CARBOXYLIC ACIDS

Saturated monocarboxylic acids have general formula of $C_nH_{2n}O_2$.

PREPARATION OF CARBOXYLIC ACIDS

(1) By Oxidation of Alcohol:

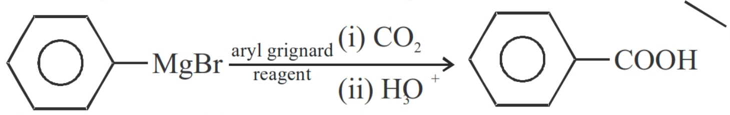
$$\underset{\substack{1^\circ\text{ alcohol}\\ \text{G.R.}}}{R-CH_2OH} \xrightarrow{[O]} \underset{\substack{\text{Carboxylic acids}\\ \text{with same number}\\ \text{of carbon atom}}}{RCOOH}$$

Oxidation ofalkene also gives carboxylic acids

$$RCH=CH-R' \xrightarrow{[O]} RCOOH + RCOOR'$$

(2) Using Grignard reagent (carbonation)

(a) $$\overset{\delta}{R}-\overset{\delta^+}{MgX} + CO_2 \longrightarrow RCOOMgX \xrightarrow{H_3O^+} RCOOH + Mg\begin{smallmatrix}X\\X\end{smallmatrix}$$

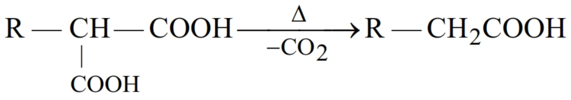
(b) 

(3) By the hydrolysis of cyanides

$$R-X \xrightarrow{\text{alc.KCN}} R-C\equiv N \xrightarrow{H_3O^+} R-COOH$$

The acid formed contain one carbon more than the parent alkyl halide.

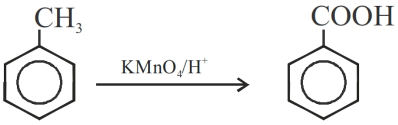
(4) By heating gem. dicarboxylic acids



$$R-\underset{\substack{|\\ COOH}}{CH}-COOH \xrightarrow[-CO_2]{\Delta} R-CH_2COOH$$

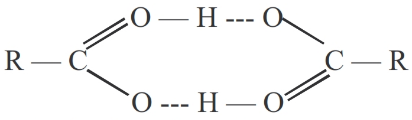
(5) Preparation of aromatic carboxylic acids

Benzoic acid is obtained by the oxidation of the alkyl benzene provided the carbon bonded directly to benzene contains at least one hydrogen atom.



PROPERTIES OF CARBOXYLIC ACIDS

(1) Carboxylic acids have a higher boiling point than the corresponding alcohol. This is due to their ability to associate via intermolecular hydrogen bonding and exists as dimer. The dimer exists even in the vapour phase.



⇒ B.P. of carboxylic acids increases regularly down the homologous series.

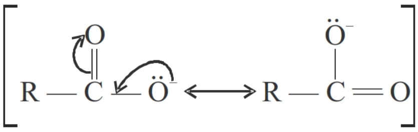
ACIDIC STRENGTH OF CARBOXYLIC ACIDS

(1) Carboxylic acids give H_3O^+ ion in water and thus acts as acid.

$$R\ COOH + H_2O \rightleftharpoons \underset{\text{carboxylate ion}}{R-COO^-} + H_3O^+$$ and

$$K_a = \frac{[RCOO^-][H_3O^+]}{[R\ COOH]}$$

$\Rightarrow$ The strength of carboxylic acid depends on its ability to lose proton.



Note: The presence of electron donating group (EDG) decreases the acidic strength and electron with drawing group (EWG) increases the acidic strength.

The decreasing acidic strength order, of few common carboxylic acids are given below,

(i) $HCOOH > CH_3COOH > C_2H_5COOH$

(ii) $FCH_2\ COOH > ClCH_2COOH > BrCH_2COOH$

(iii) $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH$

(iv) $RCOOH > H_2O > ROH > HC\equiv CH > NH_3$

Ortho Effect :

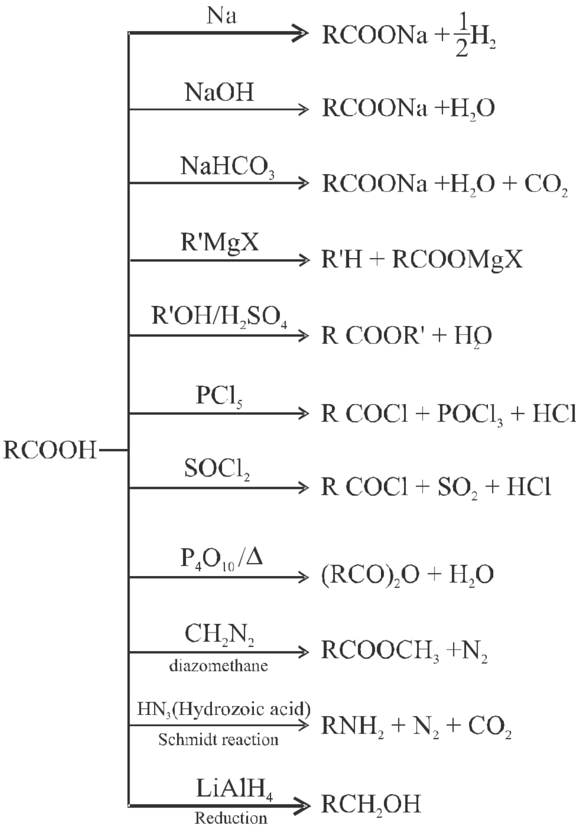
All ortho-substituted benzoic acids are stronger than benzoic acid. This is due to (a) steric factor (b) I-effect (c) chelation by H bonding. In other positions, we have to see both resonance and the inductive effect.

(i) Nitrobenzoic acid : o > p > m > benzoic acid

(ii) Hydroxybenzoic acid : o > m > p > benzoic acid

(iii) Chlorobenzoic acid : o > m > p (iv) Methyl benzoic acid : o > m > p

Chemical Reactions:



$$RCOOH \xrightarrow{Na} RCOONa + \frac{1}{2}H_2$$

$$RCOOH \xrightarrow{NaOH} RCOONa + H_2O$$

$$RCOOH \xrightarrow{NaHCO_3} RCOONa + H_2O + CO_2$$

$$RCOOH \xrightarrow{R'MgX} R'H + RCOOMgX$$

$$RCOOH \xrightarrow{R'OH/H_2SO_4} R\ COOR' + H_2O$$

$$RCOOH \xrightarrow{PCl_5} R\ COCl + POCl_3 + HCl$$

$$RCOOH \xrightarrow{SOCl_2} R\ COCl + SO_2 + HCl$$

$$RCOOH \xrightarrow{P_4O_{10}/\Delta} (RCO)_2O + H_2O$$

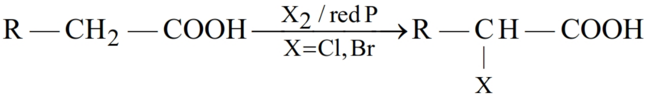
$$RCOOH \xrightarrow[\text{diazomethane}]{CH_2N_2} RCOOCH_3 + N_2$$

$$RCOOH \xrightarrow[\text{Schmidt reaction}]{HN_3\text{(Hydrozoic acid)}} RNH_2 + N_2 + CO_2$$

$$RCOOH \xrightarrow[\text{Reduction}]{LiAlH_4} RCH_2OH$$

HELL-VOLHARD-ZELINSKY REACTION :

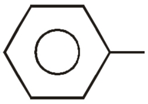
The reaction involving substitution of $\alpha -$hydrogen by halogen in pesence of red P is called HVZ reaction.



$$R - CH_2 - COOH \xrightarrow[X=Cl,Br]{X_2\,/\,\text{red P}} R - \underset{\underset{X}{|}}{C}H - COOH$$

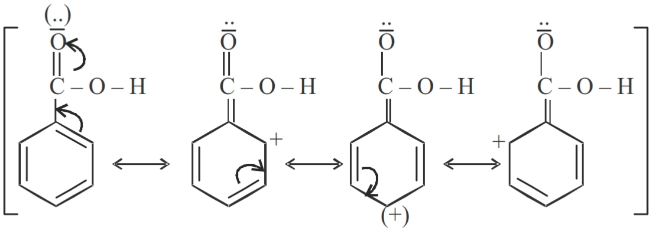
Esterification : $R - COOH + R'OH \overset{H^+}{\rightleftharpoons} \underset{\text{Ester}}{RCOOR'} + H_2O$

Esterification is an S_N2 reaction. Therefore, as the size of R group in carboxylic acid increases, the rate of esterification decreases.

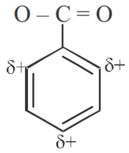
HCOOH > CH_3COOH >  COOH

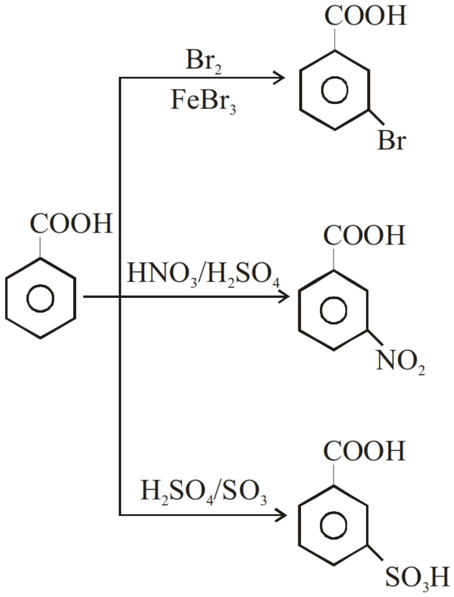
REACTIONS OF BENZOIC ACID

–COOH groups is deactivating and meta directing.



Resonance hybrid:



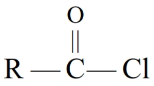


Test for carboxylic acid:

1. Acids turns blue litmus red.
2. Formic acid (It is only the carboxylic acid) gives positive Tollen’s reagent test and Fehling solution test.
3. Carboxylic acid gives brisk effervesence with $NaHCO_3$ or Na_2CO_3.

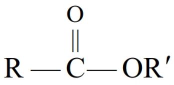
ACID DERIVATIVES

1. Acid chlorides (Acyl halides)



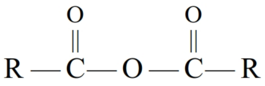
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl$$

2. Esters



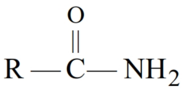
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OR'$$

3. Acid anhydrides



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-R$$

4. Amides

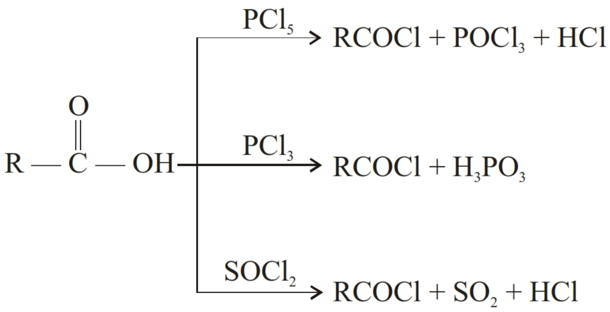


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$$

(1) ACYL HALIDES

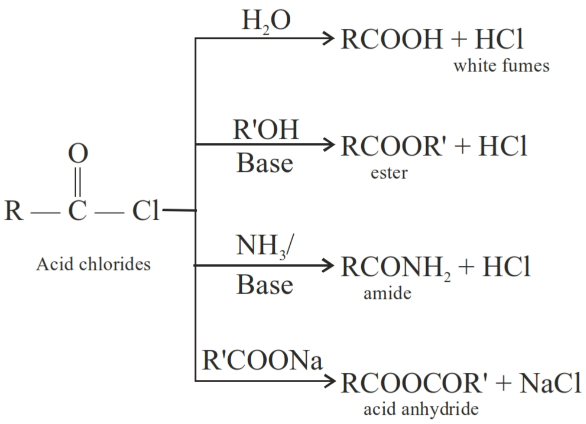
Preparation :

(i)

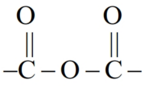


(ii) $(RCO)_2O \xrightarrow{PCl_5} 2RCOCl + POCl_3$

Acid chlorides have lower b.p. than carboxylic acid as there is no association via intermolecular hydrogen bonding. Due to weak C–Cl bond, acid chlorides are more reactive than carboxylic acids towards nucleophilic substitution reaction.



(2) ACID ANHDYRIDES

Acid anhdyrides function Group : 

$$-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-$$

Preparation

(1) Acid anhydrides are prepared by the dehydration of carboxylic acid using P_2O_5/Δ.

$$R-COOH\xrightarrow[\Delta]{P_4O_{10}}(RCO)_2O+H_2O$$

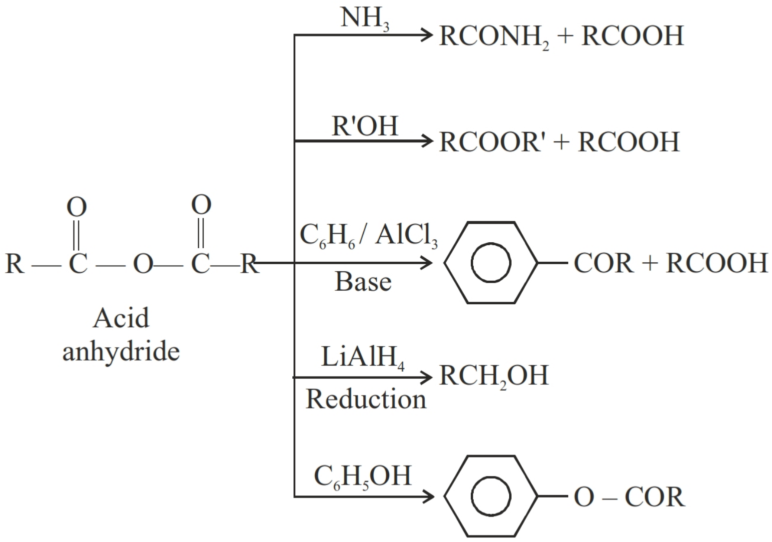
(2) Acetic anhydride is prepared commercially by heating acetic acid to 1073 K.

$$2CH_3COOH\xrightarrow{1073K}(CH_3CO)_2O+H_2O$$

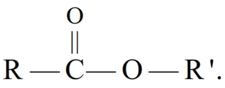
Acid anhydrides have higher b.p. than acid chlorides and are less reactive than acid chlorides.

Reactions :

Chemcial reactions of acid anhydride are shown below,



(3) ESTERS

Ester functional group is: 

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-R'.$$

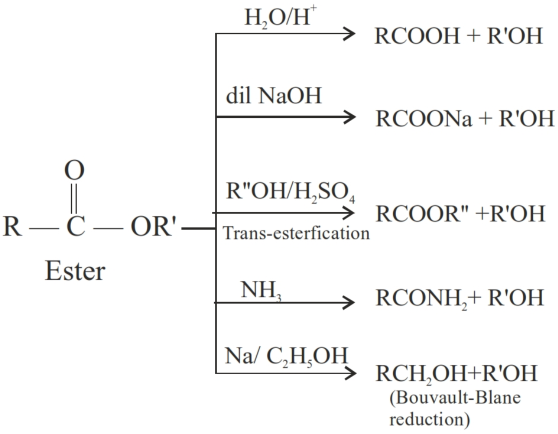
Preparation

(1) Esterification reaction: $RCOOH+R'OH\xrightleftharpoons{H_2SO_4}RCOOR'+H_2O$

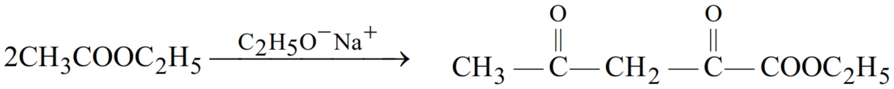
(2) From acid chlorides: $RCOCl+R'OH\xrightarrow{base}RCOOR'+HCl$

Esters of low molecular mass are soluble in water and solubility decreases with increasing molecular mass. Esters are less reactive than both acid chlorides or acid anhydrides.

Chemical Reactions of esters



Claisen condensation: The reaction is given by ethyl ester of carboxylic acids containing alpha hydrogen. The reaction takes place in presence of sodium ethoxide. The product obtained is β -keto ester which on hydrolysis generates β -keto acids. The β -keto acid on heating gives carbonyl compound.

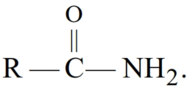


$$2CH_3COOC_2H_5 \xrightarrow{C_2H_5O^-Na^+} CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-COOC_2H_5$$

Ethyl aceto acetate
(Ethyl–4–oxo pentanoate)

(4) AMIDE

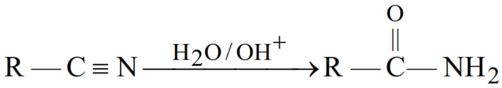
Amide functional group is



$$R-\overset{O}{\overset{\|}{C}}-NH_2.$$

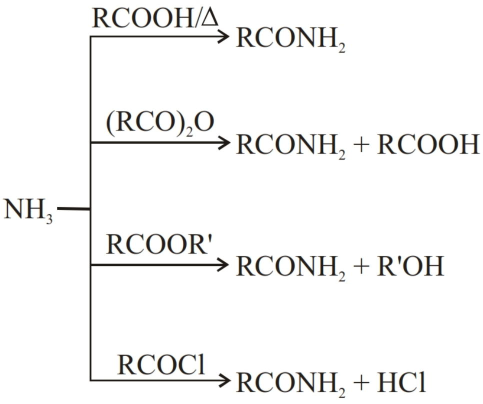
Preparations

(1) Partial hydrolysis of nitrites:



$$R-C\equiv N \xrightarrow{H_2O/OH^+} R-\overset{O}{\overset{\|}{C}}-NH_2$$

(2) Using ammonia:



Properties

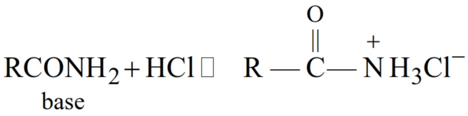
(i) Amongst all acid derivatives, amides have the highest boiling point. This is due to extensive network of intermolecular hydrogen bonding. The increasing b.p. order is

$ROCl < RCOOR < (RCO_2)_2O < RCONH_2$

(ii) Amides are the least reactive derivatives of carboxylic acid towards nucleophilic substitution reaction due to high bond enthalpy of C—N bond.

(iii) Amides are amphoteric in nature:

(a) As base:



$$\underset{\text{base}}{RCONH_2} + HCl \rightleftharpoons R-\overset{\overset{O}{\|}}{C}-\overset{+}{N}H_3Cl^-$$

(b) As acid:

$$\underset{\text{acid}}{RCONH_2} + NaOH \longrightarrow R\ COO\bar{N}a^+ + NH_3$$

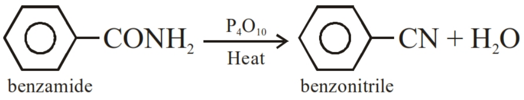
1. Hydrolysis:

$$R\ CONH_2 + H_2O \xrightarrow{H_2SO_4} RCOOH + NH_4HSO_4$$

$$R\ CONH_2 + H_2O \xrightarrow{NaOH} R\ COONa + NH_3$$

2. Dehydration:

$$R\ CONH_2 \xrightarrow[\text{Heat}]{P_4O_{10}} \underset{\text{nitriles}}{R-CN} + H_2O$$



3. Reduction:

$$RCONH_2 \xrightarrow[\text{(ii)}H_3O^+]{\text{(i)}LiAlH_4} \underset{1^\circ\ \text{amine}}{RCH_2NH_2}$$

4. Hydrolysis using HNO_2:

$RCONH_2 + HNO_2 \rightarrow RCOOH + N_2 + H_2O$

5. Hofmann bromanide reaction

Its converts amide (1°) containing α-carbon to 1° amines with one carbon less using Br_2 and alkali

$R\ CONH_2 + Br_2 + 4\ NaOH \rightarrow RNH_2 + 2Na\ Br + Na_2\ CO_3 + 2H_2O$

$\Rightarrow$ In this reaction nitrene as reaction intermediate is used.