SRI AKILANDESWARI WOMEN’S COLLEGE, WANDIWASH

CARBOXYLIC ACIDS

Class : II UG CHEMISTRY

Mrs.S. PREMA

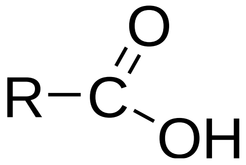
Assistant Professor

Department of Chemistry

SWAMY ABEDHANADHA EDUCATIONAL TRUST, WANDIWASH

Carboxylic acids:

R-COOH, R-CO_2H,

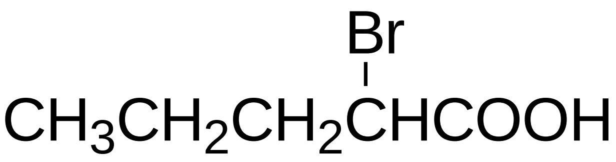


Common names:

HCO_2H	formic acid
CH_3CO_2H	acetic acid
$CH_3CH_2CO_2H$	propionic acid
$CH_3CH_2CH_2CO_2H$	butyric acid
$CH_3CH_2CH_2CH_2CO_2H$	valeric acid

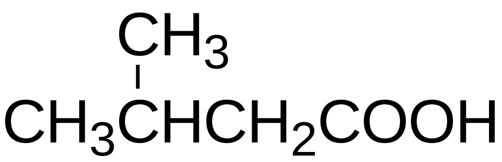
$$\underset{\delta}{\overset{5}{\mathrm{C}}}-\underset{\gamma}{\overset{4}{\mathrm{C}}}-\underset{\beta}{\overset{3}{\mathrm{C}}}-\underset{\alpha}{\overset{2}{\mathrm{C}}}-\overset{1}{\mathrm{C}}=\mathrm{O}$$

used in common names



$$\mathrm{CH_3CH_2CH_2\overset{\overset{Br}{|}}{C}HCOOH}$$

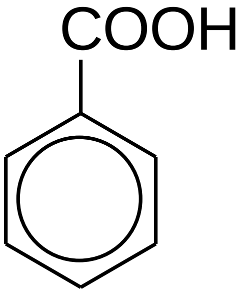
$\alpha-$ bromovaleric acid



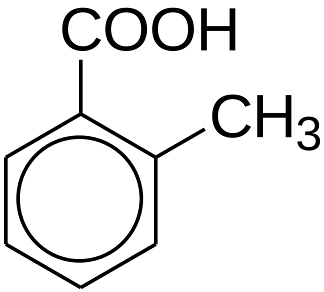
$$\mathrm{CH_3\overset{\overset{CH_3}{|}}{C}HCH_2COOH}$$

β-methylbutyric acid

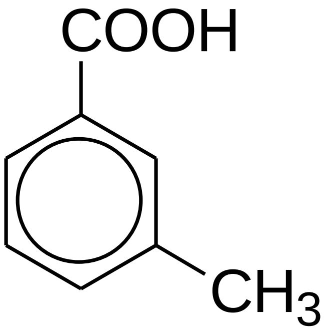
isovaleric acid



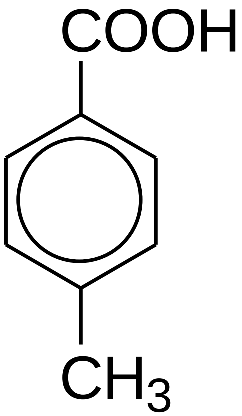
benzoic acid



o-toluic acid



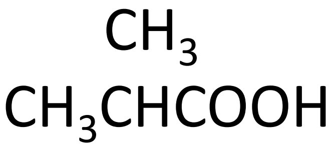
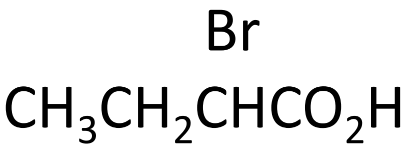
m-toluic acid



p-toluic acid

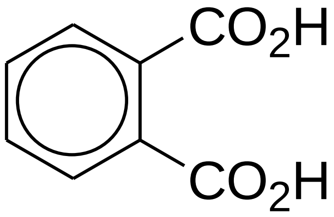
IUPAC nomenclature for carboxylic acids:

parent chain = longest, continuous carbon chain that contains the carboxyl group → alkane, drop –e, add –oic acid

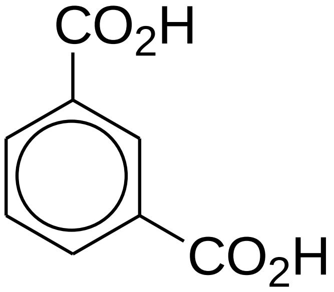
HCOOH	methanoic acid
CH_3CO_2H	ethanoic acid
$CH_3CH_2CO_2H$	propanoic acid
 $CH_3\overset{CH_3}{C}HCOOH$	2-methylpropanoic acid
 $CH_3CH_2\overset{Br}{C}HCO_2H$	2-bromobutanoic acid

Dicarboxylic acids

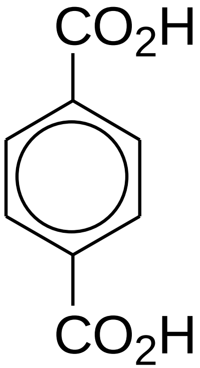
$HOOC\text{-}COOH$	oxalic acid
$HO_2C\text{-}CH_2\text{-}CO_2H$	malonic acid
$HO_2C\text{-}CH_2CH_2\text{-}CO_2H$	succinic acid
$HO_2C\text{-}CH_2CH_2CH_2\text{-}CO_2H$	glutaric acid
$HOOC\text{-}(CH_2)_4\text{-}COOH$	adipic acid
$HOOC\text{-}(CH_2)_5\text{-}COOH$	pimelic acid



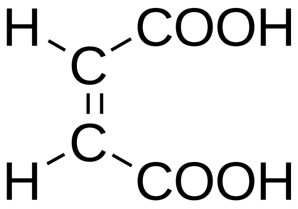
phthalic acid



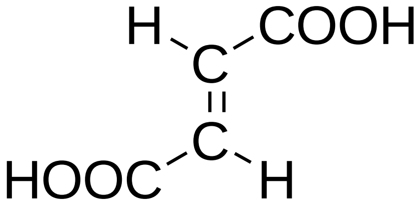
isophthalic acid



terephthalic acid



maleic acid



fumaric acid

salts of carboxylic acids:

name of cation + name of acid: drop –ic acid, add –ate

CH_3CO_2Na	sodium acetate or sodium ethanoate
$CH_3CH_2CH_2CO_2NH_4$	ammonium butyrate ammonium butanoate
$(CH_3CH_2COO)_2Mg$	magnesium propionate magnesium propanoate

Physical Properties:

polar + hydrogen bond → relatively high mp/bp

water insoluble

exceptions: four carbons or less

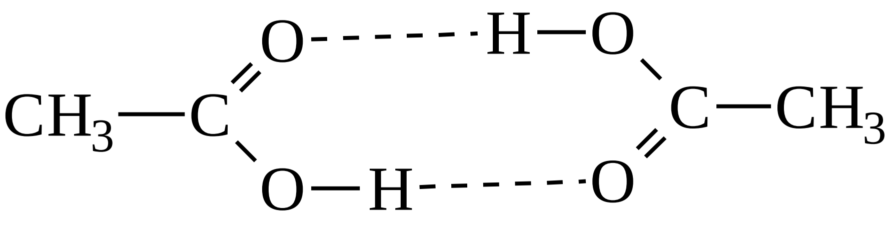
acidic turn blue litmus → red

soluble in 5% NaOH

$$RCO_2H \;+\; NaOH \;\rightarrow\; RCO_2^{-}Na^{+} \;+\; H_2O$$

stronger acid	stronger base	weaker base	weaker acid

- Two molecules of a carboxylic acid can hydrogen bond together.



RCO_2H	RCO_2^-
covalent	ionic
water insoluble	water soluble

Carboxylic acids are insoluble in water, but soluble in 5% NaOH.

1. Identification.
2. Separation of carboxylic acids from basic/neutral organic compounds.

   The carboxylic acid can be extracted with aq. NaOH and then regenerated by the addition of strong acid.

General Methods of preparation of Carboxylic Acids:

1. oxidation of 1^o alcohols:

$$CH_3CH_2CH_2CH_2\text{-}OH \quad + \quad CrO_3 \quad \rightarrow \quad CH_3CH_2CH_2CO_2H$$

n-butyl alcohol butyric acid

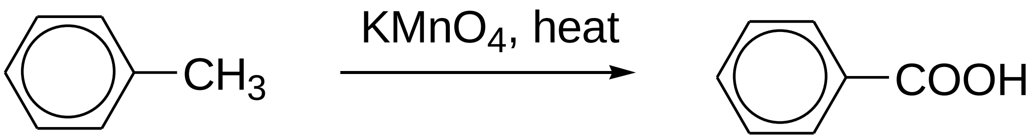
1-butanol butanoic acid

$$CH_3\overset{CH_3}{CH}CH_2\text{-}OH \quad + \quad KMnO_4 \quad \rightarrow \quad CH_3\overset{CH_3}{CH}COOH$$

isobutyl alcohol isobutyric acid

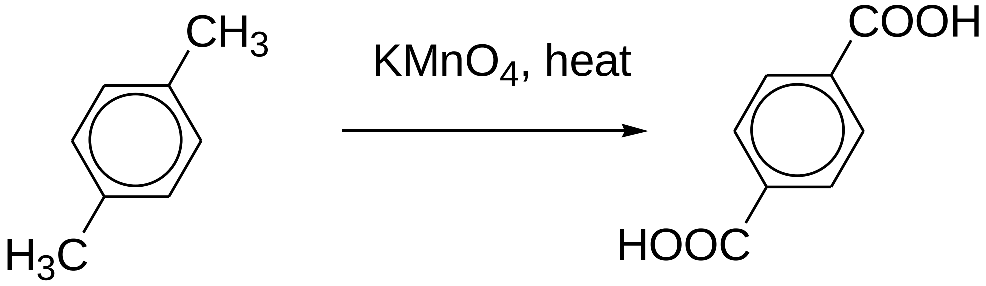
2-methyl-1-propanol` 2-methylpropanoic acid

2. Oxidation of alkylbenzenes:



toluene

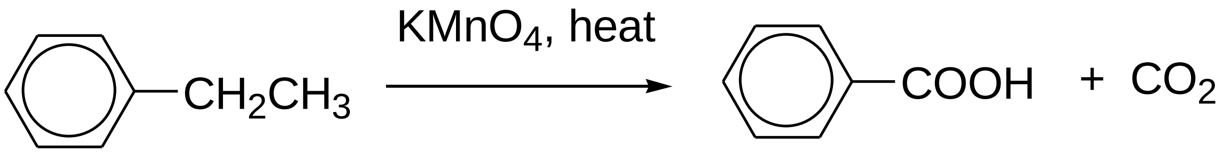
benzoic acid



p-xylene

terephthalic acid

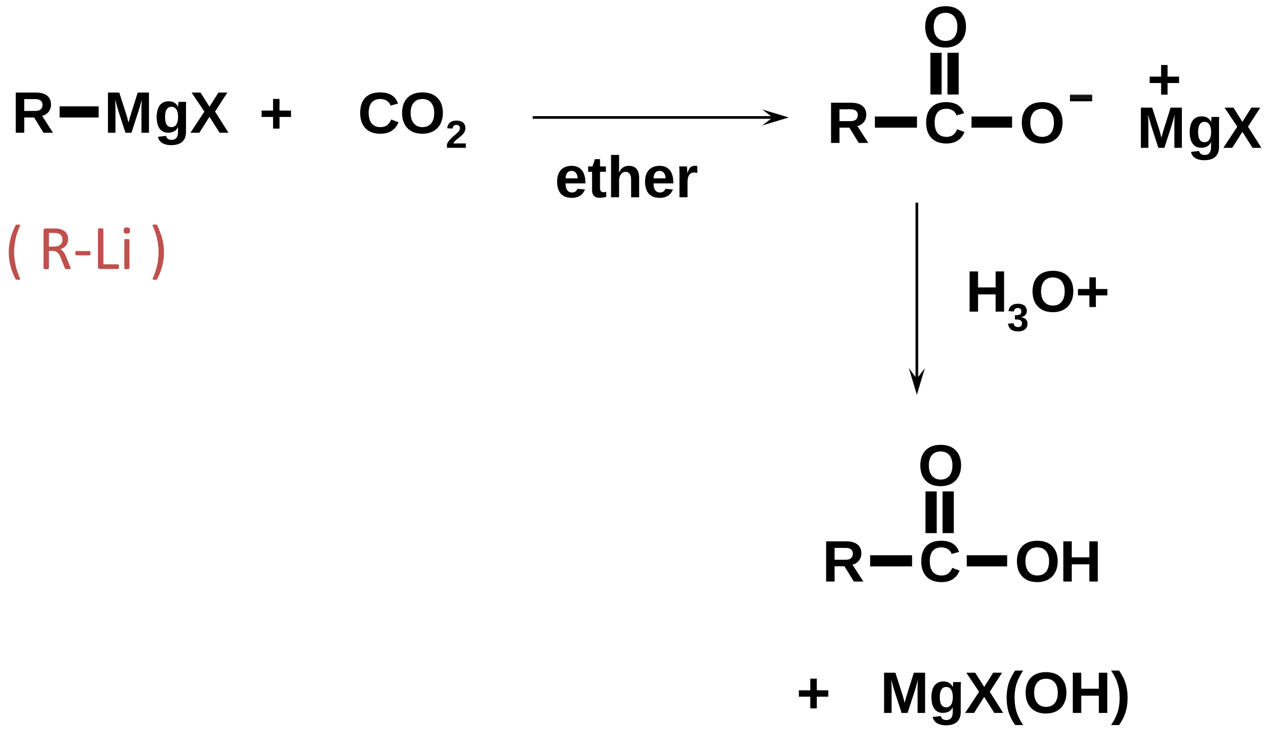
note: aromatic acids only!



ethylbenzene

benzoic acid

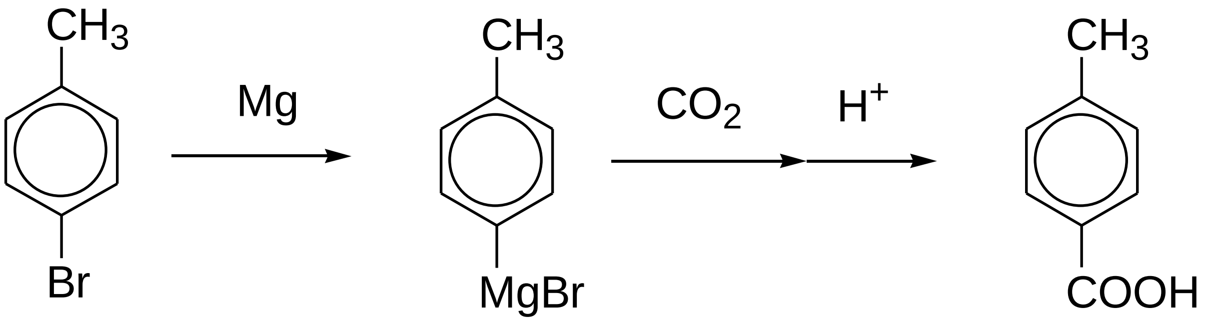
3. Carbonation of Grignard Reagents:



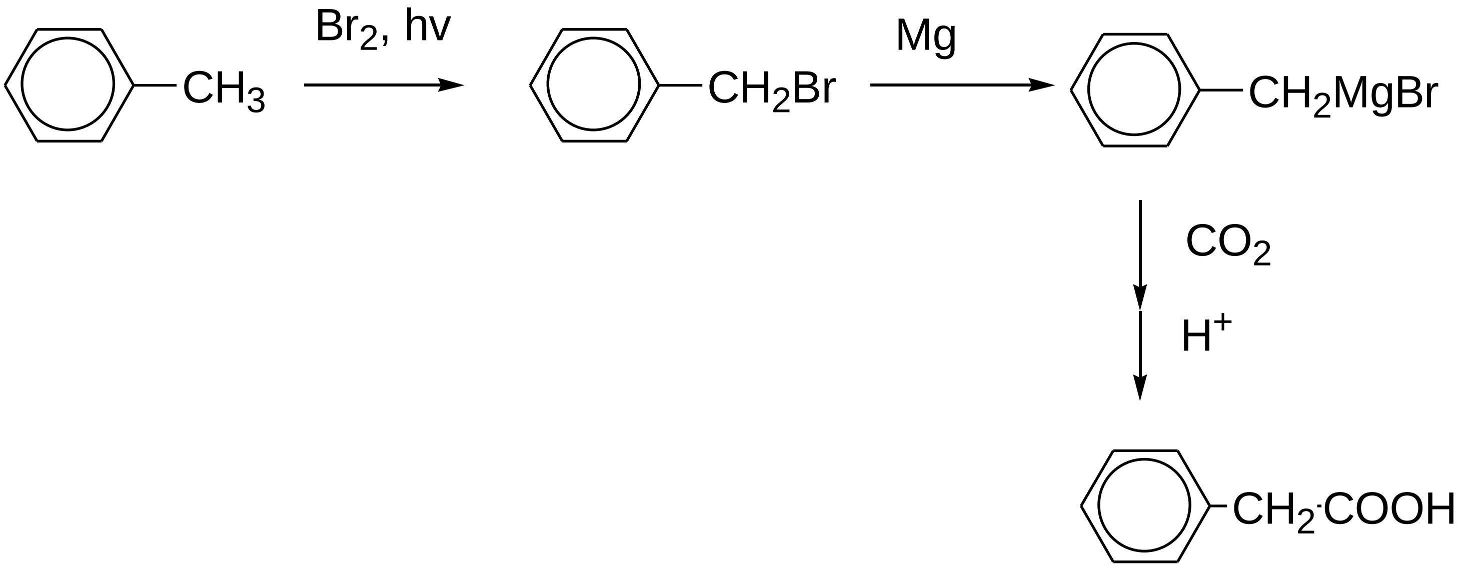
$$R{-}MgX + CO_2 \xrightarrow[\text{ether}]{} R{-}\overset{\overset{O}{\|}}{C}{-}O^{-}\ \overset{+}{M}gX$$

(R-Li)

$$\xrightarrow{H_3O^+} R{-}\overset{\overset{O}{\|}}{C}{-}OH + MgX(OH)$$

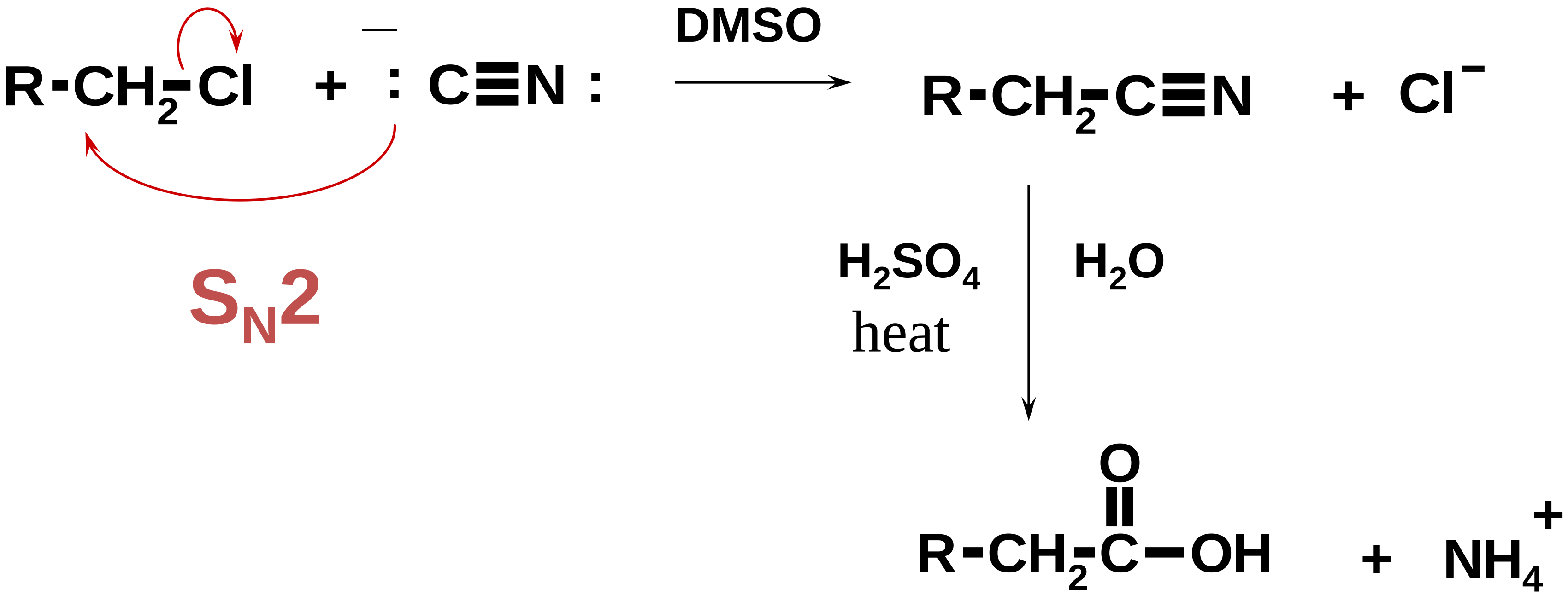


p-toluic acid



phenylacetic acid

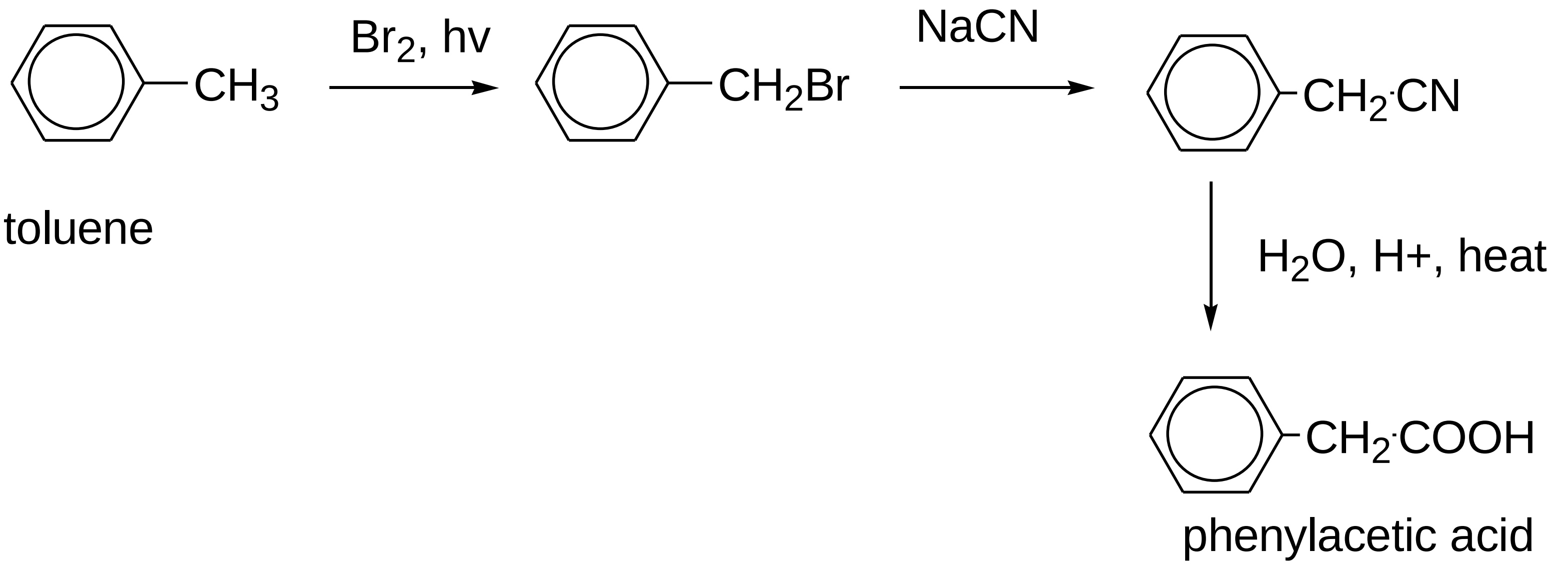
Hydrolysis of Nitriles



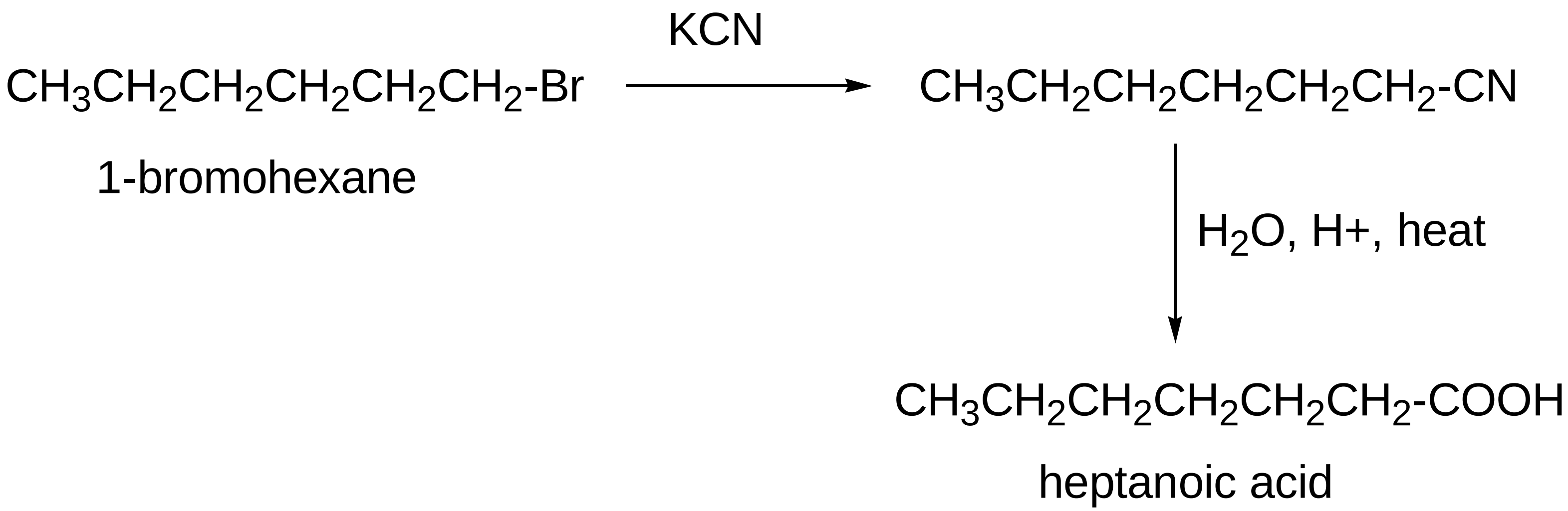
$$R\text{-}CH_2\text{-}Cl \;+\; \overset{-}{:}C\equiv N: \xrightarrow{DMSO} R\text{-}CH_2\text{-}C\equiv N \;+\; Cl^-$$

S_N2

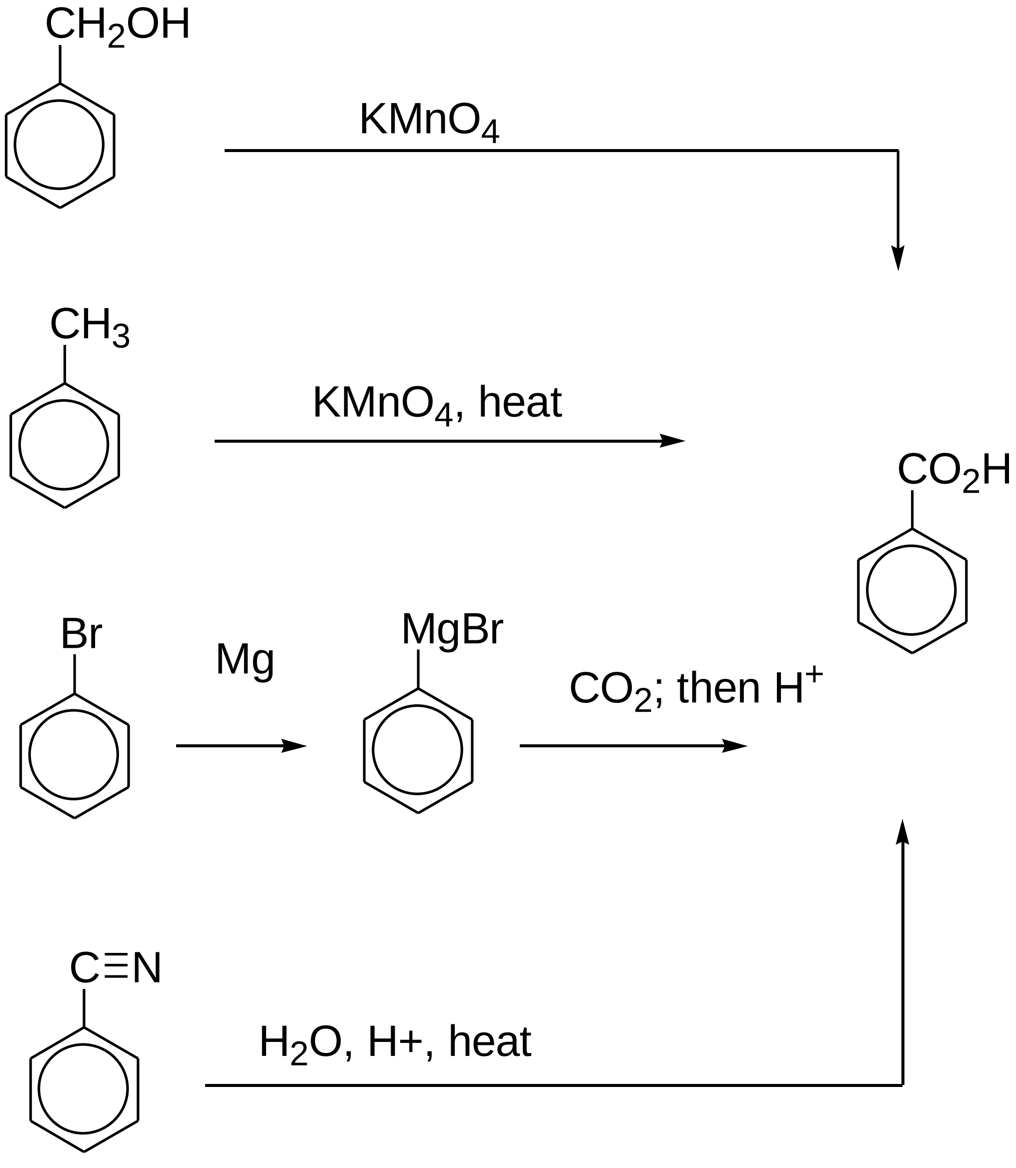
$$R\text{-}CH_2\text{-}C\equiv N \xrightarrow[\text{heat}]{H_2SO_4 \quad H_2O} R\text{-}CH_2\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}OH \;+\; NH_4^+$$



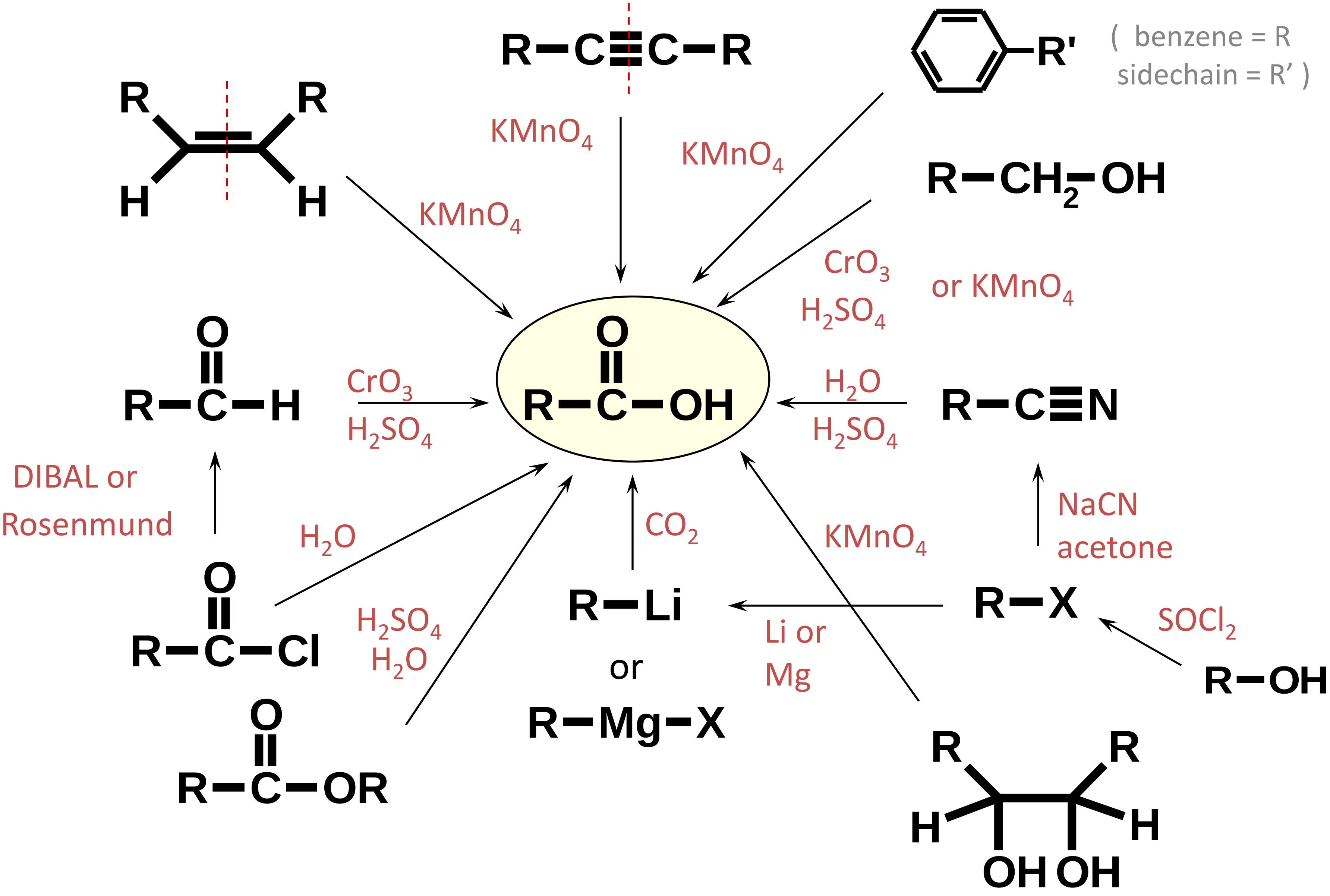
CH_3
toluene
Br_2, hv
CH_2Br
NaCN
$CH_2{\cdot}CN$
H_2O, H+, heat
$CH_2{\cdot}COOH$
phenylacetic acid



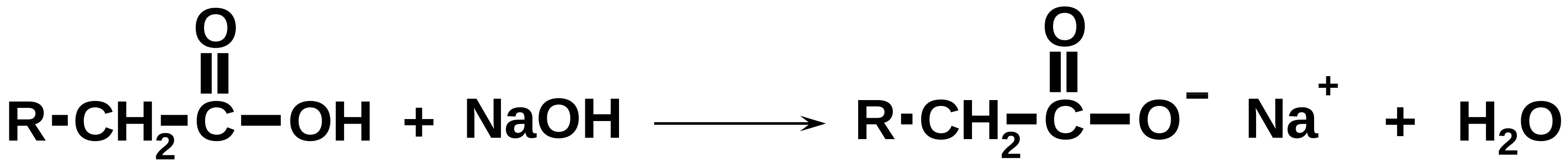
$CH_3CH_2CH_2CH_2CH_2CH_2$-Br
1-bromohexane
KCN
$CH_3CH_2CH_2CH_2CH_2CH_2$-CN
H_2O, H+, heat
$CH_3CH_2CH_2CH_2CH_2CH_2$-COOH
heptanoic acid


CH2OH
KMnO4
CH3
KMnO4, heat
CO2H
Br
Mg
MgBr
CO2; then H+
C≡N
H2O, H+, heat

SYNTHESIS OF CARBOXYLIC ACIDS



Carboxylate Ion Formation



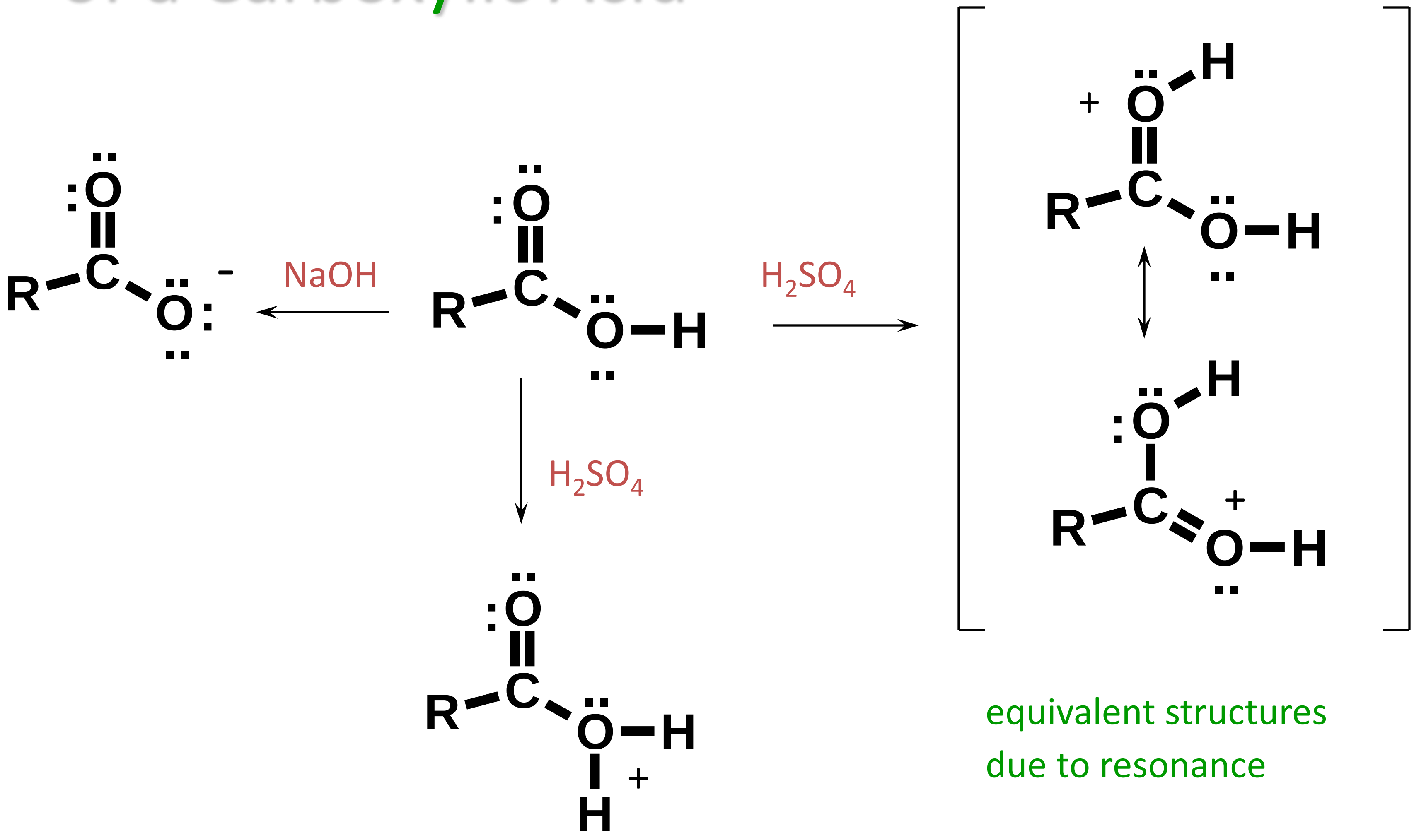
$$R\text{-}CH_2\text{-}\overset{\overset{O}{\|}}{C}\text{-}OH + NaOH \longrightarrow R\text{-}CH_2\text{-}\overset{\overset{O}{\|}}{C}\text{-}O^- \; Na^+ + H_2O$$

carboxylic acid

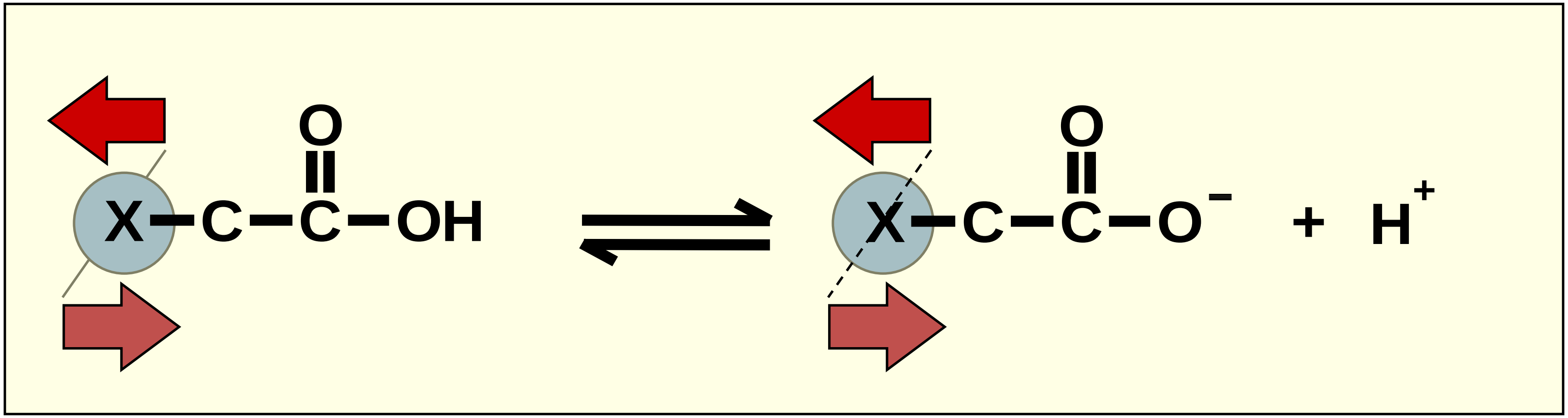
carboxylate ion

$pK_a \approx 5$

Protonation and Deprotonation of a Carboxylic Acid

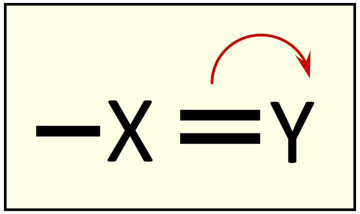


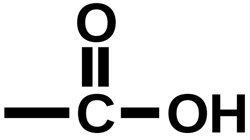
equivalent structures
due to resonance



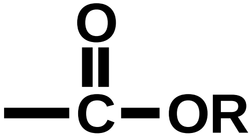
- ⬅ **Electron-withdrawing Groups**:
  - strengthen acids
  - weaken bases
- ➡ **Electron-releasing Groups:**
  - weaken acids
  - strengthen bases

Substituents with Electron-Withdrawing Resonance (- R) Effects

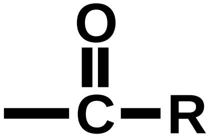

$-X=Y$


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

$-NO_2$ nitro


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

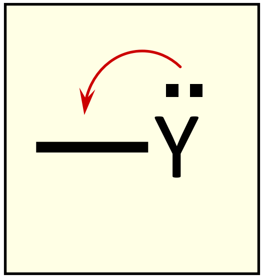
$-C\equiv N$ cyano

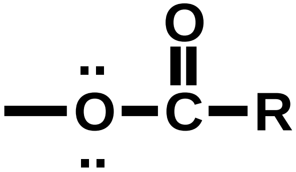

$-\overset{\overset{\displaystyle O}{\|}}{C}-R$ acyl

$-SO_3H$ sulfo

-R substituents strengthen acids and weaken bases

Substituents with Electron-Releasing Resonance (+ R) Effects

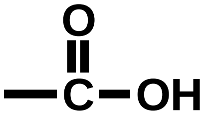
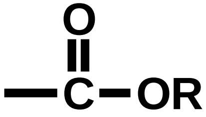
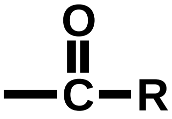


$-\underset{\cdot\cdot}{\ddot{\mathrm{O}}}\mathrm{H}$	hydroxy	$-\underset{\cdot\cdot}{\ddot{\mathrm{O}}}\mathrm{R}$	alkoxy
$-\underset{\cdot\cdot}{\ddot{\mathrm{S}}}\mathrm{H}$	mercapto	 $-\underset{\cdot\cdot}{\ddot{\mathrm{O}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{R}$	acyloxy
$-\mathrm{CH_3}$	methyl	$-\mathrm{CR_3}$	alkyl
$-\ddot{\mathrm{N}}\mathrm{H_2}$	amino	$-\ddot{\mathrm{N}}\mathrm{R_2}$	dialkylamino
$-\underset{\cdot\cdot}{\ddot{\mathrm{F}}}:$	fluoro	$-\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}:$	chloro
$-\underset{\cdot\cdot}{\ddot{\mathrm{Br}}}:$	bromo	$-\underset{\cdot\cdot}{\ddot{\mathrm{I}}}:$	iodo

+R substituents weaken acids and strengthen bases

Substituents with Electron-Withdrawing (- I) Inductive Effects

$\rightarrow X$

 $-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{OH}$	carboxyl
 $-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{OR}$	alkoxycarbonyl
 $-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{R}$	acyl
$-OH$	hydroxyl
$-SH$	mercapto
$-NH_2$	amino
$-Cl$	chloro
$-NO_2$	nitro

$-C\equiv N$	cyano
$-SO_3H$	sulfonic acid
$-OR$	alkoxy
$-NR_2$	dialkylamino
$-F$	fluoro
$-Br$	bromo
$-I$	iodo
$-\overset{+}{N}(CH_3)_3$	trimethylammonium

-I substituents strengthen acids and weaken bases

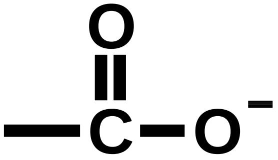
Substituents with Electron-Releasing Inductive (+ I) Effects

$R \longrightarrow$

$-CH_3$ methyl

$-CR_3$ alkyl

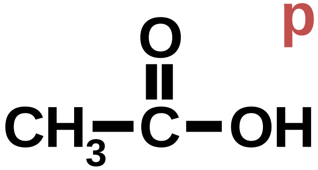
$-O^-$ oxide



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

carboxylate

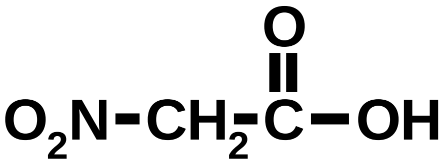
+I substituents <u>weaken acids</u> and <u>strengthen bases</u>



$CH_3-\overset{O}{\overset{\|}{C}}-OH$

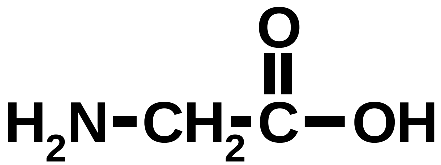
pK$_a$ = 4.75

increasing acidity



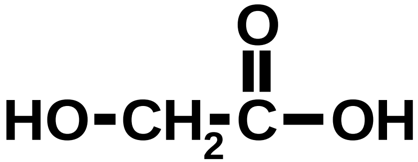
$O_2N-CH_2-\overset{O}{\overset{\|}{C}}-OH$

3.83



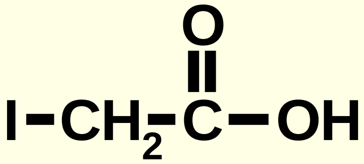
$H_2N-CH_2-\overset{O}{\overset{\|}{C}}-OH$

2.34



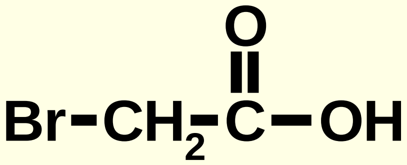
$HO-CH_2-\overset{O}{\overset{\|}{C}}-OH$

1.68



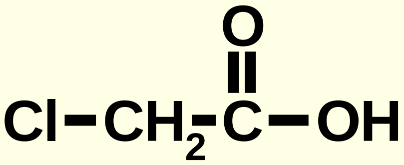
$I-CH_2-\overset{O}{\overset{\|}{C}}-OH$

3.12



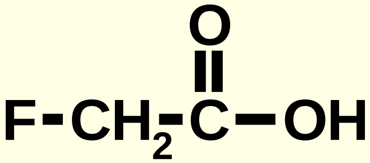
$Br-CH_2-\overset{O}{\overset{\|}{C}}-OH$

2.86



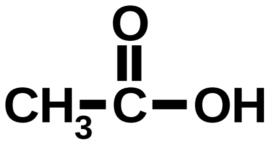
$Cl-CH_2-\overset{O}{\overset{\|}{C}}-OH$

2.86



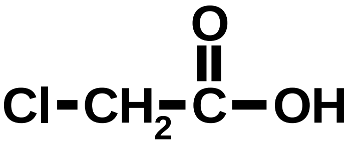
$F-CH_2-\overset{O}{\overset{\|}{C}}-OH$

2.66



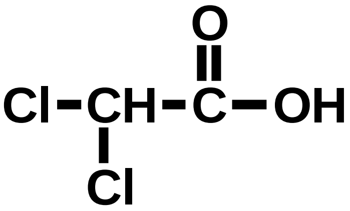
CH_3COOH

$pK_a = 4.75$



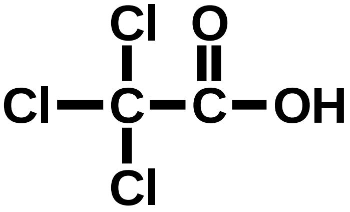
$ClCH_2COOH$

2.86



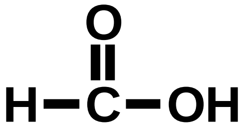
$Cl_2CHCOOH$

1.29



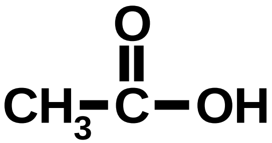
Cl_3CCOOH

0.65



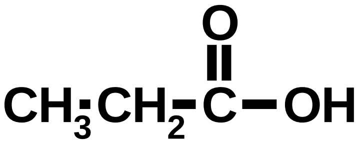
$HCOOH$

3.77



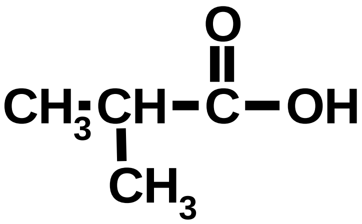
CH_3COOH

4.75



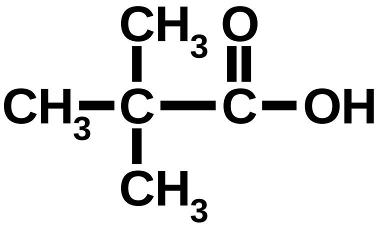
CH_3CH_2COOH

4.88



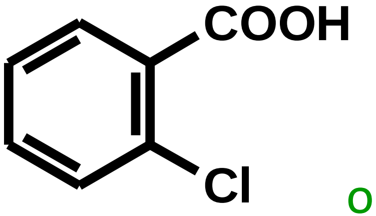
$(CH_3)_2CHCOOH$

4.86



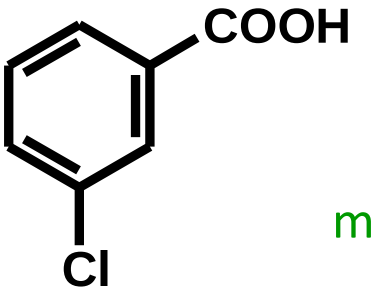
$(CH_3)_3CCOOH$

5.05



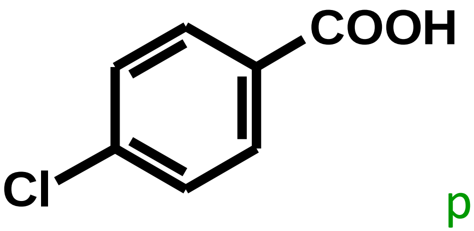
$pK_a = 2.92$

ortho



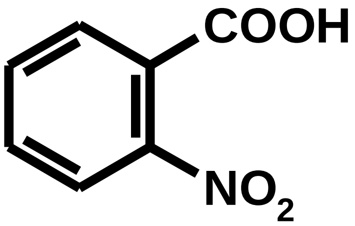
3.82

meta



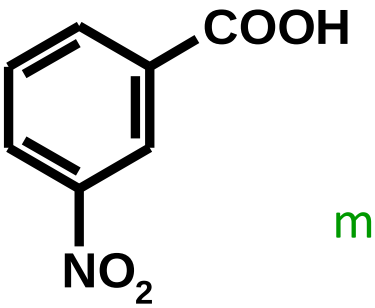
3.98

para



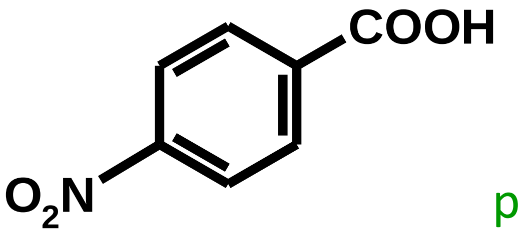
2.16

ortho



3.47

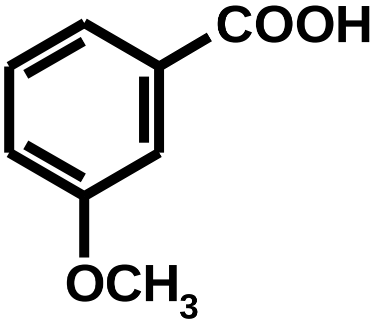
meta



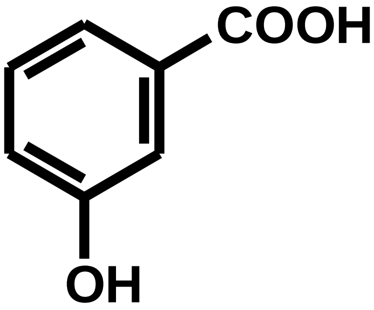
3.41

para

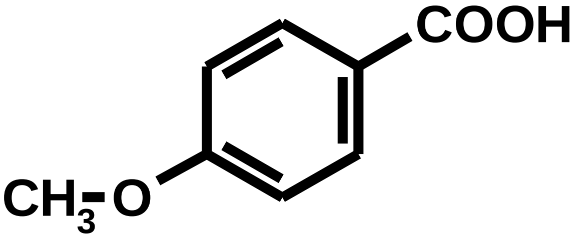
Benzoic Acid: $pK_a = 4.19$



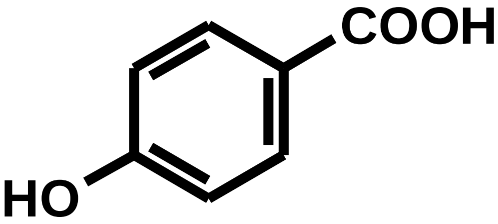
4.08



4.06

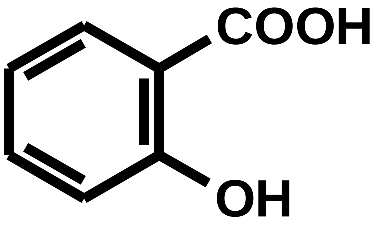


4.46



4.48

Benzoic Acid: pK_a = 4.19



2.97

Chemical Properties of Carboxylic Acids:

1. as acids
2. conversion into functional derivatives
    a) → acid chlorides
    b) → esters
    c) → amides
3. reduction
4. alpha-halogenation
5. EAS

1) Salt formation:

a) **with active metals**

$RCO_2H + Na \rightarrow RCO_2^-Na^+ + H_2(g)$

b) **with bases**

$RCO_2H + NaOH \rightarrow RCO_2^-Na^+ + H_2O$

c) **relative acid strength?**

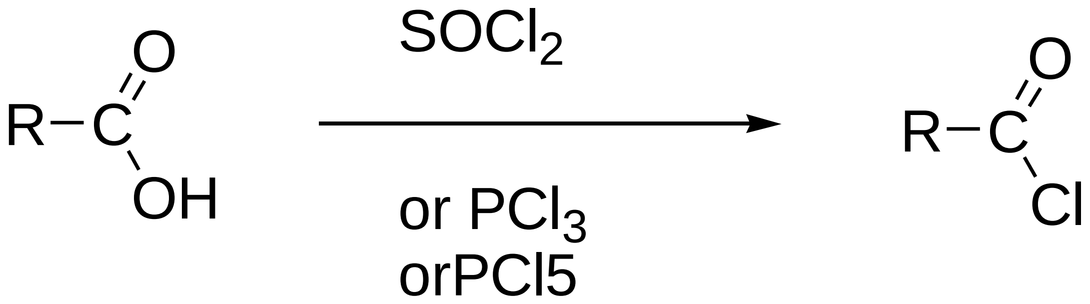
$CH_4 < NH_3 < HC{\equiv}CH < ROH < HOH < H_2CO_3 <$ **RCO_2H** $< HF$

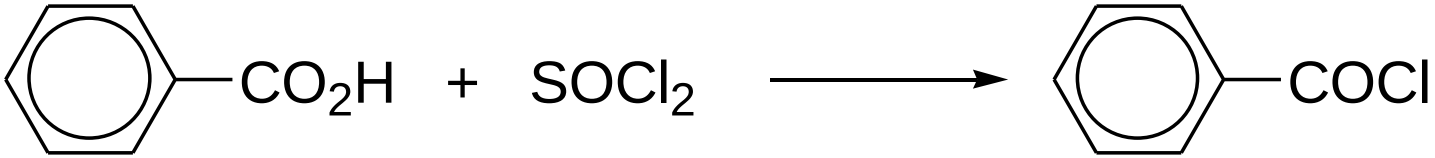
d) **quantitative**

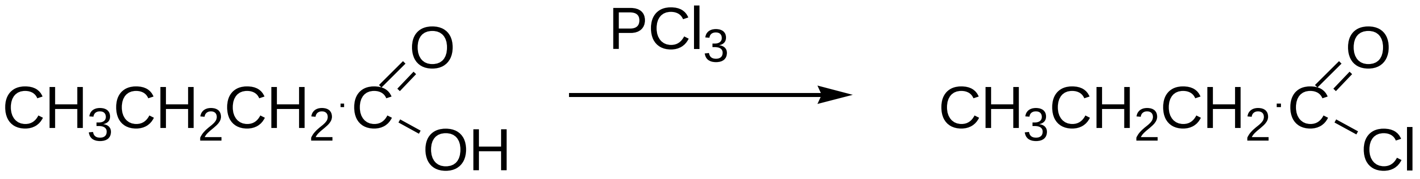
$HA + H_2O \leftrightarrows H_3O^+ + A^-$ ionization in water

$Ka = [H_3O^+]\,[A^-] / [HA]$

2) Formation of acid chlorides:







3) Formation of esters:

“direct” esterification:

$$\mathrm{RCOOH} \;+\; \mathrm{R'OH} \;\overset{H^+}{\leftrightarrows}\; \mathrm{RCO_2R'} \;+\; \mathrm{H_2O}$$

-reversible and often does not favor the ester

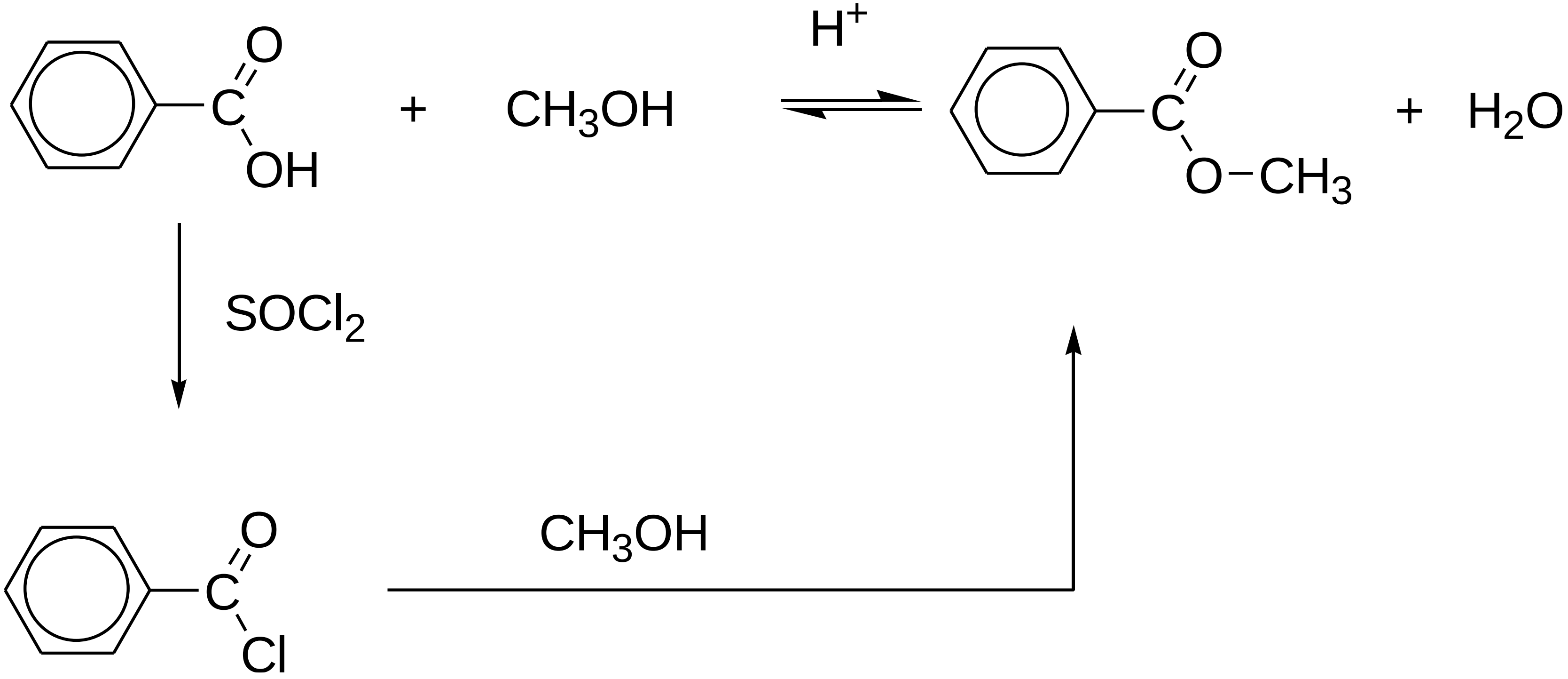
-use an excess of the alcohol or acid to shift equilibrium

-or remove the products to shift equilibrium to completion

“indirect” esterification:

$$\mathrm{RCOOH} \;+\; \mathrm{PCl_3} \;\rightarrow\; \mathrm{RCOCl} \;+\; \mathrm{R'OH} \;\rightarrow\; \mathrm{RCO_2R'}$$

-convert the acid into the acid chloride first; not reversible

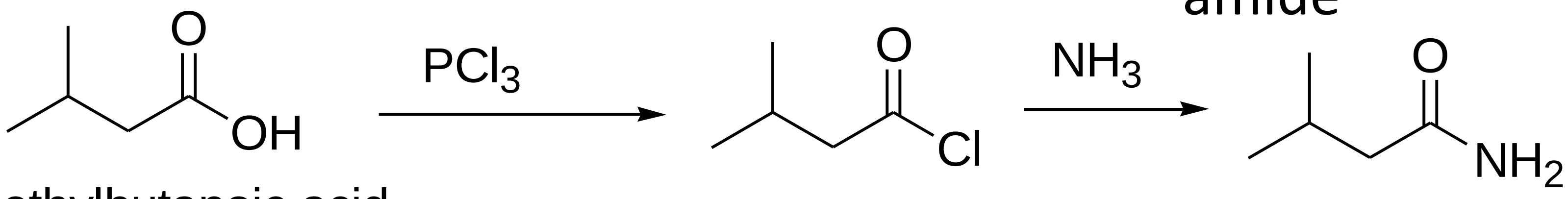

O
C
OH
+
CH3OH
H+
O
C
O−CH3
+
H2O
SOCl2
O
C
Cl
CH3OH

4) Formation of amides:

“indirect” only.

$RCOOH + SOCl_2 \rightarrow RCOCl + NH_3 \rightarrow RCONH_2$

amide

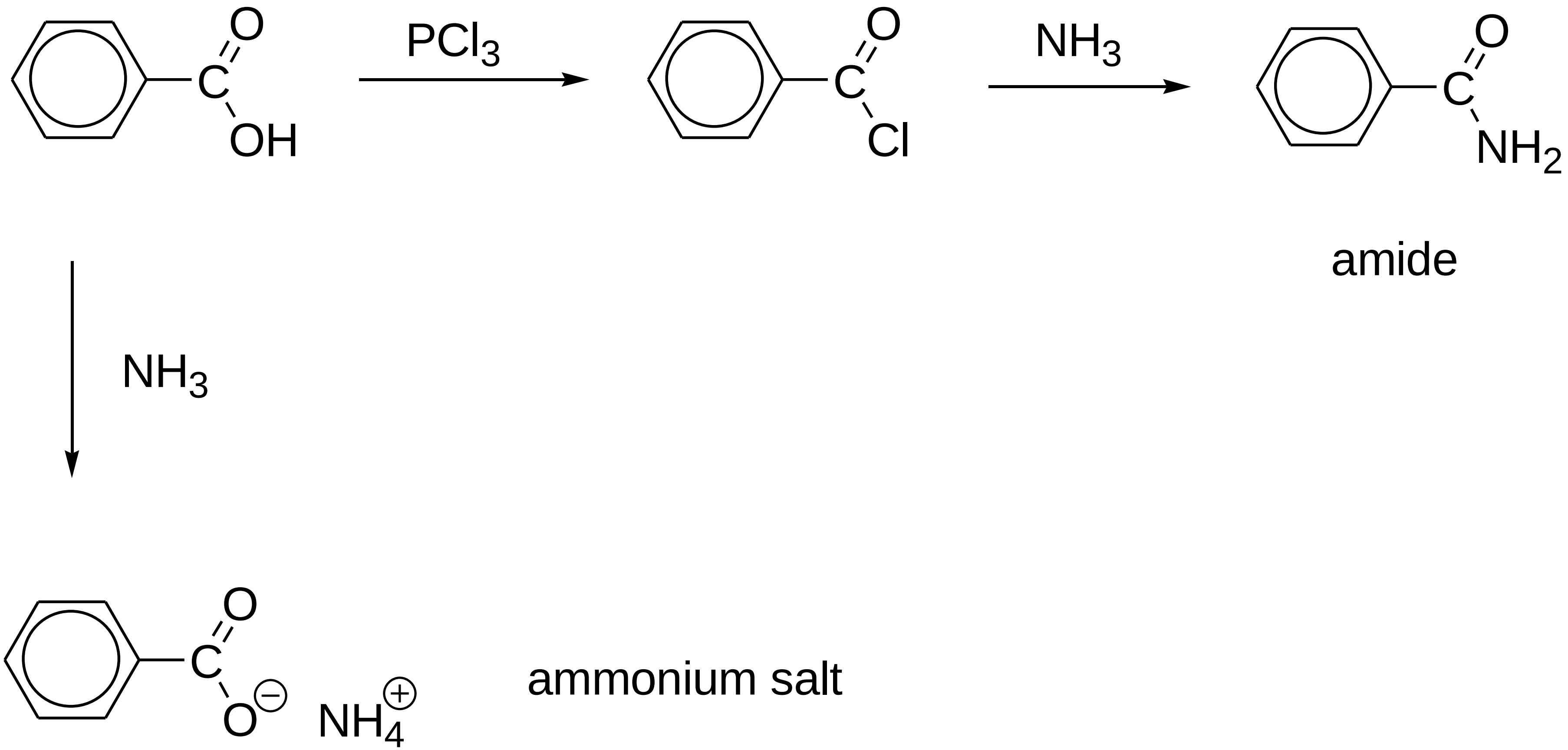


3-Methylbutanoic acid

Directly reacting ammonia with a carboxylic acid results in an ammonium salt:

$RCOOH + NH_3 \rightarrow RCOO^-NH_4^+$

acid base



amide

ammonium salt

5) Reduction:

$$RCO_2H \quad + \quad LiAlH_4;\ \text{then}\ H^+ \quad \rightarrow \quad RCH_2OH$$

1° alcohol

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2COOH \xrightarrow{LiAlH_4} \xrightarrow{H^+}$$

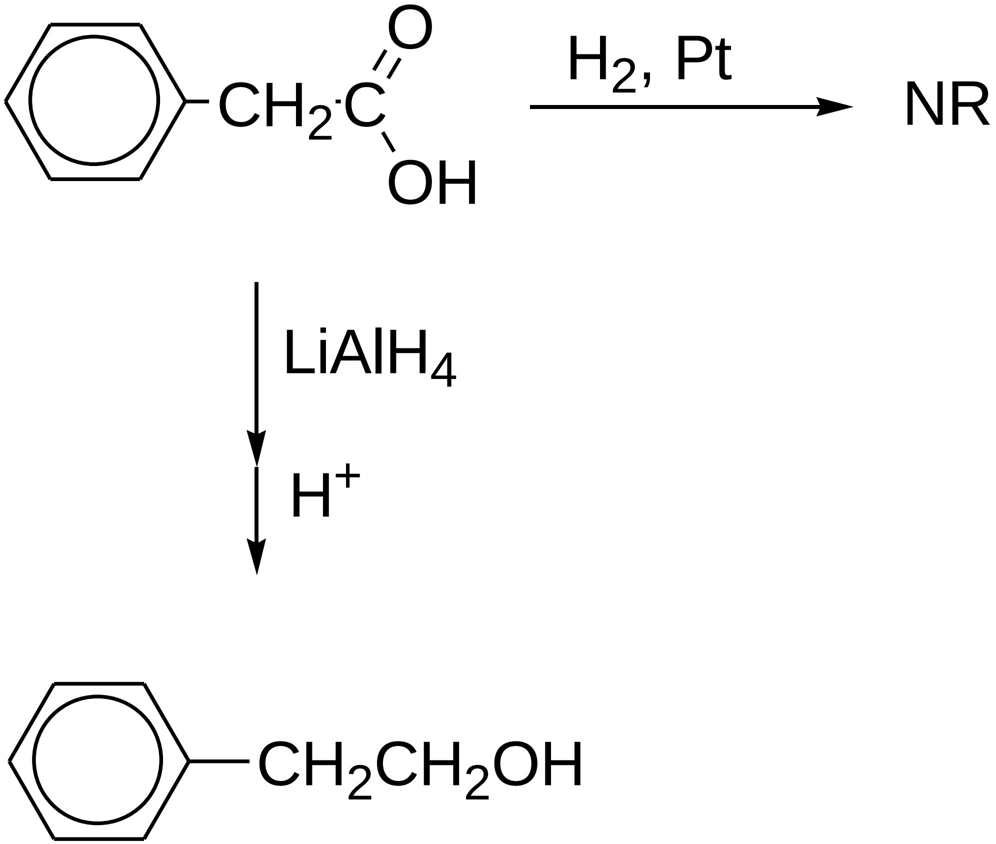
Octanoic acid
(Caprylic acid)

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2OH$$

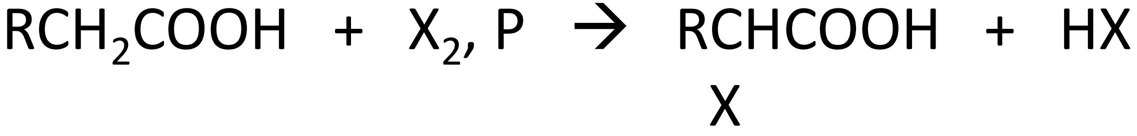
1-Octanol

Carboxylic acids resist catalytic reduction under normal conditions.

$$RCOOH \quad + \quad H_2,\ Ni \quad \rightarrow \quad \text{No Reaction (NR)}$$


CH2-C
O
OH
H2, Pt
NR
LiAlH4
H+
CH2CH2OH

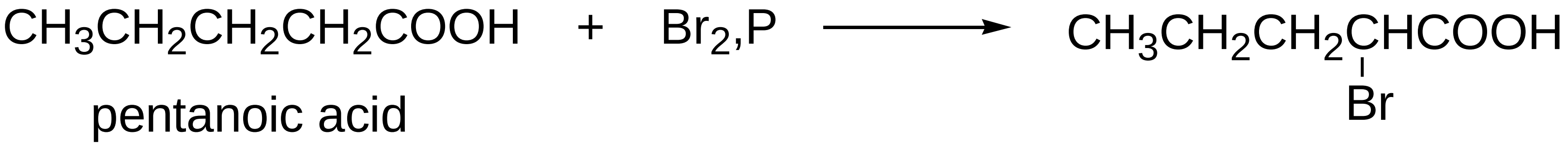
6) Halogenation of alkyl groups (Hell-Volhard-Zelinsky reaction):



$$\mathrm{RCH_2COOH} \;+\; \mathrm{X_2,\ P} \;\rightarrow\; \mathrm{R}\underset{\mathrm{X}}{\mathrm{C}}\mathrm{HCOOH} \;+\; \mathrm{HX}$$

α-haloacid

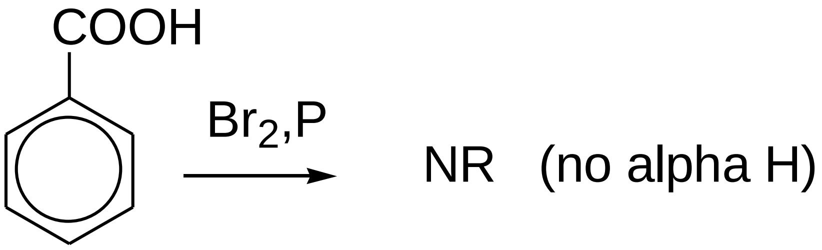
$X_2 = Cl_2, Br_2$



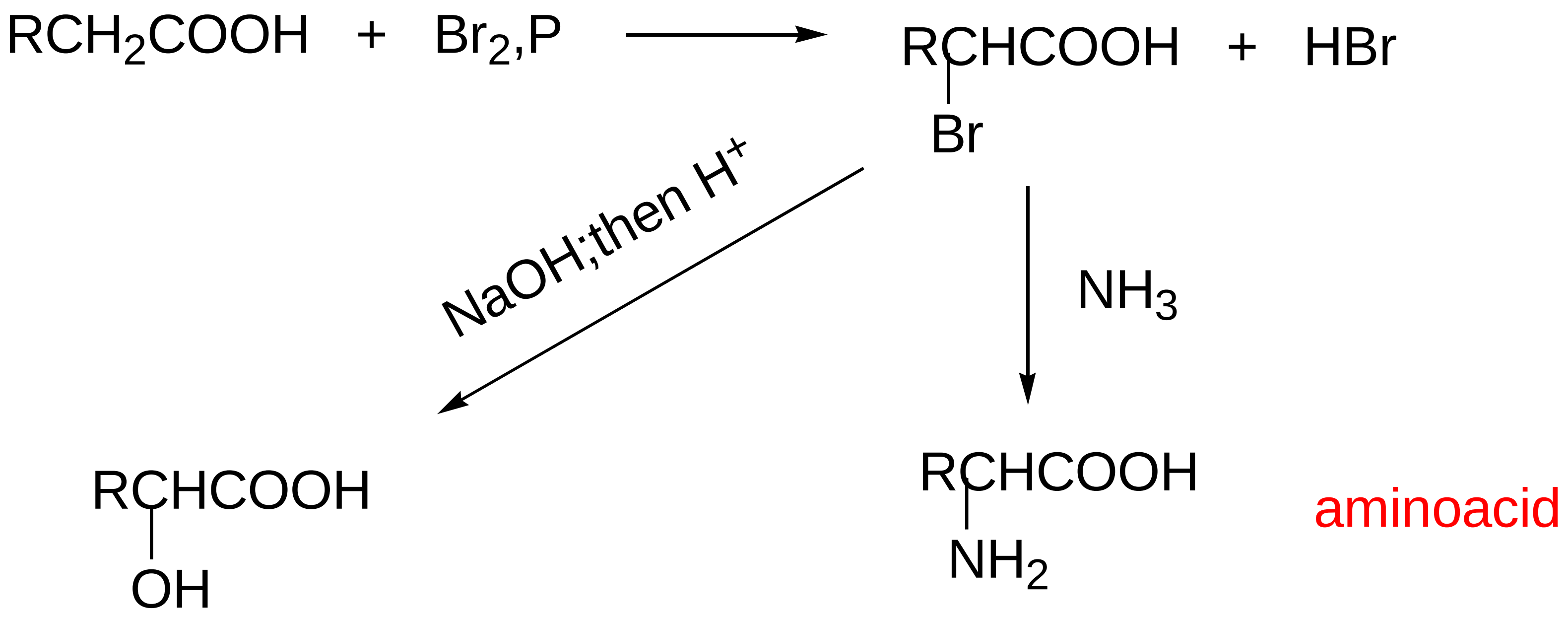
$$\mathrm{CH_3CH_2CH_2CH_2COOH} \;+\; \mathrm{Br_2,P} \longrightarrow \mathrm{CH_3CH_2CH_2}\underset{\mathrm{Br}}{\mathrm{C}}\mathrm{HCOOH}$$

pentanoic acid

2-bromopentanoic acid



$\xrightarrow{Br_2,P}$ NR (no alpha H)

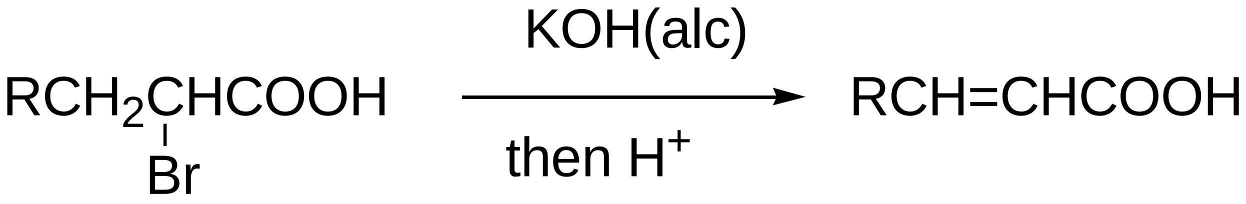


$$RCH_2COOH + Br_2,P \longrightarrow \underset{Br}{RCHCOOH} + HBr$$

$$\underset{Br}{RCHCOOH} \xrightarrow{\text{NaOH;then } H^+} \underset{OH}{RCHCOOH}$$

$$\underset{Br}{RCHCOOH} \xrightarrow{NH_3} \underset{NH_2}{RCHCOOH}$$

aminoacid



$$RCH_2\underset{Br}{C}HCOOH \xrightarrow[\text{then } H^+]{\text{KOH(alc)}} RCH{=}CHCOOH$$

5) Aromatic Substitution:

(-COOH is deactivating and *meta*- directing)