Aromatic acids

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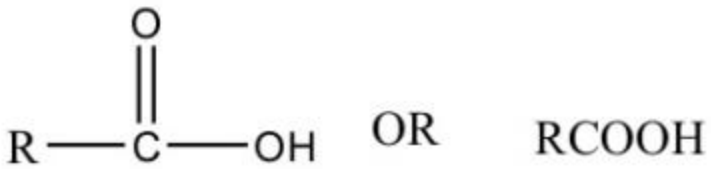
PhD

Carboxylic acid

- Organic compounds which contain the carboxyl functional group are called as carboxylic acids.
- The name carboxyl is derived from carbonyl(C=O) and hydroxyl(OH) because in the carboxyl group these two groups are directly bonded to each other.

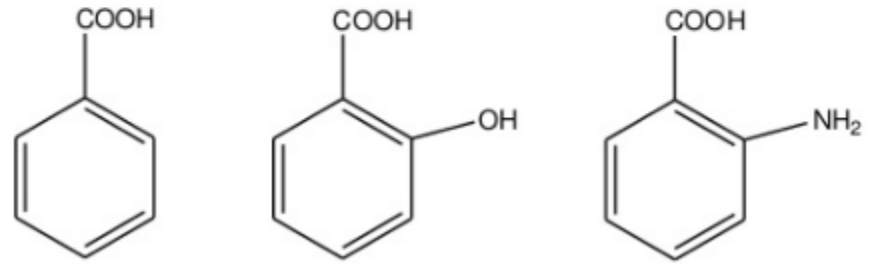


OR RCOOH

- Carboxyl group are further classified as monocarboxylic acid, dicarboxylic acid, tricarboxylic acid.
- The long chain monocarboxylic acids are commonly known as fatty acid.

Aromatic acid

- The compounds in which one or more carboxyl group are attached directly to the aromatic ring.



benzoic acid | 2-hydroxybenzoic acid | 2-aminobenzoic acid

Acidity of carboxylic acid

- Carboxylic acid are weak acids and ionize in water according to the following equation.

The equilibrium constant, K_{eq}

$$K_{eq} = \frac{[RCOO^-][H_3O^+]}{[RCOOH][H_2O]}$$

K_a value of carboxylic acid falls within the range of 10^{-4}-10^{-5}, the Ka value for acetic acid=1.74×10^{-5}

The ionization Constant: K_a

$$K_a = K_{eq}[H_2O] = \frac{[RCOO^-][H^+]}{[RCOOH]}$$

pK_a value of carboxylic acids falls within the range 4-5

pK_a value of acetic acid =4.76

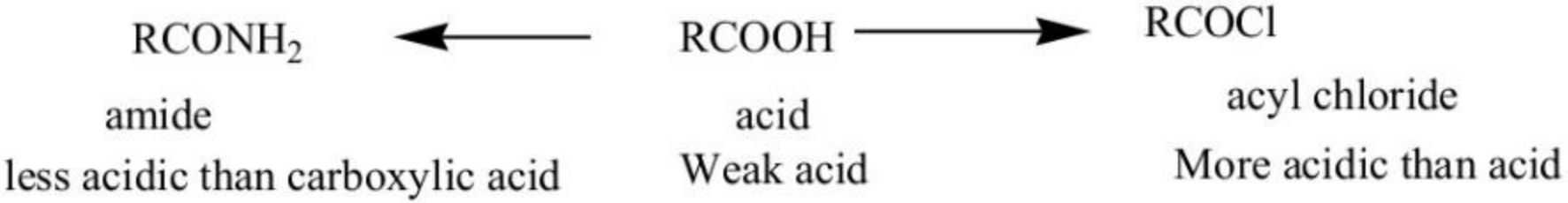
$$pK_a = -\log K_a$$

Acidity of aromatic acids

- The π electron plays important role in acidity of carboxylic acid.
- The negative charge of the carboxylate ion is shared by the two carboxylate oxygen atoms cannot be effectively delocalized by aromatic ring.
- Acidity influence by inductive effect

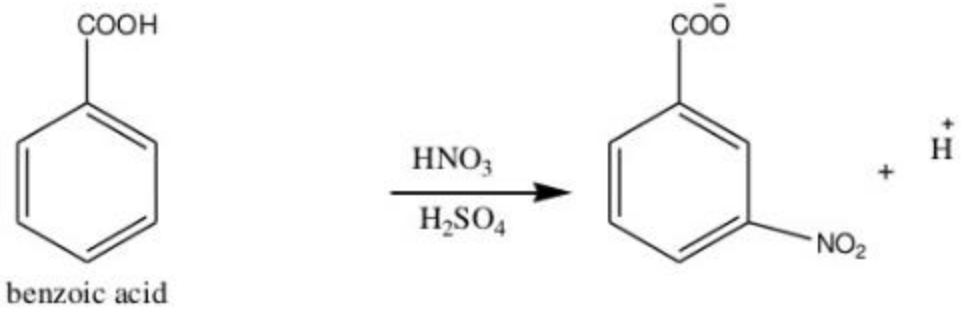
Effect of substituent's on acidity of carboxylic acid.

- Electron withdrawing group(Cl, Br, F) increases acidity- Electron withdrawing group withdraws electron density from the carboxyl group and equilibrium shifted to right that increases acidity of carboxylic acid.
- Electron donating group(OH, NH2) decreases the acidity- Electron donating group adds electron density to carboxyl group and equilibrium shifted to left that decreases acidity of carboxylic acid.



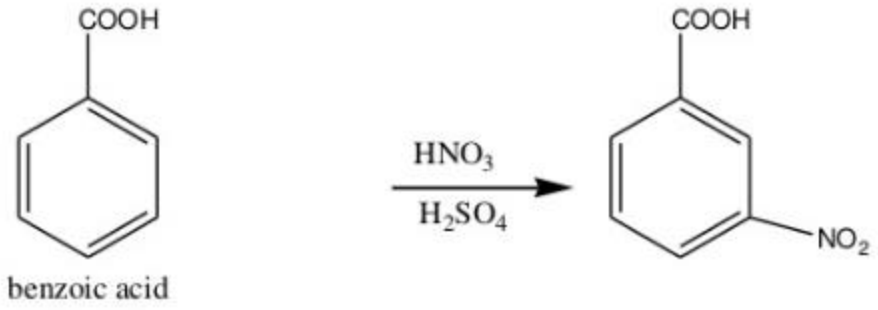
Factor affecting on acidity of benzoic acid

- The electron withdrawing group increases the acidity of a benzoic acid.
- The electronegative atom stabilizes anion
- An electron releasing on meta or para position decreases acidity of benzoic acid.
- Ortho substitution by electrophilic or nucleophilic group increases acidity due to steric effect.



Why carboxylic acid is called as deactivating?

- Benzoic acid undergoes electrophilic substitution is more slowly than benzene because carboxyl group withdraws electron from the ring by resonance.
- It decreases electron density of the ring and makes it less attractive to an incoming electrophile. hence electrophilic substitution is slow
- It requires vigorous reagent and condition

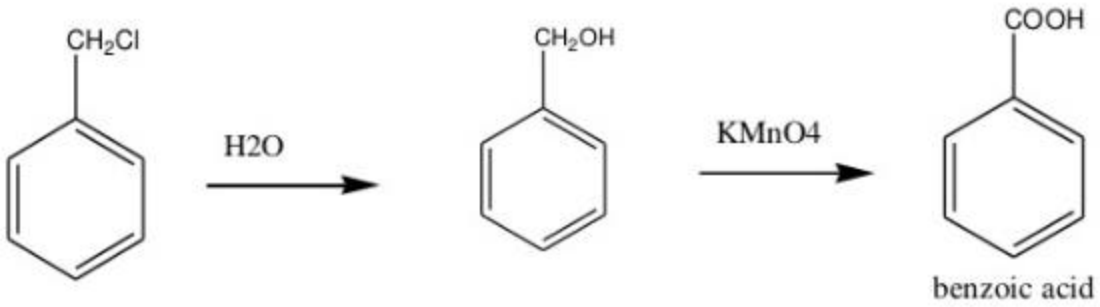


Preparation of aromatic acid

1. Oxidation of benzyl chloride
2. Reaction of phenyl magnesium bromide with carbon dioxide
3. Acid hydrolysis of benzonitrile
4. Basic hydrolysis of benzotrichloride
5. Hydrolysis of phenyl benzoate

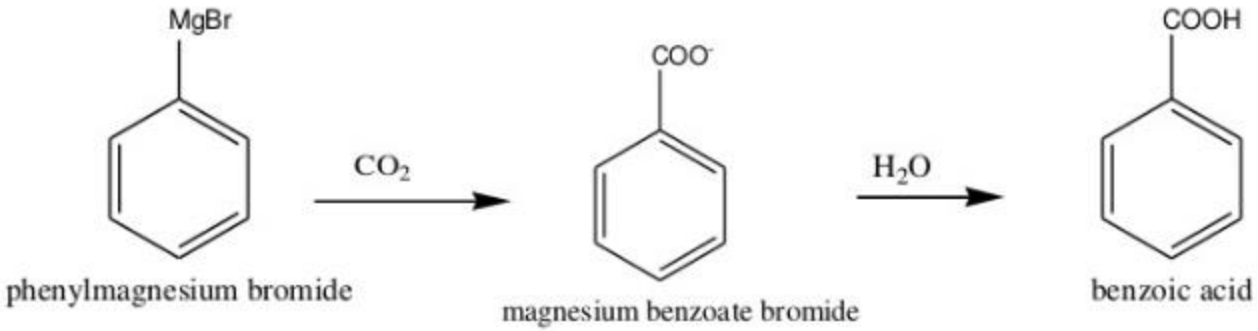
1.Oxidation of Benzyl chloride

Oxidation of Benzyl chloride with acidic potassium permanganate or sodium dichromate

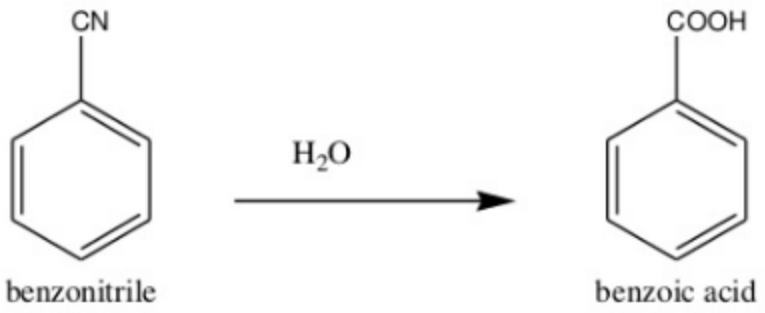


2.Reaction of phenyl magnesium bromide with carbon dioxide

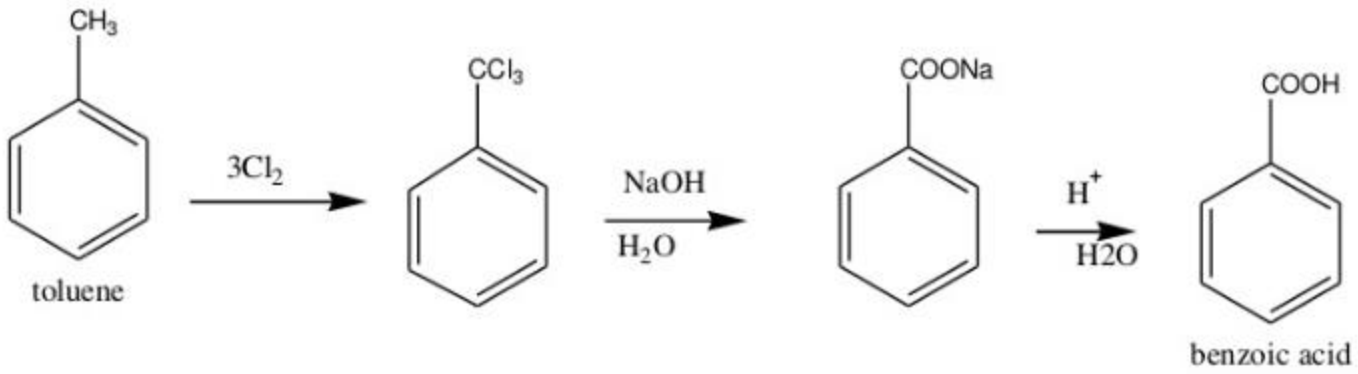
- The reaction of phenyl magnesium bromide with carbon dioxide followed by acid hydrolysis.



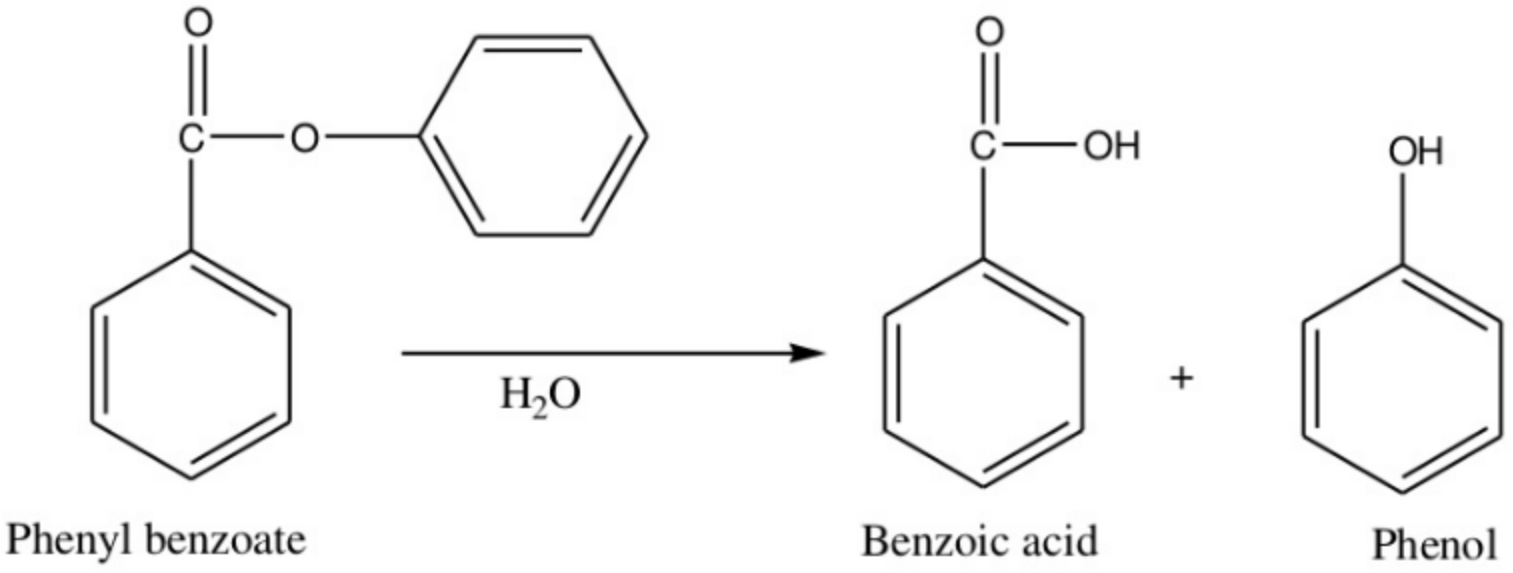
3.Acid hydrolysis of benzonitrile



4.Basic hydrolysis of benzotrichloride



5. Hydrolysis of Phenyl benzoate



Phenyl benzoate

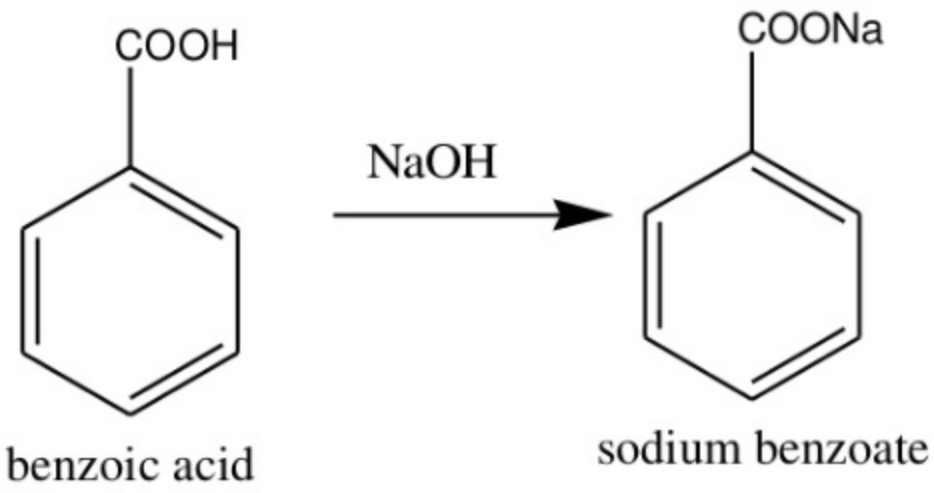
Benzoic acid

Phenol

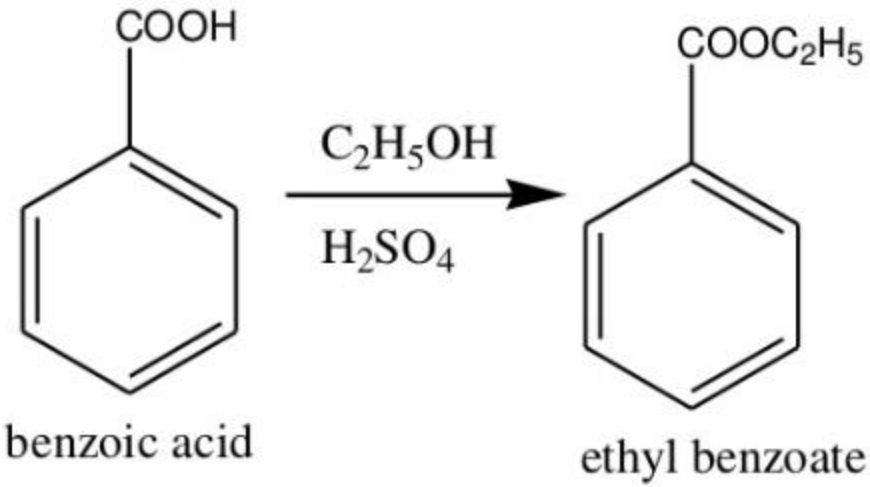
Reactions of aromatic acid

1. Salt formation
2. Ester formation
3. Acyl halide formation
4. Reduction to benzyl alcohol
5. Decarboxylation
6. Electrophilic substitution

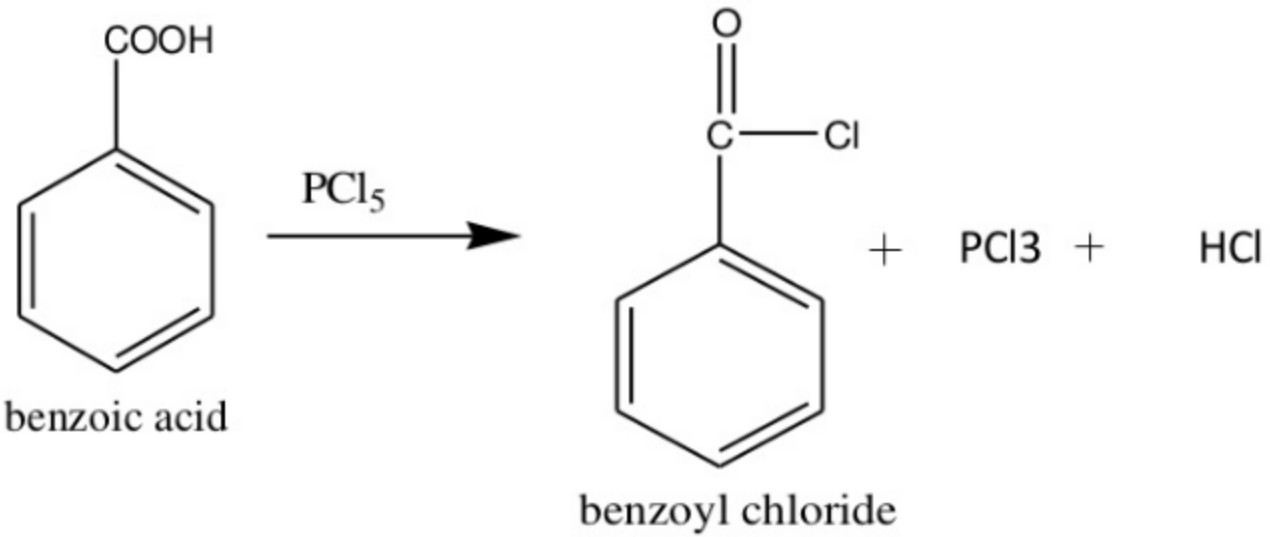
1.Salt formation



2.Ester formation

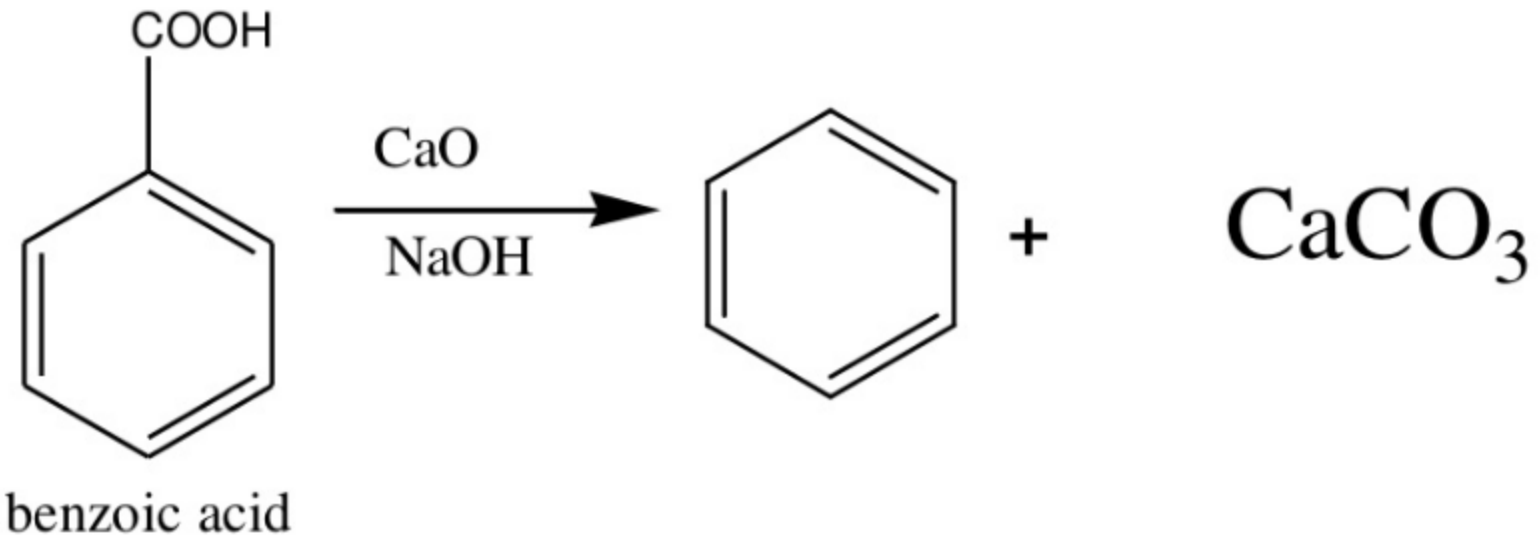


3.Acyl halide formation



4.Reduction to benzyl alcohol

5. Decarboxylation



benzoic acid

6. Electrophilic substitution