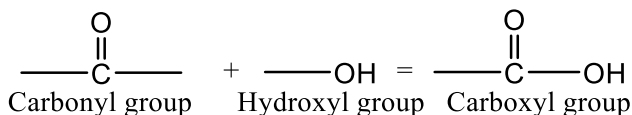


14.1 Aliphatic and Aromatic carboxylic acids

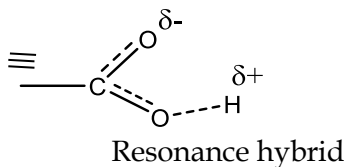
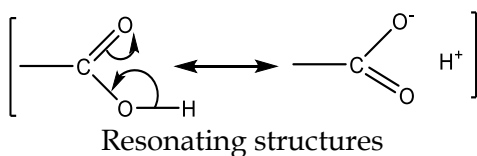
Introduction

The organic functional group **-COOH** is called the carboxyl group because it is formed by the combination of the carbonyl group ($>\text{CO}$) and hydroxyl group ($-\text{OH}$).

Its structure is

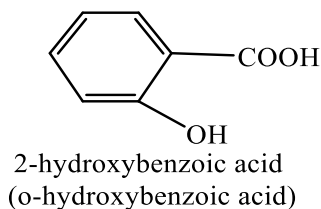
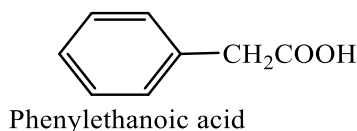
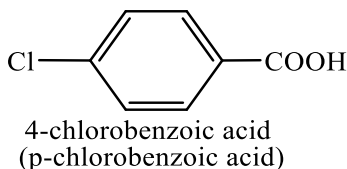
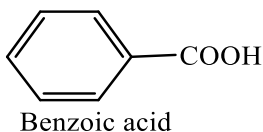


However, due to the resonating structures, the compounds containing the carboxyl group have entirely different properties than both carbonyl compounds and alcohols.

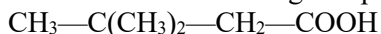


Carboxylic acid is one of the very reactive functional groups among the organic compounds.

Carboxylic acids are named by adding the **-oic acid** as a secondary suffix replacing -e in the name of parent hydrocarbon alkane, i.e., alkanoic acid.



1. Write the name of following compound according to the IUPAC rule.



2

2. Name: $\text{CH}_3\text{—CH}_2\text{—C(CH}_3)_2\text{—CH}_2\text{—COOH}$ according to IUPAC rule.

Isomerism

I. Functional Isomerism

Carboxylic acid can form functional isomers with esters.

e.g. $C_2H_4O_2$ can exist as;



Ethanoic acid (acetic acid)



Methylmethanoate

3. What is functional isomer of Ethanoic acid? Give its IUPAC name. 2
4. Write down the functional isomer of Methylmethanoate. 1

II. Chain Isomerism

Carboxylic acids having more than 3 carbon atoms exhibit chain isomerism.

e.g. following two isomers are possible for the formula $C_4H_8O_2$.



Butanoic acid



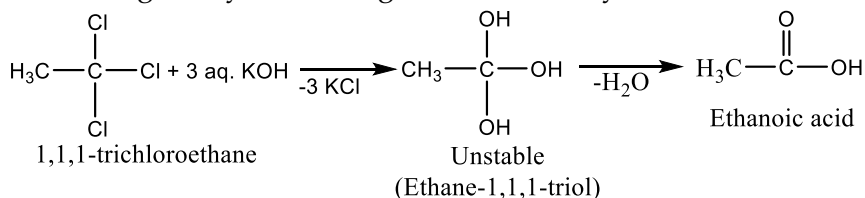
2-methylpropanoic acid

1. Carboxylic acids are functional isomers of
 - a. Alcohols
 - b. Esters
 - c. Aldehydes and ketones
 - d. Acid anhydride
2. $C_3H_6O_2$ does not represent
 - a. A monocarboxylic acid
 - b. An ethyl ester
 - c. A methyl ester
 - d. A dicarboxylic acid
3. Vinegar contains
 - a. 10-20% acetic acid
 - b. 7-8% acetic acid
 - c. 10% acetic acid
 - d. 100% acetic acid
4. A carboxylic acid, P, has no chain isomers. It reacts with an alcohol, Q, that has only one positional isomer.
What could be the ester formed from a reaction between P and Q?
A butyl propanoate
B ethyl butanoate
C pentyl ethanoate
D propyl pentanoate

General methods of preparations of monocarboxylic acids

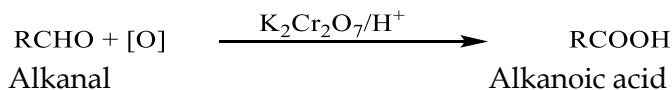
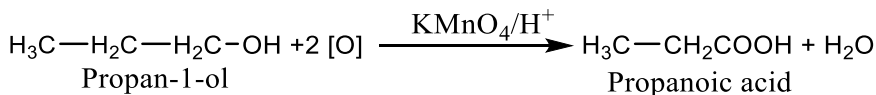
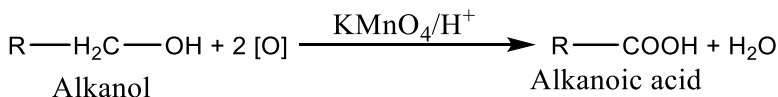
I. From trihaloalkanes

Hydrolysis of 1,1,1-trihaloalkanes produce unstable trihydroxy alkanes which undergo dehydration to give monocarboxylic acid.



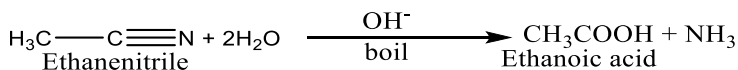
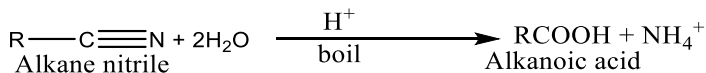
II. By oxidation of 1° alcohols and aldehydes (studied in alcohols and aldehydes- ketones chapters already)

Primary alcohols and aldehydes get oxidized in the presence of strong oxidizing agents like alkaline or acidified KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$ etc., carboxylic acids are produced.



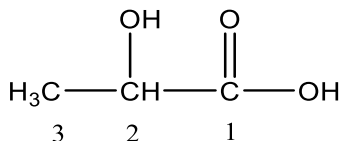
III. By hydrolysis of nitriles

Alkanenitriles on acidic or basic hydrolysis produce acids (via amide and ammonium salt).



5. An organic compound 'A' undergoes ozonolysis to give two carbonyl compounds B and C. The compound B, on reduction with $\text{Zn-Hg}/\text{H}^+$, gives propane. The compound C reacts with HCN and followed by

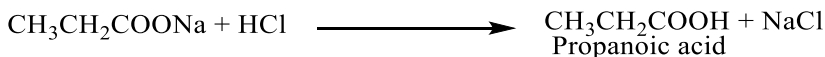
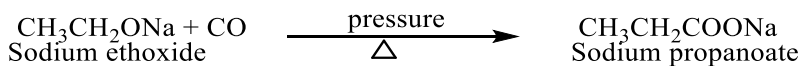
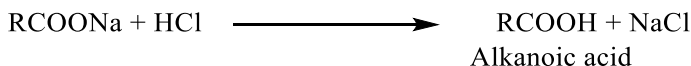
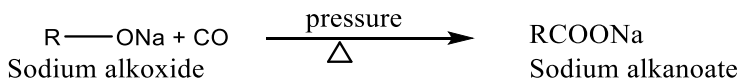
hydrolysis to produce 2-hydroxypropanoic acid as the major product. Write the chemical reaction involved and give the IUPAC name of A, B and C. 5



2-hydroxypropanoic acid

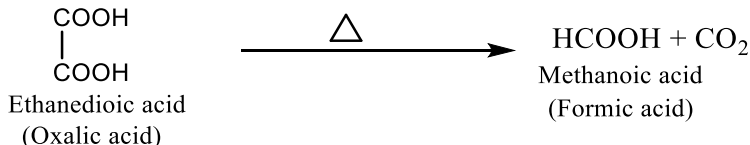
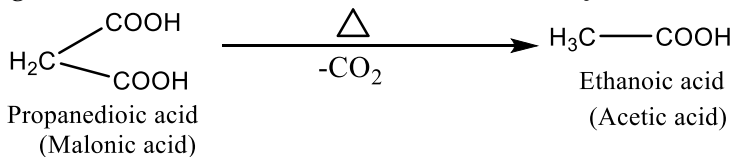
IV. From sodium alkoxide

Sodium alkoxide when heated with carbon monoxide under pressure gives sodium alkanoate which on acidification gives carboxylic acids.



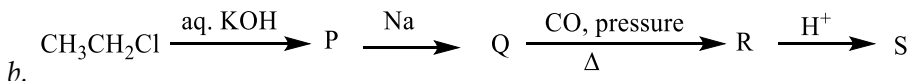
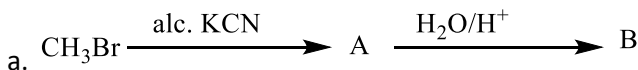
v. From dicarboxylic acids

Dicarboxylic acids when heated yield monocarboxylic acids and carbon dioxide gas. This reaction is also known as **decarboxylation reaction**.



6. Give chemical reactions for the preparation of Ethanoic acid from
i) 1,1,1-trichloroethane ii) Ethanenitrile iii) Sodium ethoxide 3
7. Suggest any three suitable chemical reactions for the preparation of
Ethanoic acid. 3
8. Write an example of carboxylation reaction. 1

9. What is meant by carboxylation reaction? Give an example. 2
10. Write the correct reactions for the preparation of Ethanoic acid from following set of compounds
 a. CH_3CN b. CH_3ONa 2
11. Make the following conversions.



5. Methylbut-2-ene reacts with HBr at room temperature to produce compound X as a major product.

Compound X reacts with KCN in ethanol to produce compound Y.

Compound Y is hydrolysed with acid to produce compound Z.

What is compound Z?

A 2,2-dimethylbutanoic acid

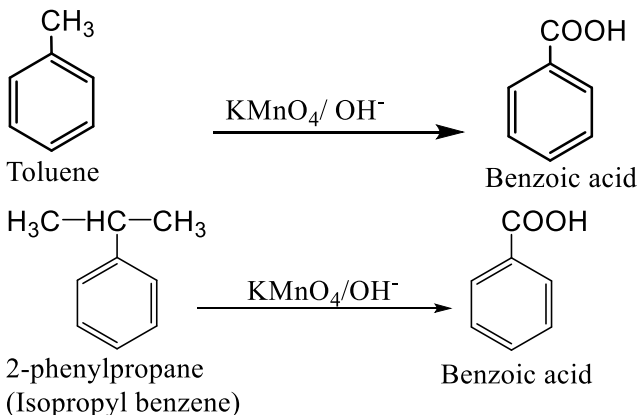
B 2,3-dimethylbutanoic acid

C 2-methylpentanoic acid

D 3-methylpentanoic acid

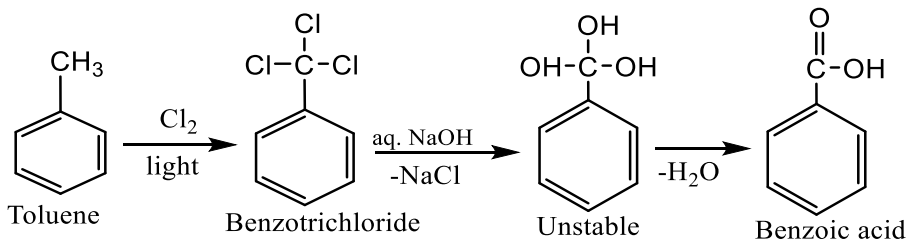
Preparation of Benzoic acid from alkyl benzene

Irrespective of the chain length of the alkyl group, alkyl benzenes are oxidized by **alkaline KMnO_4** or **dil. HNO_3** as oxidizing agent into benzoic acid.



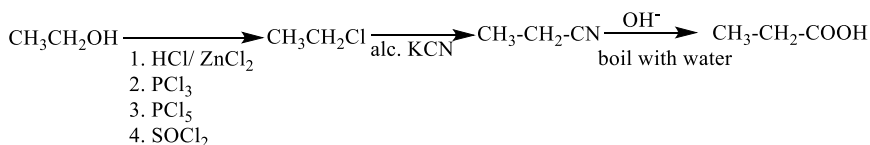
Manufacture of Benzoic acid

Benzoic acid is prepared in industrial scale by bubbling chlorine through the boiling toluene in presence of ultra violet light. The Benzotrichloride obtained is hydrolyzed by alkali to benzoic acid.

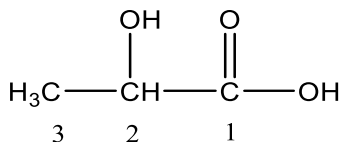


12. How is Benzoic acid prepared from Benzene? 2

13. Convert Ethanol to Propanoic acid. 2



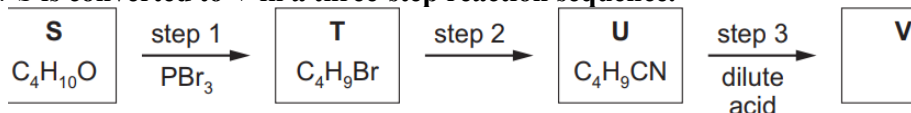
14. An organic compound 'A' undergoes ozonolysis to give two carbonyl compounds B and C. The compound B, on reduction with Zn-Hg/H⁺, gives propane. The compound C reacts with HCN and followed by hydrolysis to produce 2-hydroxypropanoic acid as the major product. Write the chemical reaction involved and give the IUPAC name of A, B and C. 5



2-hydroxypropanoic acid

15. An organic compound A reacts with HCN to give B. On hydrolysis of B in acidic medium gives C. 'A' also produces Propane when treated with Zn-amalgum and HCl. Identify A, B and C with reaction and IUPAC names. What product would you expect when A is treated with Trichloromethane in alkaline medium? 5

16. S is converted to V in a three-step reaction sequence.



In step 1, the secondary alcohol **S** reacts with PBr_3 to produce **T**, which has molecular formula $\text{C}_4\text{H}_9\text{Br}$.

(i) Give the systematic name of **T**. [1]

(ii) Name the type of reaction that occurs in step 1. [1]

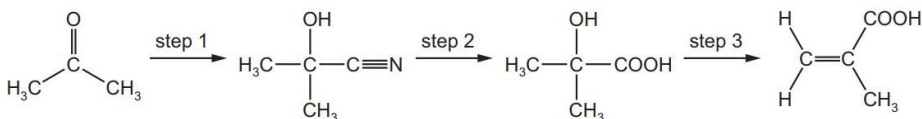
(iii) State the reagent(s) and conditions for step 2. [2]

(iv) Step 3 involves heating $\text{C}_4\text{H}_9\text{CN}$ with dilute acid to form **V**.

Complete the equation for this reaction.

..... $\text{C}_4\text{H}_9\text{CN}$ + H^+ + H_2O → [2]

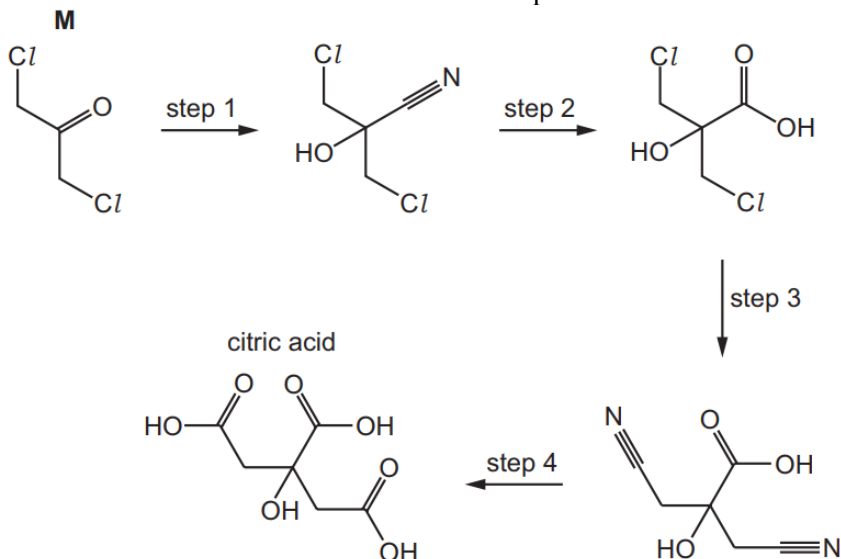
6. **K** can be made from propanone in the three-step synthesis



Complete the following table to identify the reagent(s) used and the type of reaction in each step. [2]

step	reagent(s)	type of reaction
1		
2		
3	Al_2O_3	

17. Citric acid can be made from **M** in a four-step reaction.

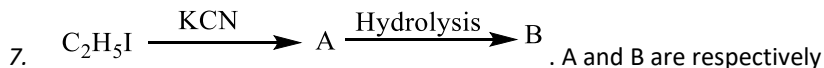


Complete the table for each step of the reaction sequence to identify:

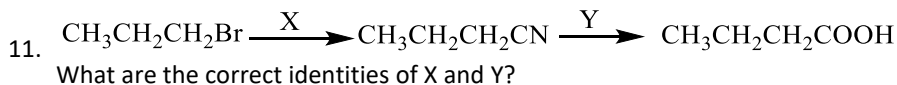
- the reagents and conditions required
- the type of reaction.

[3]

step	reagent and conditions	type of reaction
1		
2	dilute sulfuric acid	
3		
4	dilute sulfuric acid	



- C_2H_6 and $\text{C}_2\text{H}_5\text{OH}$
 - $\text{C}_2\text{H}_5\text{CN}$ and $\text{C}_2\text{H}_5\text{CH}_2\text{NH}_2$
 - $\text{C}_2\text{H}_5\text{CN}$ and $\text{C}_2\text{H}_5\text{COOH}$
 - C_2H_6 and $\text{C}_2\text{H}_5\text{CH}_2\text{NH}_2$
8. Iodoethane reacts with alc. KCN and its complete hydrolysis forms
- Acetonitrile
 - Ethyl amine
 - Ethanamine
 - Propanoic acid
9. The compound formed as a result of oxidation of ethyl benzene by KMnO_4 is:
- Acetophenone
 - Benzyl alcohol
 - Benzophenone
 - Benzoic acid
10. X and Y are the reagents required to convert 1-bromopropane into Butanoic acid in the following reaction.



	X	Y
A	HCN	HCl(aq)
B	KCN in $\text{C}_2\text{H}_5\text{OH}$	NaOH(aq)
C	KCN in $\text{C}_2\text{H}_5\text{OH}$	HCl(aq)
D	HCN	NaOH(aq)

12. Propanoic acid can be made from bromoethane using a two-stage synthesis. Which pair of reagents is most suitable?

	reagent for stage 1	reagent for stage 2
A	hydrogen cyanide	aqueous sodium hydroxide
B	aqueous sodium hydroxide	excess acidified potassium dichromate(VI)
C	ethanolic sodium hydroxide	acidified potassium manganate(VII)

D	potassium cyanide	dilute hydrochloric acid
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13. Butanoic acid can be made from 1-bromopropane in two stages.

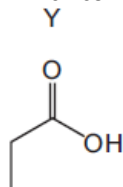
stage 1 $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$

stage 2 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$

Which types of reaction are stage 1 and stage 2?

	stage 1	stage 2
A	electrophilic addition	hydrolysis
B	electrophilic addition	oxidation
C	nucleophilic substitution	hydrolysis
D	nucleophilic substitution	oxidation

14. Which compounds can be used to make Y in a single-step reaction?



1 propanenitrile

2 ethanenitrile

3 propyl ethanoate

4 ethyl propanoate

A 1 and 3

B 1 and 4

C 2 and 3

D 2 and 4

Physical properties

I. State:

First few members are liquids and higher members are waxy solids because the intermolecular force of attraction increases with increasing molecular mass.

II. Solubility

The lower members of carboxylic acids are highly soluble in water owing to their polar nature and the capacity to form hydrogen bond with water.

But the solubility decreases gradually moving up the homologous series as the non-polar alkyl part gets bigger and hence dominant.

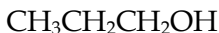
III. Melting and boiling points

The melting and boiling points of carboxylic acids are higher relative to corresponding compounds of other class of organic compounds of comparable molecular mass. This is because of strong hydrogen bond formed between two molecules, which results dimers, making the effective molecular mass double. e.g.



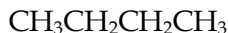
Molecular wt = 60

Boiling point = 118°C



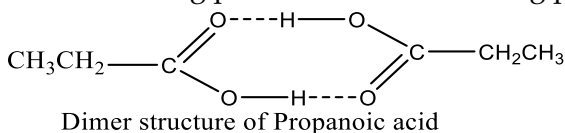
Molecular wt = 60

Boiling point = 97°C



Molecular wt=58

Boiling point = -1°C



18. Boiling point of Methanoic acid is higher than Ethanol though they have same molecular mass. Explain. 2

15. Which of the following has maximum boiling point?

- b. Methanoic acid
- c. Ethanoic acid
- d. Propanoic acid
- e. Butanoic acid

16. Which is the correct order for the boiling points

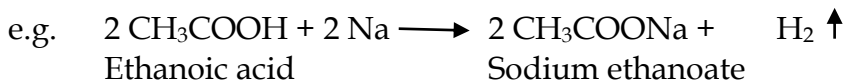
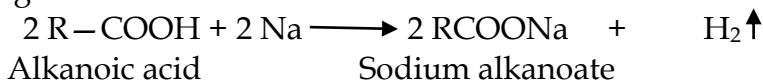
- a. 1-aminopropane > Ethanoic acid > Methoxypropane > Propan-1-ol
- b. Ethanoic acid > 1-aminopropane > Propan-1-ol > Methoxymethane
- c. Propan-1-ol > Methoxymethane > Ethanoic acid > 1-aminopropane
- d. 1-aminopropane > Ethanoic acid > Propan-1-ol > Methoxymethane

Chemical properties

I. Acidic nature

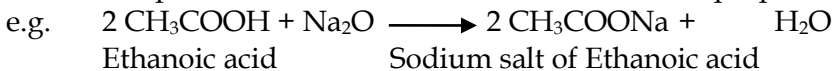
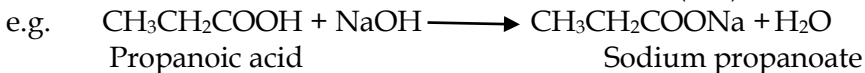
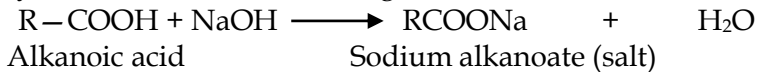
1. Reaction with active metal (Na)

Active metals like alkali and alkaline earth metal replace hydrogen from acids.



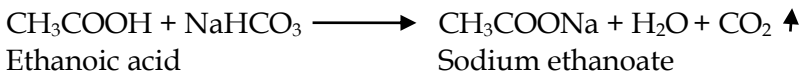
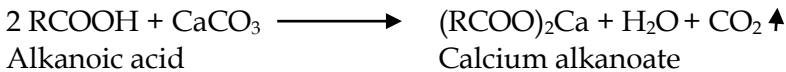
2. Reaction with base (NaOH or Na₂O etc.)

Carboxylic acids react with base to give salt and water.

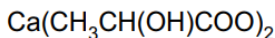
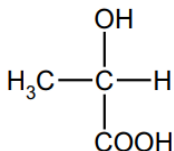


3. Reaction with metal carbonates and bicarbonates

Carboxylic acids react with metal carbonates and bicarbonates evolving carbon-dioxide gas. This reaction is used for the test of carboxylic acid functional group in organic compounds.



19. What product is obtained when CH_3COOH is allowed to react with NaOH ? 1
20. Calcium carbonate reacts with 2-hydroxypropanoic acid to form product **Y**.
2-hydroxypropanoic acid **Y**



Identify the **two** other products of the reaction of 2-hydroxypropanoic acid with calcium carbonate. [0.5]

17. Ethanedioic acid has the formula $\text{HO}_2\text{CCO}_2\text{H}$.
What is the formula of aluminium ethanedioate?
A $\text{Al C}_2\text{O}_4$ **B** $\text{Al (C}_2\text{O}_4)_3$ **C** $\text{Al}_2\text{C}_2\text{O}_4$ **D** $\text{Al}_2(\text{C}_2\text{O}_4)_3$
18. Which of the following reaction is used to distinguish carboxylic acid with other organic compounds?
- Reaction with sodium metal
 - Reaction with bicarbonate
 - Reaction with magnesium metal

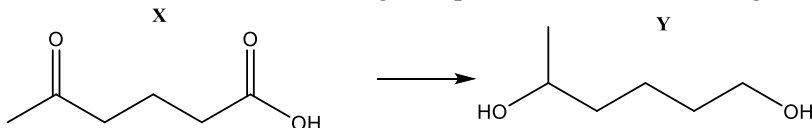
d. Reaction with chlorine

19. Propanoic acid is treated with reagent X at room temperature. The organic product of the reaction is sodium propanoate. No gas is produced during the reaction.

What could be reagent X?

A $\text{NaHCO}_3(\text{aq})$ **B** $\text{NaOH}(\text{aq})$ **C** $\text{Na}_2\text{CO}_3(\text{aq})$ **D** $\text{Na}_2\text{SO}_4(\text{aq})$

20. **Y** is formed from **X** in a single-step reaction, as shown in figure



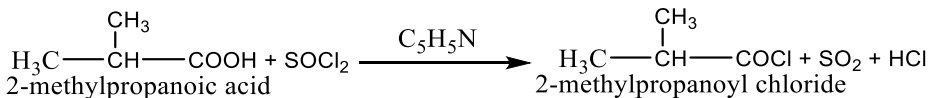
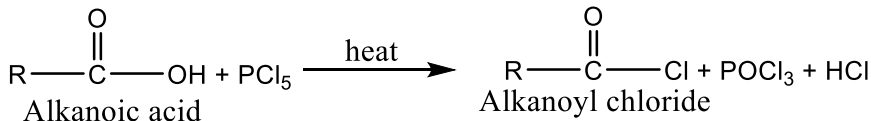
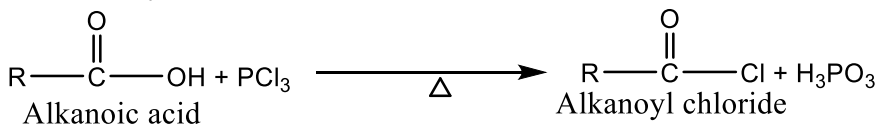
Complete Table 5.2 with the expected observations that occur when the reagents shown are added to separate solutions of **X** and **Y**. Do **not** refer to temperature changes in your answer. [2]

reagent	observation on addition to X	observation on addition to Y
aqueous sodium carbonate		
2,4-dinitrophenylhydrazine (2,4-DNPH reagent)		
alkaline aqueous iodine		

II. Reaction involving -OH group

1. Reaction with PCl_3

The hydroxyl group of the carboxylic acid is replaced by the chloride group forming acid chloride on treatment with these reagents in presence of pyridine.



21. How does Ethanoic acid react with PCl_5 ?

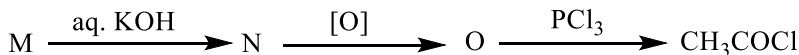
1

22. What happens when Ethanoic acid is treated with SOCl_2 ?

1

23. How would you prepare acid chloride from a carboxylic acid? Show pertinent equations.

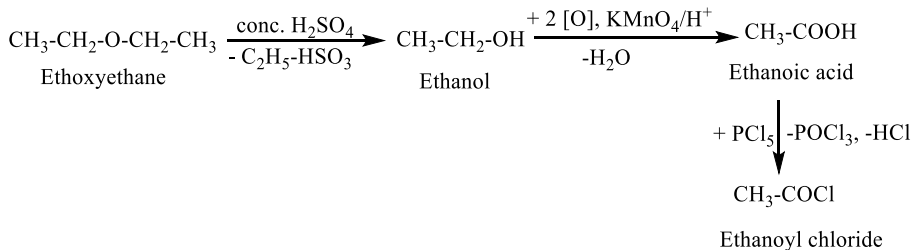
24. Identify M, N and O in following reaction sequence.



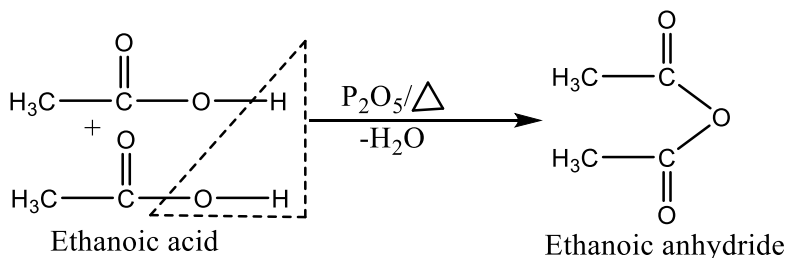
25. Convert Ethoxyethane to Ethanoyl chloride.

2

Solution:



2. Dehydration (Formation of acid anhydrides - reaction with P₂O₅)



26. What happens when Ethanoic acid is treated with P₂O₅?

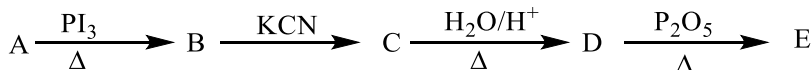
1

27. Write suitable reaction to convert Ethanoic acid into Ethanoic anhydride.

28. Write down the functional isomer of Methyl methanoate. What product would you expect when the isomer is heated with P₂O₅?

2

29. Consider the following reaction

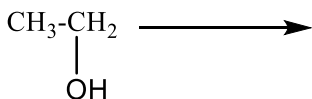


The compound A is a primary alcohol which gives iodoform test. Identify the organic compounds A, B, C, D and E; giving complete reaction.

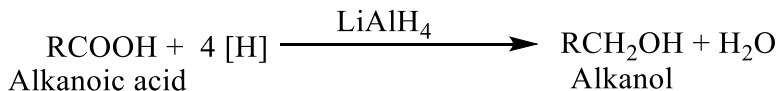
5

{Hint:

The only primary alcohol that gives iodoform test is Ethanol. Therefore A must be Ethanol.



4. Reduction with LiAlH_4 (partial reduction)



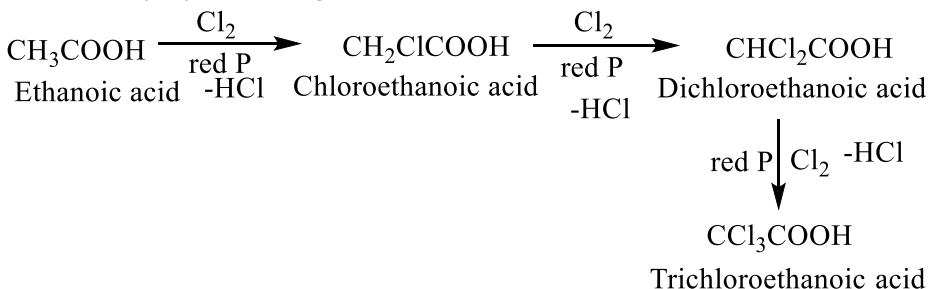
2. What products are obtained when CH_3COOH is allowed to react with LiAlH_4 ? 1

3. Predict the major product of $\text{CH}_3\text{COOH} \xrightarrow{\text{LiAlH}_4}$ 1

III. Reaction involving side chain (alkyl group)

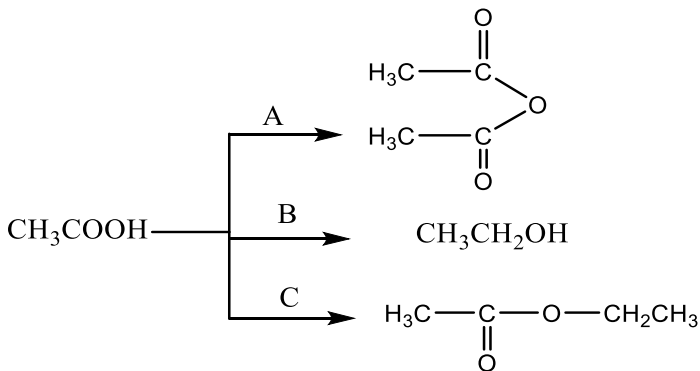
1. Halogenation of side chain (Hell-Volhard-Zelinsky -HVZ reaction)

When carboxylic acids are treated with Cl_2 or Br_2 in the presence of red phosphorous, all the α -hydrogen atoms of carboxylic acids are replaced successively by the halogen atoms.



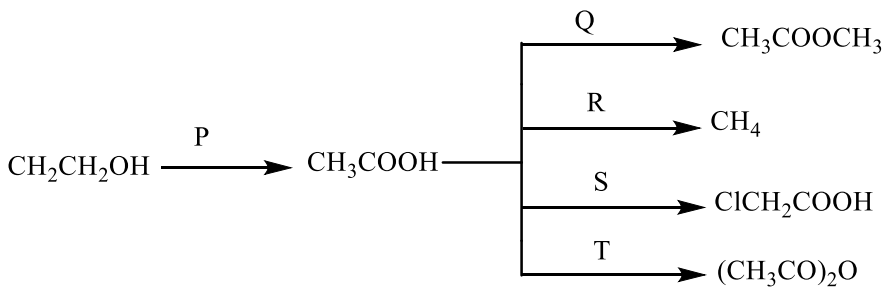
30. Give an example of Hell-vollard zelinsky reaction.

31. How would you bring about the following conversions?



3

32. Complete the following reaction sequence using suitable reagents and conditions in P, Q, R, S and T.



5

33. An alkene A on ozonolysis yields acetone and an aldehyde. The aldehyde is easily oxidized to an acid B. When B is treated with Br_2/P it yields C which on hydrolysis gives a hydroxyl acid D. This acid can also be obtained from Acetone by the reaction of HCN followed by hydrolysis. Identify the compounds A, B, C and D.

5

21. Acetic acid is reduced with LiAlH_4 to give

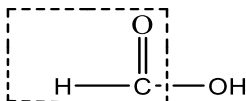
- a. Ethane b. Ethanol c. Methanol d. Ethanal

22. Which of the following is suitable for the preparation of α -chloroacetic acid?

- b. Hell-Volhard Zelinsky reaction
 c. Perkin's reaction
 d. Claisen reaction
 e. Cannizaro's reaction.

Abnormal properties of Formic acid

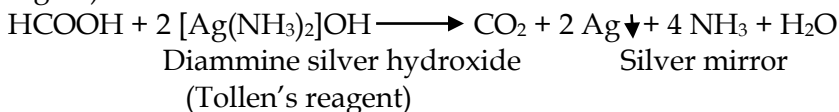
Formic acid or Methanoic acid apart from being a carboxylic acid resembles somewhat with aldehyde functional group. Thus, it gives few reactions which other carboxylic acids don't.



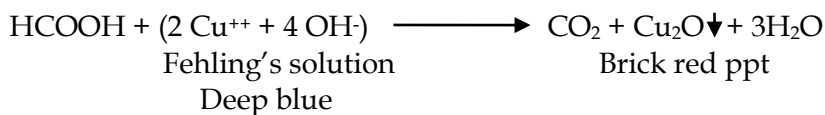
Therefore, formic acid can be distinguished from other acids by following chemical reactions.

I. Reaction with Tollen's reagent

Formic acid gives silver mirror with ammonical silver nitrate (Tollen's reagent).

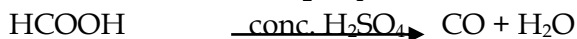


II. Reaction with Fehling's solution



34. Write a chemical reaction to distinguish Ethanoic acid from Methanoic acid. 2
35. 'Methanoic acid gives Tollen's test but Ethanoic acid does not' give reason. 1
36. Why does formic acid give silver mirror with Tollen's reagent? 2
37. What happens when Methanoic acid is warmed with Ammonical silver nitrate? 1
38. You are given two test tubes, one containing Methanoic acid and other Ethanoic acid. Suggest a suitable chemical test to identify them. Give chemical reaction too. 1
39. How does Methanoic acid act upon Fehling's solution? 1
40. How does formic acid act upon Tollen's reagent? 1

III. Reaction with conc. H_2SO_4

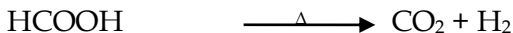


41. How does Methanoic acid act upon conc. H_2SO_4 ? 1

IV. Reaction with acidified KMnO_4



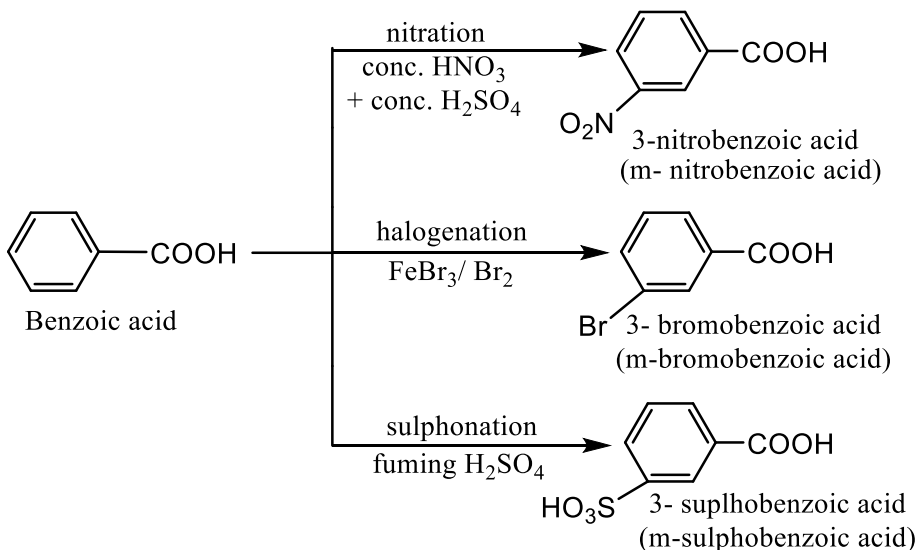
V. Action of heat



42. Formic acid is the first member of carboxylic acid and naturally found in ant stings and venom of bee.
- Draw the molecular formula of formic acid and write its IUPAC name. [1]
 - How is formic acid prepared from
 - Chloroform
 - Ethane-1,2-dioic acid? [1+1]
 - Distinguish formic acid from acetic acid with a chemical reaction. [1]
 - Why is formic acid more acidic than acetic acid? [1]
23. Which of the following cannot reduce Fehling's solution?
a. Formic acid b. Acetic acid c. Formaldehyde d. *Acetaldehyde*
24. What is formed by the dehydration of formic acid conc. H_2SO_4 ?
c. CO b. CO_2 c. Both d. None
25. The reaction of HCOOH and conc. H_2SO_4 gives
a. Carbon dioxide b. carbon monoxide
b. Oxalic acid d. acetic acid
26. Formic acid and formaldehyde can be distinguished by
a. Ammonical silver nitrate
b. NaHCO_3
c. Fehlings solution
d. Both a and c.
27. Which of the following reduces Tollen's reagent?
a. HCOOH b. $(\text{COOH})_2$ c. CH_3COOH d. CH_3COCH_3

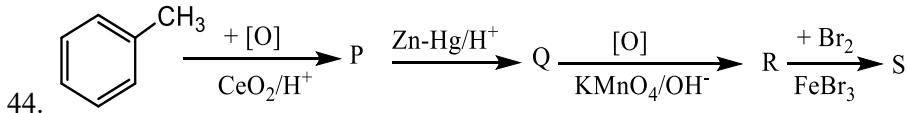
Electrophilic aromatic substitution reaction of Benzoic acid

Carboxylic group is an electron-withdrawing group and meta director, therefore undergo nitration, sulphonation and halogenations reactions at meta position rather difficulty.



43. What happens when Benzoic acid is nitrated?

2



Complete the above reaction sequence with side products and IUPAC name.

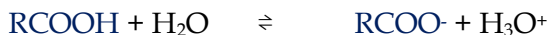
Acidity of Carboxylic acids

The acidity of carboxylic acids can be explained on the basis of the following two facts:

Ionization constant

When carboxylic acid is dissolved in water, it ionizes to give protons to the water molecules. The stronger acids give up most of their ionizable protons while weaker acids transfer only a small proportion.

The dissociation of carboxylic acid can be represented as:



The equilibrium (K_c) of the process is given by the expression:

$$K_c = \frac{[\text{H}_3\text{O}^+][\text{RCOO}^-]}{[\text{RCOOH}][\text{H}_2\text{O}]}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{RCOO}^-]}{[\text{RCOOH}]}$$

A stronger acid has a larger K_a . The value of K_a , therefore, the acidity decreases in the following order.

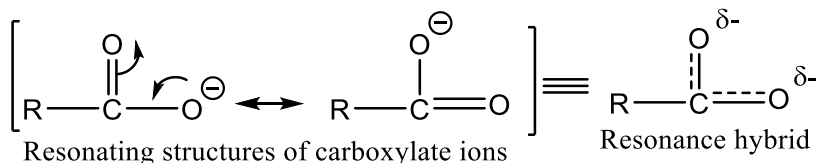
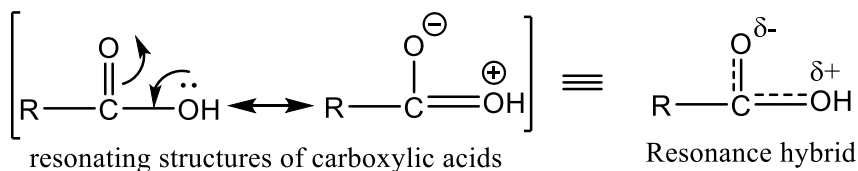
Formic acid > Acetic acid > Propionic acid > n-butyric acid

Trichloroacetic acid > Dichloroacetic acid > Chloroacetic acid > Acetic acid

Resonance stabilization

Carboxylic acids are quite strong acids because of the presence of polar O-H group. They ionize to give protons.

Carboxylic acids as well as its carboxylate anion both are stabilized by resonance.



However, carboxylate anion is more stabilized by resonance because its contributing structures are exactly identical and does not include charge separation as in carboxylic acid. Therefore, the above equilibrium lies very much towards ionized form. Hence carboxylic acids behave as fairly strong acids. These are stronger acids in comparison to alcohols and phenols which is attributed to the stable resonating structure of carboxylate ion.

Effects of Substitution on Acidity of Carboxylic Acids

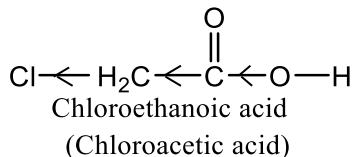
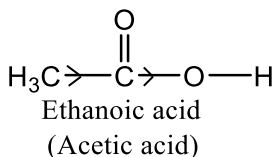
The factors which increase the stability of the carboxylate ion more than carboxylic acid increase the acidic strength.

Therefore, electron withdrawing groups stabilize the carboxylate ion by dispersal of the negative charge and increase the acid strength. On the

other hand, the electron releasing groups destabilize the carboxylate ion and decrease the acid strength.

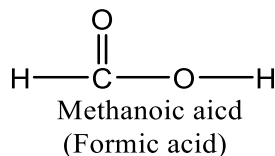
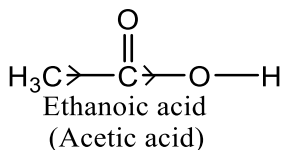
45. Why is chloroacetic acid stronger acid than acetic acid? 2

The greater the tendency of acid to release proton i.e., H^+ ion, stronger the acidic character. In acetic acid, methyl group is electron releasing group, due to this proton of acid does not loose easily but in chloroacetic acid, chlorine is electron withdrawing group and withdraws the electron, due to this proton of acid is lost easily. Therefore, chloroacetic acid is stronger acid than acetic acid.



46. Why is Ethanoic acid weaker acid than Methanoic acid? 2

The greater the tendency of acid to release proton i.e., H^+ ion, stronger the acidic character. In acetic acid, methyl group is electron releasing group, due to this proton of acid does not loose easily. Therefore, acetic acid is weaker acid than formic acid.



In other words, the carboxylate ion of the acetic acid is destabilized by the electron releasing methyl group in comparison to formic acid. That makes acetic acid weaker acid than formic acid.

47. Arrange the following compounds according to their ascending order of acidic strength and justify your order.



3

28. The correct decreasing order of acidic strength of 0.1 M solution of following acids is

- $\text{F}_2\text{CHCOOH} > \text{FCH}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{CH}_3\text{COOH}$
- $\text{FCH}_2\text{COOH} > \text{FCH}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{CH}_3\text{COOH}$
- $\text{ClCH}_2\text{COOH} > \text{FCH}_2\text{COOH} > \text{F}_2\text{CHCOOH} > \text{CH}_3\text{COOH}$
- $\text{CH}_3\text{COOH} > \text{ClCH}_2\text{COOH} > \text{FCH}_2\text{COOH} > \text{F}_2\text{CHCOOH}$

29. Q is a compound with the molecular formula $C_4H_{10}O$. Q can be oxidised with acidified potassium dichromate (VI). Q cannot be made by reducing a carboxylic acid with $LiAlH_4$. What is the structure of Q?
- | | |
|-------------------------|-------------------------|
| e. $CH_3CH(OH)CH_2CH_3$ | c. $CH_3CH_2CH_2CH_2OH$ |
| f. $(CH_3)_3COH$ | d. $(CH_3)_2CHCH_2OH$ |