Organic Chemistry

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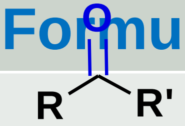
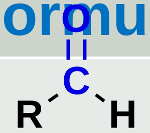
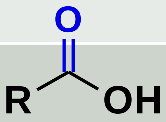
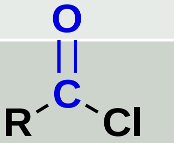
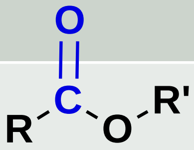
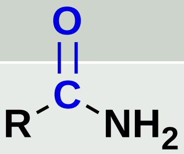
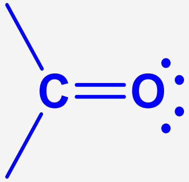
CHAPTER 2 : Aldehydes and Ketones

Common Classes of Carbonyl Compounds

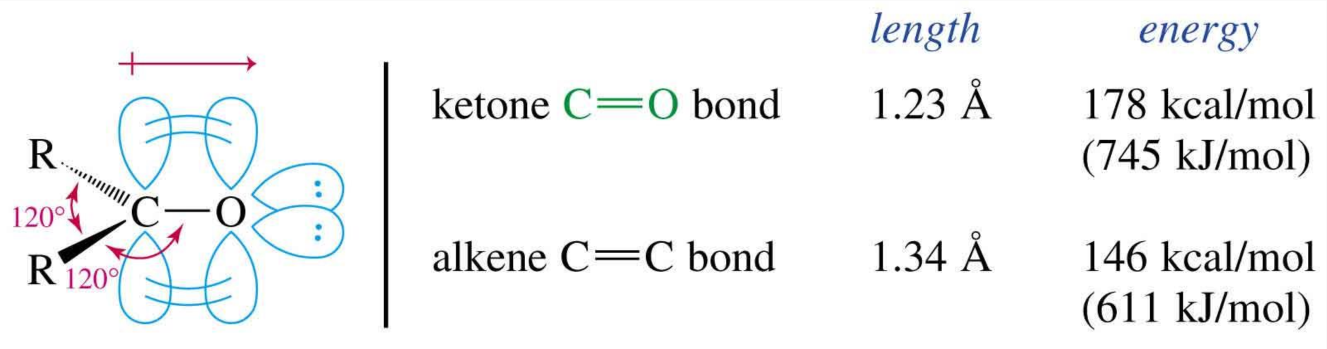
Class	General Formula	Class	General Formula
Ketones		Aldehydes	
Carboxylic acids		Acid Chlorides	
Esters		Amides	

The Carbonyl Group



The carbonyl group

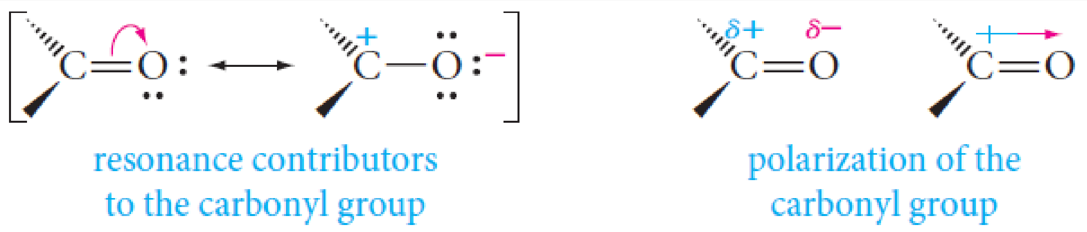
- The carbon–oxygen double bond consists of a sigma bond and a pi bond.
- The carbon atom is sp^2-hybridized.
- The three atoms attached to the carbonyl carbon lie in a plane with bond angles of 120°.
- The pi bond is formed by overlap of a *p* orbital on carbon with an oxygen *p* orbital.
- There are also two unshared electron pairs on the oxygen atom.
- The C=O bond distance is 1.24A, shorter than the C-O distance in alcohols and ethers (1.43A).



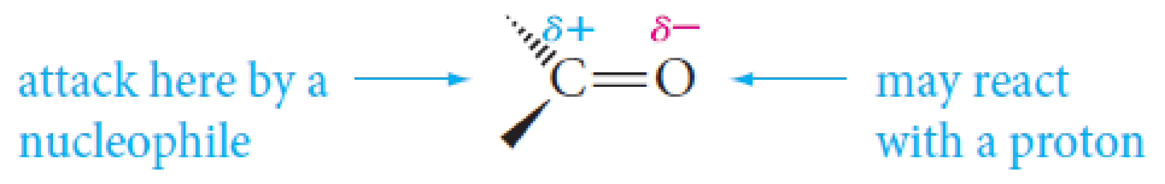
	length	*energy*
ketone C=O bond	1.23 Å	178 kcal/mol (745 kJ/mol)
alkene C=C bond	1.34 Å	146 kcal/mol (611 kJ/mol)

The Carbonyl Group

- Oxygen is much more electronegative than carbon. Therefore, the electrons in the C=O bond are attracted to the oxygen, producing a highly polarized bond.

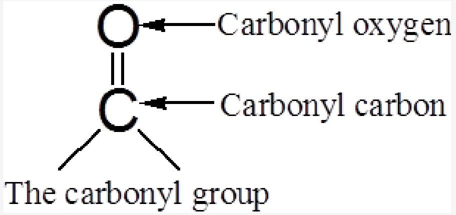


- As a consequence of this polarization, *most carbonyl reactions involve* nucleophilic attack *at the carbonyl carbon,* often accompanied by addition of a proton to the oxygen (electron rich).



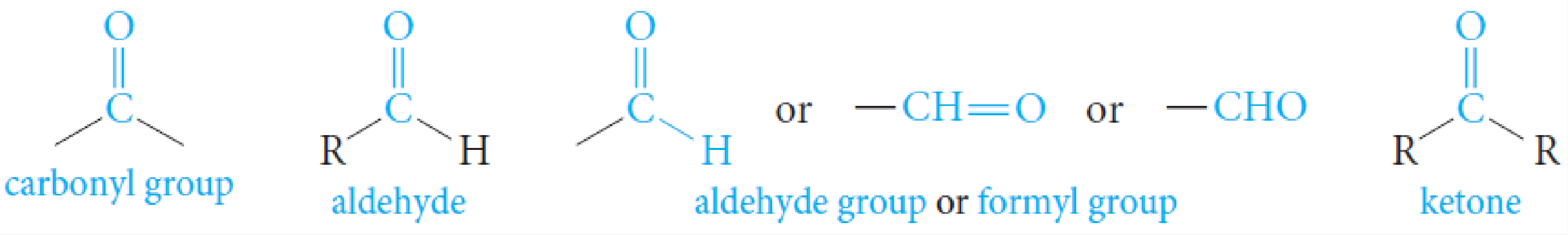
Structure of Aldehydes and Ketones

- **Aldehydes and ketones** are characterized by the presence of the carbonyl group.



The carbonyl group

- **Aldehydes** have at least one hydrogen atom attached to the carbonyl carbon atom. *The remaining group may be another hydrogen atom or any aliphatic or aromatic organic group*. The -CH=O group characteristic of aldehydes is often called a formyl group.
- In **ketones,** the carbonyl carbon atom is connected to two other carbon atoms.

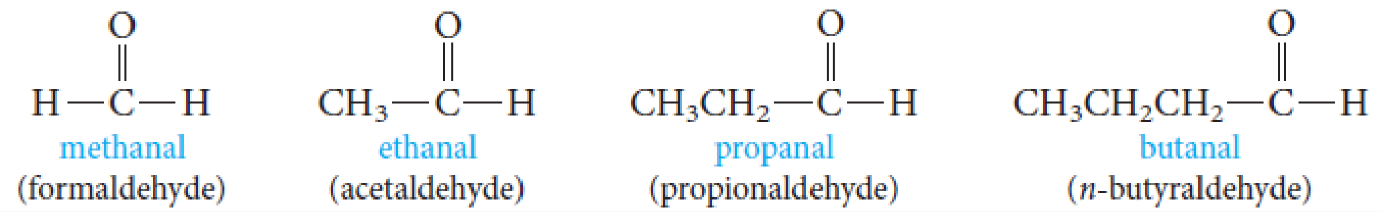


IUPAC System

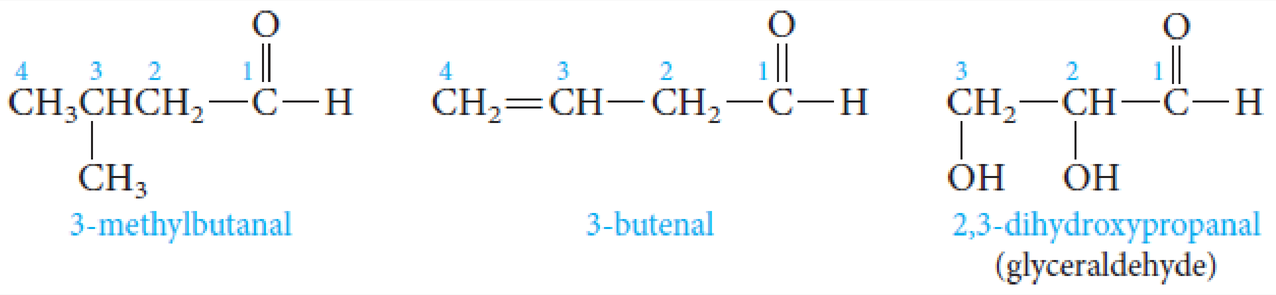
Nomenclature of Aldehydes

- ***Aliphatic aldehydes*** *are named by dropping the suffix -e from the name of the hydrocarbon that has the same carbon skeleton as the aldehyde and replacing it with the suffix -al.*

Alkane - e+ *al = Alkanal*



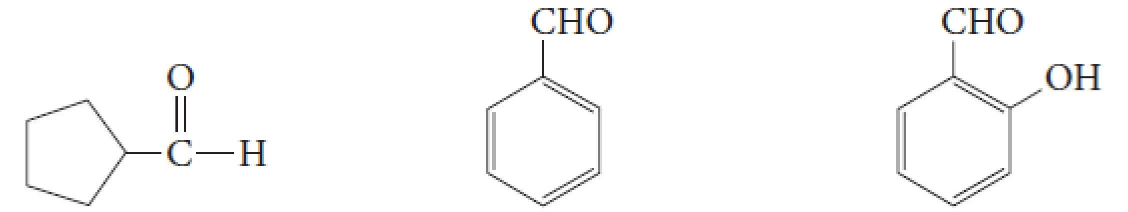
- ***Substituted aldehydes,*** *we number the chain starting with the aldehyde carbon.*
  - *-CH=O group is assigned the number 1 position.*
  - *Aldehyde group has priority over a double bond or hydroxyl group.*



Nomenclature of Aldehydes

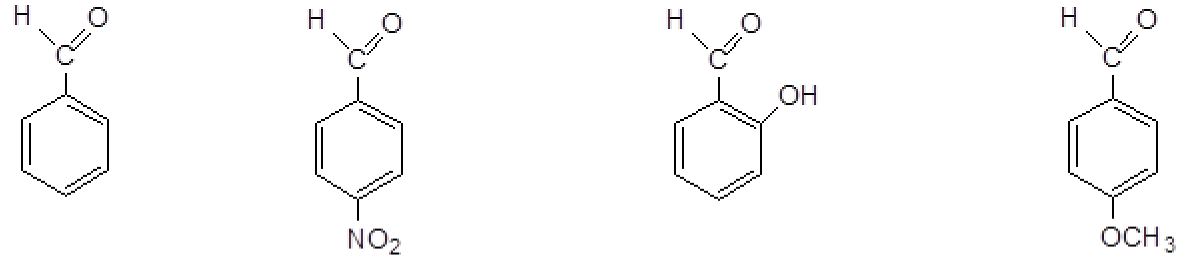
IUPAC System

- ○ ***Cyclic aldehydes,*** *the suffix –carbaldehyde is used.*



cyclopentanecarbaldehyde (formylcyclopentane) | benzaldehyde (benzenecarbaldehyde) | salicylaldehyde (2-hydroxybenzenecarbaldehyde)

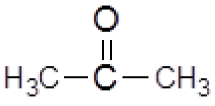
- ○ ***Aromatic aldehydes*** *are usually designated as derivatives of the simplest aromatic aldehyde, benzaldehyde.*



Benzaldehyde | *p*-Nitrobenzaldehyde | *o*-Hydroxybenzaldehyde (Salicylaldehyde) | *p*-Methoxybenzaldehyde (Anisaldehyde)

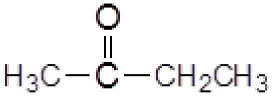
Common Names

- Common names of ketones are formed by adding the word *ketone* to the names of the alkyl or aryl groups attached to the carbonyl carbon. Alkyl ketone.



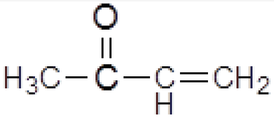
$H_3C-\overset{\overset{\large O}{\|}}{C}-CH_3$

Acetone
(Dimethyl ketone)



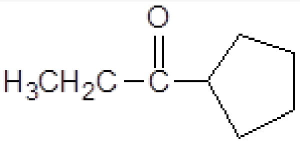
$H_3C-\overset{\overset{\large O}{\|}}{C}-CH_2CH_3$

Methyl ethyl ketone

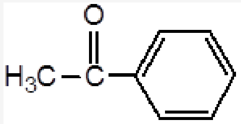


$H_3C-\overset{\overset{\large O}{\|}}{C}-\underset{H}{C}=CH_2$

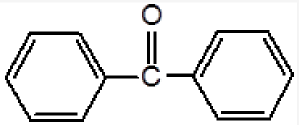
Methyl vinyl ketone



Ethyl cyclopentyl ketone



Methyl phenyl ketone
(Acetophenone)

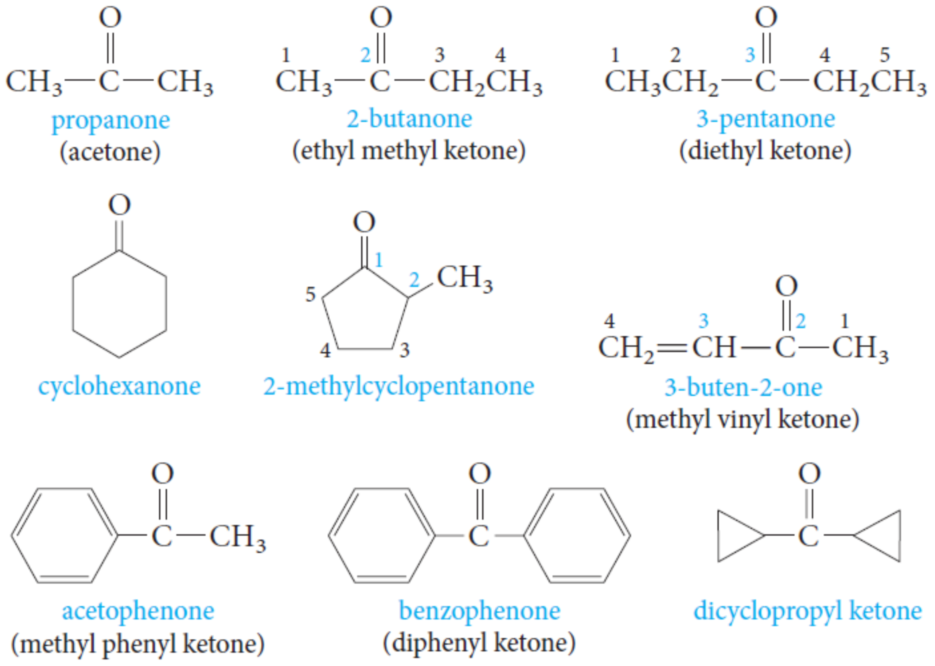


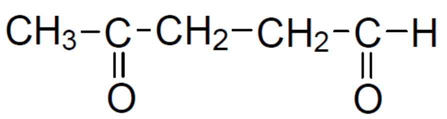
Diphenyl ketone
(Benzophenone)

Nomenclature of Ketones

IUPAC System

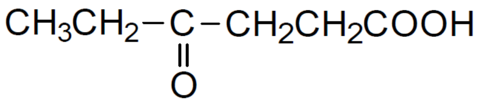
- In the IUPAC system, the ending for ketones is -one.
- The chain is numbered so that the carbonyl carbon has the lowest possible number.
- For cyclic ketones, numbering always starts from the C=O group.
- The prefix "oxo" is used when the ketone is not the principal functional group.





$CH_3-C(=O)-CH_2-CH_2-C(=O)-H$

4-oxopentanal



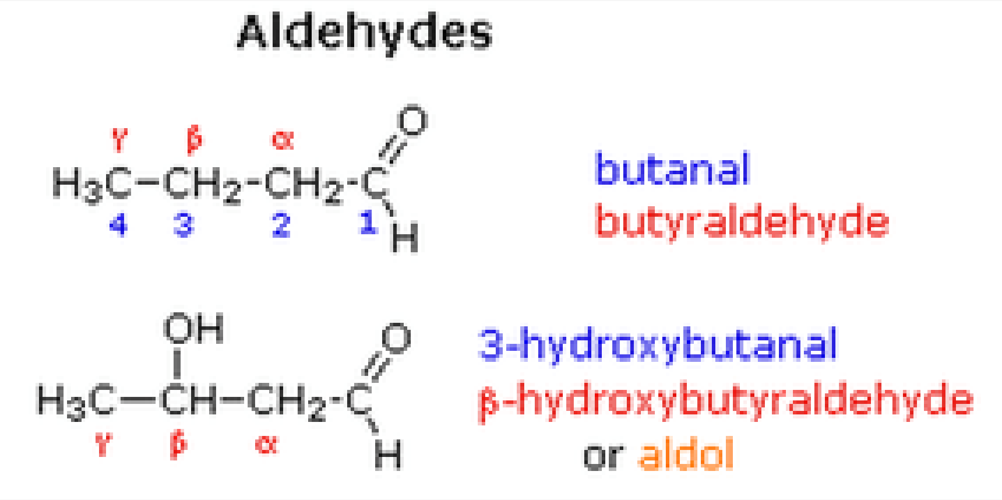
$CH_3CH_2-C(=O)-CH_2CH_2COOH$

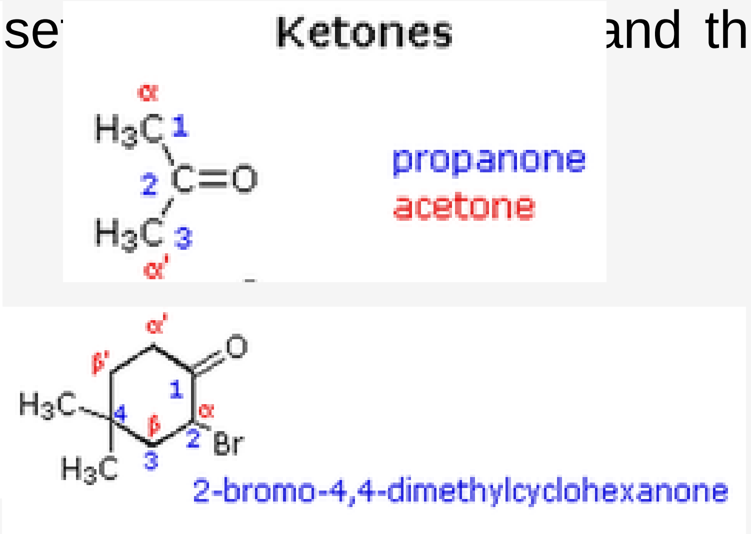
4-oxohexanoic acid

NOTES

Nomenclature of Aldehydes and Ketones

- **In common names** carbon atoms near the carbonyl group are often designated by Greek letters.
- The atom adjacent to the function is *alpha (α)*, the next removed is *beta (β)* and so on. Since ketones h se and the other *α′*, *β′* etc.





- **The functional group priority order in nomenclature system** is as following:
  Acid and derivatives >aldehyde> ketone> alcoho > amine > alkene > alkyne > ether

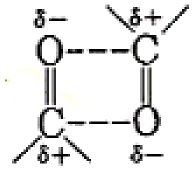
Physical Properties of Aldehydes and Ketones

○ Boiling Points

- Carbonyl compounds boil at higher temperatures than hydrocarbons, but at lower temperatures than alcohols of comparable molecular weight.

$CH_3(CH_2)_4CH_3$	$CH_3(CH_2)_3CH{=}O$	$CH_3(CH_2)_3CH_2OH$
hexane (bp 69°C)	pentanal (bp 102°C)	pentanol (bp 118°C)

- This is due to the intermolecular forces of attraction, called dipole-dipole interactions, which is stronger than van der Waals attractions but not as strong as hydrogen bonds.

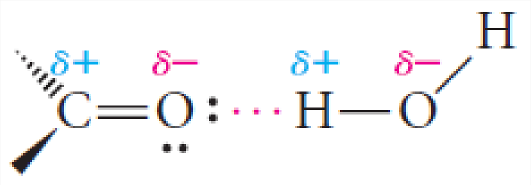


Dipole-dipole attractions among carbonyl compounds

Physical Properties of Aldehydes and Ketones

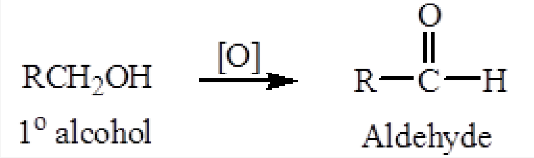
○ Solubility

- Carbonyl compounds as aldehydes and ketones have a C=O bond, but no O-H bond, cannot form hydrogen bonds with themselves.
- The polarity of the carbonyl group also affects the solubility properties of aldehydes and ketones.
- Carbonyl compounds with low molecular weights are soluble in water as they can form hydrogen bonds with O-H or N-H compounds.

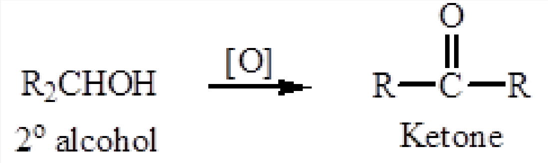


Preparation of Aldehydes and Ketones

1) Oxidation of Primary and Secondary Alcohols



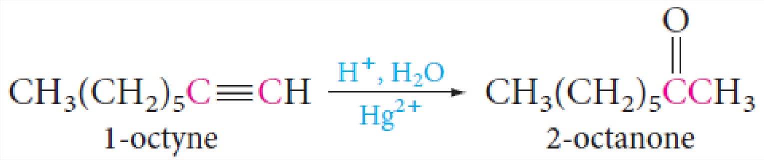
$$\underset{1^\circ\text{ alcohol}}{RCH_2OH} \xrightarrow{[O]} \underset{\text{Aldehyde}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-H}$$



$$\underset{2^\circ\text{ alcohol}}{R_2CHOH} \xrightarrow{[O]} \underset{\text{Ketone}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-R}$$

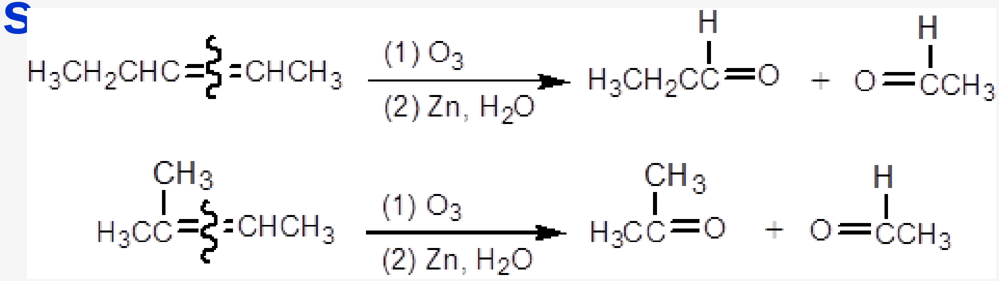
2) Hydration of Alkynes

Hydration of terminal alkynes EXCEPT acetylene yields ketones (catalyzed by acid and mercuric).



$$\underset{\text{1-octyne}}{CH_3(CH_2)_5C{\equiv}CH} \xrightarrow[Hg^{2+}]{H^+,\ H_2O} \underset{\text{2-octanone}}{CH_3(CH_2)_5\overset{\overset{\displaystyle O}{\|}}{C}CH_3}$$

3) Ozonolysis of Alkenes



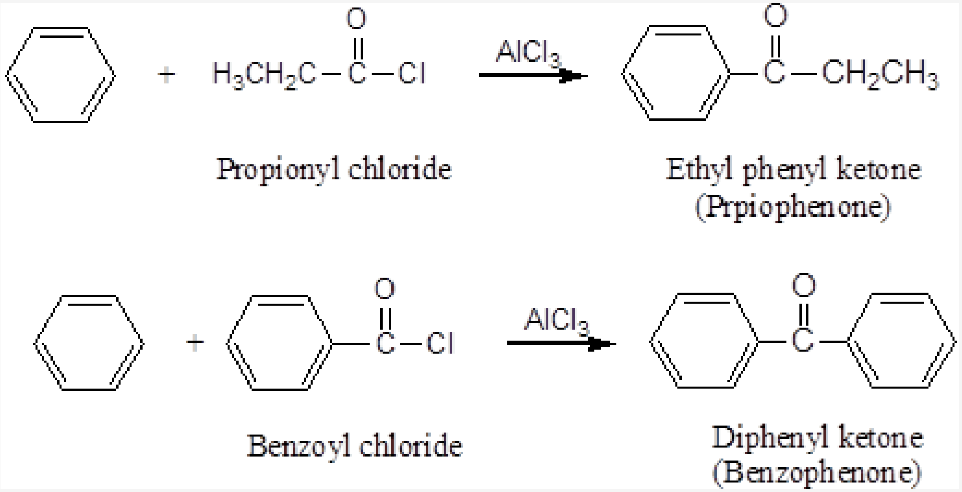
$$H_3CH_2CHC{=}{=}CHCH_3 \xrightarrow[(2)\ Zn,\ H_2O]{(1)\ O_3} H_3CH_2C\overset{\overset{\displaystyle H}{|}}{C}{=}O + O{=}\overset{\overset{\displaystyle H}{|}}{C}CH_3$$

$$H_3C\overset{\overset{\displaystyle CH_3}{|}}{C}{=}{=}CHCH_3 \xrightarrow[(2)\ Zn,\ H_2O]{(1)\ O_3} H_3C\overset{\overset{\displaystyle CH_3}{|}}{C}{=}O + O{=}\overset{\overset{\displaystyle H}{|}}{C}CH_3$$

Preparation of Aldehydes and Ketones

4) Friedel-Crafts Acylation

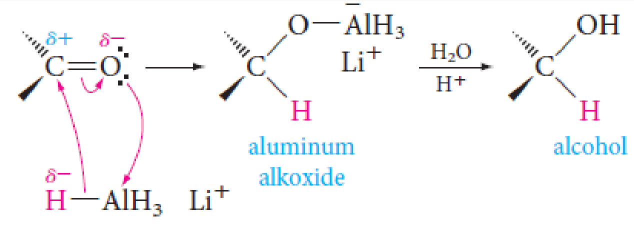
Preparing ketones that contain an aromatic ring.



Reactions of Aldehydes and Ketones

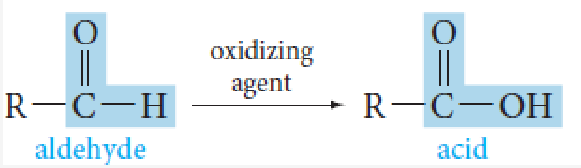
A) Reduction of Carbonyl Compounds

- Aldehydes and ketones are easily reduced to primary and secondary alcohols, respectively.
- The most common metal hydrides used to reduce carbonyl compounds are lithium aluminum hydride ($LiAlH_4$) and sodium borohydride ($NaBH_4$).



B) Oxidation of Carbonyl Compounds

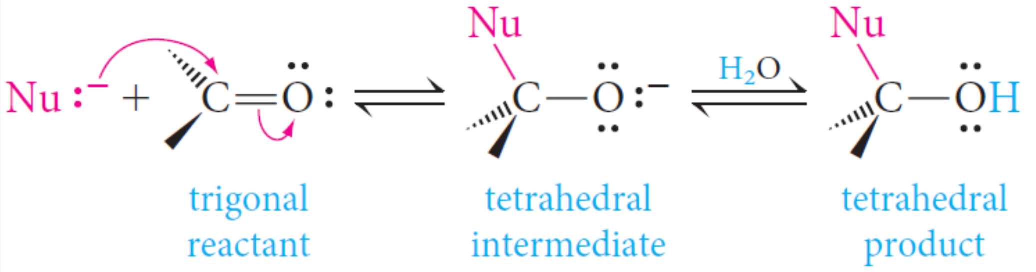
- Oxidation of aldehydes gives a carboxylic acid with the same number of carbon atoms.
- Because the reaction occurs easily, many oxidizing agents, such as $KMnO_4$, CrO_3, Ag_2O and peracids will work.



Reactions of Aldehydes and Ketones

C) Nucleophilic Addition Reactions

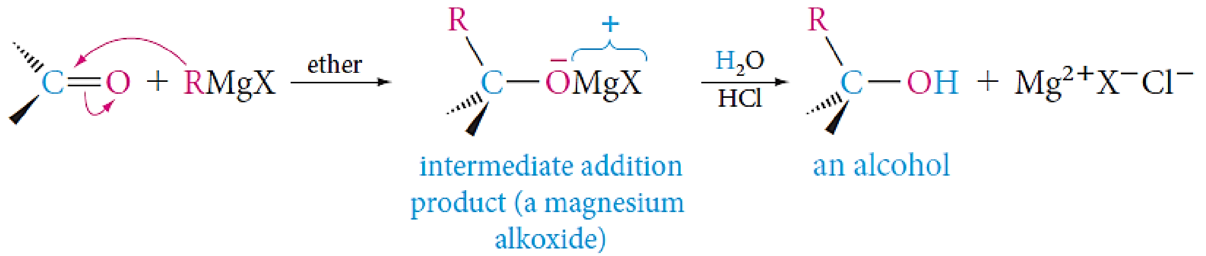
- Nucleophiles attack the carbon atom of a carbon-oxygen double bond because that carbon has a partial positive charge.
- The overall reaction involves addition of a nucleophile and a proton across the pi bond of the carbonyl group (when carried out in alcohol or water).

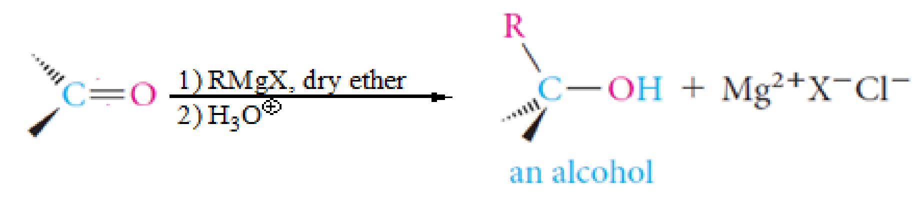


C) Nucleophilic Addition Reactions

1) Addition of Grignard Reagents: Formation of Alcohols

- *Grignard reagents act as carbon nucleophiles toward carbonyl compounds.*
- The reaction of a Grignard reagent with a carbonyl compound provides a useful route to alcohols.



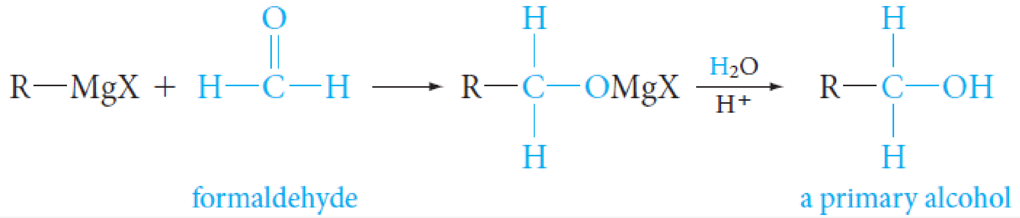


- The type of carbonyl compound chosen determines the class of alcohol produced.

C) Nucleophilic Addition Reactions

1) Addition of Grignard Reagents: Formation of Alcohols

- *Formaldehyde gives primary alcohols.*

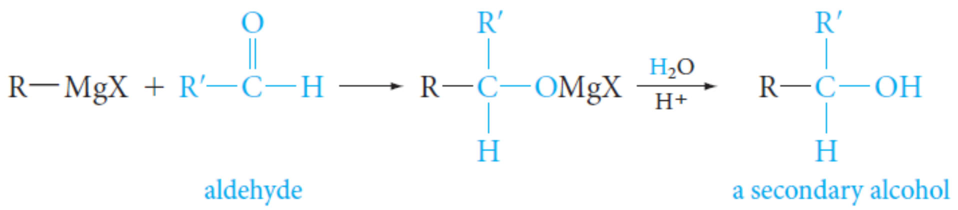


$$R{-}MgX + H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H \longrightarrow R{-}\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}{-}OMgX \xrightarrow[H^+]{H_2O} R{-}\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}{-}OH$$

formaldehyde

a primary alcohol

- *Other aldehydes give secondary alcohols*

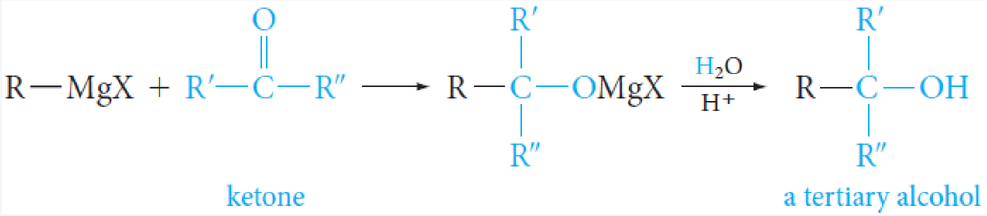


$$R{-}MgX + R'{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H \longrightarrow R{-}\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle R'}{|}}{C}}{-}OMgX \xrightarrow[H^+]{H_2O} R{-}\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle R'}{|}}{C}}{-}OH$$

aldehyde

a secondary alcohol

- *Ketones give tertiary alcohols.*



$$R{-}MgX + R'{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R'' \longrightarrow R{-}\underset{\underset{\displaystyle R''}{|}}{\overset{\overset{\displaystyle R'}{|}}{C}}{-}OMgX \xrightarrow[H^+]{H_2O} R{-}\underset{\underset{\displaystyle R''}{|}}{\overset{\overset{\displaystyle R'}{|}}{C}}{-}OH$$

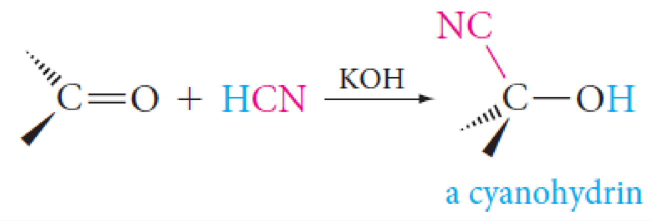
ketone

a tertiary alcohol

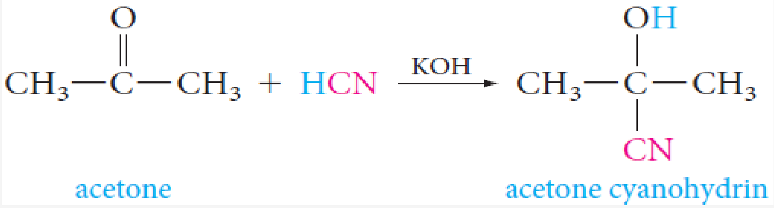
C) Nucleophilic Addition Reactions

2) Addition of Hydrogen Cyanide: Formation of Cyanohydrins

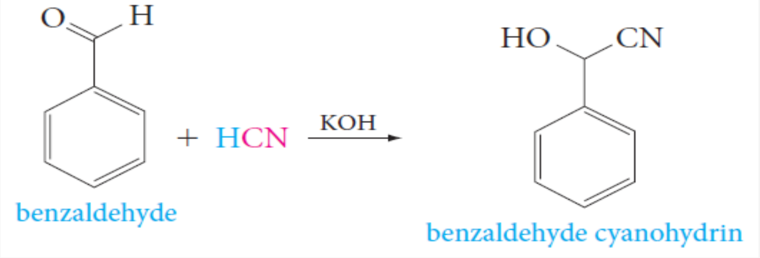
- Hydrogen cyanide adds to the carbonyl group of aldehydes and ketones to form cyanohydrins, compounds with a hydroxyl and a cyano group attached to the same carbon.



- **Example**



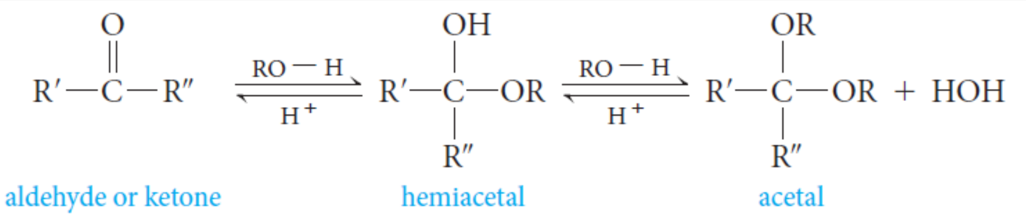
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + HCN \xrightarrow{KOH} CH_3-\underset{\underset{\displaystyle CN}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_3$$



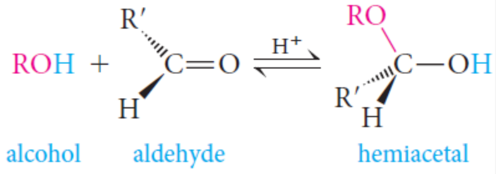
C) Nucleophilic Addition Reactions

3) Addition of Alcohols: Formation of Hemiacetals and Acetals

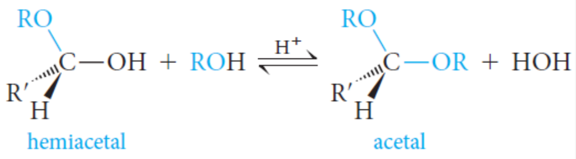
- *Alcohols add to the C=O bond, the OR group becoming attached to the carbon and the proton becoming attached to the oxygen.*
- Aldehydes and ketones react with alcohols to form, first, hemiacetals and then, if excess alcohol is present, acetals.



- Hemiacetals; it contains both alcohol and ether functional groups on the same carbon atom.



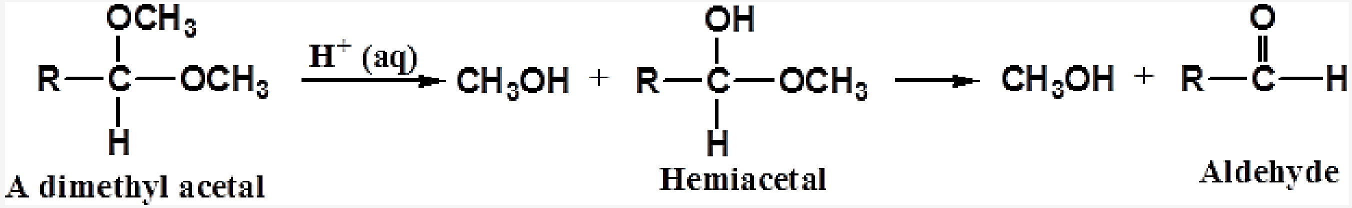
- Acetals have two ether functions at the same carbon atom.

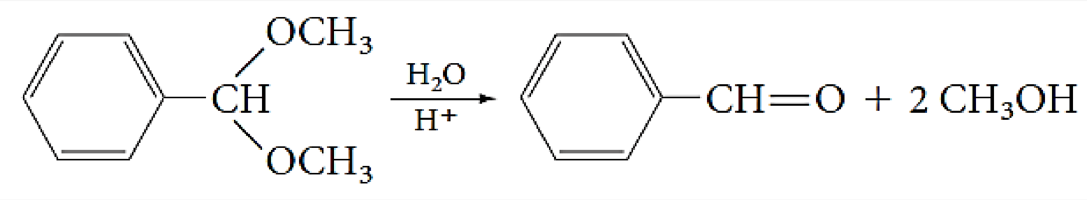


C) Nucleophilic Addition Reactions

3) Addition of Alcohols: Formation of Hemiacetals and Acetals

- The reverse of acetal formation, called acetal hydrolysis.
- Acetal can be hydrolyzed to its aldehyde or ketone and alcohol components by treatment with excess water in the presence of an acid catalyst.

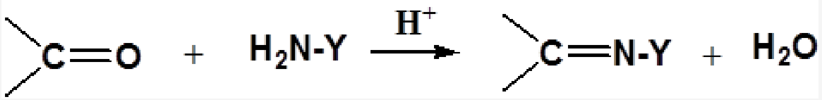


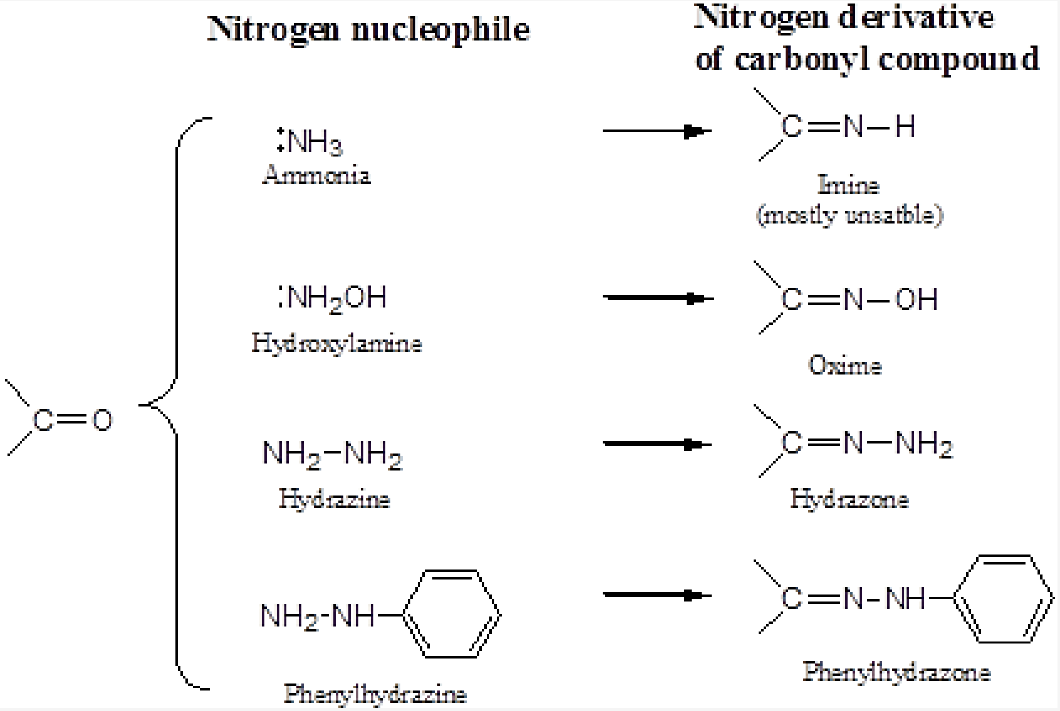


C) Nucleophilic Addition Reactions

4) Addition of Ammonia and Ammonia Derivatives

The addition of nitrogen nucleophile, such as ammonia(NH_3) and substituted ammonia (NH_2-Y).





Organic Chemistry

Department of Chemistry
University of Mosul
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Dr. Nameer S. Ezzat and Dr. Ghufran Th. Sediq

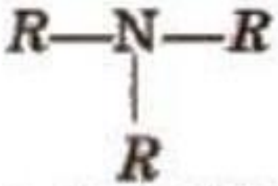
Amines

Amines

Amines constitute an important class of organic compounds derived by replacing one or more hydrogen atoms ofNH 3 molecule by alkyl/aryl group(s).

$R\text{—}NH_2$
primary (1°)

$R\text{—}NH\text{—}R$
secondary (2°)



$R\text{—}\underset{\displaystyle R}{\underset{|}{N}}\text{—}R$

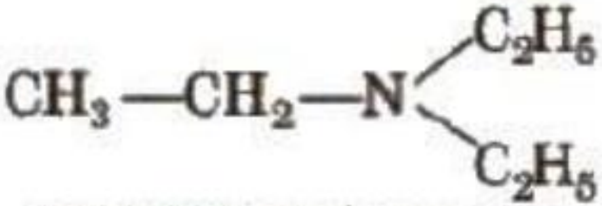
tertiary (3°)

$C_6H_5\text{—}NH_2$
aromatic amine

In the IUPAC system, the amines are regarded as alkanamines, e.g.,

$CH_3\text{—}CH_2\text{—}NH_2$,
ethanamine

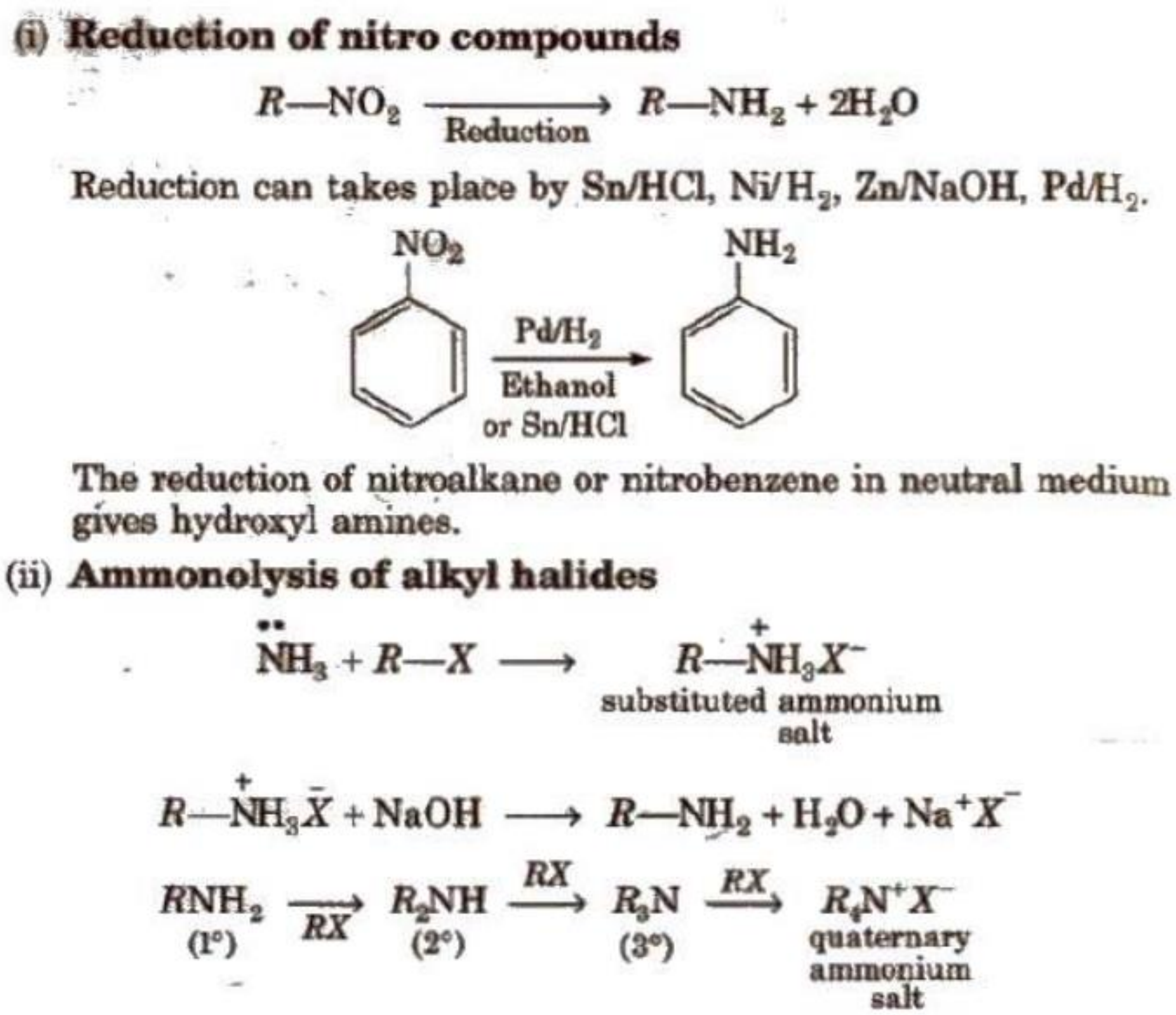
$CH_3CH_2\text{—}NH\text{—}CH_3$
N-methyl ethanamine



$CH_3\text{—}CH_2\text{—}N\begin{matrix} \diagup C_2H_5 \\ \diagdown C_2H_5 \end{matrix}$

N,N-diethylethanamine

Preparation of Amines



(i) Reduction of nitro compounds

$$R\text{—}NO_2 \xrightarrow[\text{Reduction}]{} R\text{—}NH_2 + 2H_2O$$

Reduction can takes place by Sn/HCl, Ni/H_2, Zn/NaOH, Pd/H_2.

The reduction of nitroalkane or nitrobenzene in neutral medium gives hydroxyl amines.

(ii) Ammonolysis of alkyl halides

$$\ddot{N}H_3 + R\text{—}X \longrightarrow \underset{\text{substituted ammonium salt}}{R\text{—}\overset{+}{N}H_3X^-}$$

$$R\text{—}\overset{+}{N}H_3\bar{X} + NaOH \longrightarrow R\text{—}NH_2 + H_2O + Na^+X^-$$

$$\underset{(1^\circ)}{RNH_2} \xrightarrow[RX]{} \underset{(2^\circ)}{R_2NH} \xrightarrow{RX} \underset{(3^\circ)}{R_3N} \xrightarrow{RX} \underset{\text{quaternary ammonium salt}}{R_4N^+X^-}$$

Preparation of Amines

However, primary amine is obtained as a major product by taking large excess of NH_3.

Order of reactivity of halides ‘with amines is RI > RBr > RCI.

Aromatic amines could not be prepared since aryl halides are much less reactive towards nucleophilic substitution reactions.

(iii) Reduction of nitriles or cyanides

$$R{-}C{\equiv}N \xrightarrow[\text{Na(Hg)/}C_2H_5OH]{\text{Ni/}H_2} R{-}CH_2NH_2$$

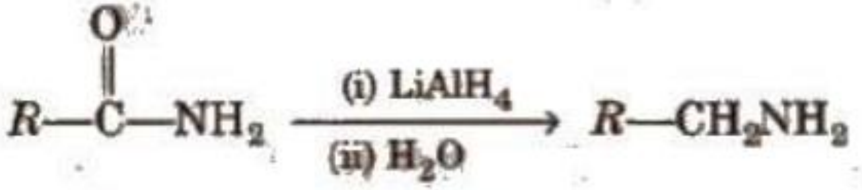
(iv) **Schmidt reaction**

$$RCOOH + \underset{\text{hydrazoic acid}}{N_3H} \xrightarrow{\text{Conc } H_2SO_4} \underset{\text{alkylamine}}{R{-}NH_2} + N_2 + CO_2$$

It is a modification of Curtius degradation.

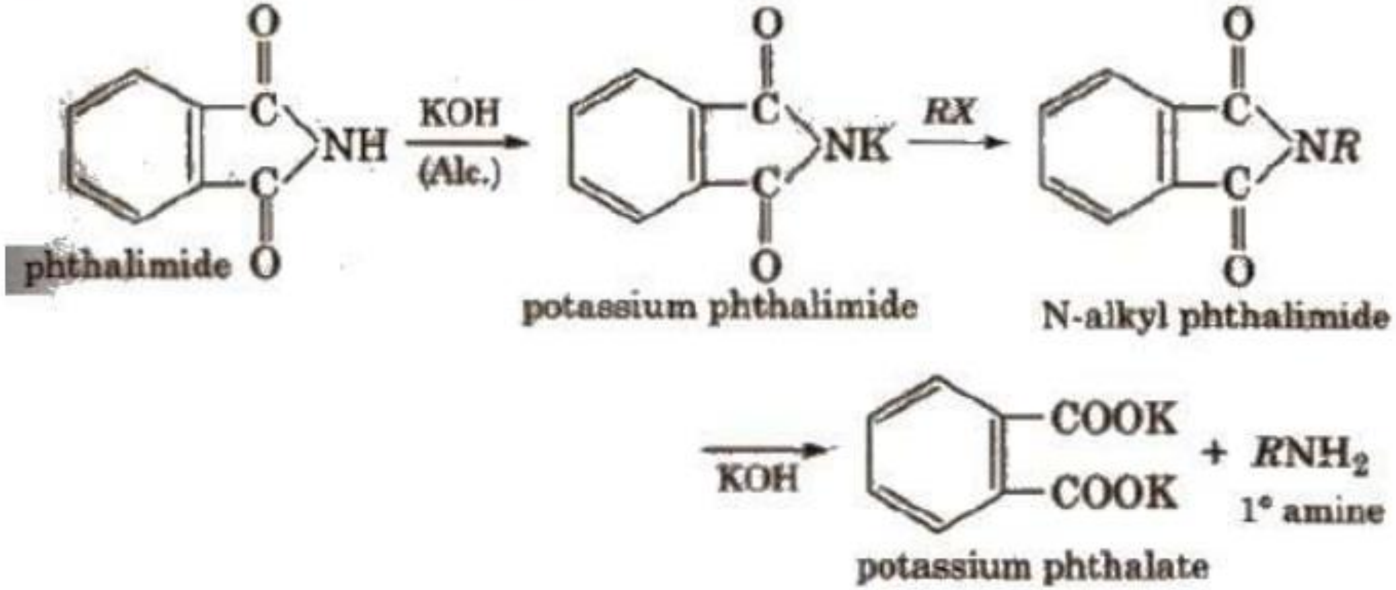
Preparation of Amines

(v) Reduction of amides



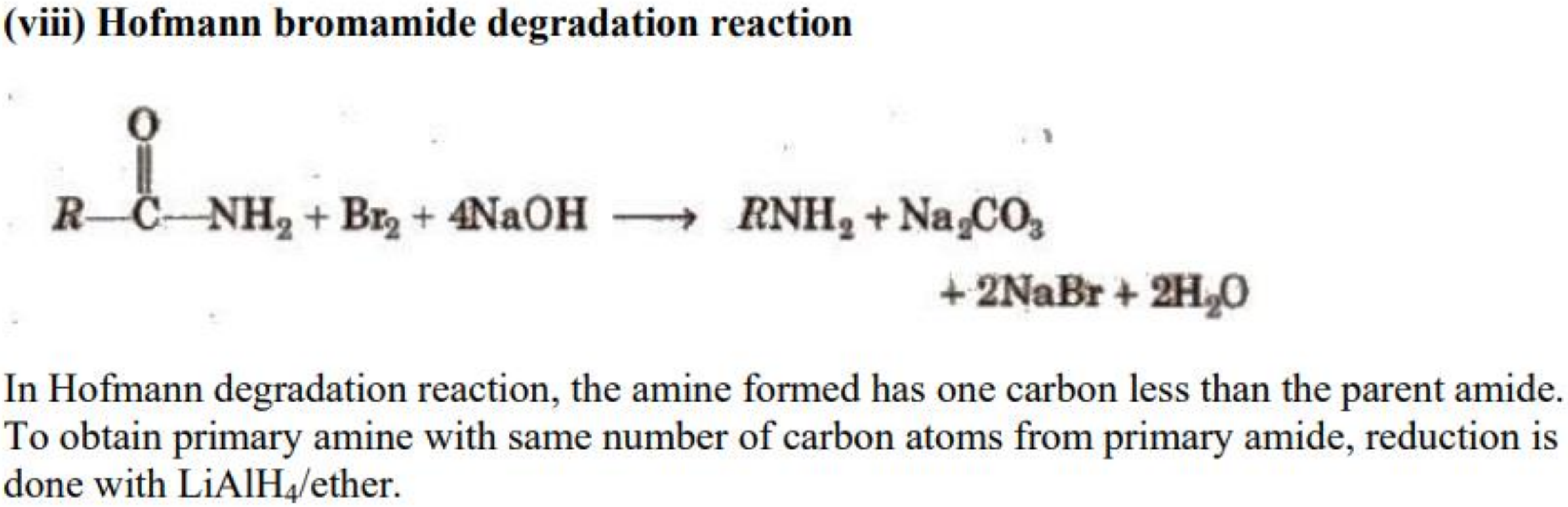
$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} R-CH_2NH_2$$

(vi) Gabriel's phthalimide reaction



It only produces 1 0 amines. This method is not suitable for 1° arylamine because aryl halide does not give nucleophilic substitution reaction.

Preparation of Amines



(viii) Hofmann bromamide degradation reaction

$$R-\overset{\overset{O}{\|}}{C}-NH_2 + Br_2 + 4NaOH \longrightarrow RNH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

In Hofmann degradation reaction, the amine formed has one carbon less than the parent amide. To obtain primary amine with same number of carbon atoms from primary amide, reduction is done with $LiAlH_4$/ether.

Physical properties of Amines

Physical Properties of Amines

1. The lower aliphatic amines are gases with fishy smell.
2. Primary amines with three or more carbon atoms are liquid and higher members are all solids.
3. Lower aliphatic amines are water soluble because they can form hydrogen bonds with water molecules, however, the solubility decreases with increase in hydrophobic alkyl group.
4. Boiling points order primary > secondary > tertiary
5. Tertiary amines does not have intermolecular association due to the absence of hydrogen atom available for hydrogen bond formation.

Basic Strength of Amines

Amines act as Lewis bases due to the presence of lone pair of electrons on the nitrogen atom.

More the Kb (dissociation constant of base), higher is the basicity of amines. Lesser the pKb‘ higher is the basicity of amines.

Aliphatic amines (CH_3NH_2) are stronger bases than NH_3 due to the electron releasing +/ effect of the alkyl group.

Among aliphatic methyl amines, the order of basic strength in aqueous solution is as follows

$$(C_2H_5NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$$

$$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$$

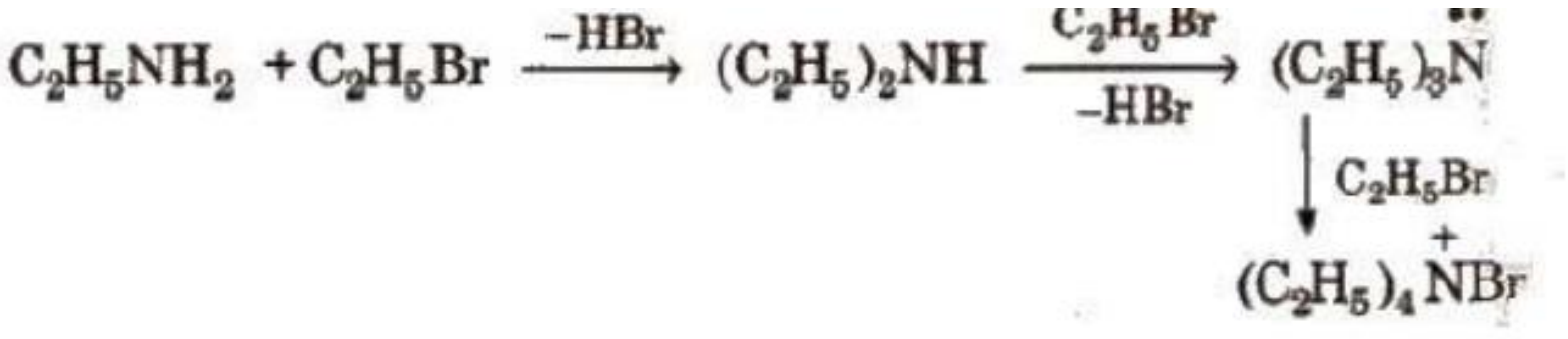
Basic Strength of Amines

Aromatic amines are weaker base than aliphatic amines and NH_3,due to the fact that the electron pair on the nitrogen atom is involved in resonance with the π-electron pairs of the ring.
Electron releasing groups (e.g.,$-CH_3$,$-OCH_3$,$-NH_2$ etc.) increase the basic strength of aromatic amines while electron withdrawing groups (like – NO_2, -X,-CN etc.) tend to decrease the same.
o-substituted aromatic amines are usually weaker base than aniline irrespective of the nature of substituent whether electron releasing or electron withdrawing. This is called ortho effect and is probably due to Sterk and electronic factors.

Reactions of Amines

(i) Alkylation

All the three types of amines react with alkyl halides to form quaternary ammonium salt as the final product provided alkyl halide is present in excess



$$C_2H_5NH_2 + C_2H_5Br \xrightarrow{-HBr} (C_2H_5)_2NH \xrightarrow[-HBr]{C_2H_5Br} (C_2H_5)_3\ddot{N}$$

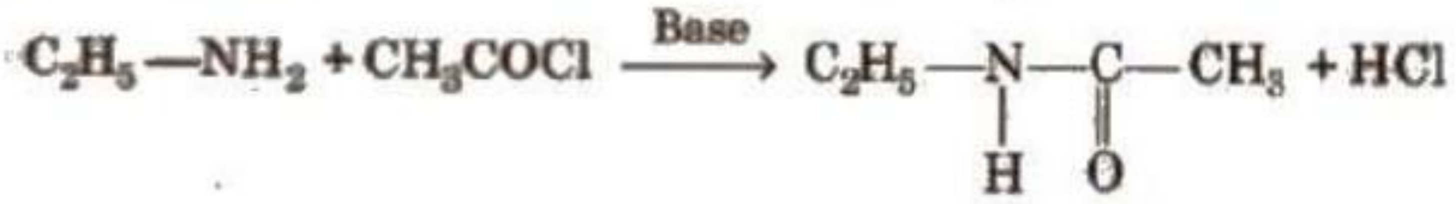
$$\downarrow C_2H_5Br$$

$$(C_2H_5)_4\overset{+}{N}Br$$

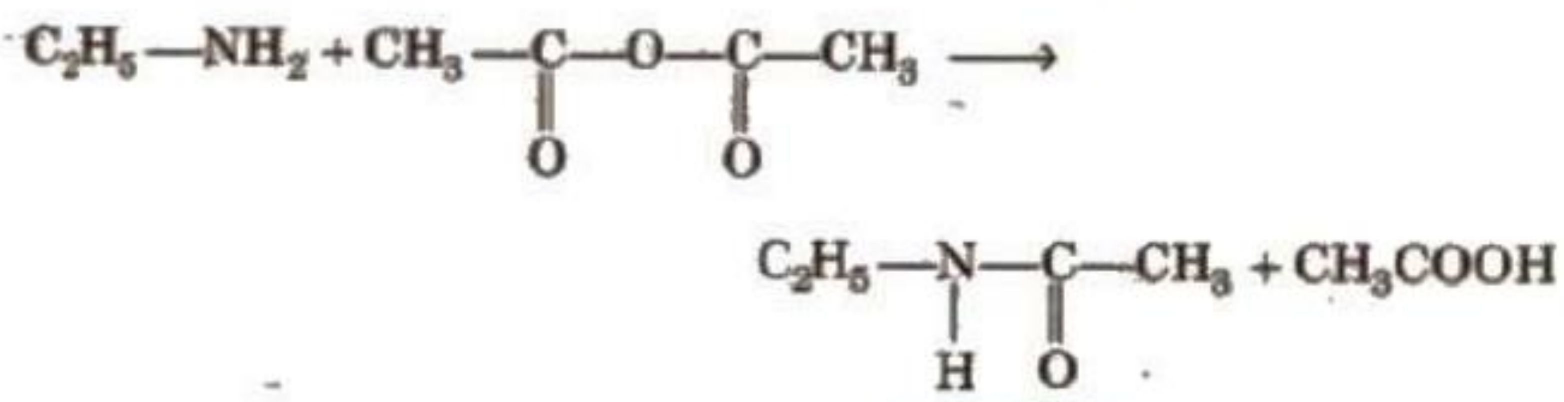
Aromatic amines also undergo alkylation as given below.

Reactions of Amines

(ii) Acylation



$$C_2H_5-NH_2 + CH_3COCl \xrightarrow{\text{Base}} C_2H_5-\underset{H}{\underset{|}{N}}-\underset{O}{\underset{\|}{C}}-CH_3 + HCl$$



$$C_2H_5-NH_2 + CH_3-\underset{O}{\underset{\|}{C}}-O-\underset{O}{\underset{\|}{C}}-CH_3 \longrightarrow C_2H_5-\underset{H}{\underset{|}{N}}-\underset{O}{\underset{\|}{C}}-CH_3 + CH_3COOH$$

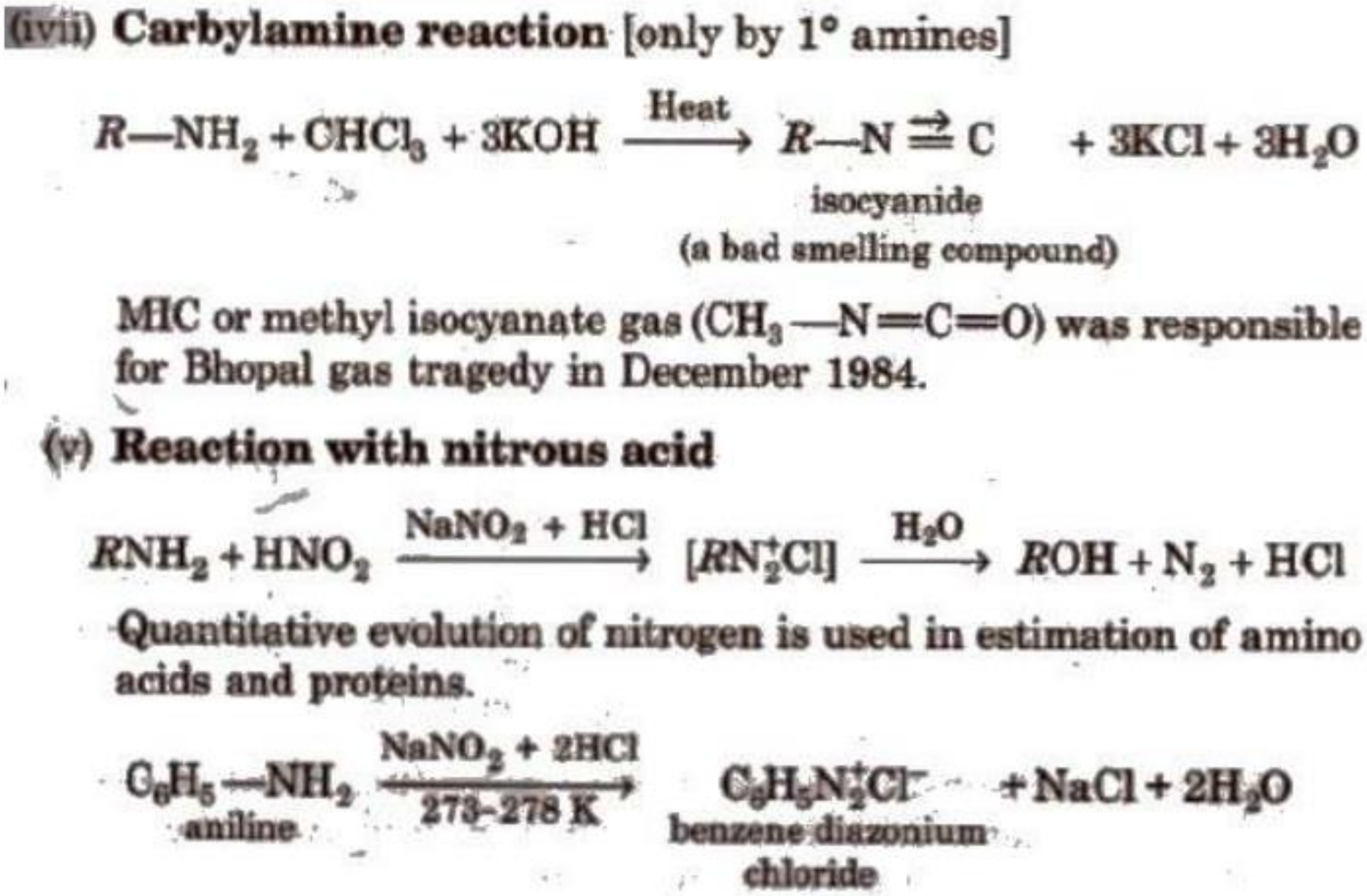
acetanilide

(iii) Benzoylation

$$CH_3NH_2 + C_6H_5COCl \xrightarrow{\text{Pyridine}} CH_3NHCOC_6H_5 + HCl$$

Benzoylation of aniline is known as **Schotten Baumann reaction.**

Reactions of Amines



(ivii) Carbylamine reaction [only by 1° amines]

$$R{-}NH_2 + CHCl_3 + 3KOH \xrightarrow{\text{Heat}} \underset{\substack{\text{isocyanide} \\ \text{(a bad smelling compound)}}}{R{-}N \overset{\rightarrow}{=} C} + 3KCl + 3H_2O$$

MIC or methyl isocyanate gas ($CH_3{-}N{=}C{=}O$) was responsible for Bhopal gas tragedy in December 1984.

(v) Reaction with nitrous acid

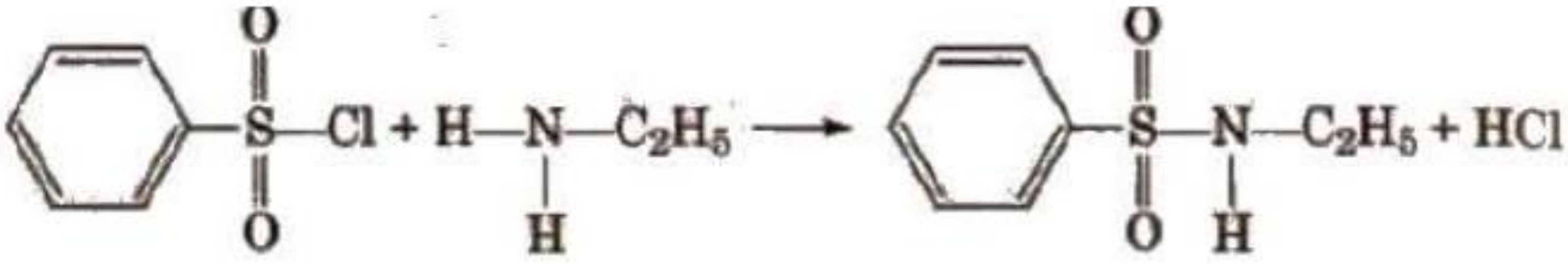
$$RNH_2 + HNO_2 \xrightarrow{NaNO_2 + HCl} [RN_2^+Cl] \xrightarrow{H_2O} ROH + N_2 + HCl$$

Quantitative evolution of nitrogen is used in estimation of amino acids and proteins.

$$\underset{\text{aniline}}{C_6H_5{-}NH_2} \xrightarrow[273\text{–}278\ K]{NaNO_2 + 2HCl} \underset{\substack{\text{benzene diazonium} \\ \text{chloride}}}{C_6H_5N_2^+Cl^-} + NaCl + 2H_2O$$

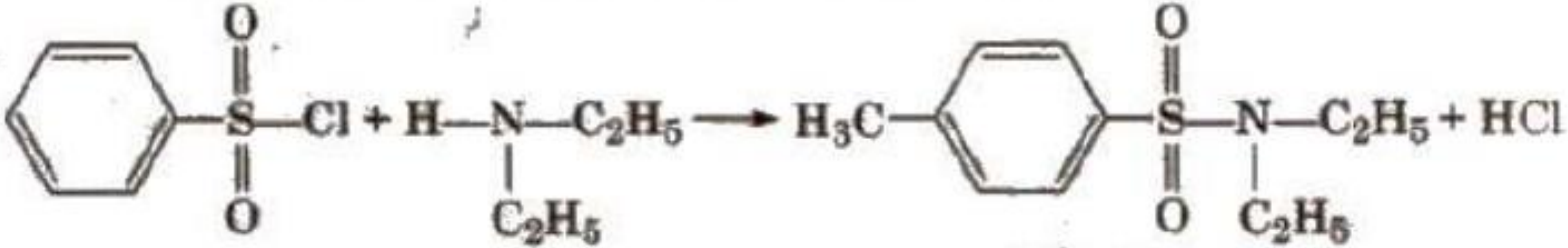
Reactions of Amines

(vi) Reaction with aryl sulphonyl chloride [Hinsberg reagent] The reaction of benzenesulphonyl chloride with primary amine yield N-ethyl benzenesulphonyl amide.



(soluble in alkali)

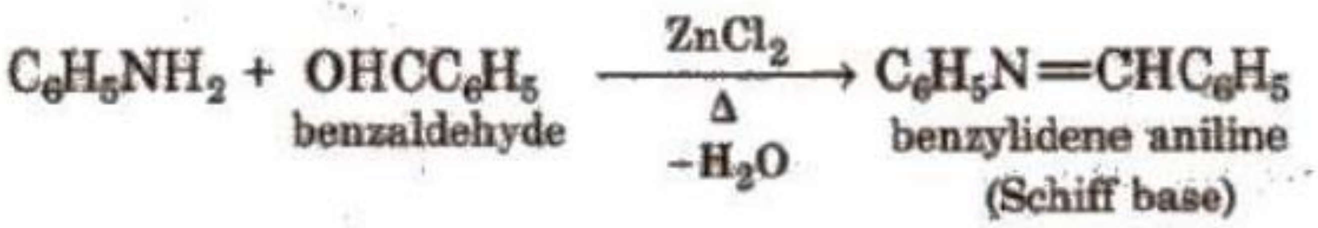
The reaction of benzenesulphonyl chloride with secondary amine yields N,N-diethyl benzene sulphonamide.



(insoluble in alkali)

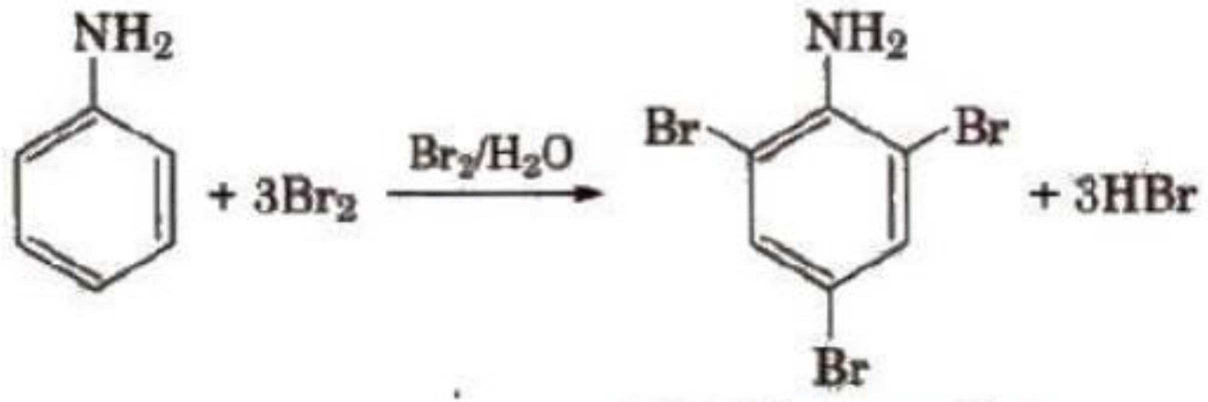
Reactions of Amines

(vii) Reaction with aldehydes Schiff base is obtained.



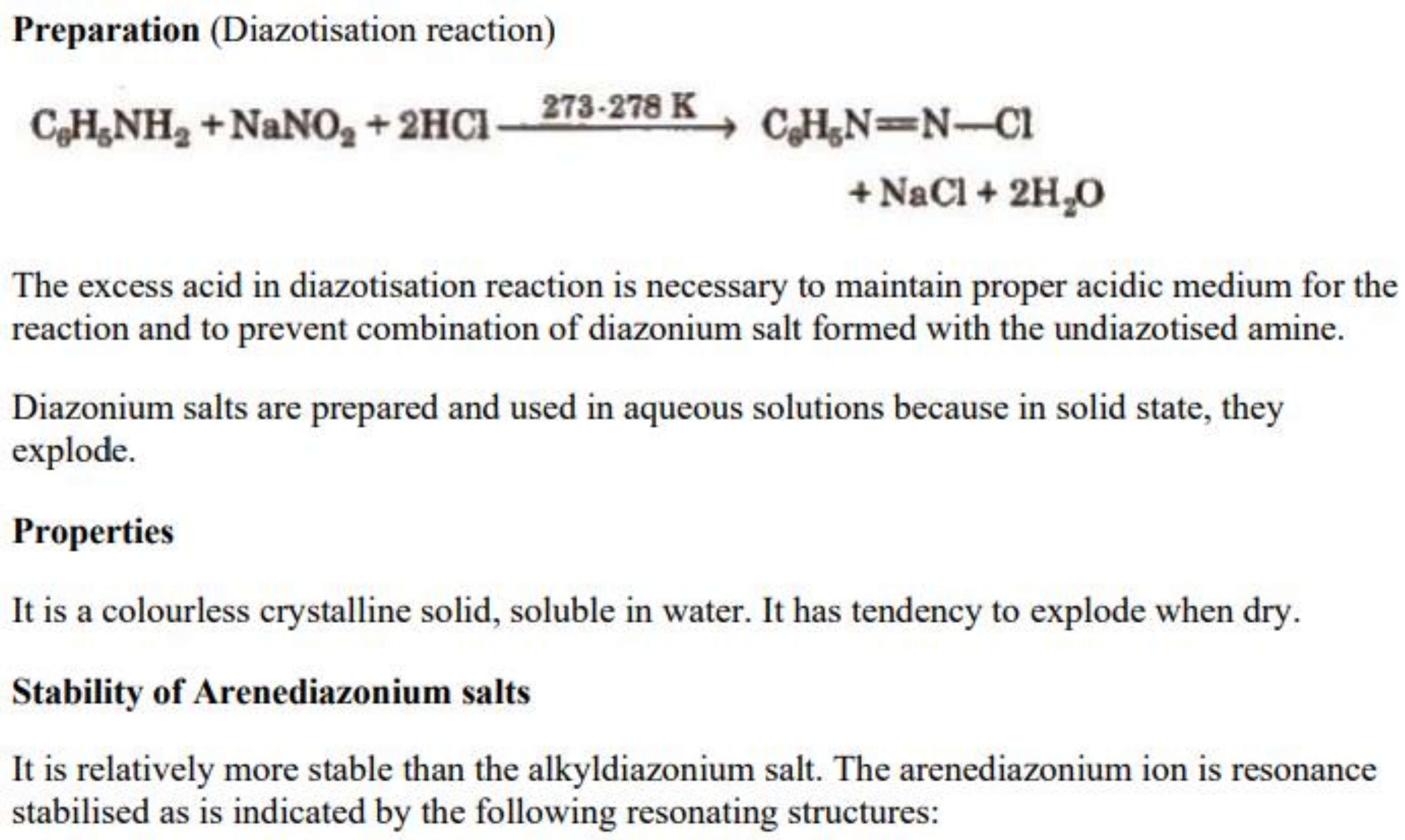
$$\underset{\text{}}{C_6H_5NH_2} + \underset{\text{benzaldehyde}}{OHCC_6H_5} \xrightarrow[\Delta \; -H_2O]{ZnCl_2} \underset{\substack{\text{benzylidene aniline} \\ \text{(Schiff base)}}}{C_6H_5N{=}CHC_6H_5}$$

(viii) Electrophihc substitution reactions Aniline is ortho and para directing towards electrophilic substitution reaction due to high electron density at ortho and para-positions.



2,4,6-tribromoaniline
(light yellow ppt)

Benzene Diazonium Chloride



Preparation (Diazotisation reaction)

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273\text{-}278\ K} C_6H_5N{=}N{-}Cl + NaCl + 2H_2O$$

The excess acid in diazotisation reaction is necessary to maintain proper acidic medium for the reaction and to prevent combination of diazonium salt formed with the undiazotised amine.

Diazonium salts are prepared and used in aqueous solutions because in solid state, they explode.

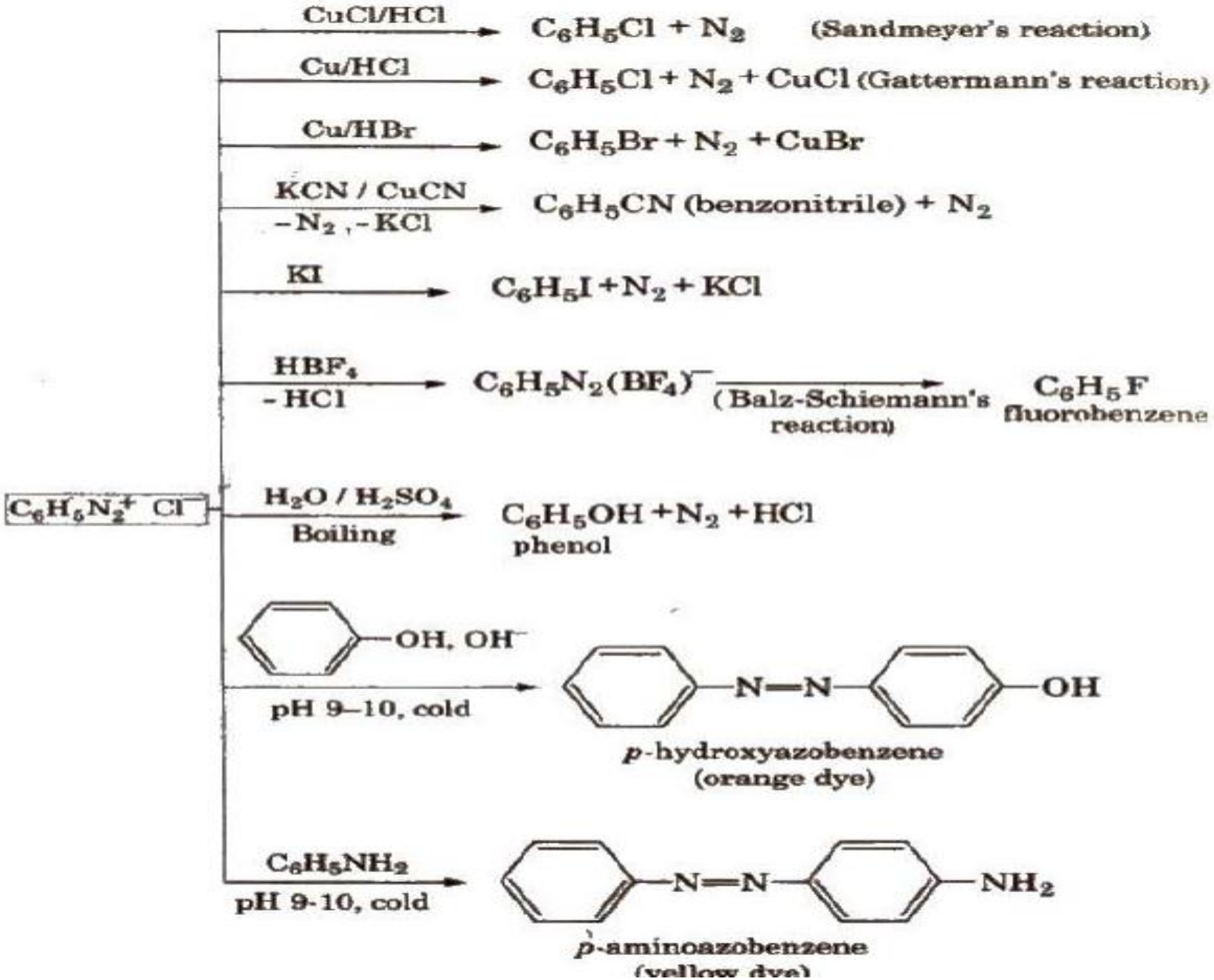
Properties

It is a colourless crystalline solid, soluble in water. It has tendency to explode when dry.

Stability of Arenediazonium salts

It is relatively more stable than the alkyldiazonium salt. The arenediazonium ion is resonance stabilised as is indicated by the following resonating structures:

Benzene Diazonium Chloride



$C_6H_5N_2^+Cl^- \xrightarrow{CuCl/HCl} C_6H_5Cl + N_2$ (Sandmeyer's reaction)

$C_6H_5N_2^+Cl^- \xrightarrow{Cu/HCl} C_6H_5Cl + N_2 + CuCl$ (Gattermann's reaction)

$C_6H_5N_2^+Cl^- \xrightarrow{Cu/HBr} C_6H_5Br + N_2 + CuBr$

$C_6H_5N_2^+Cl^- \xrightarrow[-N_2,\ -KCl]{KCN\ /\ CuCN} C_6H_5CN$ (benzonitrile) $+ N_2$

$C_6H_5N_2^+Cl^- \xrightarrow{KI} C_6H_5I + N_2 + KCl$

$C_6H_5N_2^+Cl^- \xrightarrow[-HCl]{HBF_4} C_6H_5N_2(BF_4)^- \xrightarrow[\text{(Balz-Schiemann's reaction)}]{} C_6H_5F$ fluorobenzene

$C_6H_5N_2^+Cl^- \xrightarrow[\text{Boiling}]{H_2O\ /\ H_2SO_4} C_6H_5OH + N_2 + HCl$ phenol

Organic Chemistry

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Carboxylic Acid Derivatives

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?**

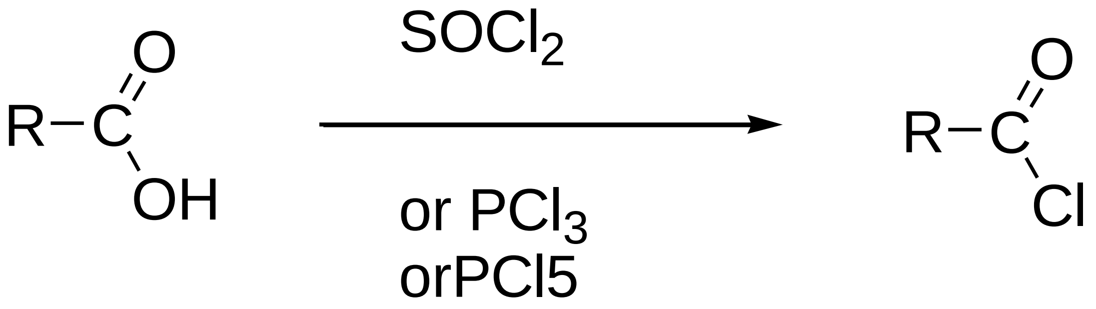
$CH_4 < NH_3 < HC{\equiv}CH < ROH < HOH < H_2CO_3 < \mathbf{RCO_2H} < HF$

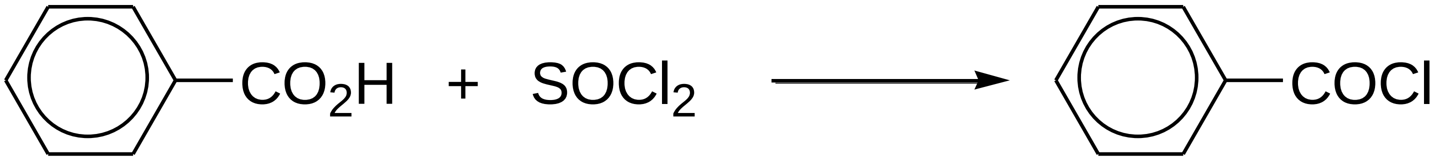
d) **quantitative**

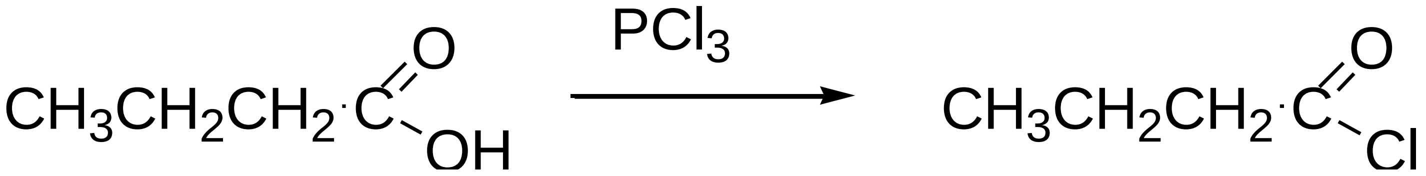
$HA + H_2O \leftrightarrows H_3O^+ + A^-$ ionization in water

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

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

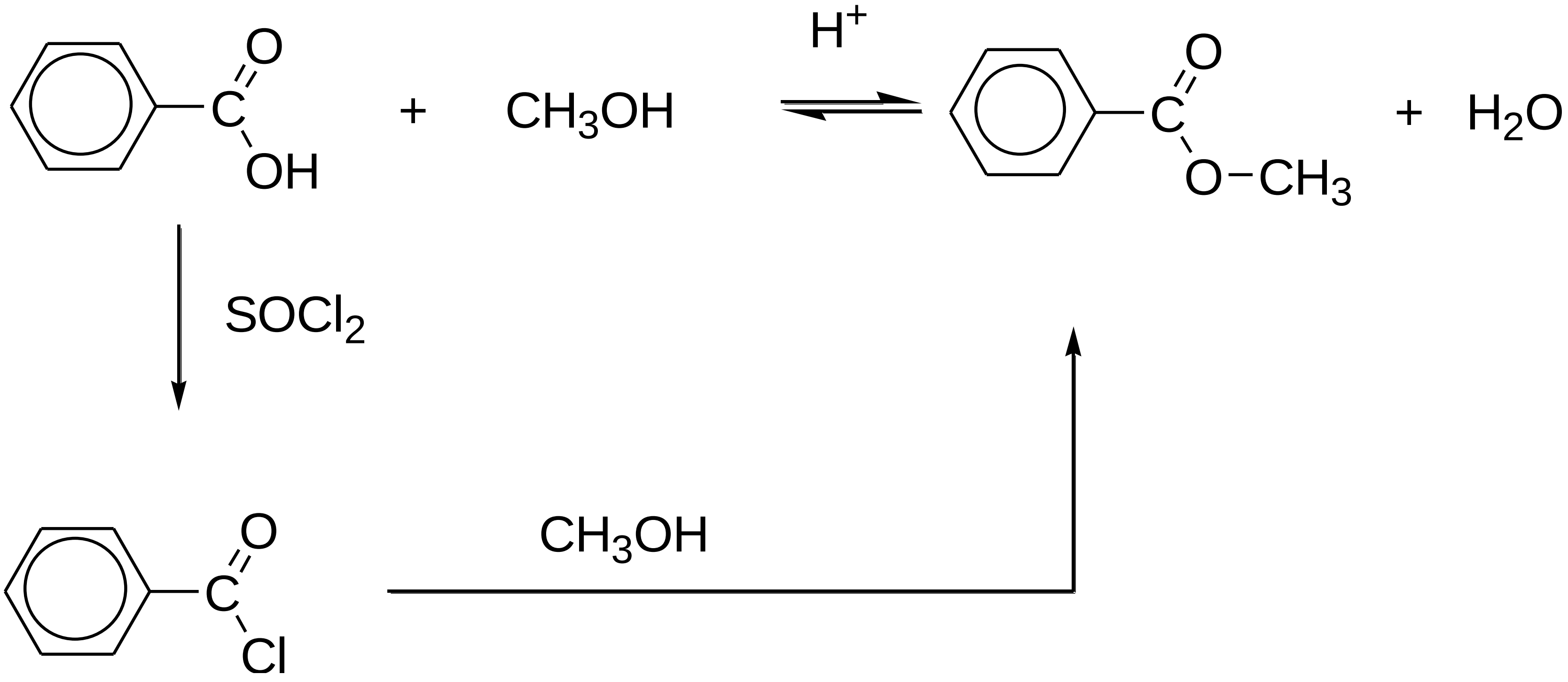
-use an excess of the alcohol or acid to shift equilibrium

-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

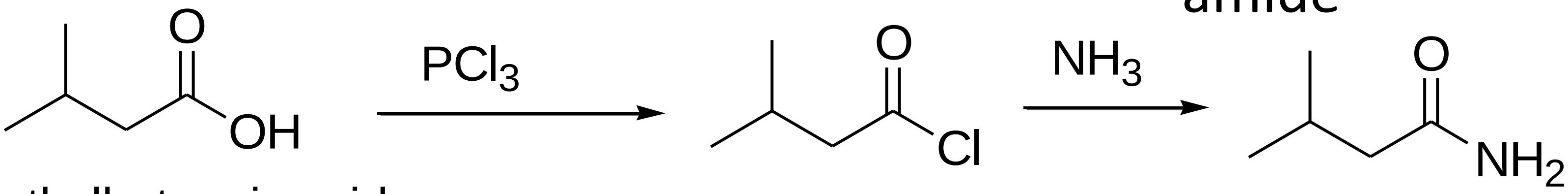

O
C
OH
+
CH3OH
H+
O
C
O–CH3
+
H2O
SOCl2
O
C
Cl
CH3OH

4) Formation of amides:

“indirect” only.

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

amide

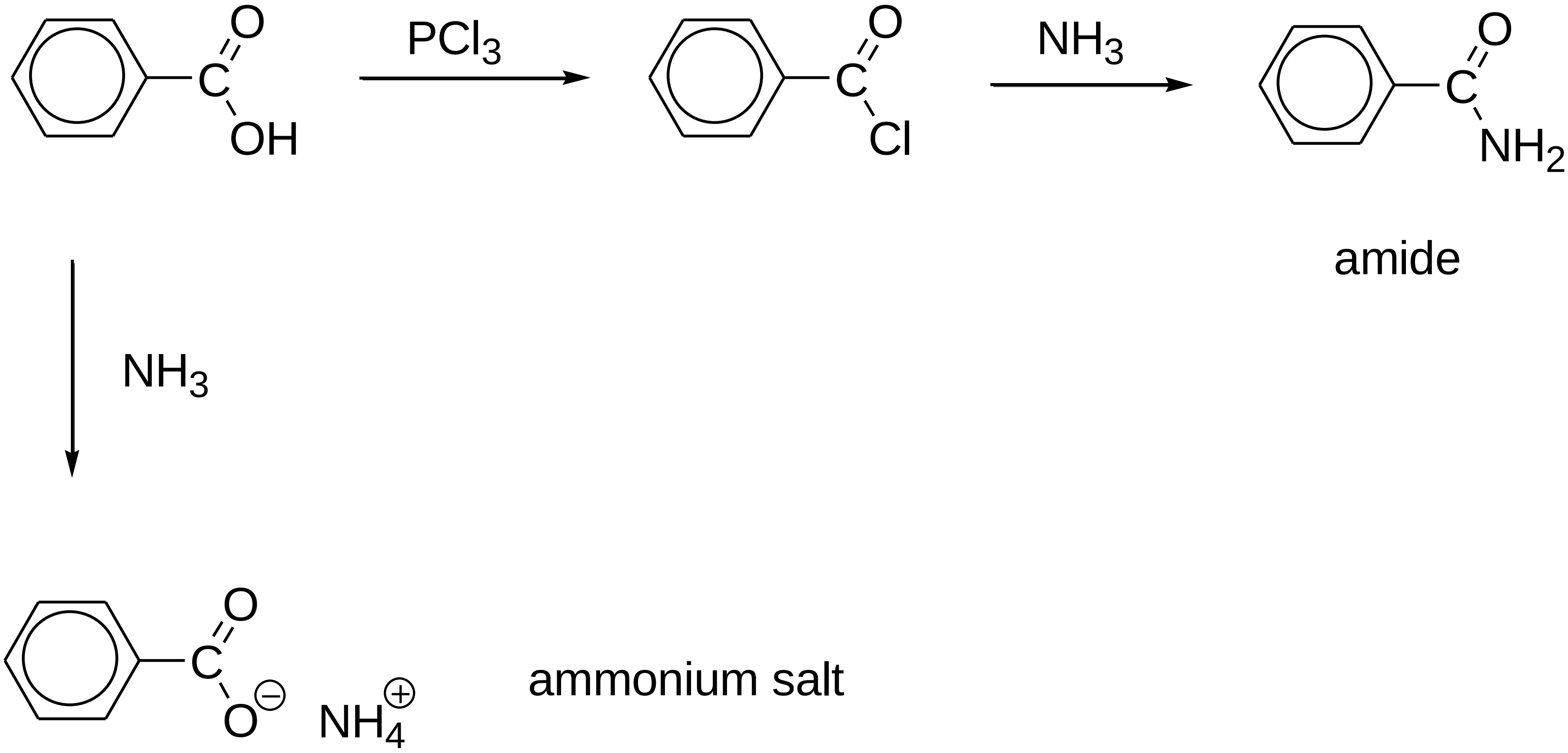


3-Methylbutanoic acid

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

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

acid base


O
C
OH
PCl3
O
C
Cl
NH3
O
C
NH2
amide
NH3
O
C
O
NH4
ammonium salt

5) Reduction:

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

1° alcohol

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

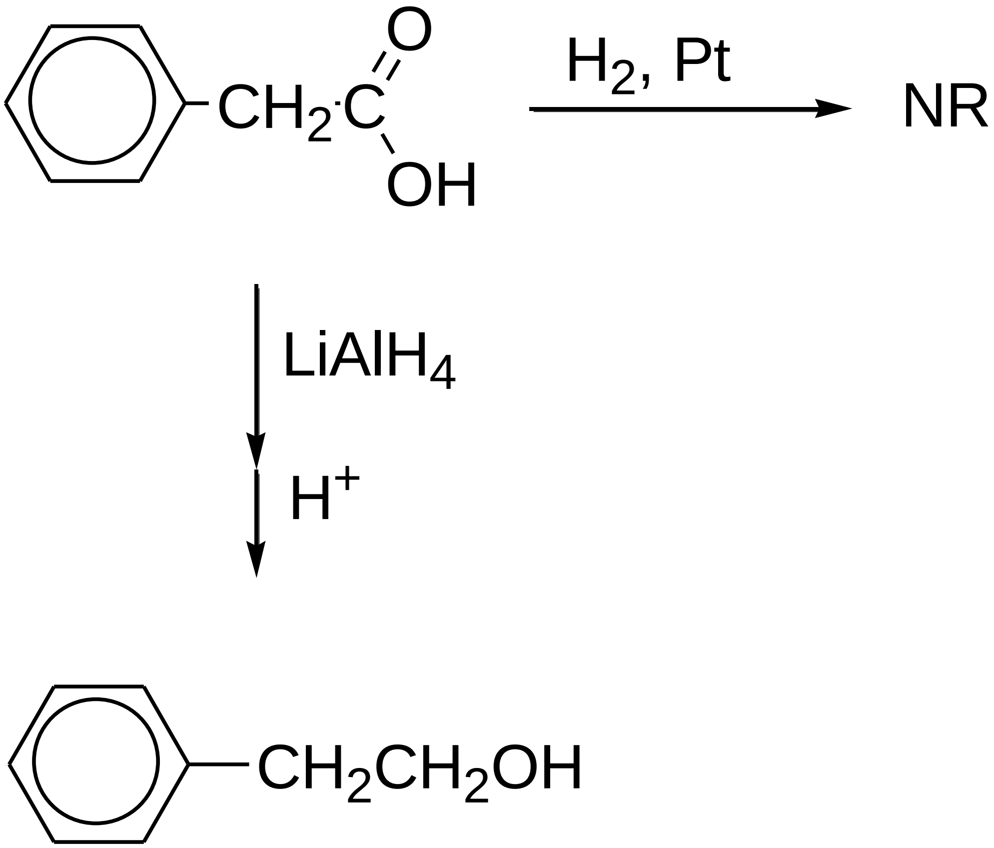
Octanoic acid
(Caprylic acid)

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2OH$$

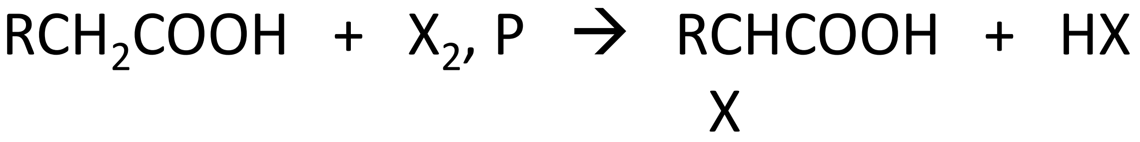
1-Octanol

Carboxylic acids resist catalytic reduction under normal conditions.

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


CH2C
O
OH
H2, Pt
NR
LiAlH4
H+
CH2CH2OH

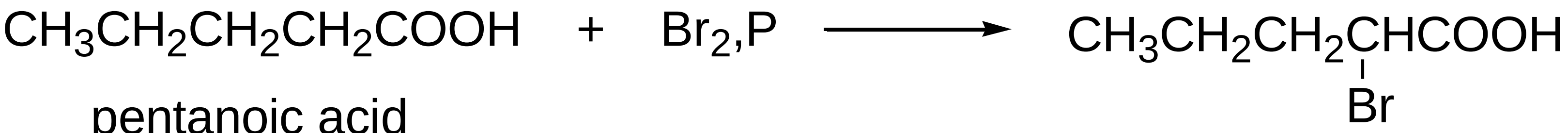
6) Halogenation of alkyl groups (Hell-Volhard-Zelinsky reaction):



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

α-haloacid

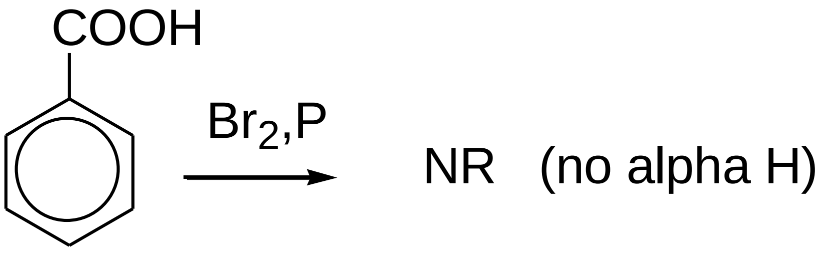
$X_2 = Cl_2, Br_2$



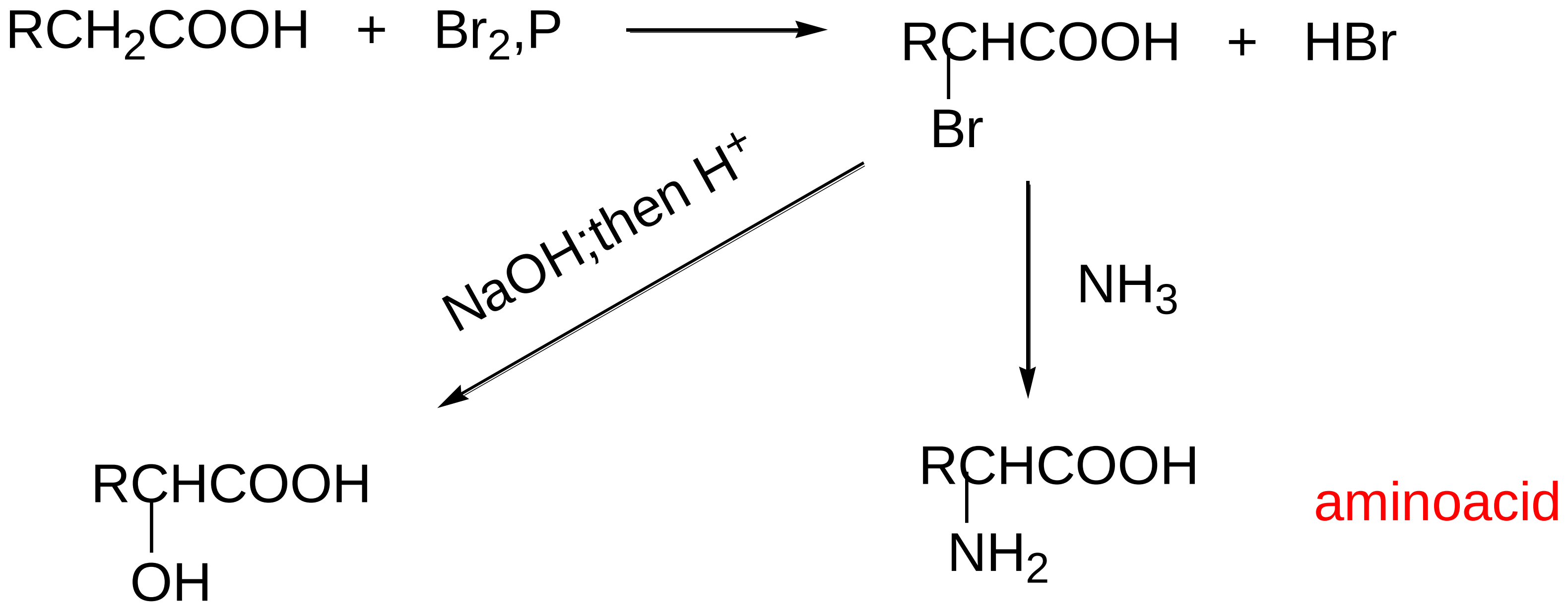
$$\mathrm{CH_3CH_2CH_2CH_2COOH} + \mathrm{Br_2,P} \longrightarrow \mathrm{CH_3CH_2CH_2}\underset{\mathrm{Br}}{\mathrm{C}}\mathrm{HCOOH}$$

pentanoic acid

2-bromopentanoic acid



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

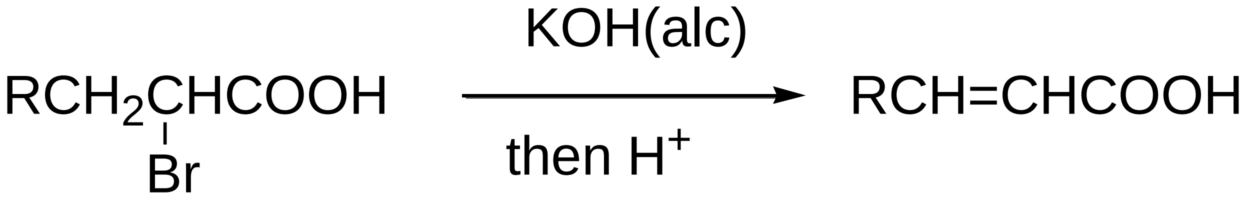


$$RCH_2COOH + Br_2,P \longrightarrow R\underset{Br}{C}HCOOH + HBr$$

$$R\underset{Br}{C}HCOOH \xrightarrow{NaOH;\text{then } H^+} R\underset{OH}{C}HCOOH$$

$$R\underset{Br}{C}HCOOH \xrightarrow{NH_3} R\underset{NH_2}{C}HCOOH$$

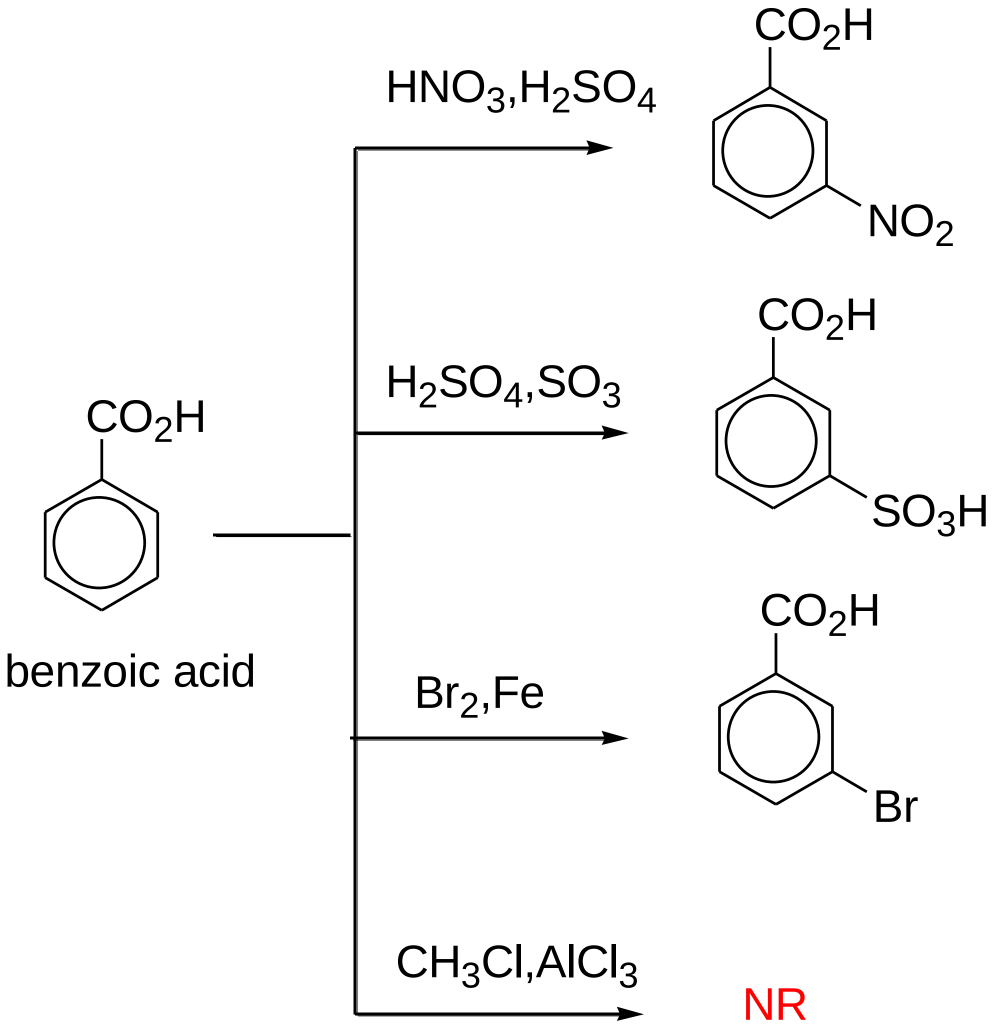
aminoacid



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

5) Aromatic Substitution:

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



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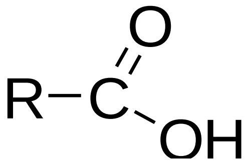
Carboxylic Acids

Carboxylic acids:

$R\text{-}COOH$, $R\text{-}CO_2H$,



$R-C(=O)OH$

Common names:

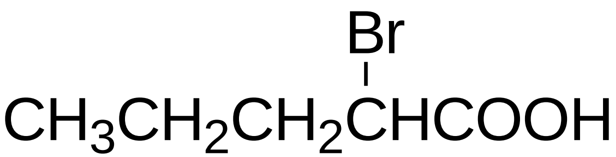
HCO_2H	formic acid
CH_3CO_2H	acetic acid
$CH_3CH_2CO_2H$	propionic acid
$CH_3CH_2CH_2CO_2H$	butyric acid
$CH_3CH_2CH_2CH_2CO_2H$	valeric acid

5 4 3 2 1

C—C—C—C—C=O

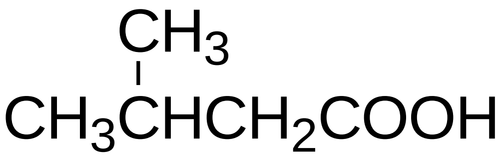
δ γ β α

used in common names



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

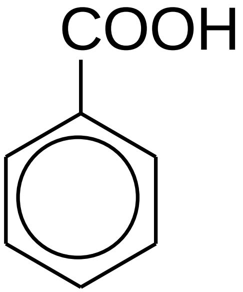
α– bromovaleric acid



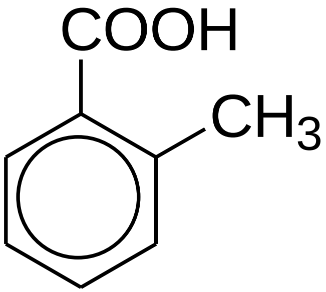
$$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2COOH$$

β-methylbutyric acid

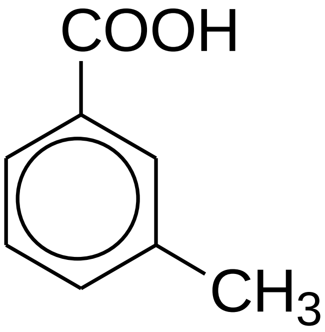
isovaleric acid



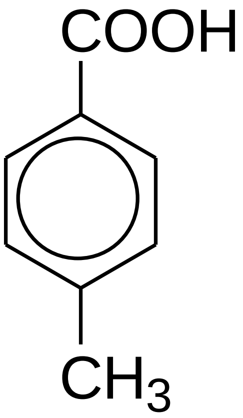
benzoic acid



o-toluic acid



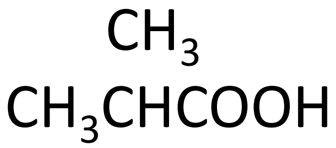
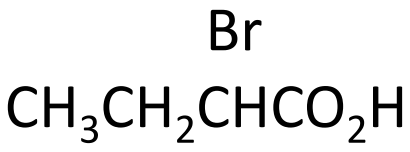
m-toluic acid



p-toluic acid

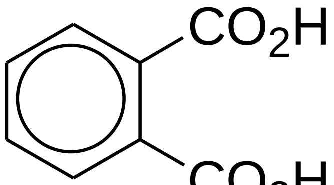
IUPAC nomenclature for carboxylic acids:

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

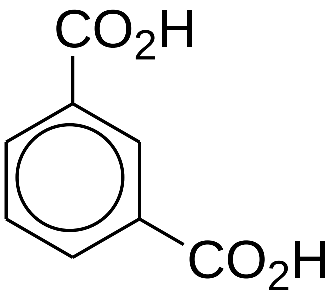
HCOOH	methanoic acid
CH_3CO_2H	ethanoic acid
$CH_3CH_2CO_2H$	propanoic acid
 $CH_3\overset{CH_3}{CH}COOH$	2-methylpropanoic acid
 $CH_3CH_2\overset{Br}{CH}CO_2H$	2-bromobutanoic acid

Dicarboxylic acids

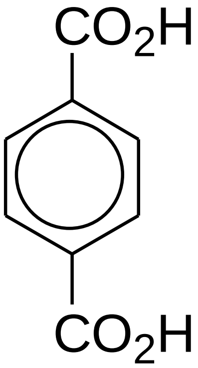
$HOOC\text{-}COOH$	oxalic acid
$HO_2C\text{-}CH_2\text{-}CO_2H$	malonic acid
$HO_2C\text{-}CH_2CH_2\text{-}CO_2H$	succinic acid
$HO_2C\text{-}CH_2CH_2CH_2\text{-}CO_2H$	glutaric acid
$HOOC\text{-}(CH_2)_4\text{-}COOH$	adipic acid
$HOOC\text{-}(CH_2)_5\text{-}COOH$	pimelic acid



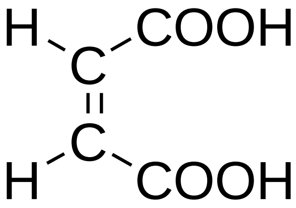
phthalic acid



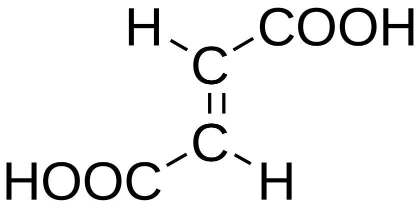
isophthalic acid



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

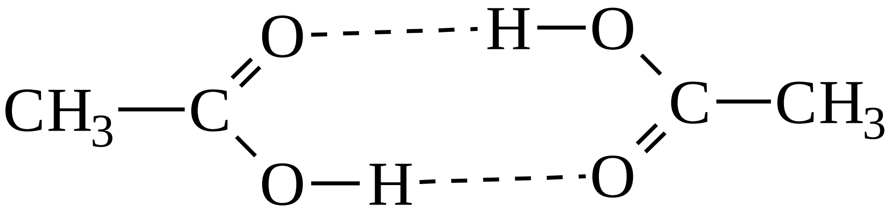
acidic turn blue litmus → red

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

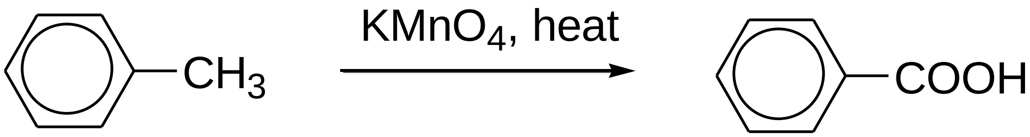
1-butanol butanoic acid

$$\overset{CH_3}{CH_3CHCH_2\text{-}OH} \quad + \quad KMnO_4 \quad \rightarrow \quad \overset{CH_3}{CH_3CHCOOH}$$

isobutyl alcohol isobutyric acid

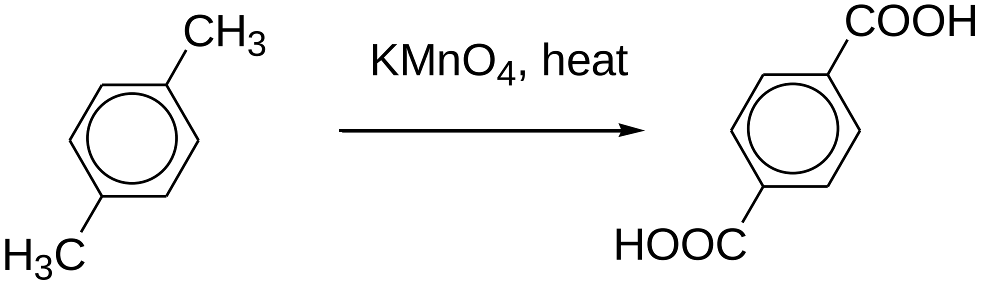
2-methyl-1-propanol` 2-methylpropanoic acid

2. Oxidation of alkylbenzenes:



toluene

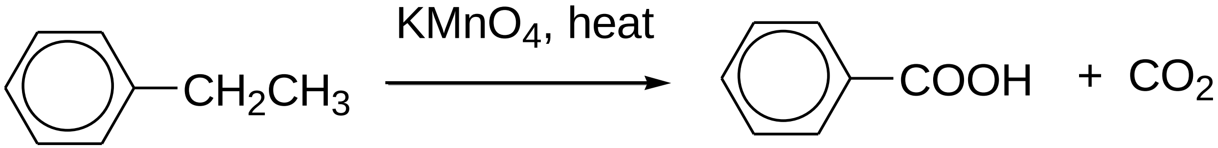
benzoic acid



p-xylene

terephthalic acid

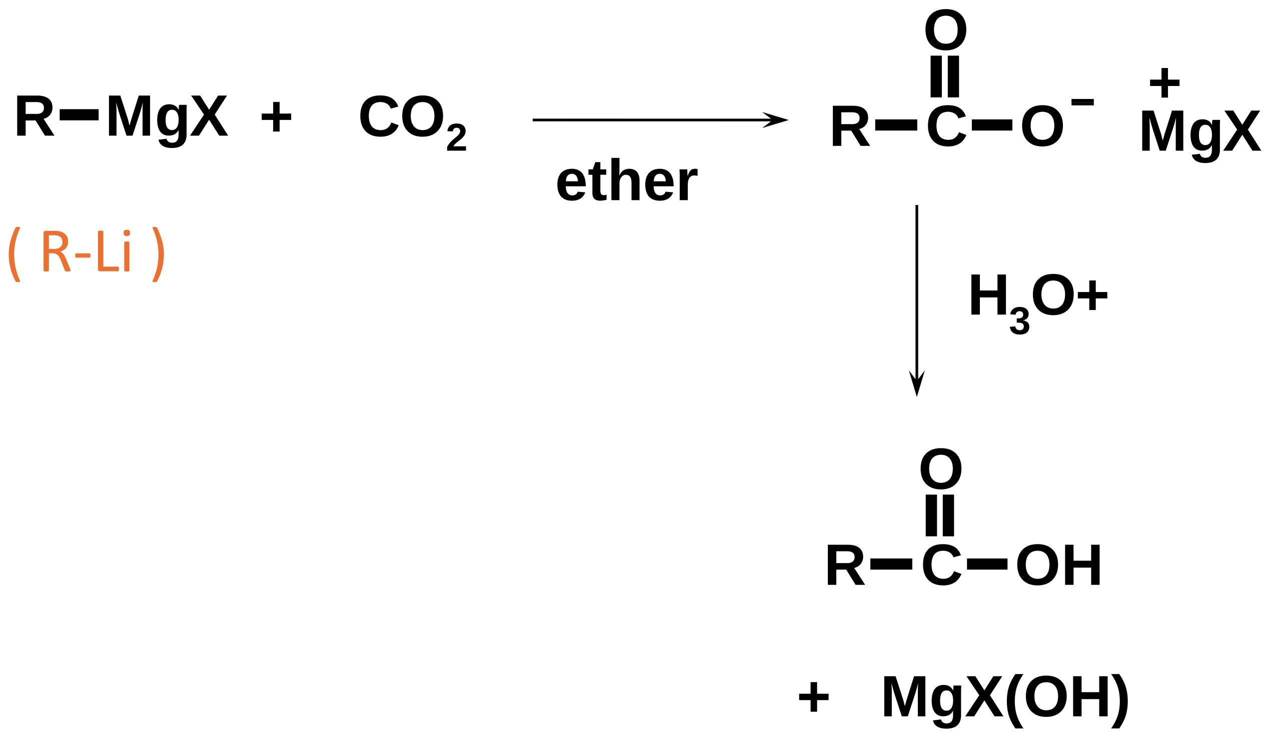
note: aromatic acids only!



ethylbenzene

benzoic acid

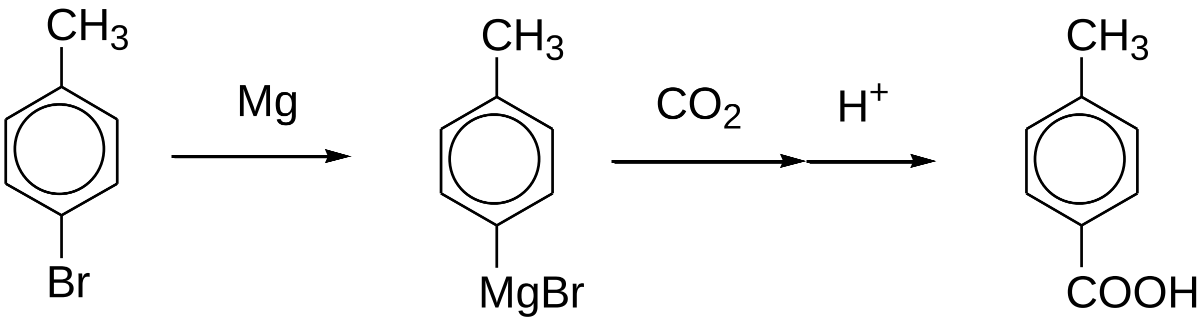
3. Carbonation of Grignard Reagents:



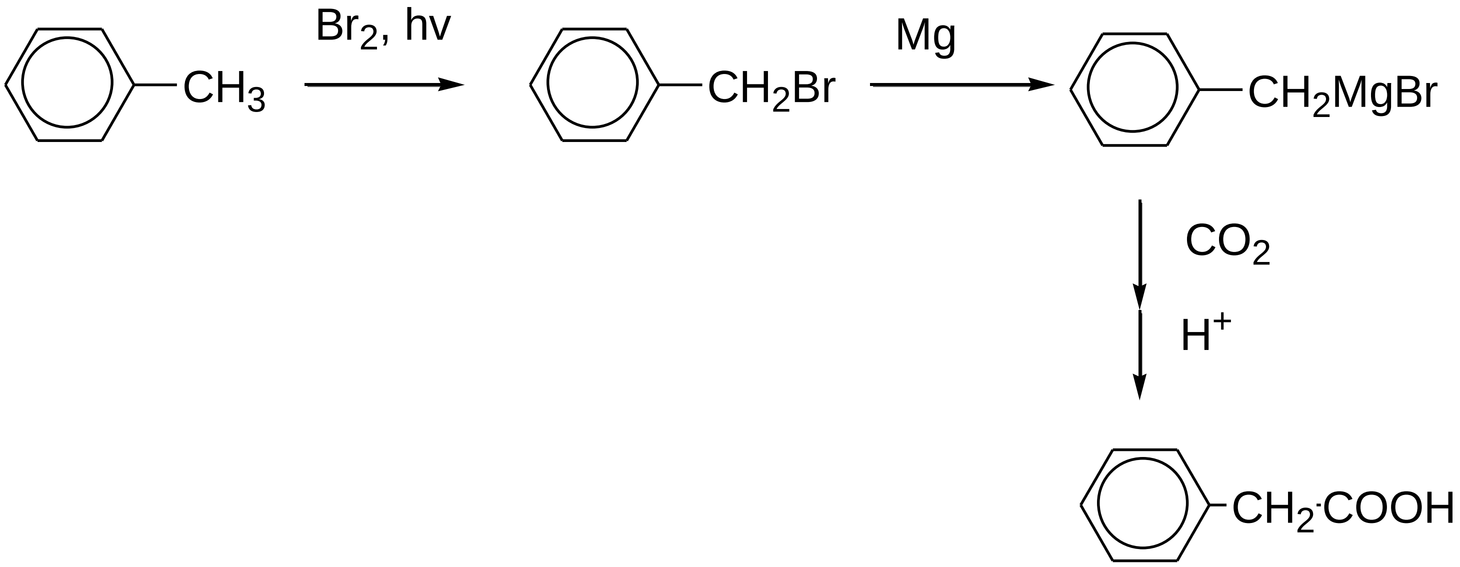
$$R{-}MgX + CO_2 \xrightarrow[\text{ether}]{} R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O^{-}\ \overset{+}{MgX}$$

(R-Li)

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

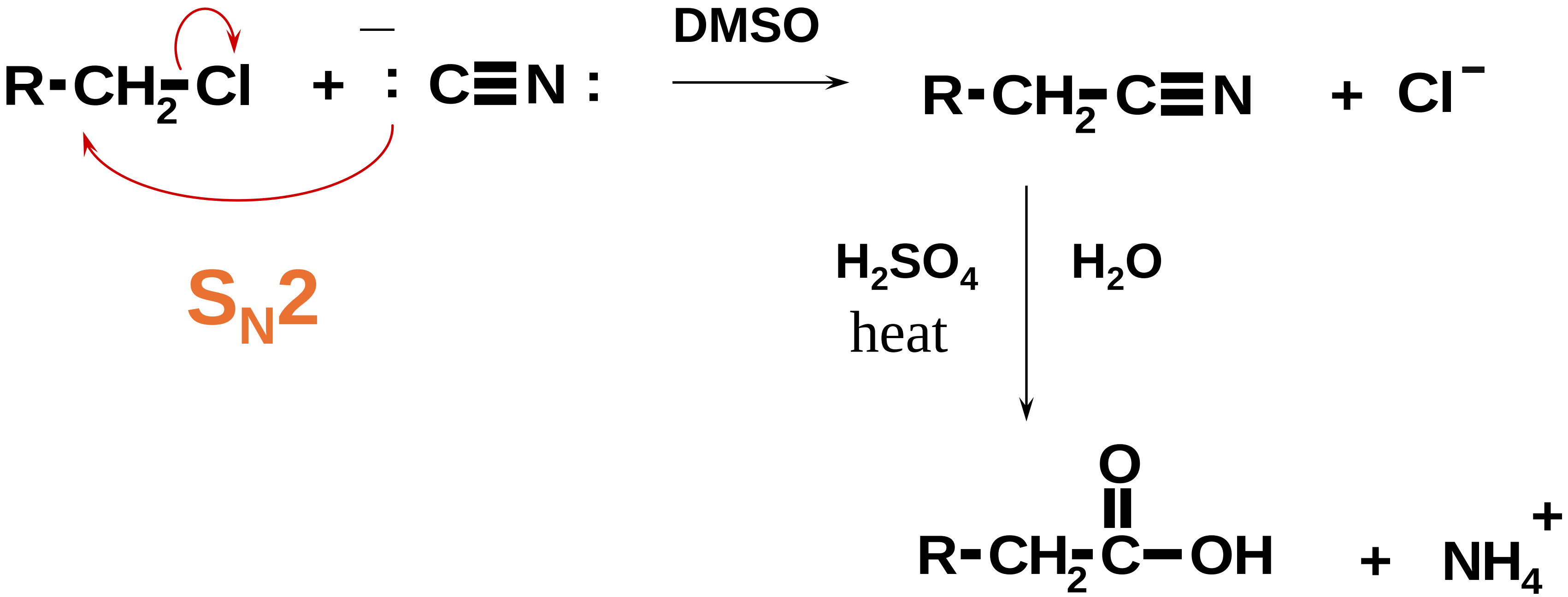


p-toluic acid



phenylacetic acid

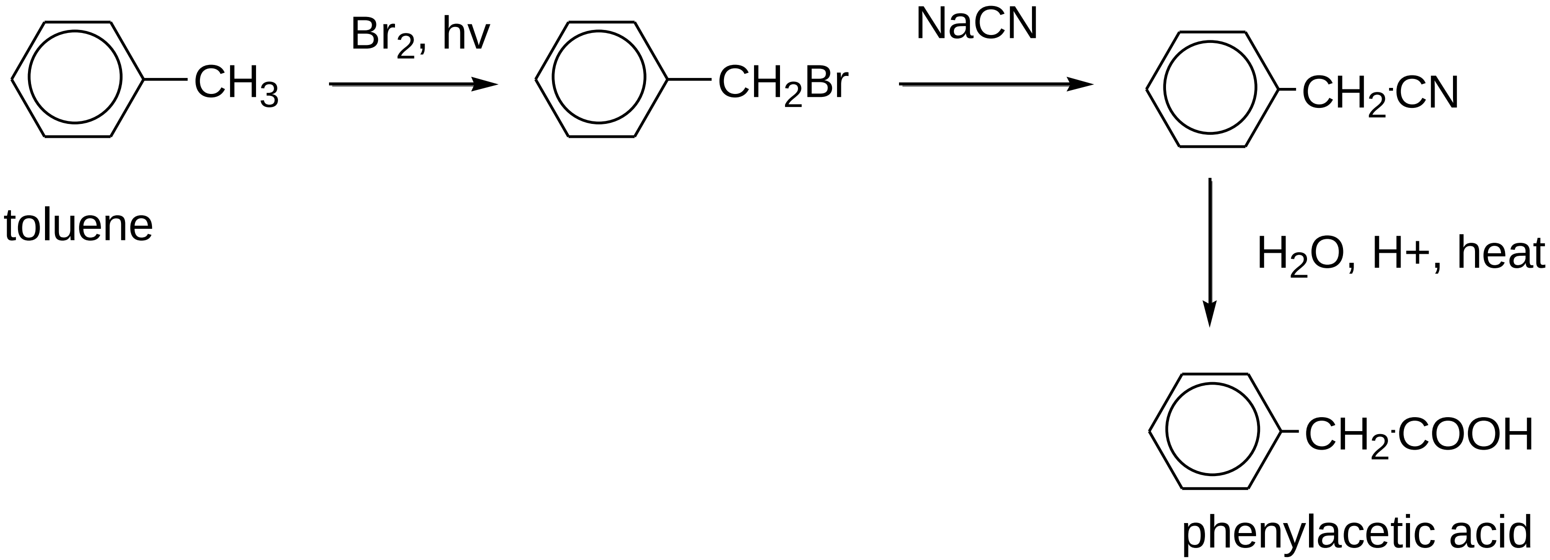
Hydrolysis of Nitriles



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

S_N2

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



toluene

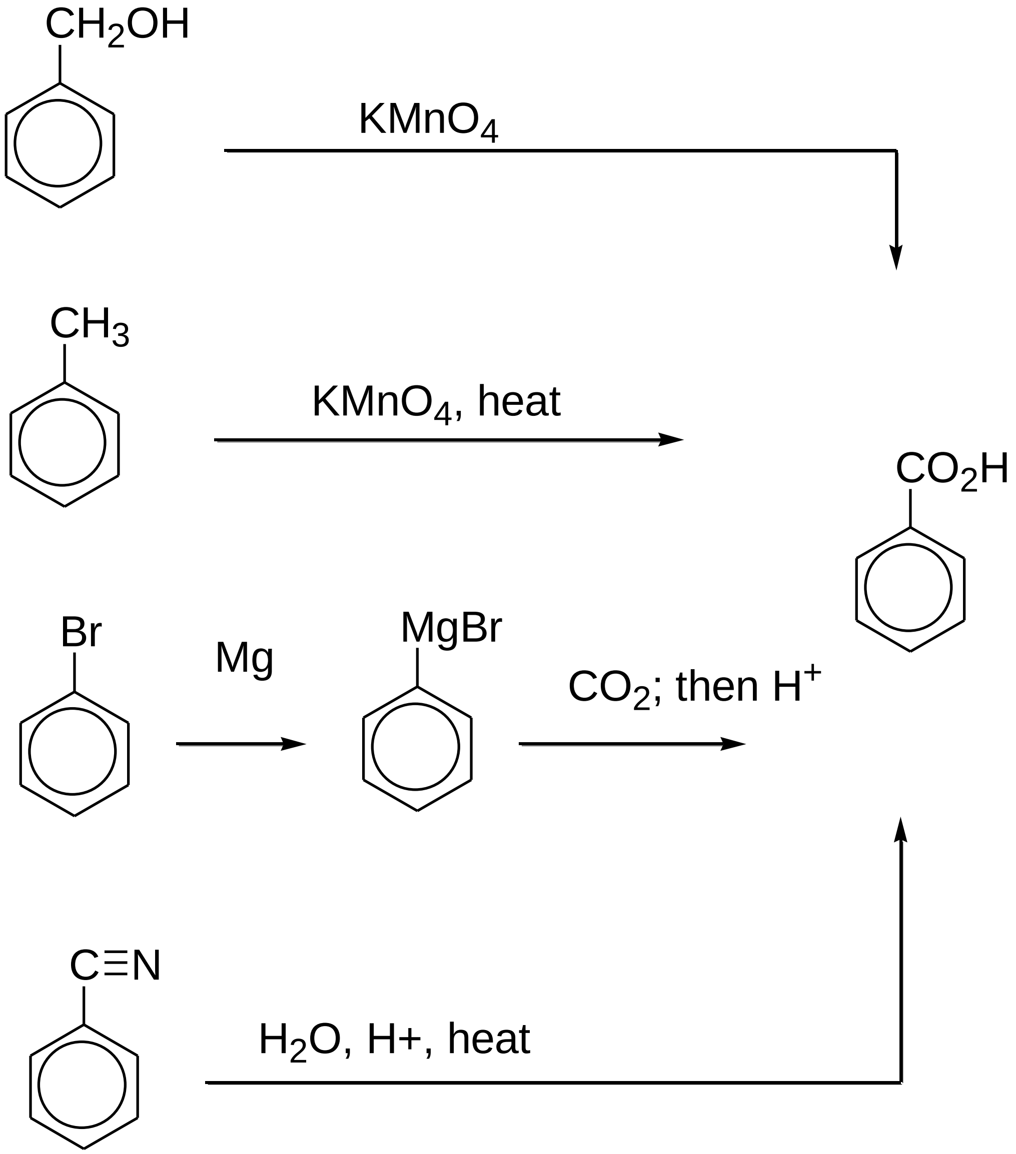
phenylacetic acid

$$\mathrm{CH_3CH_2CH_2CH_2CH_2CH_2\text{-}Br} \xrightarrow{\mathrm{KCN}} \mathrm{CH_3CH_2CH_2CH_2CH_2CH_2\text{-}CN}$$

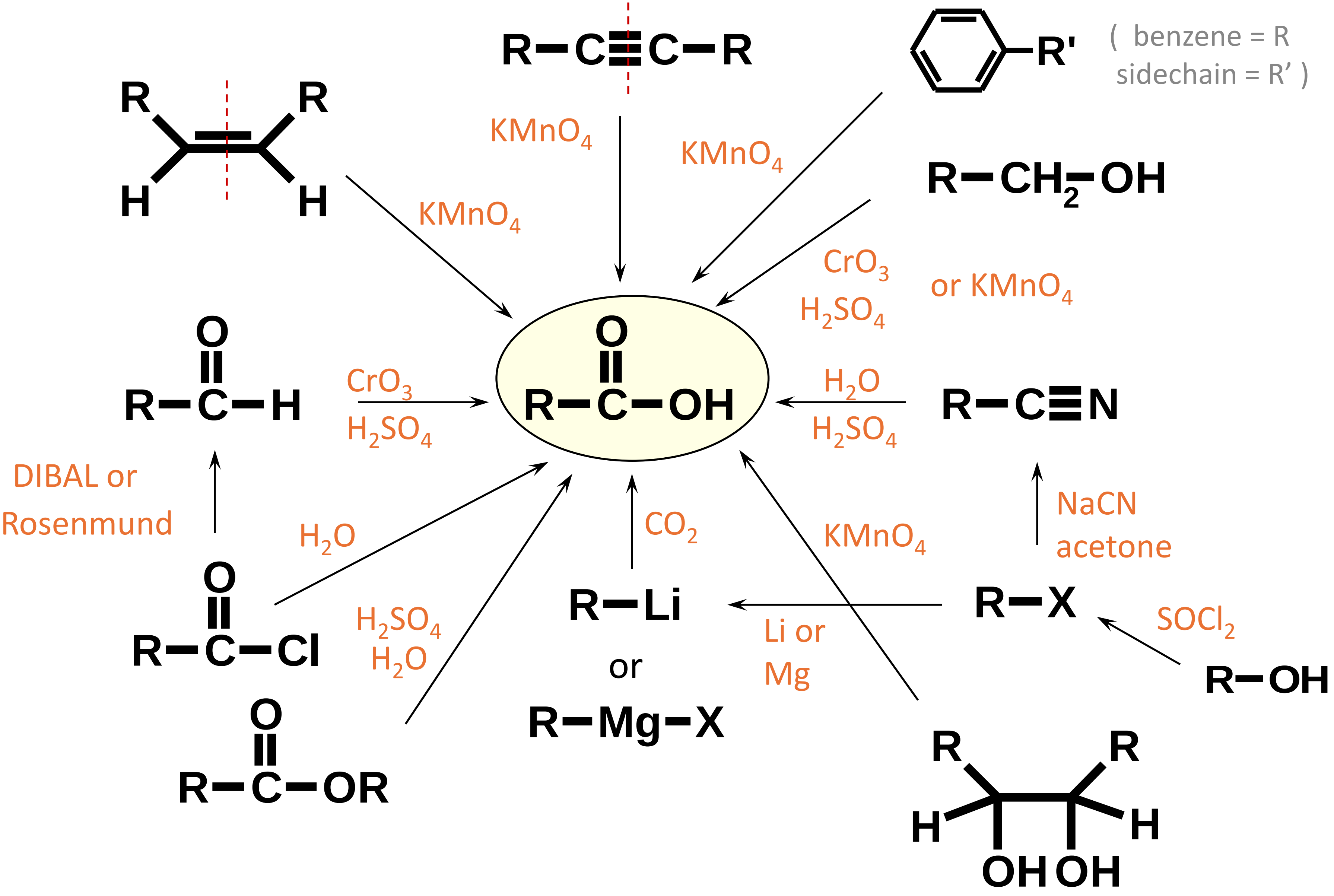
1-bromohexane

$$\xrightarrow{\mathrm{H_2O,\ H+,\ heat}} \mathrm{CH_3CH_2CH_2CH_2CH_2CH_2\text{-}COOH}$$

heptanoic acid


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

SYNTHESIS OF CARBOXYLIC ACIDS



$R-C\equiv C-R$

(benzene = R
sidechain = R')

$KMnO_4$

$KMnO_4$

$KMnO_4$

$R-CH_2-OH$

CrO_3
H_2SO_4

or $KMnO_4$

CrO_3
H_2SO_4

H_2O
H_2SO_4

$R-C\equiv N$

DIBAL or
Rosenmund

H_2O

H_2SO_4
H_2O

CO_2

$KMnO_4$

NaCN
acetone

$R-Li$
or
$R-Mg-X$

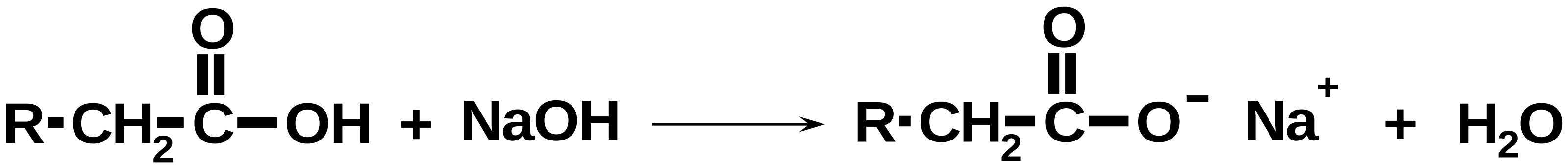
Li or
Mg

$R-X$

$SOCl_2$

$R-OH$

Carboxylate Ion Formation



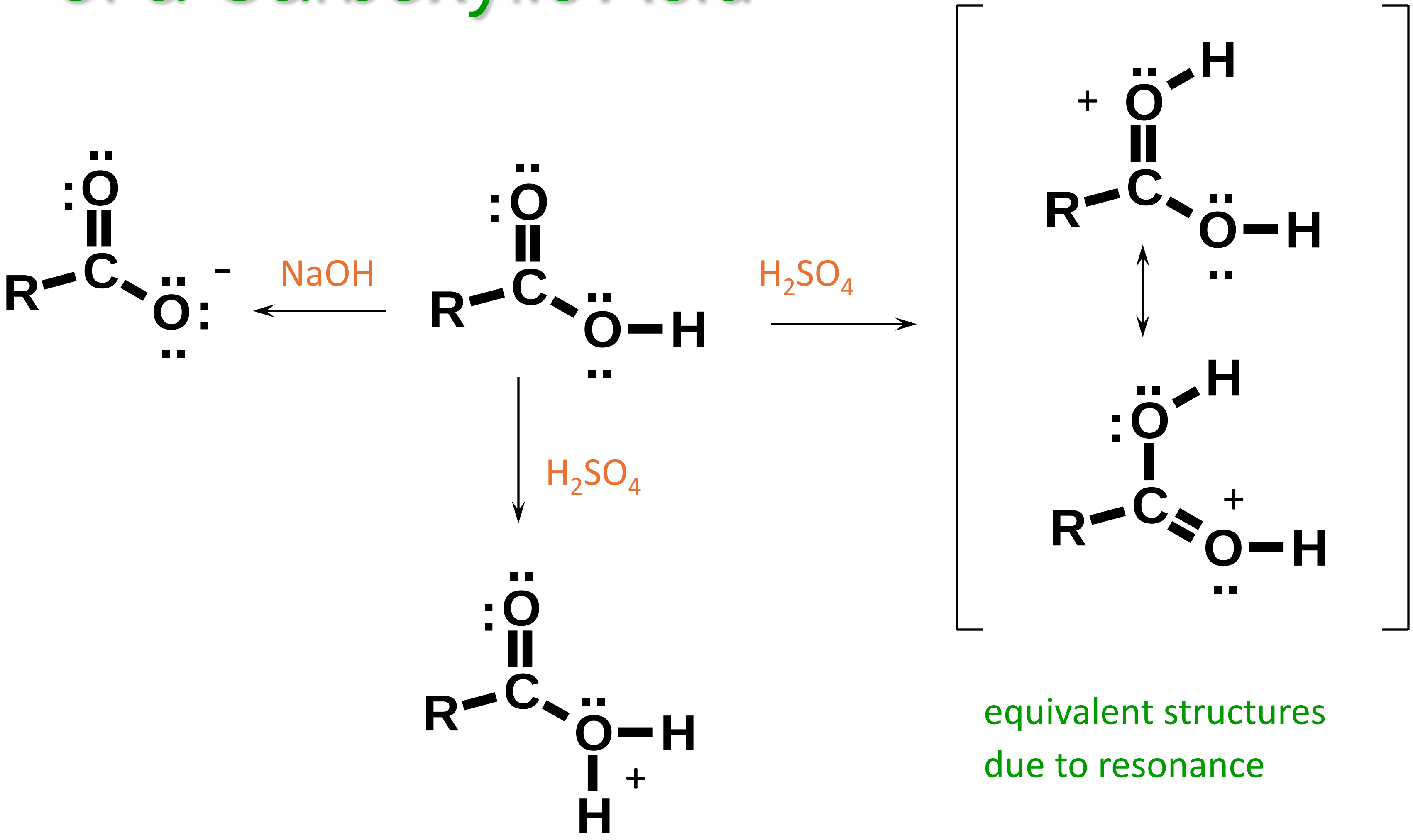
$$R-CH_2-\overset{O}{\overset{\|}{C}}-OH + NaOH \longrightarrow R-CH_2-\overset{O}{\overset{\|}{C}}-O^- \; Na^+ + H_2O$$

carboxylic acid

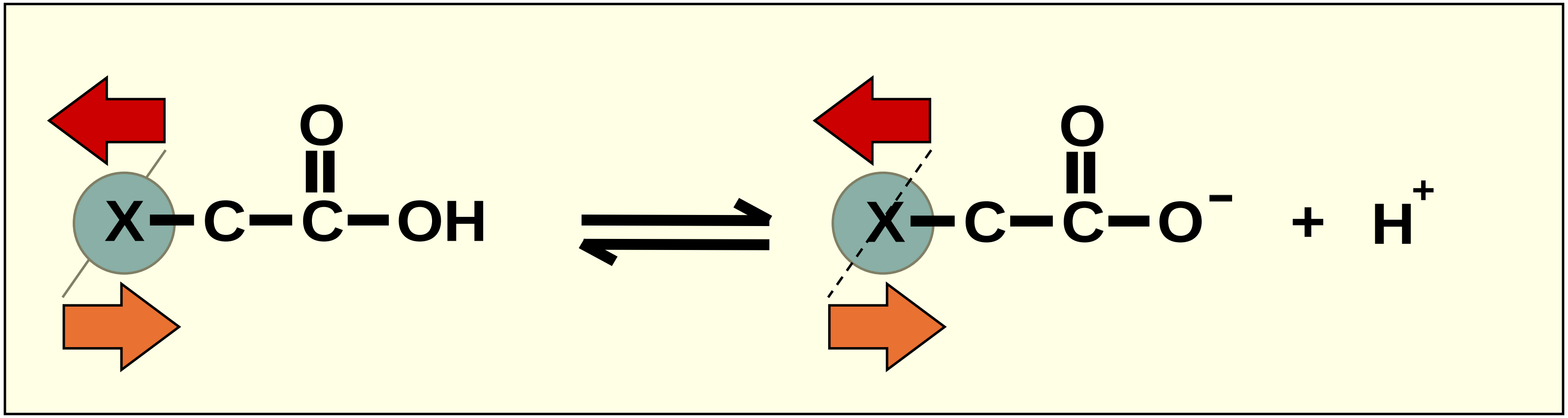
carboxylate ion

$pK_a \approx 5$

Protonation and Deprotonation of a Carboxylic Acid



equivalent structures
due to resonance

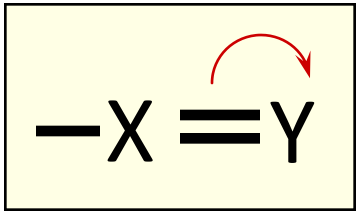


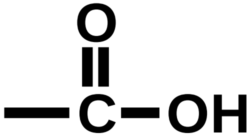
⬅

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

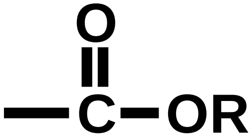
➡

Substituents with Electron-Withdrawing Resonance (- R) Effects

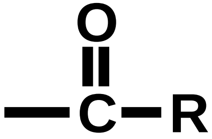



$-\overset{\overset{O}{\|}}{C}-OH$

carboxyl


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

alkoxycarbonyl


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

acyl

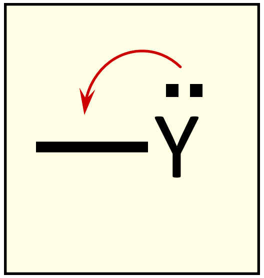
$-NO_2$ **nitro**

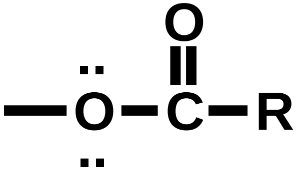
$-C\equiv N$ **cyano**

$-SO_3H$ **sulfo**

-R substituents strengthen acids and weaken bases

Substituents with Electron-Releasing Resonance (+ R) Effects

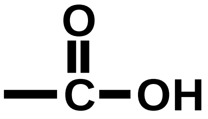
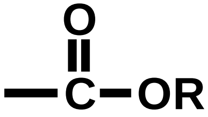
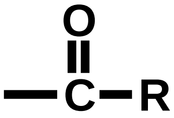


$-\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}\mathrm{H}$	hydroxy	$-\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}\mathrm{R}$	alkoxy
$-\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{S}}}\mathrm{H}$	mercapto	 $-\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}-\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}-\mathrm{R}$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

+R substituents weaken acids and strengthen bases

Substituents with Electron-Withdrawing (- I) Inductive Effects

$\rightarrow X$

 $-\overset{O}{\overset{\Vert}{C}}-OH$	carboxyl
 $-\overset{O}{\overset{\Vert}{C}}-OR$	alkoxycarbonyl
 $-\overset{O}{\overset{\Vert}{C}}-R$	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

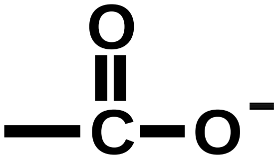
Substituents with Electron-Releasing Inductive (+ I) Effects

R →

$-CH_3$ methyl

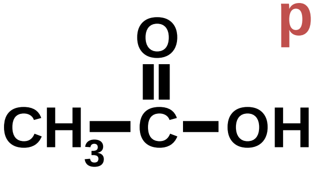
$-CR_3$ alkyl

$-O^-$ oxide



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

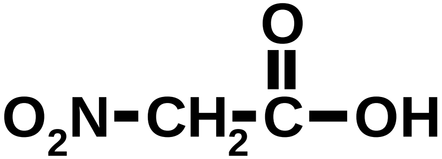
+I substituents weaken acids and strengthen bases



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

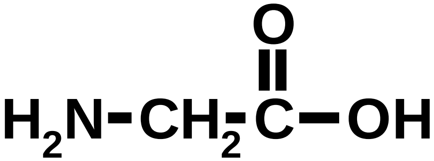
$pK_a = 4.75$

increasing acidity



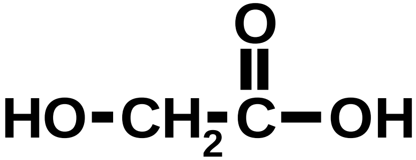
$O_2N-CH_2-\overset{\overset{O}{\|}}{C}-OH$

3.83



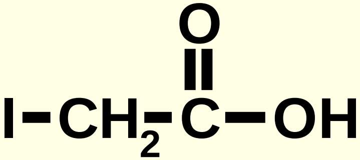
$H_2N-CH_2-\overset{\overset{O}{\|}}{C}-OH$

2.34



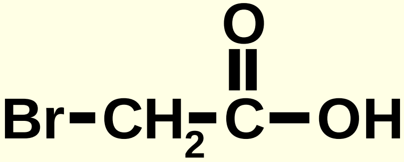
$HO-CH_2-\overset{\overset{O}{\|}}{C}-OH$

1.68



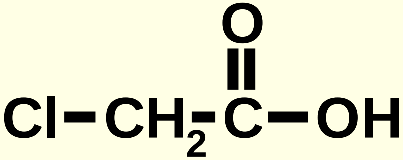
$I-CH_2-\overset{\overset{O}{\|}}{C}-OH$

3.12



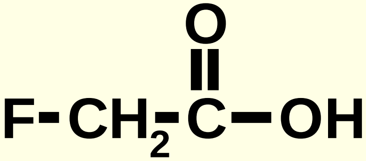
$Br-CH_2-\overset{\overset{O}{\|}}{C}-OH$

2.86



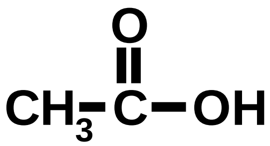
$Cl-CH_2-\overset{\overset{O}{\|}}{C}-OH$

2.86



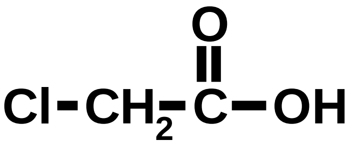
$F-CH_2-\overset{\overset{O}{\|}}{C}-OH$

2.66



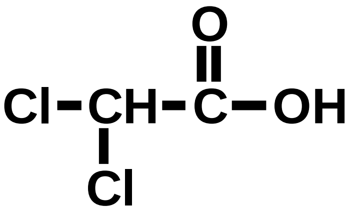
$\mathrm{CH_3-\overset{\overset{O}{\|}}{C}-OH}$

$pK_a = 4.75$



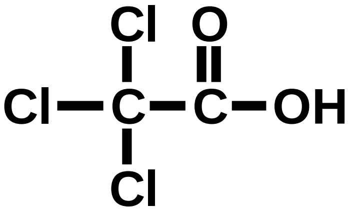
$\mathrm{Cl-CH_2-\overset{\overset{O}{\|}}{C}-OH}$

2.86



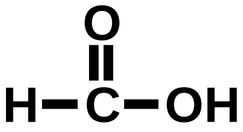
$\mathrm{Cl-\underset{\underset{Cl}{|}}{CH}-\overset{\overset{O}{\|}}{C}-OH}$

1.29



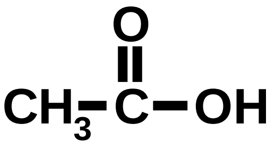
$\mathrm{Cl-\overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{C}}-\overset{\overset{O}{\|}}{C}-OH}$

0.65



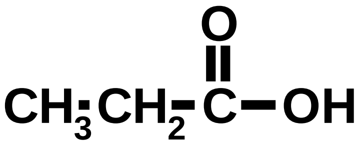
$\mathrm{H-\overset{\overset{O}{\|}}{C}-OH}$

3.77



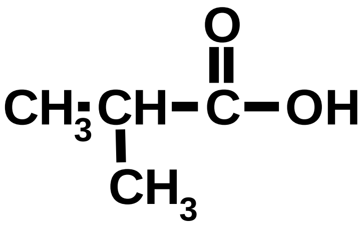
$\mathrm{CH_3-\overset{\overset{O}{\|}}{C}-OH}$

4.75



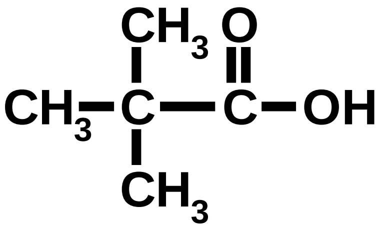
$\mathrm{CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OH}$

4.88



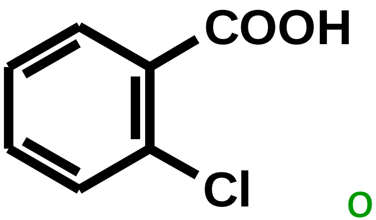
$\mathrm{CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-OH}$

4.86



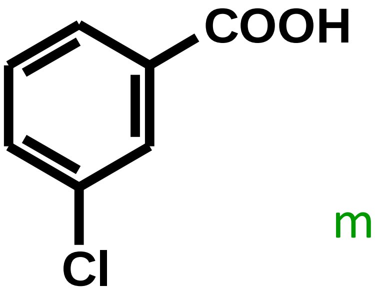
$\mathrm{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\overset{\overset{O}{\|}}{C}-OH}$

5.05



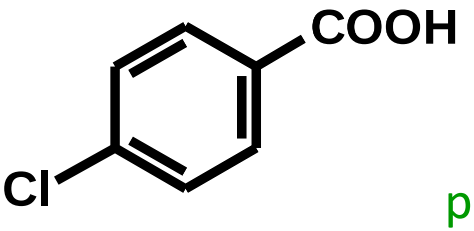
pK_a = 2.92

ortho



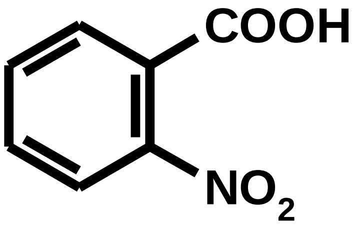
3.82

meta



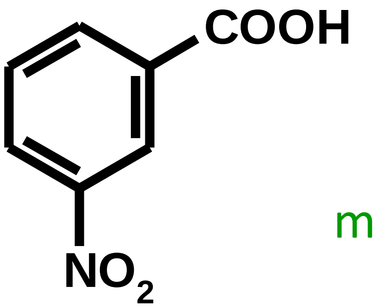
3.98

para



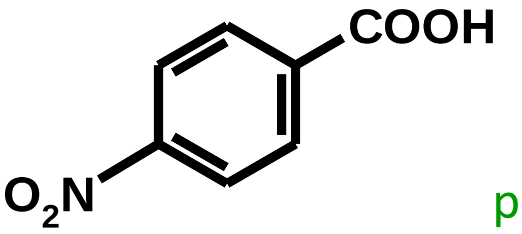
2.16

ortho



3.47

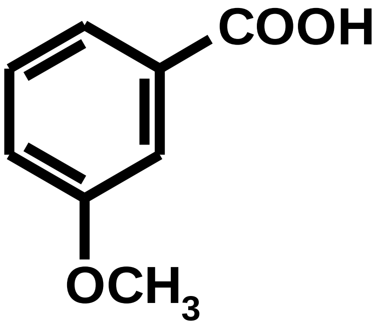
meta



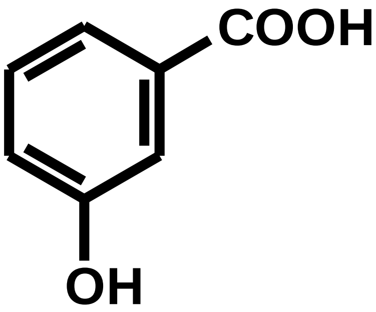
3.41

para

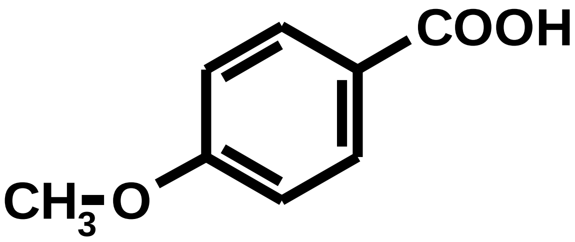
Benzoic Acid: pK_a = 4.19



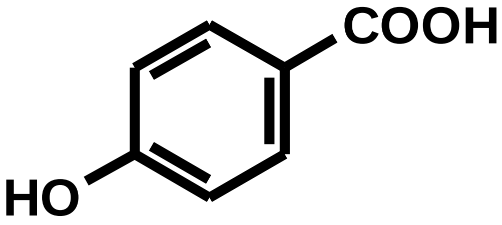
4.08



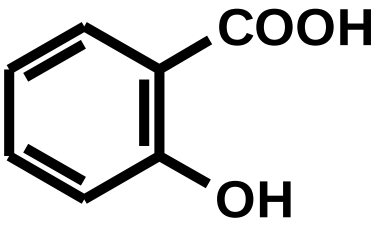
4.06



4.46



4.48



2.97

Benzoic Acid: pK_a = 4.19

Chem. 108

Ethers and Epoxides

Chapter 8

Organic Chemistry

Department of Chemistry
University of Mosul
College of Education and pure science

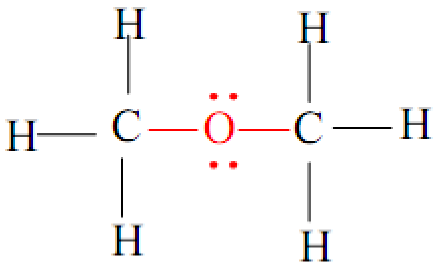
Dr. Nameer S. Ezzat and Dr. Ghufran Th. Sediq

Ethers

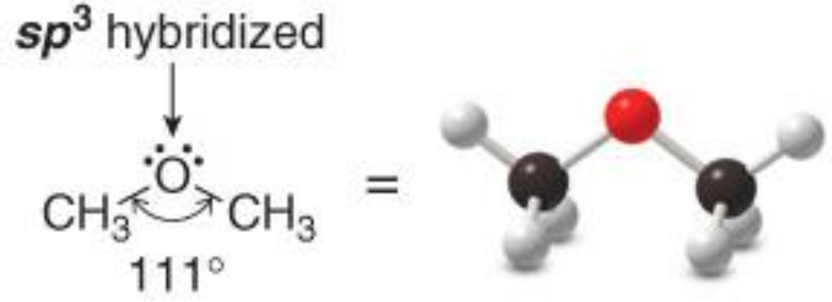
Ethers

Ether is a class of organic compounds that contain an ether group R–O–R.

For the simplest ether, Dimethyl ether



Lewis structure



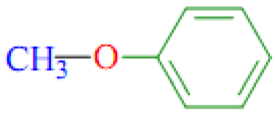
Classification of Ethers

(I) Aliphatic Ethers

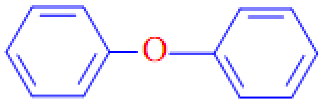
(II) Aromatic Ethers

$CH_3CH_2CH_2CH_2-O-CH_3$

Butylmethylether



Methyl phenylether



Diphenylether

Types of Ethers

1- Simple Ethers or Symmetrical Ethers

$CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_3$

Diethyl ether

2- Mixed Ethers or Unsymmetrical Ethers

$CH_3—O—CH_2—CH_3$

Ethylmethyl ether

Nomenclature

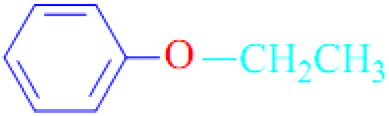
Common Names

The two-alkyl groups bonded to the functional group (- O -) are written alphabetically followed by the word ether.

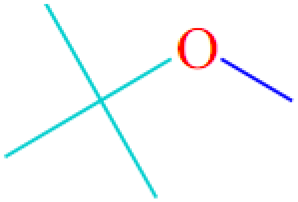
Examples:

$CH_3 - O - C_2H_5$

Ethyl methyl ether



Ethyl phenyl ether

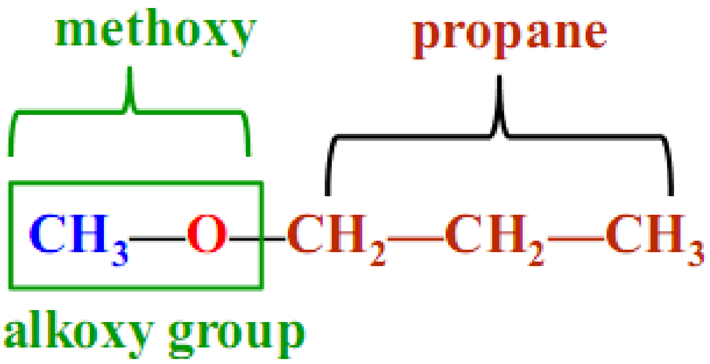


Methyl t-butylether

IUPAC System

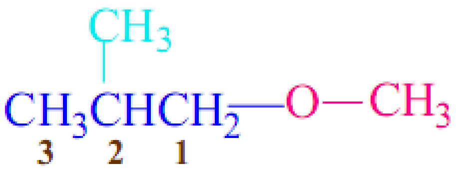
The shorter alkyl group and the oxygen are named as an alkoxy group attached to the longer alkane.

They are named as alkoxyalkanes.



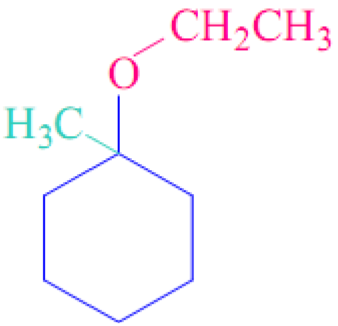
methoxypropane

Examples:

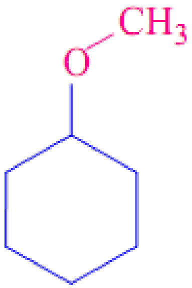


$$\overset{\displaystyle CH_3}{\overset{|}{CH_3CHCH_2}}—O—CH_3$$

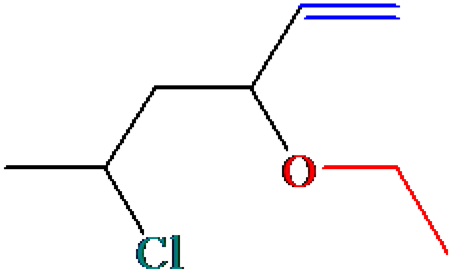
1-Methoxy-2-methyl propane



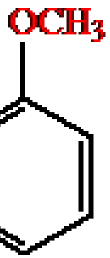
1-Ethoxy-1-methyl Cyclohexane



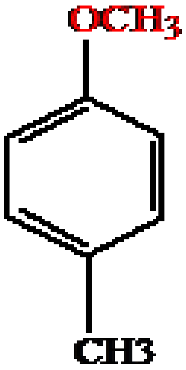
Methoxy cylohexane



5-Chloro-3-ethoxy-hex-1-ene



Methoxybenzene

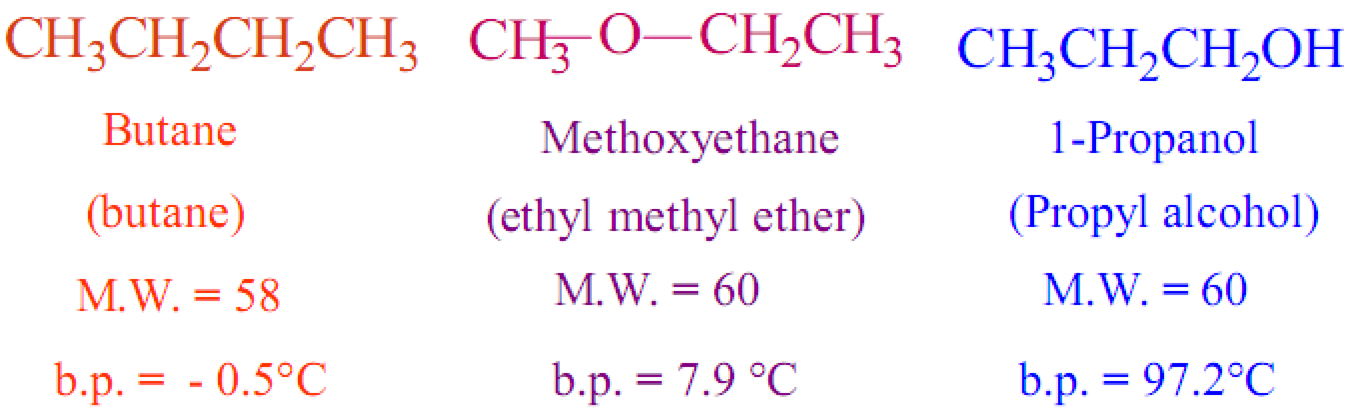


P-Methoxytoluene

Physical Properties

Boiling Points of Ethers:

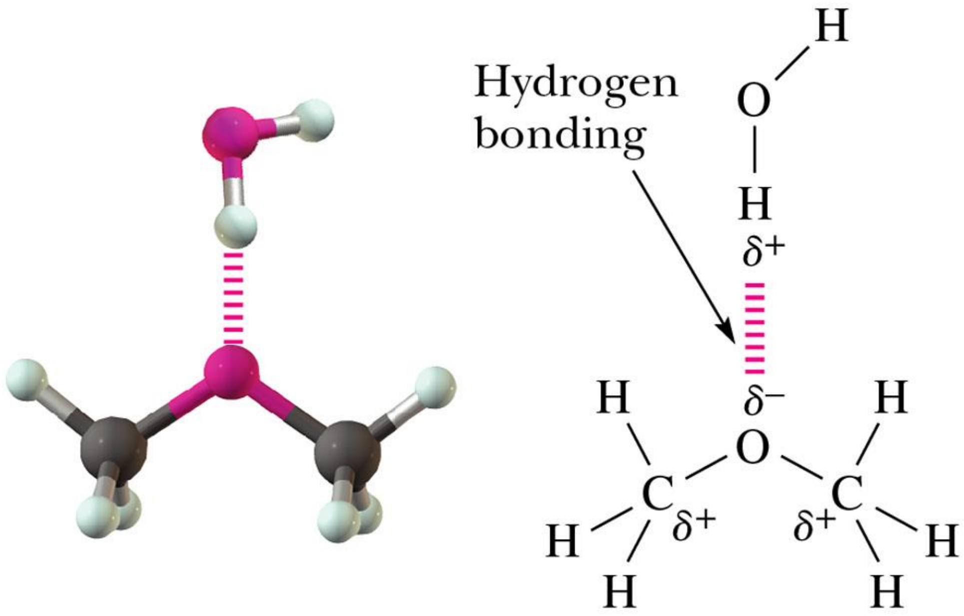
hydrogen bonds cannot form between ether molecules



$CH_3CH_2CH_2CH_3$	$CH_3—O—CH_2CH_3$	$CH_3CH_2CH_2OH$
Butane	Methoxyethane	1-Propanol
(butane)	(ethyl methyl ether)	(Propyl alcohol)
M.W. = 58	M.W. = 60	M.W. = 60
b.p. = - 0.5°C	b.p. = 7.9 °C	b.p. = 97.2°C

Solubility of Ethers:

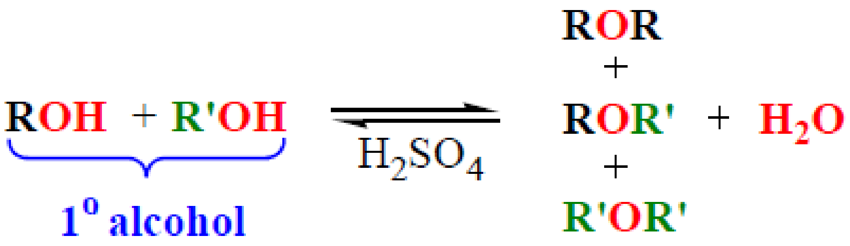
Ethers are soluble in water, due to their hydrogen bond formation with water molecules.



The solubility decreases with increase in the number of carbon atoms.

Preparation of Ethers

1- Dehydration of Alcohols



$$\underbrace{ROH + R'OH}_{1^{o}\ \text{alcohol}} \underset{H_2SO_4}{\rightleftharpoons} \begin{array}{c} ROR \\ + \\ ROR' \\ + \\ R'OR' \end{array} + H_2O$$

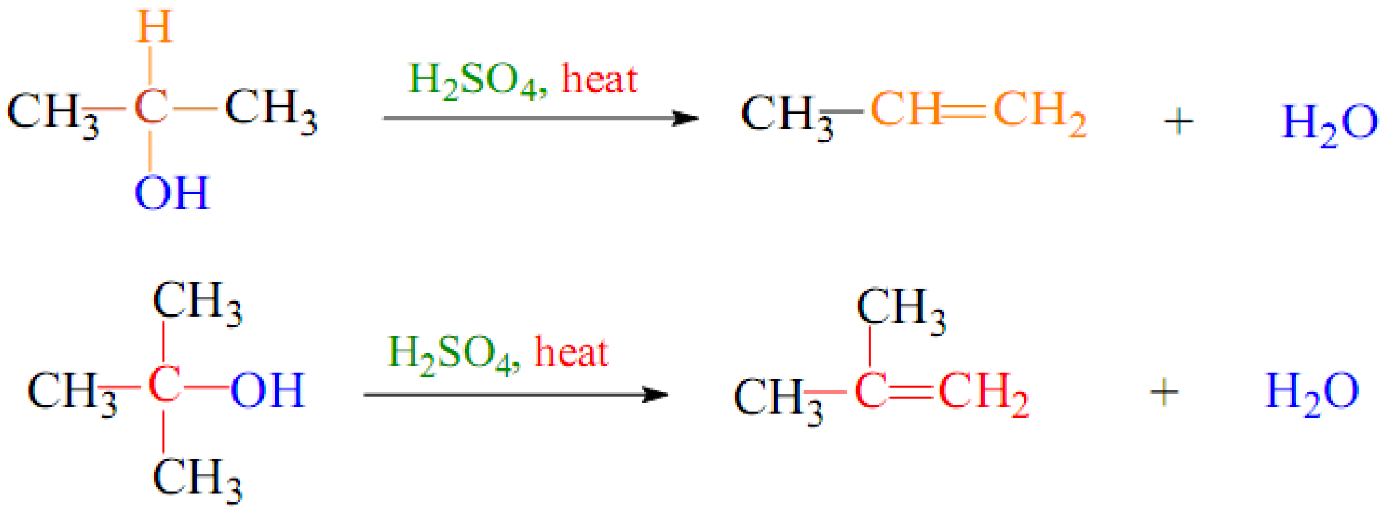
$$2\ R{-}OH \xrightarrow[140\ ^{0}C]{H_2SO_4} R{-}O{-}R + H_2O$$

Example:

$$2\ CH_3CH_2OH \xrightarrow[140^\circ\ C]{H_2SO_4} CH_3CH_2{-}O{-}CH_2CH_3 + H_2O$$

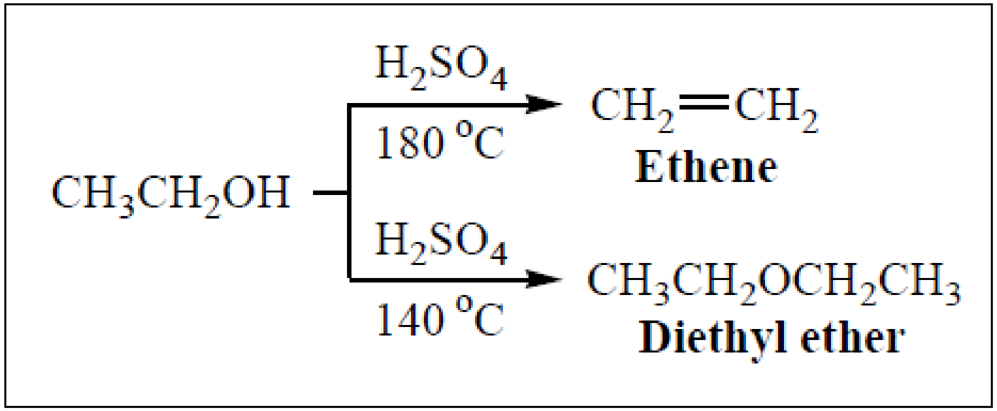
Ethanol **Diethylether**

- The dehydration of 2° and 3° alcohol is unsuccessful to get ethers as alkenes are formed easily.



$$CH_3-\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}-CH_3 \xrightarrow{H_2SO_4,\ \text{heat}} CH_3-CH=CH_2 + H_2O$$

$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-OH \xrightarrow{H_2SO_4,\ \text{heat}} CH_3-\overset{\displaystyle CH_3}{C}=CH_2 + H_2O$$



$$CH_3CH_2OH \xrightarrow[180\ ^oC]{H_2SO_4} CH_2=CH_2$$

Ethene

$$CH_3CH_2OH \xrightarrow[140\ ^oC]{H_2SO_4} CH_3CH_2OCH_2CH_3$$

Diethyl ether

2- Williamson Synthesis

- The reaction of a sodium alkoxide RONa or a sodium phenoxidex ArONa with an alkyl halide to form an ether.
- The reaction involves nucleophilic substitution of an alkoxide ion for a halide ion.

$$R{-}O^{-}\,Na^{+} + R'{-}X \longrightarrow R{-}O{-}R' + NaX$$

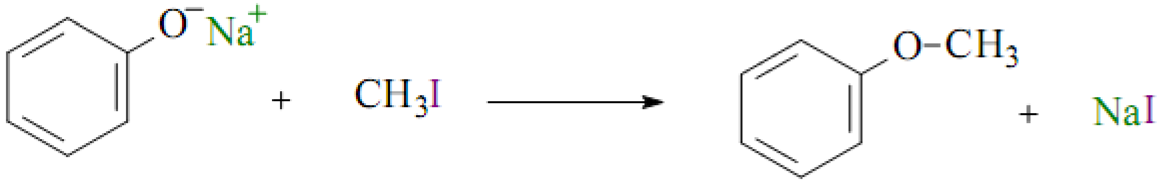
Sodium alkoxide **Alkyl halide** **Alkyl ether**

$$Ar{-}O^{-}\,Na^{+} + R'{-}X \longrightarrow Ar{-}O{-}R' + NaX$$

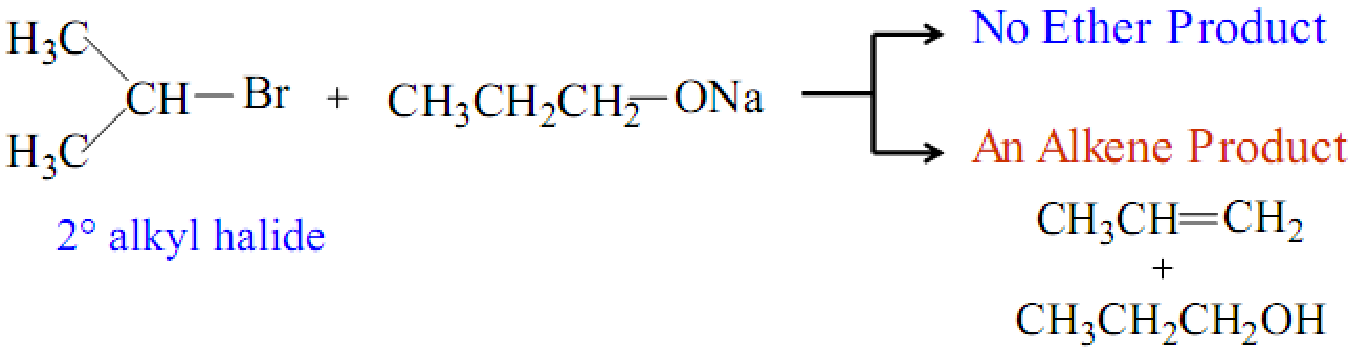
Sodium phenoxide **Alkyl halide** **Aryl ether**

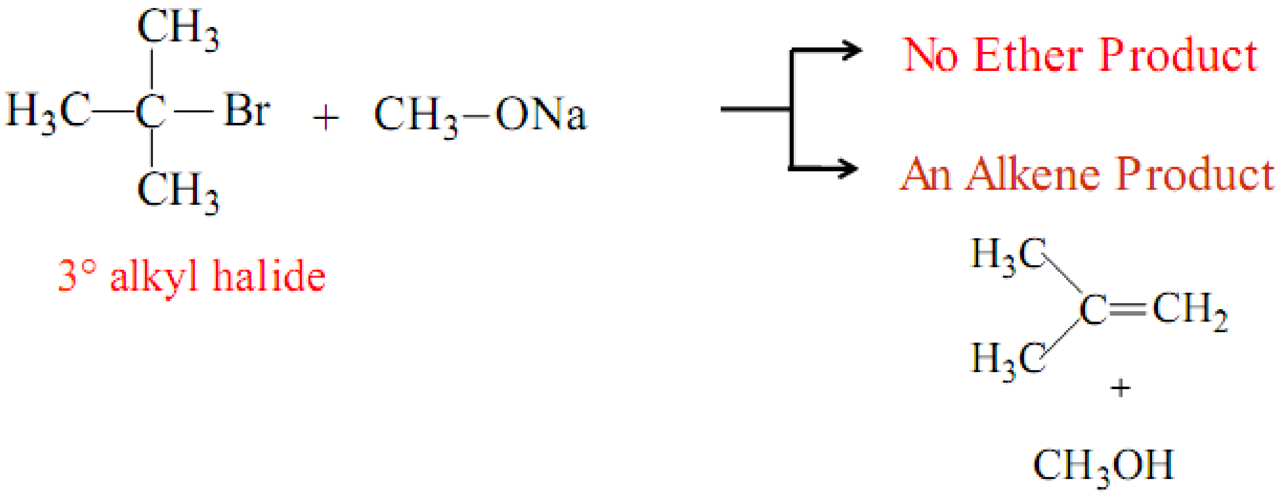
Examples:

$$CH_3CH_2Br + CH_3CH_2{-}O^{-}\,Na^{+} \longrightarrow CH_3CH_2{-}O{-}CH_2CH_3 + NaBr$$



- If a secondary (2°) or tertiary alkyl halide (3°) is used, an alkene is the only reaction product and no ether is formed.





Reactions of Ethers

Cleavage of Ethers by Acids

Substitution Reactions with strong acids HX,
X could be; I or Br.

Ethers are cleaved by HX to an alcohol and a haloalkane

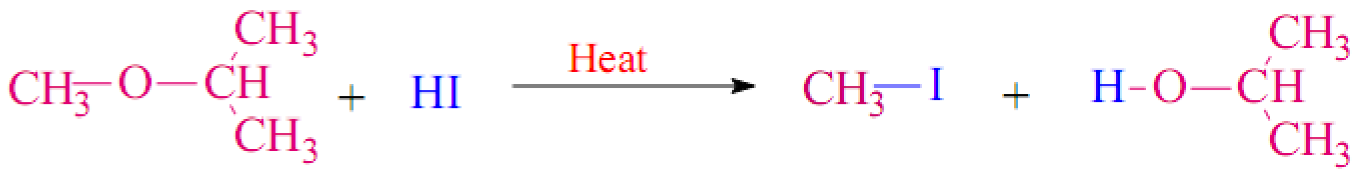
$$R-O-R' + HX \xrightarrow{\text{Heat}} R-X + R'-OH$$

Ether **Conc. acid** **Alkyl halide** **alcohol**

Examples:

$$CH_3-O-CH_3 + HBr \xrightarrow{\text{Heat}} CH_3-Br + HO-CH_3$$

Dimethyl ether **Hydrogen bromide** **Methyl bromide** **Methyl alcohol**



$$CH_3-O-CH(CH_3)_2 + HI \xrightarrow{\text{Heat}} CH_3-I + H-O-CH(CH_3)_2$$

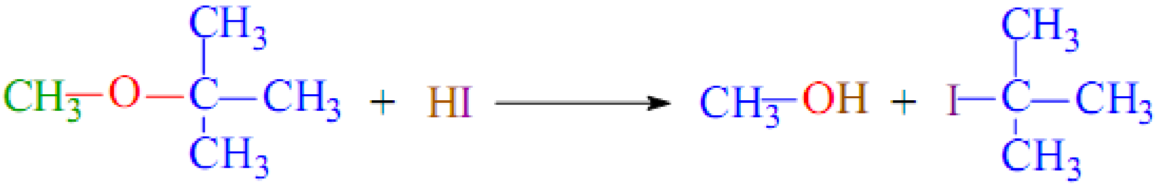
Methyl isopropyl ether **Hydrogen iodide** **Methyl iodide** **isopropylalcohol**

Point of cleavage:

- If both the alkyl groups are primary or secondary, the smaller alkyl group gets converted to the alkyl halide predominantly.

$$CH_3-O-C_2H_5 + HI \longrightarrow CH_3I + C_2H_5OH$$

- If one of the alkyl group is tertiary, the point of cleavage is such that the tertiary alkyl halide is formed as the major product



$$CH_3-O-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3 + HI \longrightarrow CH_3-OH + I-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3$$

- If two or more equivalents of acid are used further dehydration can occur on formed alcohols which may react further to form a second mole of alkyl halide.

$$CH_3CH_2OCH_2CH_3 + 2\ HBr \xrightarrow{Heat} 2\ CH_3CH_2Br + H_2O$$

Diethyl ether **Excess Hydrogen bromide** **Ethyl bromide**

Epoxides (Cyclic Ethers)

Epoxide: a cyclic ether in which oxygen is one atom of .a three-membered ring

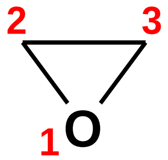
epoxide or oxirane

Nomenclature

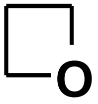
Although cyclic ethers have IUPAC names, their common names are more widely used.

IUPAC: prefix ox- shows oxygen in the ring

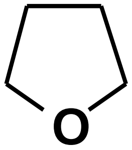
the suffixes -irane, -etane, -olane, and -ane show three, four, five, and six atoms in a saturated ring.



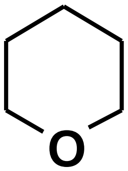
Oxirane
(Ethylene oxide)



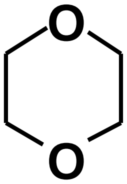
Oxetane



Oxolane
(Tetrahydrofuran)



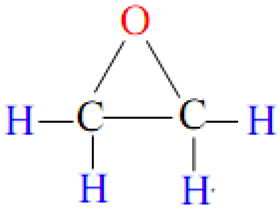
Oxane
(Tetrahydropyran)

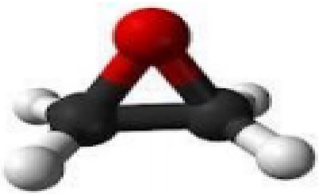


1,4-Dioxane

Preparation of Epoxides

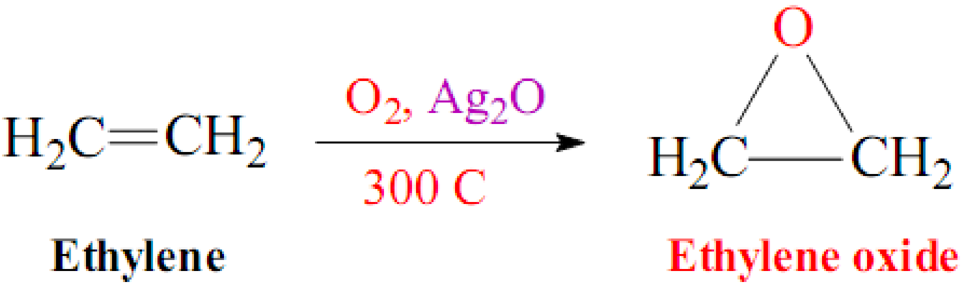
The simplest and the most important epoxide is ethylene oxide.





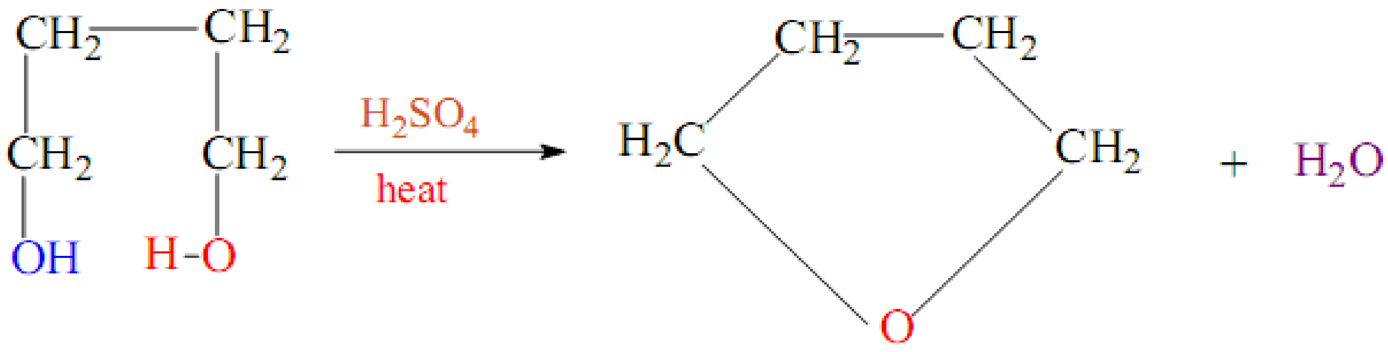
1. Air Oxidation of Ethylene

By air oxidation of ethylene and silver oxide catalyst.

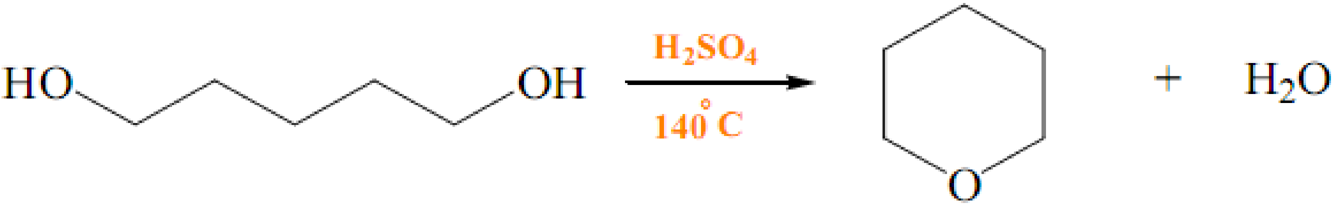


2. Dehydration of dialcohols

Examples:



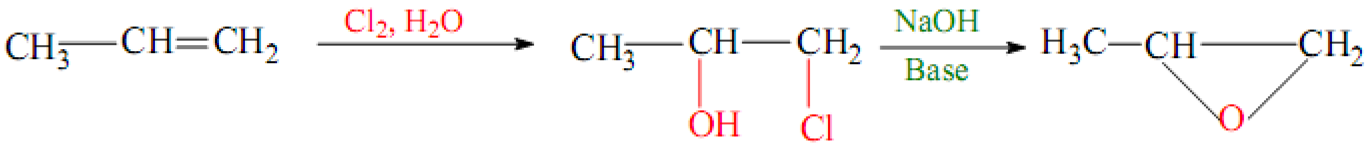
1,4- Butanediol **Tetrahydrofuran (THF)**



1,5- pentanediol **Tetrahydropyran**

3-Conversion of Vicinal Halohydrins to Epoxides

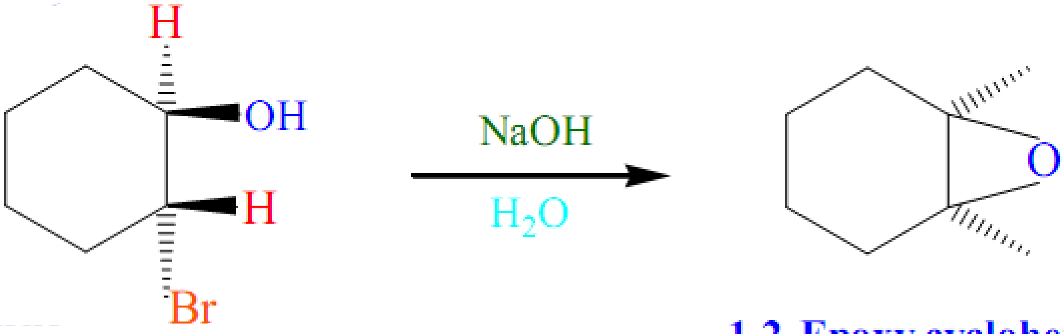
Examples:



Alkene

Halohvdrin

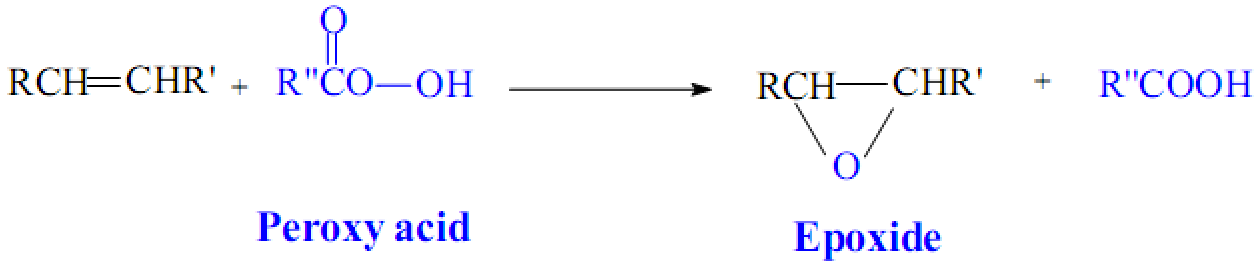
Epoxide



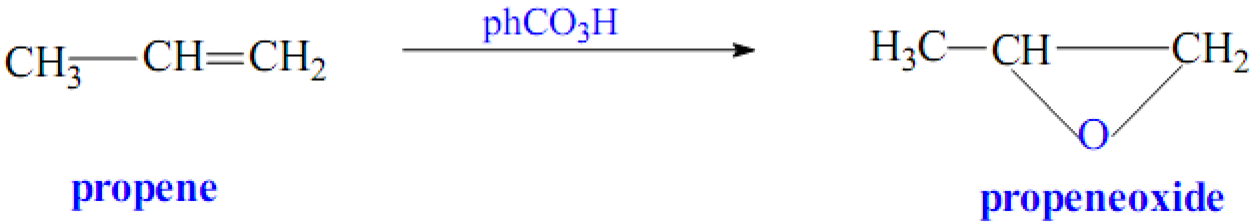
1,2-Epoxy cyclohexane

4. Epoxidation method

Epoxides are often prepared from reacting with organic peroxy acids (peracids) ex; $CH_3C(O)OOH$ in a process called epoxidation.

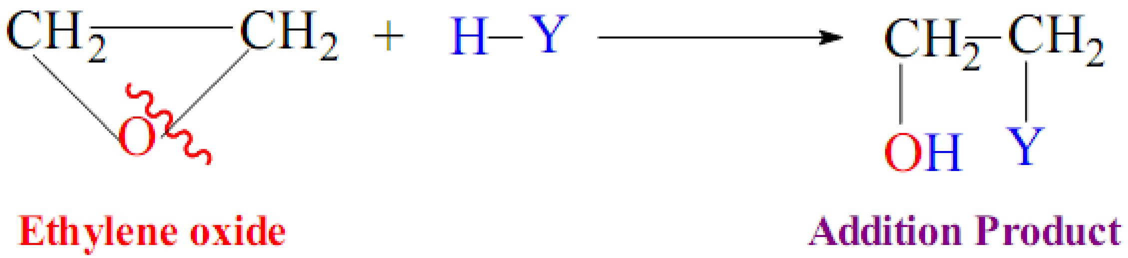


Example:



Reactions of Epoxids

Epoxides are highly strained and easily undergo ring-opening reactions under both acidic and basic conditions.



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