CHEMISTRY STUDY MATERIALS FOR CLASS 12

(NCERT Based Notes of Chapter - 11)

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Aldehyde, Ketones and Carboxylic Acid

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 or by potassium dichromate ($K_2Cr_2O_7$) and chromium trioxide (CrO_3) in acidic media.

$$R\text{-}CH_2OH \xrightarrow{\text{alkaline KMnO4/H3O+}} R\text{-}COOH$$

$$CH_3\text{-}CH_2\text{-}OH \xrightarrow{\text{CrO3/H2SO4}} CH_3\text{-}COOH$$

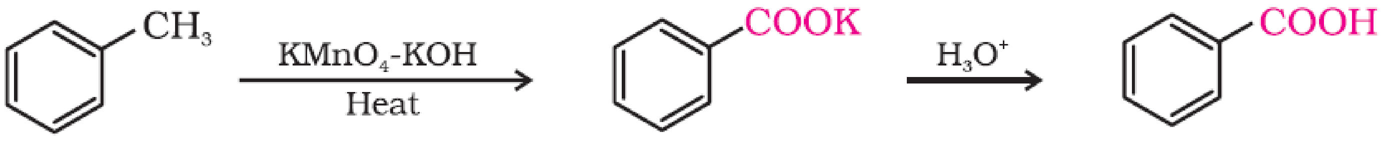
Aldehydes on oxidation with mild oxidising agents like CrO_3 or Tollen's reagent to give carboxylic acids.

$$R\text{-}CHO \xrightarrow{[O]} R\text{-}COOH$$

$$CH_3\text{-}CHO \xrightarrow{[O]} CH_3\text{-}COOH$$

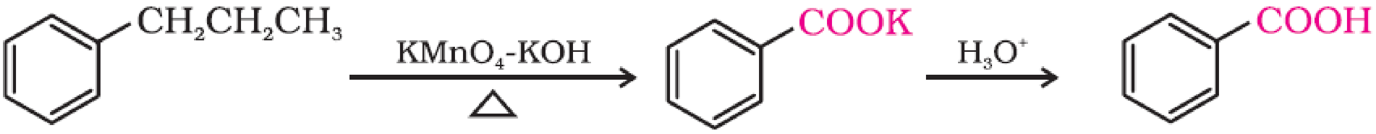
2. From alkyl benzenes:

Aromatic carboxylic acids can be prepared by vigorous oxidation of alkyl benzenes with chromic acid or acidic or alkaline potassium permanganate. The entire side chain is oxidised to the carboxyl group irrespective of length of the side chain. Primary and secondary alkyl groups are oxidised in this manner while tertiary group is not affected.



Toluene Potassium Benzoate

Benzoic acid



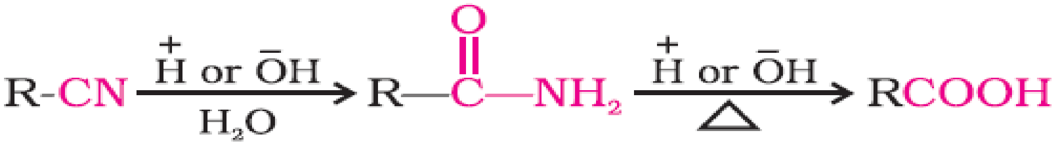
1-phenylpropane

potassium benzoate

Benzoic acid

3. From nitriles and amides:

Hydrolysis of nitriles in presence of acid or alkali as catalyst first give amides, which on further give carboxylic acids. Mild reaction conditions are used to stop the reaction at the amide stage.

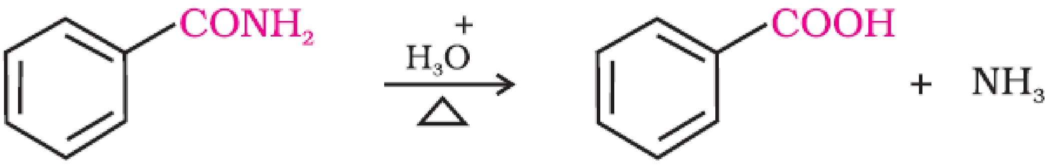


$$R\text{-}CN \xrightarrow[H_2O]{\overset{+}{H} \text{ or } \overset{-}{O}H} R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \xrightarrow[\Delta]{\overset{+}{H} \text{ or } \overset{-}{O}H} RCOOH$$

$$CH_3CONH_2 \xrightarrow[\Delta]{H_3\overset{+}{O}} CH_3COOH + NH_3$$

Ethanamide

Ethanoic acid

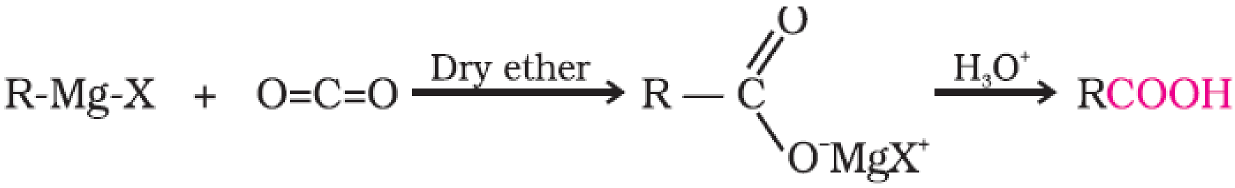


Benzamide

Benzoic acid

From Grignard reagents:

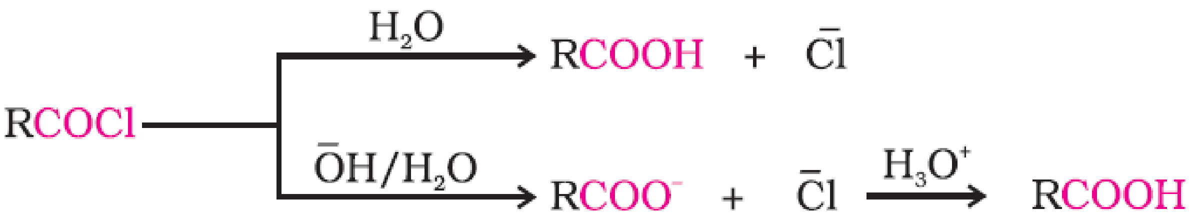
Grignard reagents react with carbon dioxide (dry ice) in dry ether to form salts of carboxylic acids which on acidification give corresponding carboxylic acids.



Grignard reagents and nitriles can be prepared from alkyl halides. So the above two reactions are used for converting alkyl halides into corresponding carboxylic acids having one carbon atom more than that present in alkyl halides.

4. From acyl halides and anhydrides:

Acid chlorides and anhydrides when hydrolysed with water give carboxylic acids. The rate of hydrolysis increases in alkaline medium.



$$RCOCl \xrightarrow{H_2O} RCOOH + \bar{Cl}$$

$$RCOCl \xrightarrow{\bar{O}H/H_2O} RCOO^- + \bar{Cl} \xrightarrow{H_3O^+} RCOOH$$

$$(C_6H_5CO)_2O \xrightarrow{H_2O} 2\ C_6H_5COOH$$

Benzoic anhydride — Benzoic acid

$$C_6H_5COOCOCH_3 \xrightarrow{H_2O} C_6H_5COOH + CH_3COOH$$

Benzoic ethanoic anhydride — Benzoic acid — Ethanoic acid

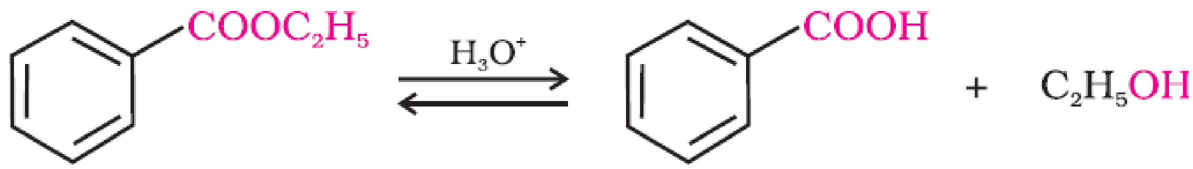
5. From esters:

Acidic hydrolysis of esters gives directly carboxylic acids while basic hydrolysis gives salt of carboxylic acids which on acidification give corresponding carboxylic acids.

$$CH_3\text{-}CH_2\text{-}COOCH_3 \underset{}{\overset{NaOH}{\rightleftharpoons}} CH_3\text{-}CH_2\text{-}COONa + CH_3OH$$

$$\downarrow$$

$$CH_3\text{-}CH_2\text{-}COOH + NaOH$$



Ethyl benzoate — Benzoic acid

Properties of carboxylic acid:

Physical properties

1. **Physical state**: Aliphatic carboxylic acids up to nine carbon atoms are colourless liquids at room temperature with unpleasant odours. The higher acids are wax like solids and are practically odourless due to their low volatility.

2. Boiling point: Carboxylic acids are higher boiling liquids than aldehydes, ketones and alcohols of comparable molecular masses. This is due to more extensive association of carboxylic acid molecules through intermolecular hydrogen bonding. Most carboxylic acids exist as dimer in the vapour phase or in the protic solvents.

3. Solubility: Simple aliphatic carboxylic acids having upto four carbon atoms are miscible in water due to the formation of hydrogen bonds with water. The solubility decreases with increasing number of carbon atoms. The simplest aromatic carboxylic acid, benzoic acid, is nearly insoluble in cold water. Carboxylic acids are also soluble in less polar organic solvents like benzene, ether, alcohol, chloroform, etc.

Chemical properties:

A. Reactions Involving Cleavage of O–H Bond:

1. Acidity:

Reactions with metals and alkalies: Like alcohols and phenols, carboxylic acids react with electropositive metals and liberate hydrogen gas.

$$2\ \text{R-COOH} + 2\ \text{Na} \longrightarrow 2\ \text{R-COONa} + \text{H}_2$$

$$\text{R-COOH} + \text{NaOH} \longrightarrow \text{R-COONa} + \text{H}_2\text{O}$$

Unlike alcohols and phenols, carboxylic acids react with sodium carbonates and bicarbonates and give brisk effervescence of carbon dioxide.

$$\text{R-COOH} + \text{NaHCO}_3 \longrightarrow \text{R-COONa} + \text{H}_2\text{O} + \text{CO}_2$$

Carboxylic acids dissociate in water to give resonance stabilized carboxylate anions and hydronium ion.

$$\text{R-COOH} + \text{H}_2\text{O} \longrightarrow \text{R-COO}^- + \text{H}_3\text{O}^+$$

Due to the formation of hydronium ion in water, carboxylic acids are acidic in nature. The acidity of a substance is expressed in terms of pKa value, which is the negative logarithm of Ka

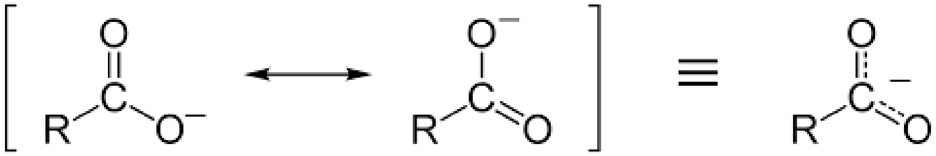
i.e. $pKa = -\log Ka$

Greater the value of Ka, smaller will be pKa and stronger will be the acid.

Comparison of acidic character

Carboxylic acids are weaker than mineral acids, but they are stronger acids than other organic compounds like alcohols and many simple phenols. The higher acidity of carboxylic acids as compared to phenols can be explained as follows:

The carboxylate ion formed from the ionization of carboxylic acid is stabilised by two equivalent resonance structures in which the negative charge is at the more electronegative oxygen atom. But the phenoxide ion formed from the ionization of phenol has non-equivalent resonance structures in which the negative charge is at the less electronegative carbon atom.



Also the negative charge is delocalized over two electronegative oxygen atoms in carboxylate ion, whereas it is less effectively delocalized over one oxygen atom and less electronegative carbon atoms in phenoxide ion. Therefore carboxylate ion is more stable than phenoxide ion and hence carboxylic acids easily donate H^+ ion and form carboxylate ion. So it is more acidic.

Effect of substituents on the acidity of carboxylic acids:

Electron withdrawing groups' increase the acidity of carboxylic acids by stabilising the carboxylate ion through delocalization of the negative charge by inductive and resonance effects. But electron donating groups decrease the acidity by destabilizing the carboxylate ion.

The effect of the following groups in increasing acidity order is

$Ph < I < Br < Cl < F < CN < NO_2 < CF_3$

Direct attachment of groups such as phenyl or vinyl to the carboxylic acid, increases the acidity of corresponding carboxylic acid. This is because of greater electronegativity of sp^2 hybridised carbon to which carboxyl carbon is attached. The presence of electron withdrawing group on the phenyl of aromatic carboxylic acid increases their acidity while electron donating groups decrease their acidity.

B. Reactions Involving Cleavage of C–OH Bond

1. **Formation of anhydride**: Carboxylic acids on heating with mineral acids like H_2SO_4 or with P_2O_5 undergo dehydration to give acid anhydrides.

$$\text{R-COOH} + \text{HOOC-R} \xrightarrow{\text{P2O5}/\Delta} (\text{R-CO})_2\text{O} + H_2O$$

$$CH_3\text{-COOH} + \text{HOOC-}CH_3 \xrightarrow{\text{H+}/\Delta} (CH_3\text{-CO})_2\text{O} + H_2O$$

Acetic acid acetic anhydride

2. **Esterification**: Carboxylic acids when heated with alcohols or phenols in the presence of a mineral acid like concentrated H_2SO_4 or HCl gas, we get esters. This reaction is reversible and is known as esterification.

$$\text{RCOOH} + \text{R'OH} \xrightleftharpoons{H^+} \text{RCOOR'} + H_2O$$

$$CH_3\text{-COOH} + CH_3\text{-OH} \xrightleftharpoons{\text{H+}} CH_3\text{-COO-}CH_3 + H_2O$$

Acetic acid methanol Methyl acetate

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