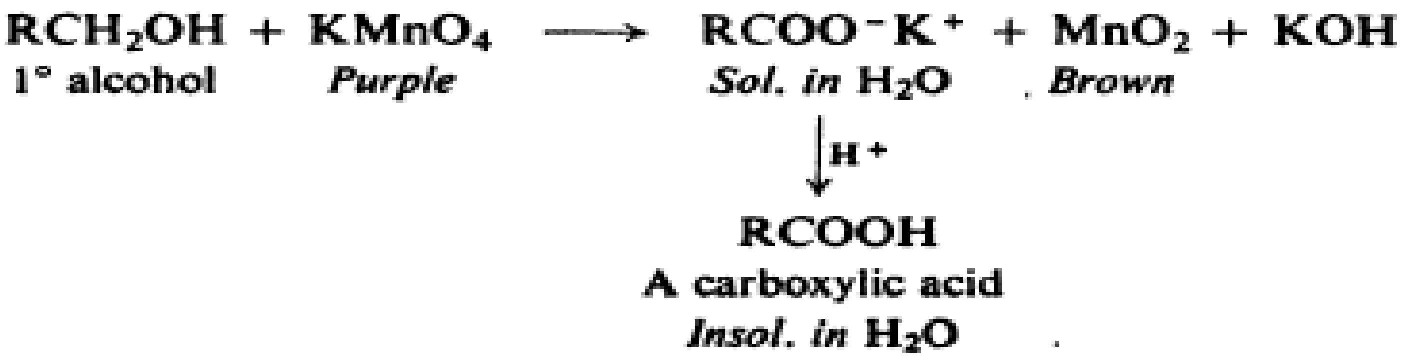
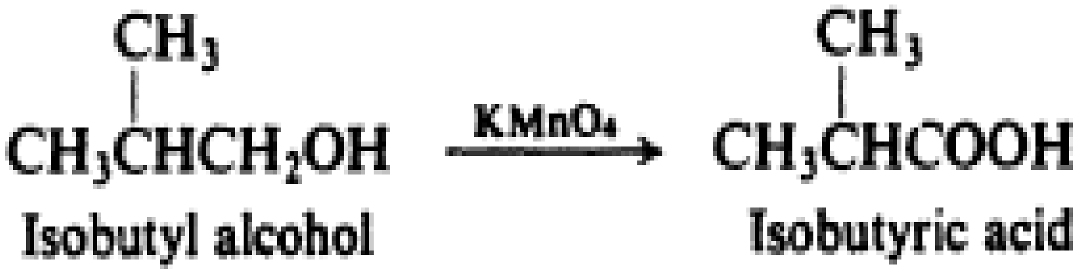
Preparation of carboxylic acid

1. Oxidation of primary alcohols



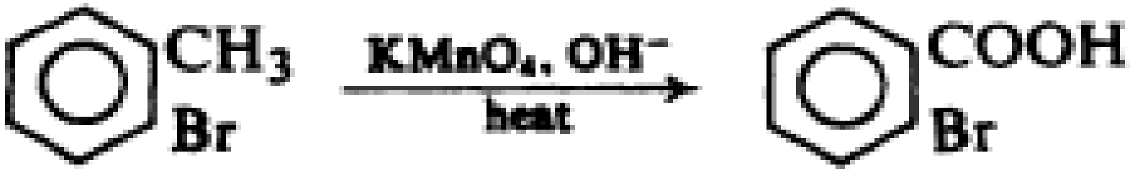
$$\begin{array}{ccccccccc} RCH_2OH & + & KMnO_4 & \longrightarrow & RCOO^-K^+ & + & MnO_2 & + & KOH \\ \text{1° alcohol} & & \textit{Purple} & & \textit{Sol. in } H_2O & & \textit{Brown} & & \\ & & & & \Big\downarrow H^+ & & & & \\ & & & & RCOOH & & & & \\ & & & & \text{A carboxylic acid} & & & & \\ & & & & \textit{Insol. in } H_2O & & & & \end{array}$$



$$\underset{\text{Isobutyl alcohol}}{CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2OH} \xrightarrow{KMnO_4} \underset{\text{Isobutyric acid}}{CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}HCOOH}$$

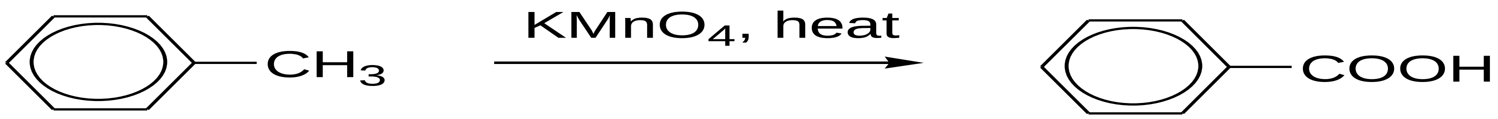
2. Oxidation of alkylbenzenes (arenes)

$$\mathrm{Ar{-}R} \xrightarrow[\mathrm{K_2C_2O_7}]{\mathrm{KMnO_4\ or\ K_2Cr_2O_7}} \mathrm{Ar{-}COOH}$$

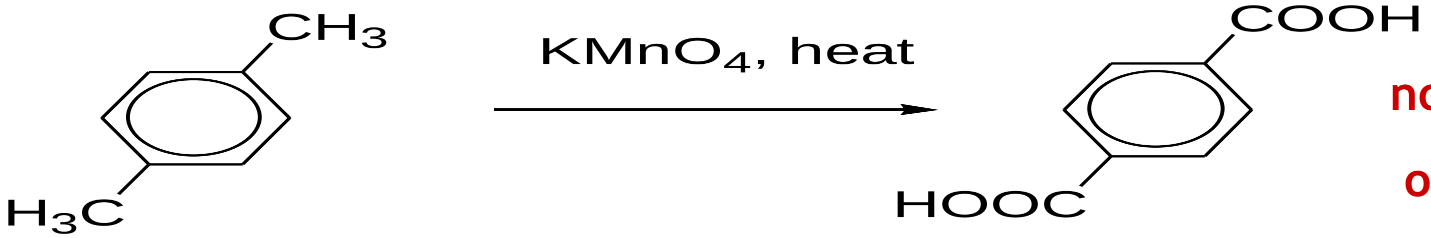


o-Bromotoluene

o-Bromobenzoic acid



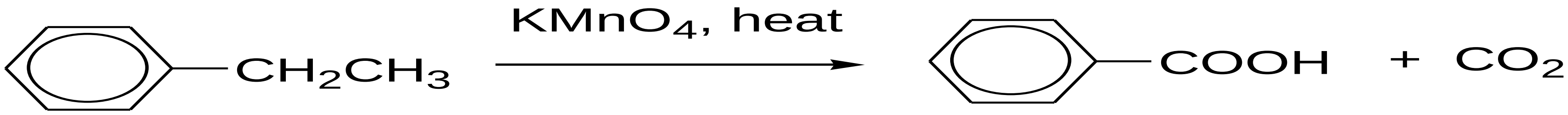
toluene benzoic acid



p-xylene terephthalic acid

note:! aromatic acids

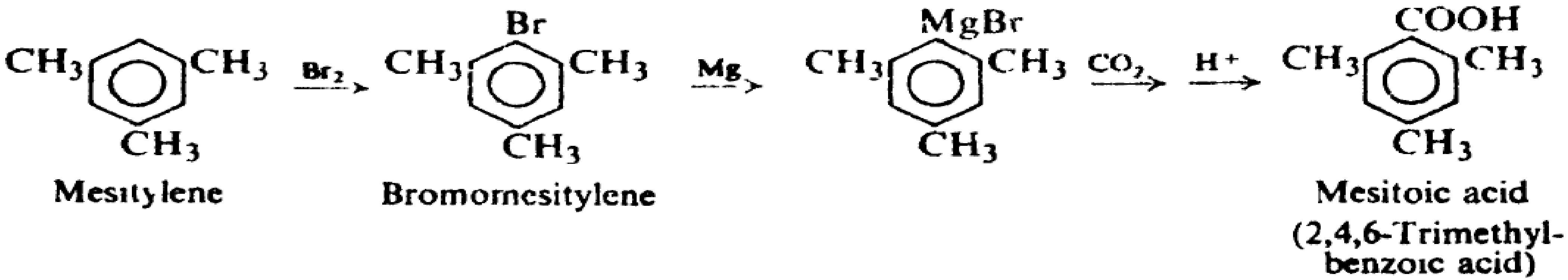
only



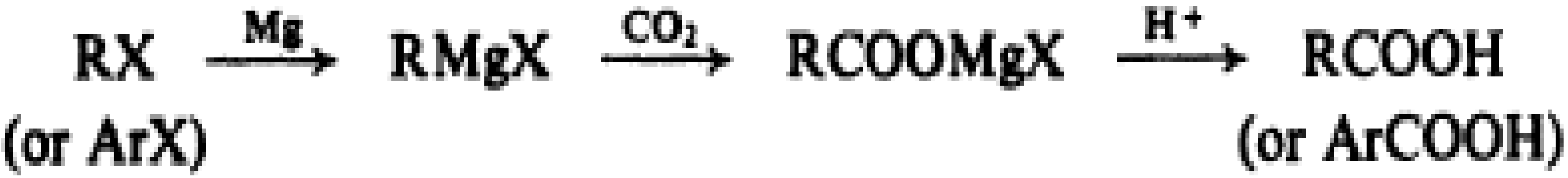
ethylbenzene benzoic acid

3-Carbonation of Grignard reagents

- The Grignard reagent can be prepared from primary, secondary, tertiary, or aromatic halides; the method is limited only by the presence of other reactive groups in the molecule.

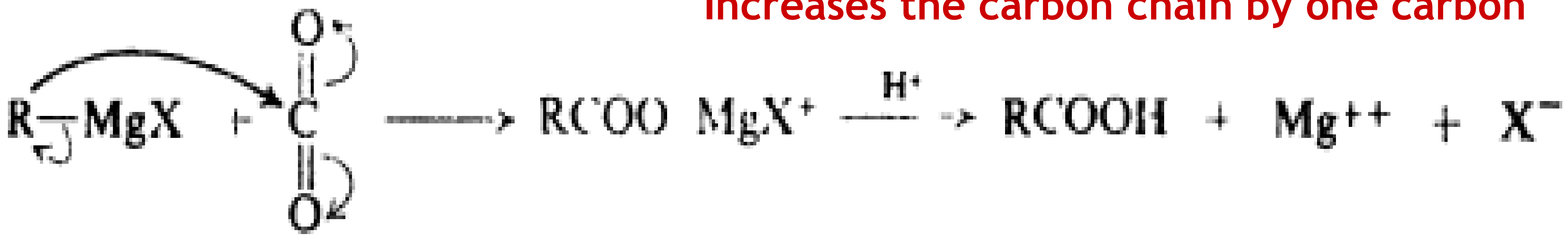


3-Carbonation of Grignard reagents

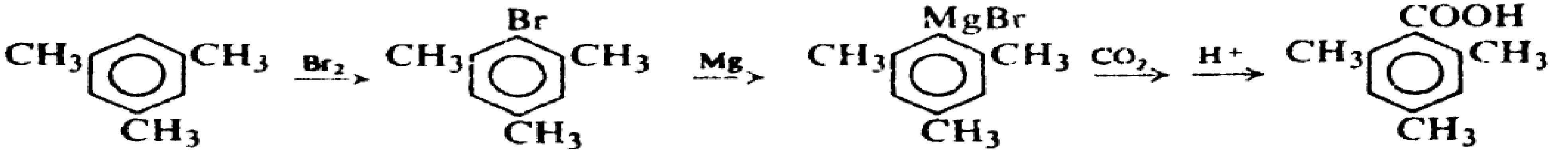


$$\underset{\text{(or ArX)}}{RX} \xrightarrow{Mg} RMgX \xrightarrow{CO_2} RCOOMgX \xrightarrow{H^+} \underset{\text{(or ArCOOH)}}{RCOOH}$$

Increases the carbon chain by one carbon



$$\underset{n\text{-propyl bromide}}{CH_3CH_2CH_2\text{-}Br} \xrightarrow{Mg} CH_3CH_2CH_2MgBr \xrightarrow[H+]{CO_2} \underset{\text{butyric acid}}{CH_3CH_2CH_2COOH}$$

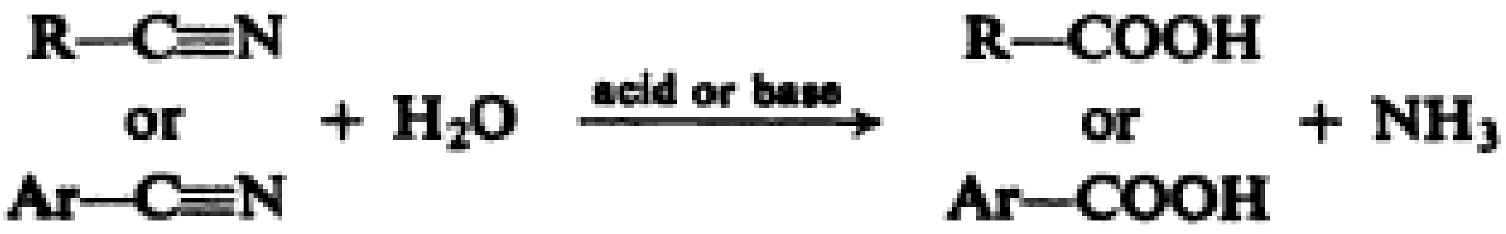


Mesitylene

Bromomesitylene

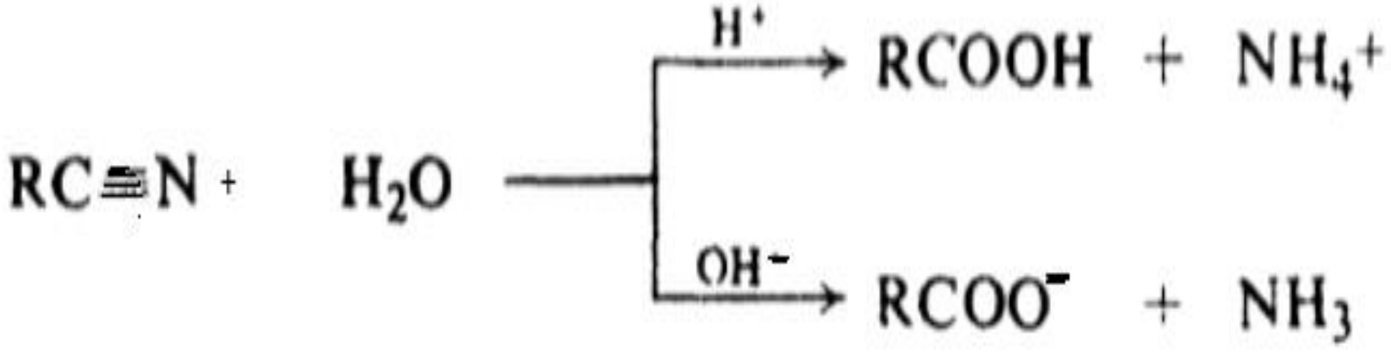
Mesitoic acid
(2,4,6-Trimethyl-
benzoic acid)

4- Hydrolysis of nitriles



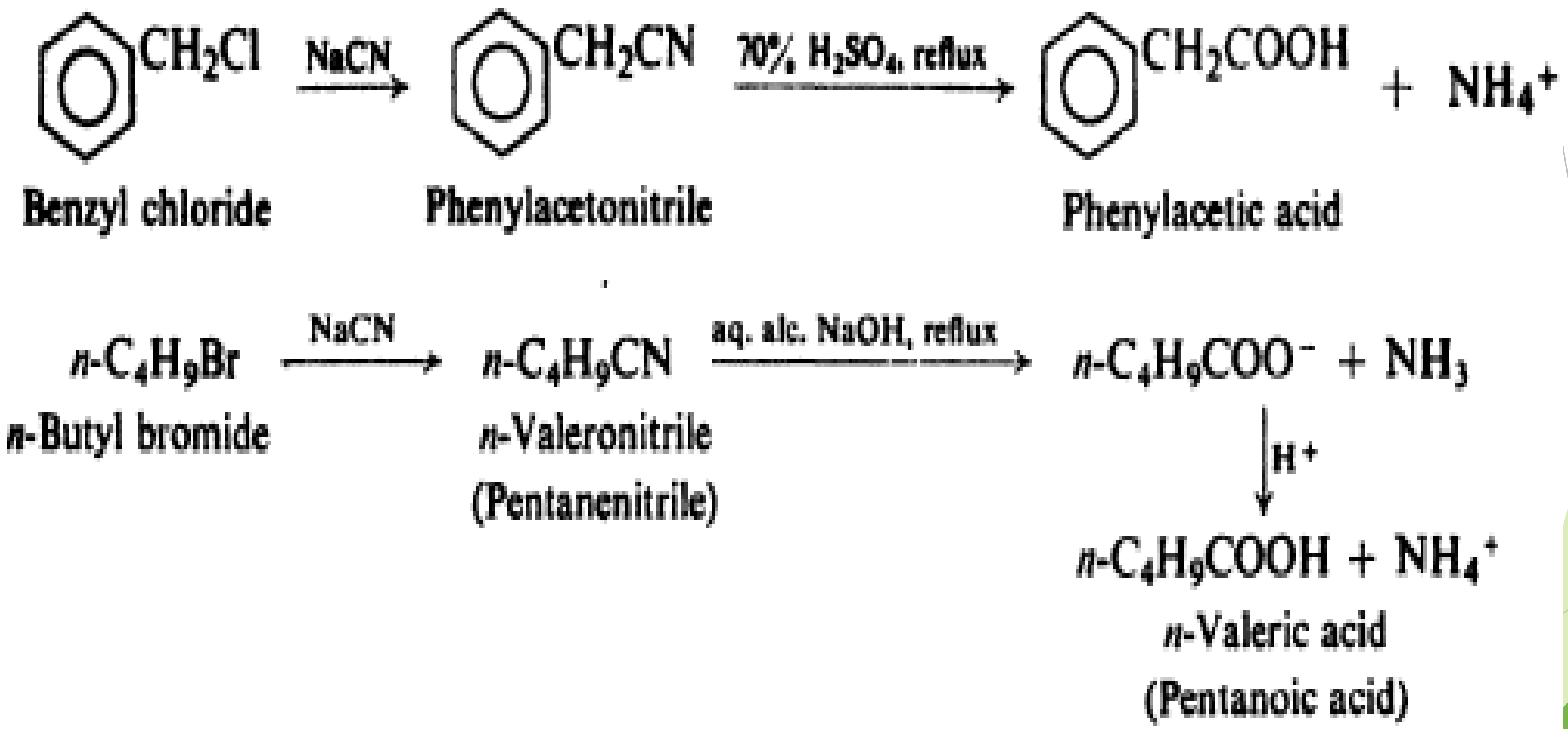
$$\begin{matrix} R{-}C{\equiv}N \\ \text{or} \\ Ar{-}C{\equiv}N \end{matrix} + H_2O \xrightarrow{\text{acid or base}} \begin{matrix} R{-}COOH \\ \text{or} \\ Ar{-}COOH \end{matrix} + NH_3$$

$$RX + CN^- \longrightarrow RC{\equiv}N + X^-$$



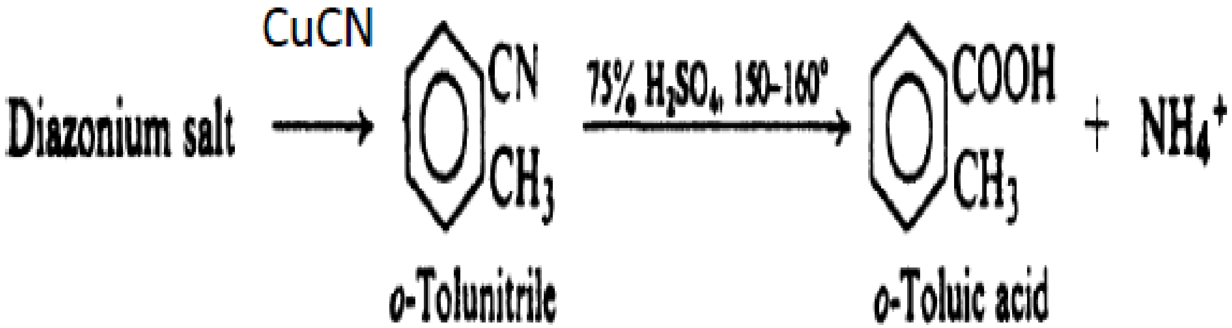
$$RC{\equiv}N + H_2O \begin{cases} \xrightarrow{H^+} RCOOH + NH_4^+ \\ \xrightarrow{OH^-} RCOO^- + NH_3 \end{cases}$$

4- Hydrolysis of nitriles



Aromatic nitriles are made, not from the unrcactive aryl halides, but from diazoniurn salts. The replacement of the diazonium group by –CN is carried out by allowing the diazonium salt to react with cuprous cyanide.

$$Ar\text{-}N_2^+X^- \xrightarrow{CuCN} Ar\text{-}CN + N_2$$



Reactions of carboxylic acids

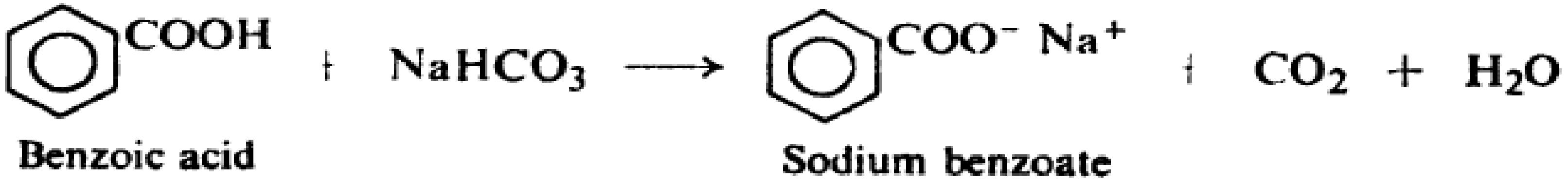
- The characteristic chemical behaviour of carboxylic acids is, of course, determined by their functional group, carboxyl COOH(This group is made up of a carbonyl group (C= O) and a hydroxyl group (OH)).

1. Acidity. Salt formation.

a-with active metals

$$\underset{\text{Acetic acid}}{2CH_3COOH} + Zn \longrightarrow \underset{\text{Zinc acetate}}{(CH_3COO^-)_2Zn^{++}} + H_2$$

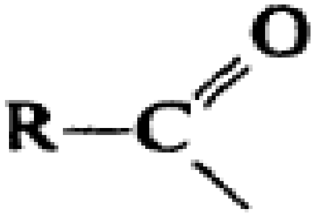
b)with bases



Acidity :the most characteristic property of the carboxylic acids is the one that gives them their name.

$$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$$

The OH of an acid can be replaced by a number of groups Cl, OR', NH_2 to yield compounds known as acid chlorides, esters, and amides. These compounds are called functional derivatives of acids; they all contain the acyl group:



Ionization of carboxylic acids. Acidity constant

$$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$$

As for any equilibrium, the concentrations of the components are related by the expression:

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

K_a = acidity constant.

Ka for carboxylic acids ≈ 10^{-5}

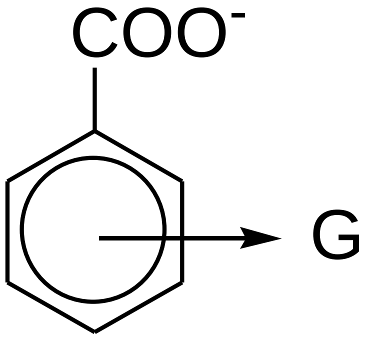
Why are carboxylic acids more acidic than alcohols?

$$ROH + H_2O \leftrightarrows H_3O^+ + RO^-$$

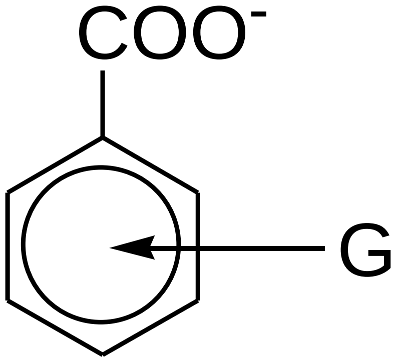
$$RCOOH + H_2O \leftrightarrows H_3O^+ + RCOO^-$$

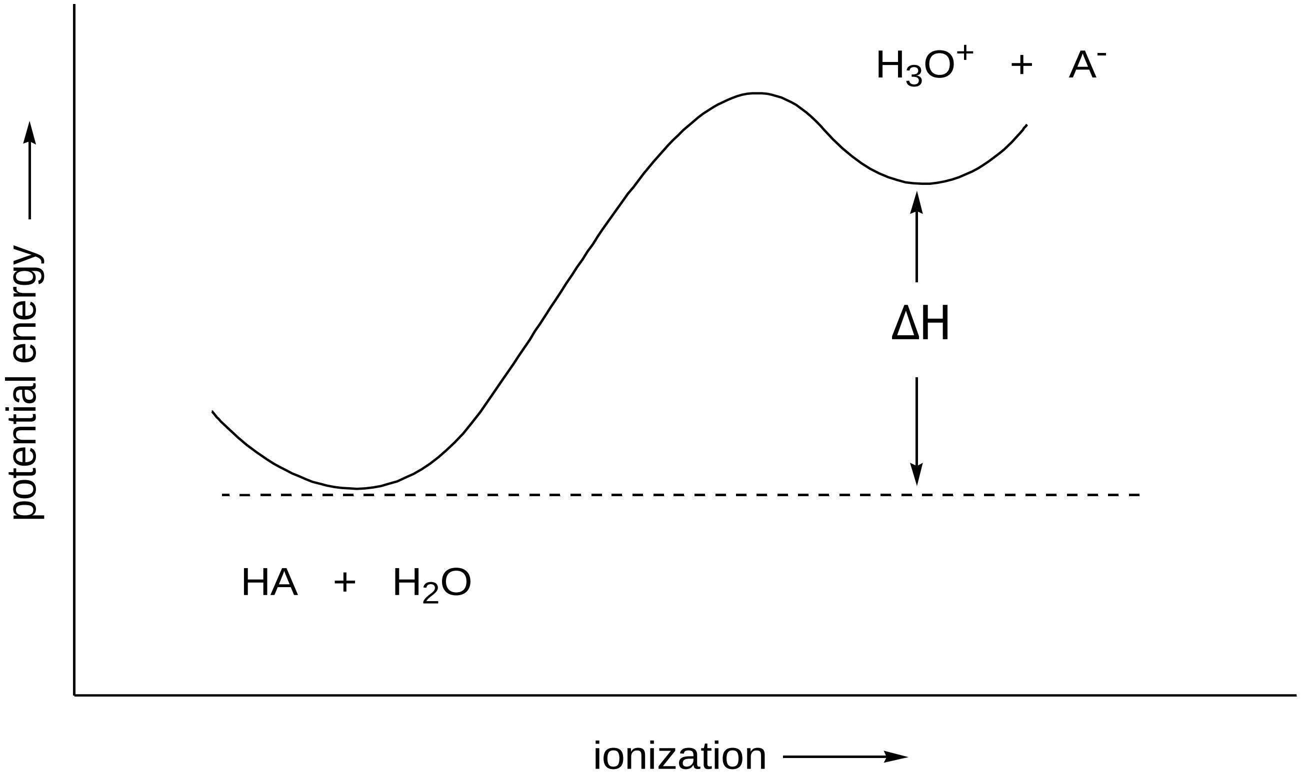
Effect of substituent groups on acid strength of benzoic acids?

- **Electron withdrawing groups** will stabilize the anion, decrease the ΔH, shift the ionization to the right, increasing the Ka, **increasing acid strength**.

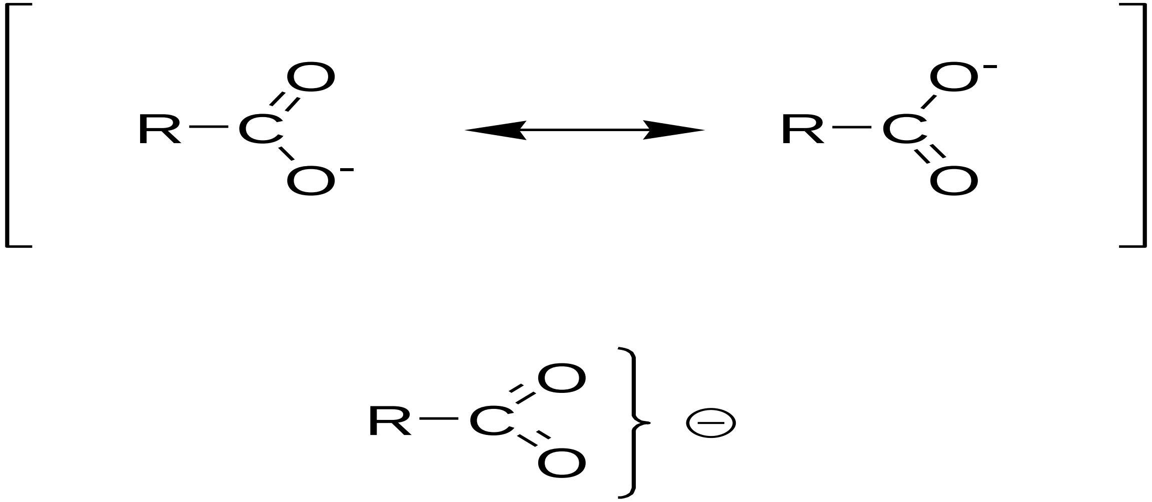


- **Electron donating groups** will destabilize the anion, increase the ΔH, shift the ionization in water to the left, decreasing the Ka, **decreasing acid strength**





The smaller the ΔH, the more the equilibrium lies to the right, giving a larger Ka (a stronger acid).



Resonance stabilization of the carboxylate ion decreases the ΔH, shifts the ionization in water to the right, increases the Ka, and results in carboxylic acids being stronger acids.

- Effect of substituent groups on acid strength?

CH_3COOH	1.75×10^{-5}
$ClCH_2COOH$	136×10^{-5}
$Cl_2CHCOOH$	$5{,}530 \times 10^{-5}$
Cl_3CCOOH	$23{,}200 \times 10^{-5}$

- -Cl is electron withdrawing and delocalizes the negative charge on the carboxylate ion, decreasing the ΔH, shifting the ionization to the right and increasing acid strength.

- $-NH_2$, $-NHR$, $-NR_2$
- $-OH$
- $-OR$

- $-NHCOCH_3$
- $-C_6H_5$
- $-R$
- $-H$

electron donating

- $-X = Cl, F, Br$
- $-CHO$, $-COR$
- $-SO_3H$
- $-COOH$, $-COOR$
- $-CN$
- $-NR_3^+$
- $-NO_2$

electron withdrawing

- Relative acid strength?

	Ka
p-aminobenzoic acid	1.4 x 10^{-5}
p-hydroxybenzoic acid	2.6 x 10^{-5}
p-methoxybenzoic acid	3.3 x 10^{-5}
p-toluic acid	4.2 x 10^{-5}
benzoic acid	6.3 x 10^{-5}
p-chlorobenzoic acid	10.3 x 10^{-5}
p-nitrobenzoic acid	36 x 10^{-5}

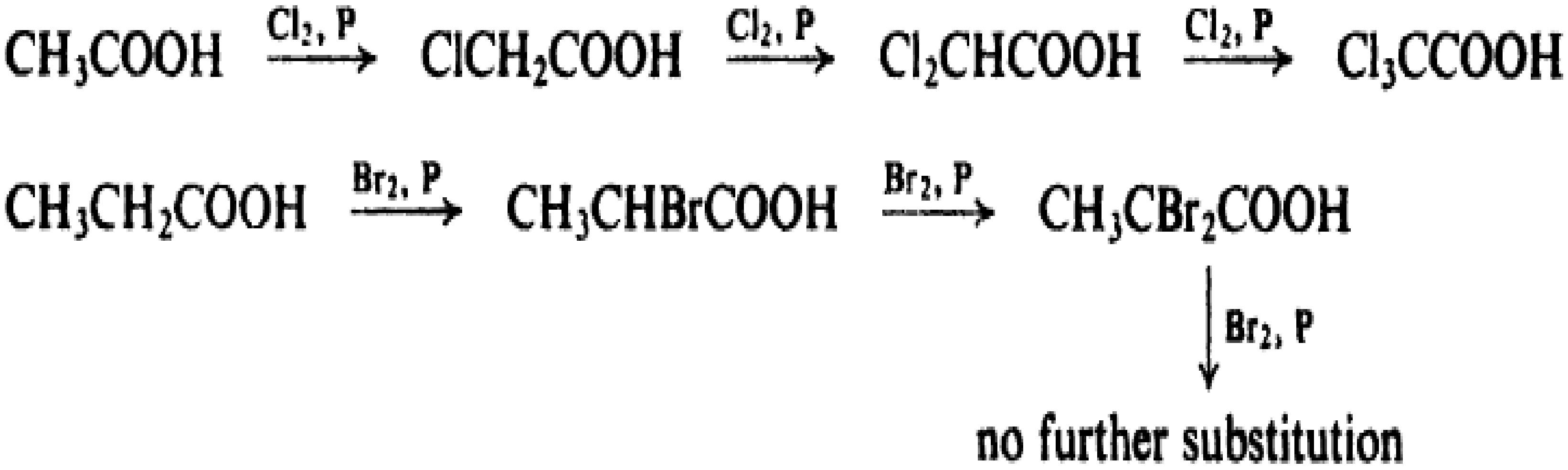
Reduction of acids to alcohol

- Lithium aluminum hydride, $LiAlH_4$, is one of the few reagents that can reduce an acid to an alcohol; the initial product is an alkoxide from which the alcohol is liberated by hydrolysis:

$$4RCOOH + 3LiAlH_4 \longrightarrow 4H_2 + 2LiAlO_2 + (RCH_2O)_4AlLi \xrightarrow{H_2O} \underset{1^\circ\ \text{alcohol}}{4RCH_2OH}$$

Halogenation of aliphatic acids. Substituted acids

- This is the Hell-Volhard-Zelinsky reaction. Aliphatic carboxylic acids react smoothly with chlorine or bromine to yield a compound in which a-hydrogen has been replaced by halogen(Cl_2or Br_2).

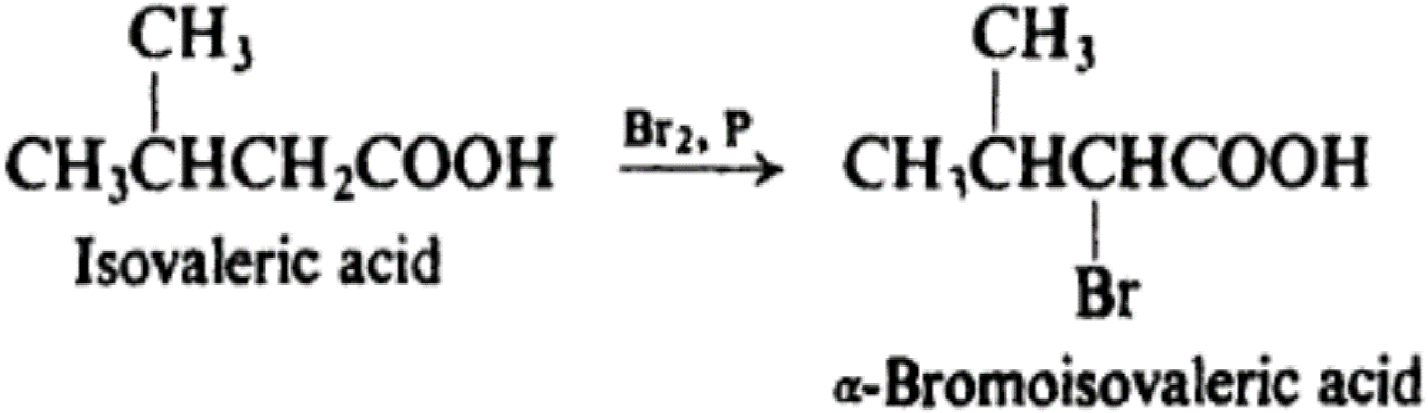


$$CH_3COOH \xrightarrow{Cl_2,\,P} ClCH_2COOH \xrightarrow{Cl_2,\,P} Cl_2CHCOOH \xrightarrow{Cl_2,\,P} Cl_3CCOOH$$

$$CH_3CH_2COOH \xrightarrow{Br_2,\,P} CH_3CHBrCOOH \xrightarrow{Br_2,\,P} CH_3CBr_2COOH$$

$$CH_3CBr_2COOH \xrightarrow{Br_2,\,P} \text{no further substitution}$$

Halogenation of aliphatic acids. Substituted acids



$$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2COOH \xrightarrow{Br_2,\,P} CH_3\overset{CH_3}{\overset{|}{C}}H\underset{Br}{\underset{|}{C}}HCOOH$$

Isovaleric acid

α-Bromoisovaleric acid