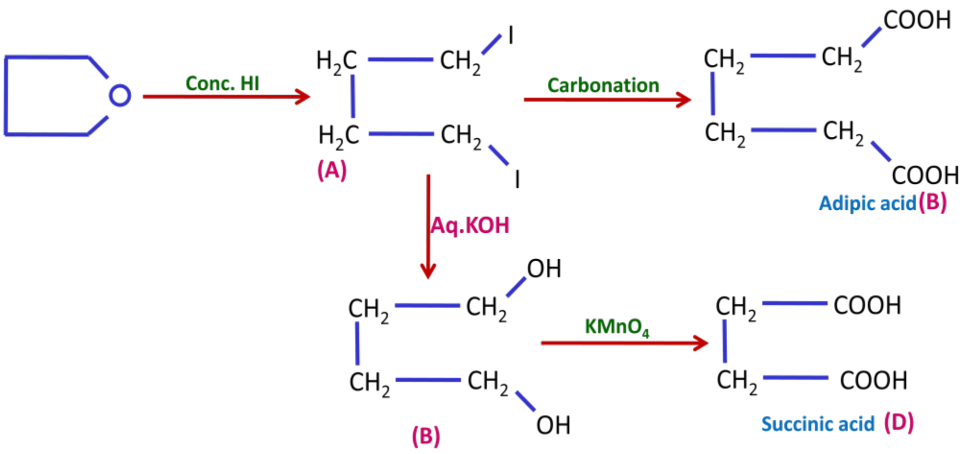


$$HC \equiv CH \xrightarrow[H_2SO_4 / HgSO_4]{H_2O} CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow[[O]]{K_2Cr_2O_7 / H^+} CH_3-\overset{O}{\overset{\|}{C}}-OH$$

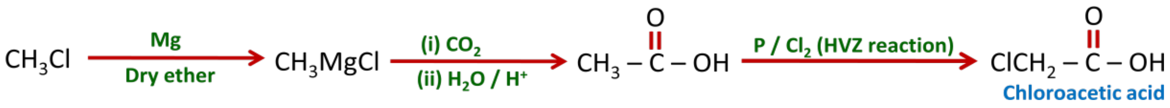
2.

$$CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{Ca(OH)_2} \underset{(A)}{(CH_3COO)_2Ca} \xrightarrow{heat} \underset{(B)}{(CH_3)_2C=O} \xrightarrow{NH_2NH_2} \underset{(c)}{(CH_3)_2C=NNH_2}$$

3.

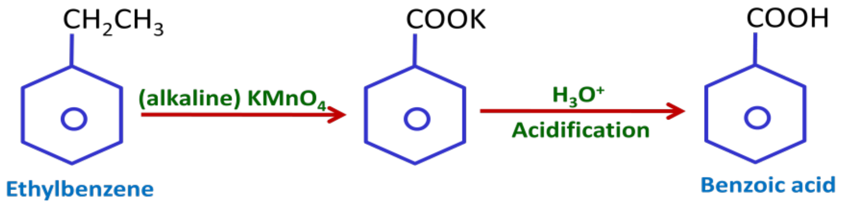


4. Following steps are involved

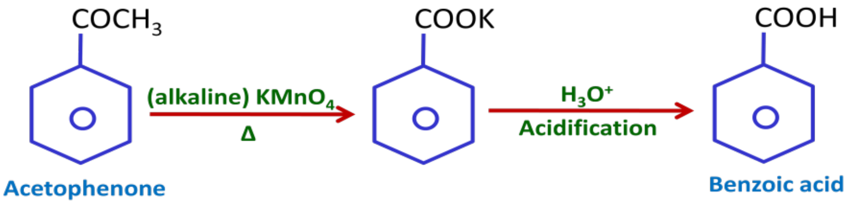


$$CH_3Cl \xrightarrow[\text{Dry ether}]{\text{Mg}} CH_3MgCl \xrightarrow[\text{(ii) } H_2O\,/\,H^+]{\text{(i) } CO_2} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow{P\,/\,Cl_2 \text{ (HVZ reaction)}} ClCH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

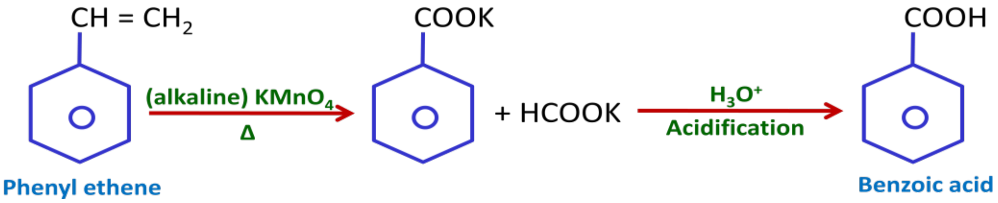
5. a.



b.



c.



IIT Questions:

1. Which of the following orders of acid strength is correct?

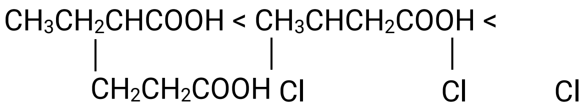
   a. $RCOOH > ROH > HOH > HC \equiv CH$
   b. $RCOOH > HOH > ROH > HC \equiv CH$
   c. $RCOOH > HOH > HC \equiv CH > ROH$
   d. $RCOOH > HC \equiv CH > HOH > ROH$

2. Which of the following orders of base strength is correct?

   a. $\overset{-}{R} > \overset{-}{NH_2} > HC \equiv \overset{-}{C} > RCOO^-$
   b. $R^- > NH_2^- > RCOO^- > HC \equiv C^-$
   c. $R^- > RCOO^- > NH_2^- > HC \equiv C^-$
   d. $HC \equiv C^- > NH_2^- > RCOO^- > R^-$

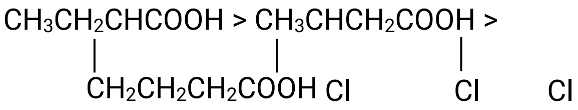
3. Which of the following orders of acid strength is correct?

a)



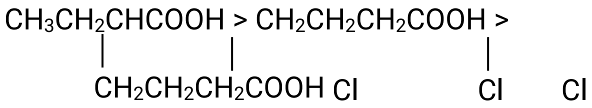
$$\begin{array}{l} CH_3CH_2CHCOOH < CH_3CHCH_2COOH < \\ \qquad\quad | \qquad\qquad\quad | \qquad\qquad\quad | \\ \qquad\quad CH_2CH_2COOH\ Cl \qquad Cl \qquad Cl \end{array}$$

b)



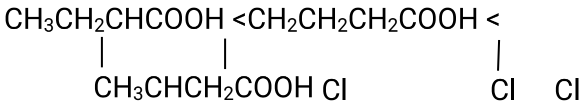
$$\begin{array}{l} CH_3CH_2CHCOOH > CH_3CHCH_2COOH > \\ \qquad\quad | \qquad\qquad\quad | \qquad\qquad\quad | \\ \qquad\quad CH_2CH_2CH_2COOH\ Cl \qquad Cl \qquad Cl \end{array}$$

c)



$$\begin{array}{l} CH_3CH_2CHCOOH > CH_2CH_2CH_2COOH > \\ \qquad\quad | \qquad\qquad\quad | \qquad\qquad\quad | \\ \qquad\quad CH_2CH_2CH_2COOH\ Cl \qquad Cl \qquad Cl \end{array}$$

d)



$$\begin{array}{l} CH_3CH_2CHCOOH < CH_2CH_2CH_2COOH < \\ \qquad\quad | \qquad\qquad\quad | \qquad\qquad\quad | \\ \qquad\quad CH_3CHCH_2COOH\ Cl \qquad Cl \qquad Cl \end{array}$$

4.The relative order of esterification of acids is

a. $RCH_2COOH > R_2CHCOOH > R_3CCOOH$
b. $RCH_2COOH < R_2CHCOOH < R_3CCOOH$
c. $RCH_2COOH < R_3CCOOH < R_2CHCOOH$
d. $R_3CCOOH > RCH_2COOH > R_2CHCOOH$

5. Acetic acid differs from formic acid in that

a. Acetic acid is stable to heat
b. formic acid is stable to heat
c. Acetic acid acts as a reducing agent
d. Acetic acid shows positive test with tollens reagent

6. The Hell-Volhard-Zelinsky reaction is used in the synthesis of

a. Aldehydes b. α-haloacids c.acid halides d. ketones

7. Which of the following sequences is correct ?

a. $pKa(p\text{-}O_2NC_6H_4COOH) > pKa\ (C_6H_5COOH) > pKa\ (p\text{-}HOC_6H_4COOH)$
b. $pKa(p\text{-}O_2NC_6H_4COOH) < pKa\ (C_6H_5COOH) < pKa\ (p\text{-}HOC_6H_4COOH)$
c. $pKa(p\text{-}O_2NC_6H_4COOH) > pKa\ (C_6H_5COOH) < pKa\ (p\text{-}HOC_6H_4COOH)$
d. $pKa(p\text{-}O_2NC_6H_4COOH) < pKa\ (C_6H_5COOH) > pKa\ (p\text{-}HOC_6H_4COOH)$

8. Which of the following sequences of rates of alkaline hydrolysis of esters is correct?

a. $CH_3CH_2COOCH_3 < (CH_3)_2CHCOOCH_3 < (CH_3)_3CCOOCH_3$
b. $CH_3CH_2COOCH_3 > (CH_3)_2CHCOOCH_3 > (CH_3)_3CCOOCH_3$
c. $CH_3CH_2COOCH_3 > (CH_3)_2CHCOOCH_3 < (CH_3)_3CCOOCH_3$
d. $CH_3CH_2COOCH_3 < (CH_3)_2CHCOOCH_3 > (CH_3)_3CCOOCH_3$

9. When propionic acid is treated with aqueous sodium bicarbonate, CO_2 is liberated. The C of CO_2 comes from :

a. Methyl group
b. Carboxylic acid group
c. Methylene group

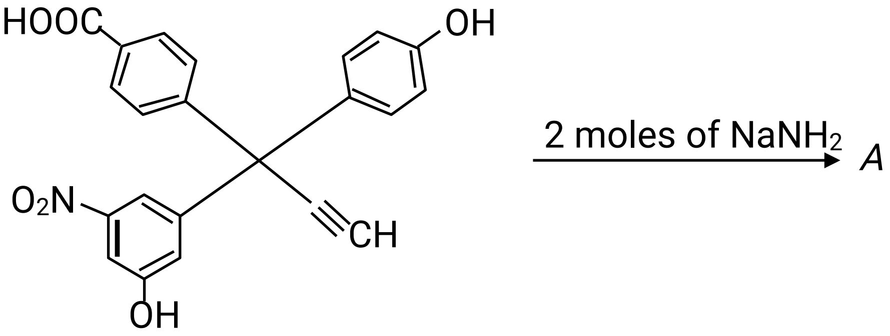
d. Bicarbonate

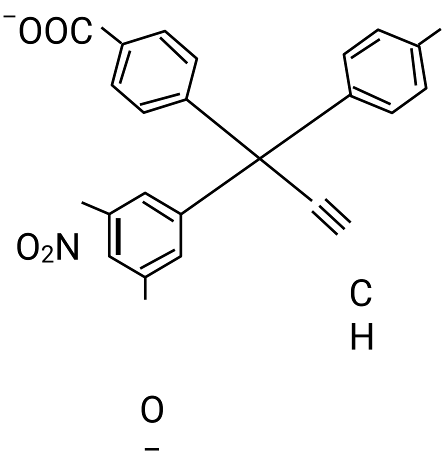
10. Benzoyl chloride is prepared from benzoic acid by :

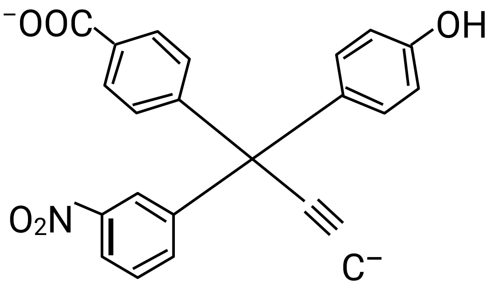
a. Cl_2, *hv*
b. SO_2Cl_2
c. $SOCl_2$
d. Cl_2, H_2O

11. Identify the correct order of boiling points of the following compounds :

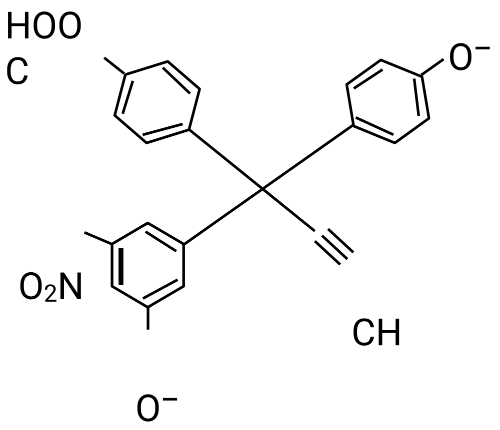
i. $CH_3CH_2CH_2CH_2OH$
ii. $CH_3CH_2CH_2CHO$,
iii. $CH_3CH_2CH_2CO$
OH a. 1 > 2 > 3
b. 3 > 1 > 2
c. 1 > 3 > 2
d. 3 > 2 > 1

12. 

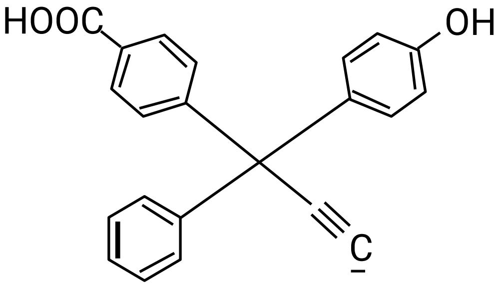
a. 

b. 

c.



d.



13. An enantiomerically pure acid is treated with racemic mixture of an alcohol having one chiral carbon. The ester formed will be :

14. Give reasons for the following in one or two sentences.
“Acetic acid be halogenated in the presence of P and Cl_2, but formic acid cannot be halogenated in the same way. “

15. Give reason in one or two sentences for the following :
“Formic acid is a stronger acid than acetic acid.”

16. A liquid *X*, having a molecular formula $C_6H_{12}O_2$ is hydrolysed with water in the presence of an acid to give a carboxylic acid *Y* and an alcohol *Z*. Oxidation of *Z* with chromic acid gives *Y*. What are the structures of *X*, *Y* and *Z*.

17. How will you bring about the following conversions?
“ Ethanoic acid to a mixture of methanoic acid and diphenyl ketone.”

18. Arrange the following as stated :
“Increasing order of acidic strength.”
$ClCH_2COOH$, CH_3CH_2COOH, $ClCH_2CH_2COOH$, $(CH_3)_2CHCOOH$, CH_3COOH

19. Give reason for the following

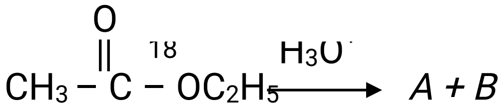
“In acylium ion the structure $R - C \equiv O^+$ is more stable than $R - C^+{=}O$”

20. Complete the following sequence of reactions with appropriate structures :

$$CH_3-CH_2-COOH \xrightarrow[\text{bromine}]{\text{P and}} A$$

$$A \xrightarrow[2.\ H^+]{1.\ \text{Alc. KOH (excess)}} B$$

21. Write the structures of the products *A* and *B*



$$CH_3-\overset{\overset{O}{\|}}{C}-\overset{18}{O}C_2H_5 \xrightarrow{H_3O^+} A + B$$

22. Five isomeric *para*-disubstituted aromatic compounds *A* to *E* with molecular formula $C_8H_8O_2$ were given for identification.

Based on the following observations, give structures of the compounds:

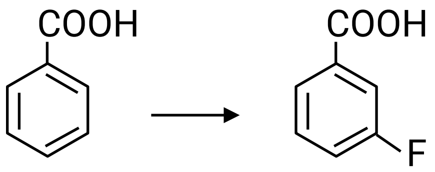
i) Both *A* and *B* form a silver mirror with Tollen's reagent; also, B gives a positive test with $FeCl_3$ solution.

ii) *C* gives positive iodoform test.

iii) *D* is readily extracted in aqueous $NaHCO_3$ solution.

iv) *E* on acid hydrolysis gives 1, 4 dihydroxy benzene.

23. Convert (in not more than 3 steps)



24. Compound A of molecular formula $C_9H_7O_2Cl$ exists in keto form and predominantly in enolic form *B*. On oxidation with $KMnO_4$, A gives m-chlorobenzoic acid. Identify *A* and *B*.

Solutions:

1. b

The order of acidic strength is RCOOH > HOH > ROH > HC ≡ CH

Electron releasing alkyl group R in ROH makes it lesser acidic than H_2O

2. a

The base strength follows the reverse order as shown by the corresponding acids. The acids are RH , NH_3, HC ≡ CH and RCOOH. Its order is

RCOOH > HC ≡ CH > NH_3 > RH. Hence, the correct order of the conjugate bases is

3. b $RCOO^- < HC{\equiv}C^- < NH_2^- < R^-$

Nearer the chlorine to the –COOH group, stronger the acidity. Hence, the correct order is

4. a $CH_3CH_2CHClCOOH > CH_3CHClCH_2COOH > CH_2ClCH_2CH_2COOH$

Increasing crowdedness near the site of esterification decreases the rate of esterification.Hence, the correct order is

5. a $RCH_2COOH > R_2CHCOOH > R_3CCOOH$

6. b Acetic acid differs from formic acid in that acetic acid is stable to heat.

7. b The Hell-Volhard-Zelinsky reaction is used in the synthesis of α-haloacids.

Electron-releasing group makes benzoic acid a weaker acid while electron- attracting group makes it a stronger the acid, lesser the value of pKa. Hence, the correct order is

$pKa(p\text{-}O_2NC_6H_4COOH) < pKa\ (C_6H_5COOH) < pKa\ (p\text{-}HOC_6H_4COOH)$

8. b

The correct order of alkaline hydrolysis is

$CH_3CH_2COOCH_3 > (CH_3)_2CHCOOCH_3 > (CH_3)_3CCOOCH_3$

9. (d) $C_2H_5COOH + NaHCO_3 \longrightarrow C_2H_5COONa + H_2O + CO_2$

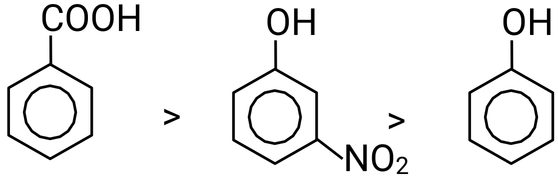
10. (c) $SOCl_2$ readily replaces –OH group of the acids by –Cl atom forming acid chloride.

$C_6H_5COOH + SOCl_2 \longrightarrow C_6H_5COCl + SO_2 + HCl$

Benzoic acid benzoyl chloride

11. (b) In theses *C* forms dimer due to hydrogen bonds and compound *A,* form hydrogen bonds. Hence in these stronger hydrogen bond is in compound *C* than compound *A.* Compound *B* does not form hydrogen bond. Thus, they follow the following order of mol. wt. 3 > 1 > 2. So they have same order in their boiling point.

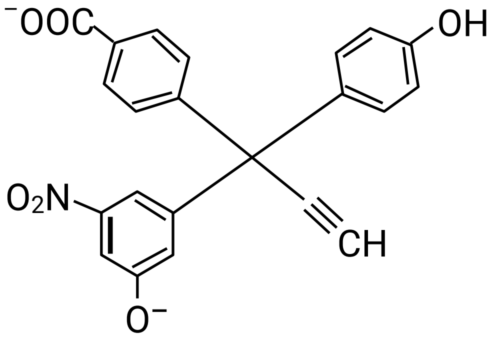
12. (a) The acidic strength of the attached groups is in the following order:



$> H-C\equiv C-H$

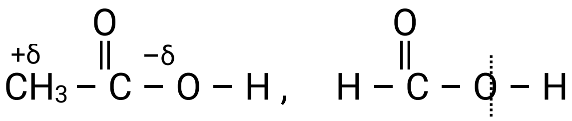
(**Note:** Due to attachment of electron attractive group acidic strength increases and carboxylic acids are more acidic than phenols.)

The two moles of NH_2^- ions will abstract two moles of a most acidic hydrogen out of the four moles of hydrogen present per mole of the given acidic compounds. Hence after abstraction of two moles of hydrogen the obtained product will be as shown:



13. When optically active acid reacts with racemic mixture of an alcohol, it forms two types of isomeric esters. In each, the configuration of the chiral center of acid will remain the same.
So, the mixture will be optically active.

14. Because acetic acid has -hydrogen atoms which can replace by halogen but formic acid does not have -hydrogen.

15. 

$\overset{+\delta}{CH_3} - \overset{O}{\overset{\|}{C}} - \overset{-\delta}{O} - H$, $H - \overset{O}{\overset{\|}{C}} - O - H$

Acetic acid + *I* effect

Acetic acid is weaker acid than formic acid due to + I effect, Hence, formic acid is stronger acid than acetic acid.

16. Since *X* is hydrolysed to give an acid *Y* and an alcohol *Z* and thus, *X* is an ester *R – COOR'*.

$$\underset{X}{RCOOR'} \xrightarrow{HOH} \underset{Y}{RCOOH} + \underset{Z}{R'OH}$$

H

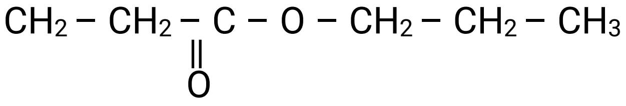
Oxidation of alcohol *Z* gives an acid *Y*, it shows that *Z* is a primary alcohol, i.e., *R – CH₂OH*

$$\underset{X}{R'OH} \xrightarrow{[O]} \underset{Y}{R - COOH}$$

$\because \quad R - CH_2OH \xrightarrow{[O]} RCOOH \qquad (\therefore R' = R - CH_2)$

So, $X = R - COOCH_2R$

$\therefore$ *X* is

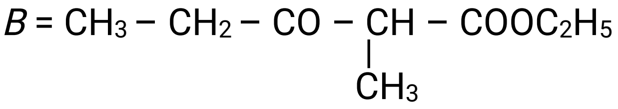


$CH_2 - CH_2 - \underset{\underset{O}{\|}}{C} - O - CH_2 - CH_2 - CH_3$

Propyl propanoate

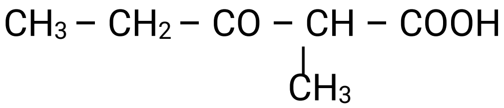
Hence, $A = CH_3 - CH_2 - COOC_2H_5$

Ethyl propanoate



$B = CH_3 - CH_2 - CO - \underset{\underset{CH_3}{|}}{CH} - COOC_2H_5$

Ethyl (2-methyl, 1,3-ketopentanoate)



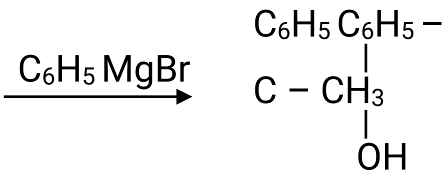
$$C = CH_3 - CH_2 - CO - \underset{\displaystyle CH_3}{\underset{|}{CH}} - COOH$$

2-methyl, 3-keto, pentanoic acid

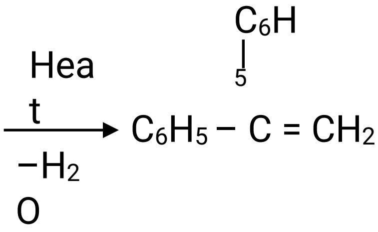
17.

$CH\ COOH \xrightarrow{\quad_5} CH\ COCl \xrightarrow{\quad_6\ _6} C\ H\ COCH$

3 ethanoic acid 3 anhydrous– $AlCl_3$ 6 5 3



$\xrightarrow{C_6H_5MgBr} C_6H_5\,C_6H_5 - \underset{OH}{\overset{|}{C}} - CH_3$



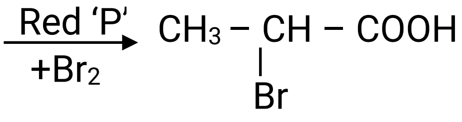
$\xrightarrow[-H_2O]{Heat} C_6H_5 - \overset{C_6H_5}{\overset{|}{C}} = CH_2$

$\xrightarrow{[O]} C_6H_5COC_6H_5 + HCOOH$

Diphenyl ketone methanoic acid

18. Increasing order of acid strength $(CH_3)_2COOH < CH_3CH_2COOH < ClCH_2CH_2COOH < CH_3COOH < ClCH_2COOH$

19. The structure $R - C \equiv O^+$ is more stable because in it all elements have complete their octet, while in $R - C^+ = O$, C – atom does not have complete its octet.

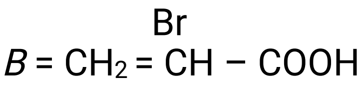


20. $CH_3 - CH_2COOH \xrightarrow[+Br_2]{Red\ 'P'} CH_3 - \underset{Br}{\underset{|}{CH}} - COOH$

Compound *A*

(This bromination takes place on -carbon atom hence, in it - hydrogen is displaced.)

$\xrightarrow[\text{2. } H^+]{\text{1. Alcoholic KOH (excess)}}$

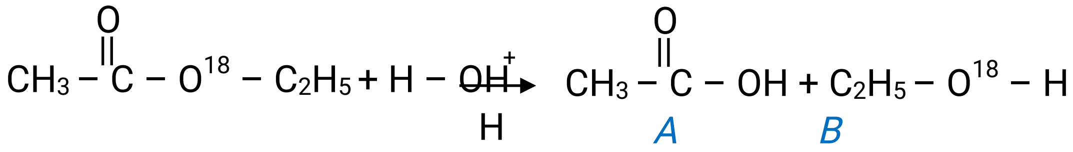


$B = CH_2 = \overset{Br}{CH} - COOH$

Thus Compound $A = CH_3 - \underset{|}{CH} - COOH$

$CH_2 = CH - COOH$ Compound *B*

21.

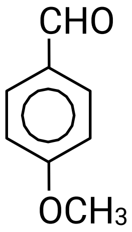


$$CH_3-\overset{\overset{O}{\|}}{C}-O^{18}-C_2H_5 + H-OH \xrightarrow{H^+} \underset{A}{CH_3-\overset{\overset{O}{\|}}{C}-OH} + \underset{B}{C_2H_5-O^{18}-H}$$

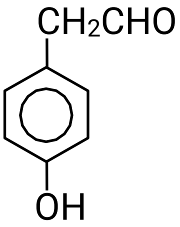
22. Five isomeric *p*-disubstituted aromatic compound *A* to *E* with molecular formula $C_8H_8O_2$, give following observations:

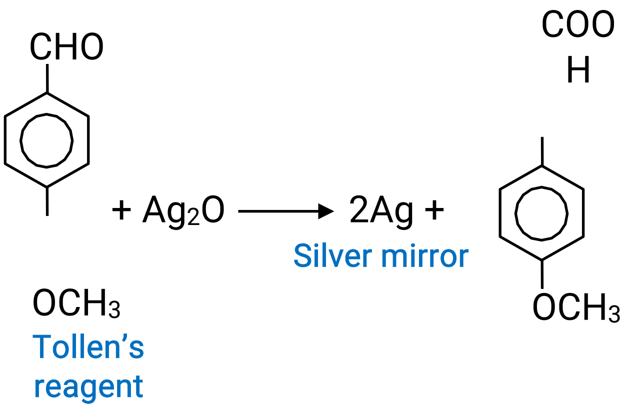
i. Both compound *A* and *B* form a silver mirror with Tollen's reagent, thus they have aldehydic group in their structures.

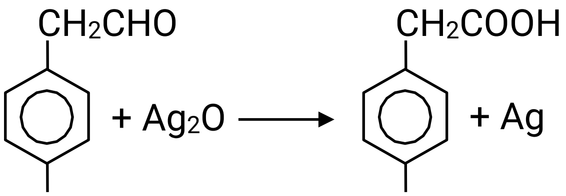
Compound '*A*'



Compound '*B*'

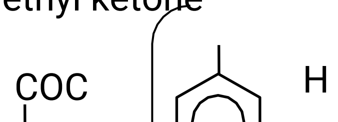


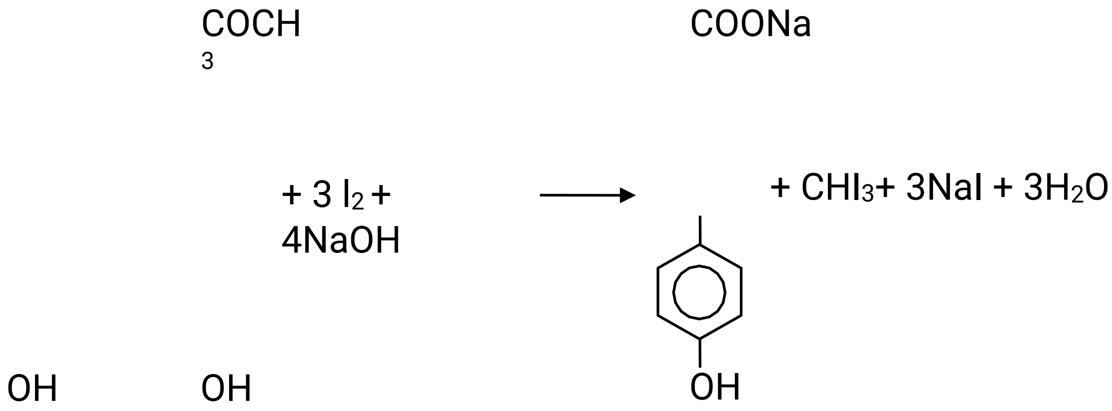




In these compound *B* gives positive test with $FeCl_3$ solution so it must have phenolic group in its structure. Hence, compound *A* is *p*-methoxy benzaldehyde and *B* is *p*-hydroxy phenyl acetaldehyde

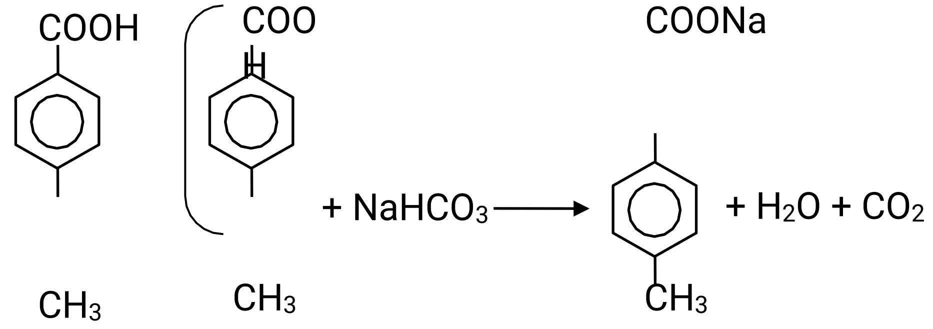
ii. Compound *C* gives positive iodoform test, so it must have CH_3CO- group in its structure. Hence compound *C* is *p*-hydroxyphenyl methyl ketone





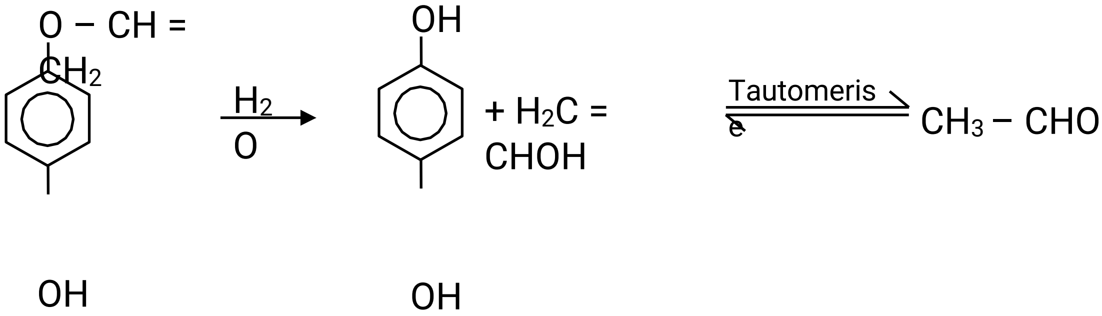
$+ 3\ I_2 + 4NaOH$ $\longrightarrow$ $+ CHI_3 + 3NaI + 3H_2O$

iii. Compound *D* is readily extracted in aqueous $NaHCO_3$, so it must have –COOH group in its structure.



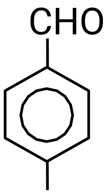
So, compound *D* is *p*-methyl benzoic acid

iv. Compound *E* on hydrolysis gives 1, 4-dihydroxy benzene,



1, 4 dihydroxy benzene

So compound *E* is *p*-hydroxylphenyl vinyl ether. Hence, compounds



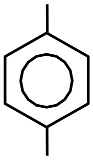
CH_2CHO COCH$_3$ COOH O – CH = CH_2

&

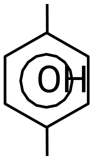
OCH_3

OH

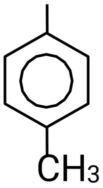
‘A’



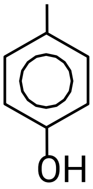
‘B’



‘C’

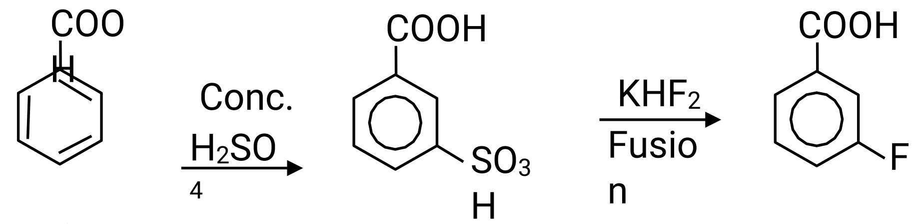


‘D’



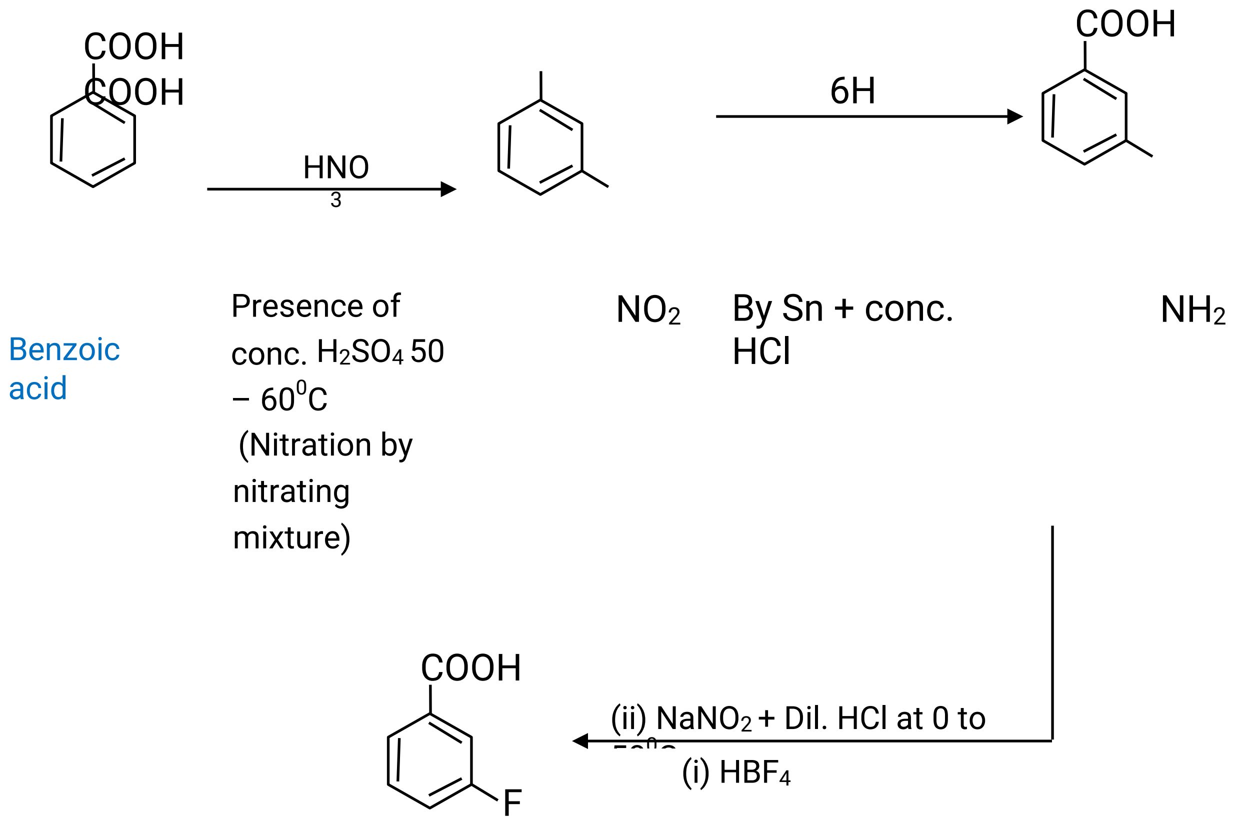
‘E’

23.



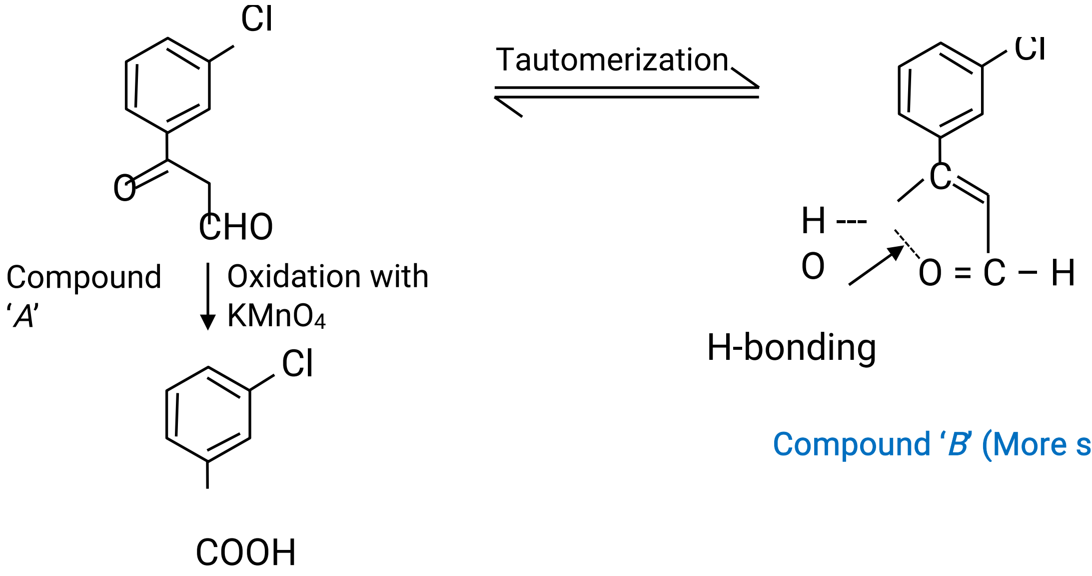
Benzoic acid

Alternatively



m-fluoro benzoic acid

24. (b) Compound *A* of molecular formula $C_9H_7O_2Cl$ exists in keto form and predominantly in enolic form *B.* Hence, compound *A* must be carbonyl compound which has -hydrogen atom because it is enolised. Enolic form *B* is predominated due to H-bonding.



Compound ‘*A*’

m-chlorobenzoic acid

Compound ‘*B*’ (More stable)