Aliphatic Chemistry

Part (1)

1st Year Education Students

Faculty of Education

General Chemistry (1)

Code: 111ch

2022/2023

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Contents

-Hydrocarbons.

- Nomenclacture

- Alkyl halides.

- Alcohols.

- Ethers.

- Thiols.

- Thioethers.

- Aldehydes and ketones.

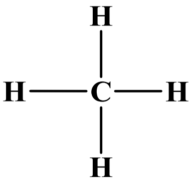
- Carboxylic acids and their derivatives.

- Amines.

Hydrocarbons

The simplest organic compounds are those composed of only two elements: carbon and hydrogen. These compounds are called hydrocarbons. Hydrocarbons themselves are separated into two types: aliphatic hydrocarbons and aromatic hydrocarbons. Aliphatic hydrocarbons are hydrocarbons based on chains of C atoms. There are three types of aliphatic hydrocarbons.

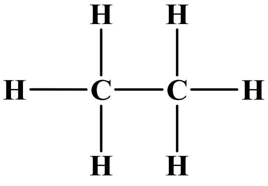
A- Alkanes are aliphatic hydrocarbons with only single covalent bonds.



$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ & & H & & \end{array}$$

CH_4

methane

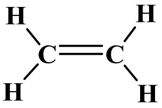


$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

C_2H_6

ethane

B- Alkenes are hydrocarbons that contain at least one C–C double bond.



C_2H_4

ethylene

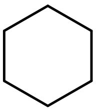
C- Alkynes are hydrocarbons that contain a C–C triple bond.

$$H-C\equiv C-H$$

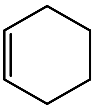
C_2H_2

acetylene

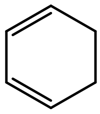
D- An aliphatic hydrocarbon with a ring of C atoms; these hydrocarbons are called cycloalkanes (or cycloalkenes or cycloalkynes).



cyclohexane



cyclohexene



cyclohexadiene

Because alkanes have the maximum number of H atoms possible

according to the rules of covalent bonds, alkanes are also referred to as saturated hydrocarbons.

Nomenclature of Molecules Containing Substituents and Functional Groups:

A- Here is a simple list of rules to follow.

Some examples are given at the end of the list.

1. **Identify the longest carbon chain. This chain is called the parent chain.**
2. **Identify all of the substituents (groups appending from the parent chain).**
3. **Number the carbons of the parent chain from the end that gives the substituents the lowest numbers.**
4. **If the same substituent occurs more than once, the location of each point on which the substituent occurs is given. In addition, the number of times the substituent group occurs is indicated by a prefix (di, tri, tetra, etc.).**
5. **If there are two or more different substituents they are listed in alphabetical order using the base name (ignore the prefixes). The only prefix which is used when putting the substituents in alphabetical order is iso as in isopropyl or isobutyl. The prefixes sec- and tert- are not used in determining alphabetical order except when compared with each other.**
6. **If chains of equal length are competing for selection as the parent chain, then the choice goes in series to:**
   a) The chain which has the greatest number of side chains.
   b) The chain whose substituents have the lowest- numbers.
   c) The chain having the greatest number of carbon atoms in the smaller side chain.
   d) The chain having the least branched side chains.

B-Priorities of Substituents and Functional Groups LISTED HERE FROM HIGHEST TO LOWEST PRIORITY, except that the substituents within Group C have equivalent priority.

Family of Compound Alkene Alkyne Structure Prefix -------- -------- Suffix -ene -yne Suffix

- ol Alcolol

-oic acid (-carboxylic acid)

-al (carbaldehyde)

-one Ketone

-amine for amines

- Suffix Alkyl R— alkyl- ----------

- Alkoxy R— O — - -----------

- NO2 nitro--------

C- Naming Molecules Containing Functional Groups from Group 1. Alkenes—Follow the same steps as for alkanes, except:

a. Number the chain of carbons that includes the C=C so that the

C=C has the lower position number, since it has a higher priority than any substituents.

b. Change "ane" to "ene" and assign a position number to the first carbon of the C=C.

Alkynes—Follow the same steps as for alkanes and change "ane" to "yne" and assign a position number to the first carbon of the triple bond.

D. Naming Molecules Containing Functional Groups from Group A—Prefix or Suffix in naming molecules containing one or more of the functional groups in Group A, the group of highest priority is indicated by suffix; the others are indicated by prefix, with priority equivalent to any other substituents.

Now that the functional groups and substituents from Groups B, and C have been described, a modified set of steps for naming organic compounds can be applied to all simple structures:

•Step 1. Find the highest priority functional group. Determine and name the longest continuous carbon chain that includes this group. •Step 2. Number the chain so that the highest priority functional group is assigned the lower number.

•Step 3. If the carbon chain includes multiple bonds (Group B), replace “ane” with “ene” for an alkene or “yne” for an alkyne. Designate the position of the multiple bond with the number of the first carbon of the multiple bond.

•Step 4. If the molecule includes Group A functional groups, replace the last “e” with the suffix of the highest priority functional group, and include its position number.

•Step 5. Indicate all Group C substituents, and Group B functional groups of lower priority, with a prefix. Place the prefixes, with appropriate position numbers, in alphabetical order before the root name.

1. Amines: prefix: amino-; suffix: -amine—substituents

2. Alcohols: prefix: hydroxy-; suffix: -ol 2-aminocyclobutan-1-ol ("1" is optional in this case) ethanol but-3-en-2-ol CH3CH2 OH H3C CH OH CH CH2 OH NH2

3. Ketones: prefix: oxo-; suffix: -one 4-(N,N-dimethylamino)pent-4-en-2-one ("1" is optional in this case) 3-hydroxybutan-2-one

4. Aldehydes: prefix: oxo-, or formyl- (O=CH-); suffix: -al (abbreviation: —CHO). An aldehyde can only be on carbon 1, so the “1” is generally omitted from the name. methanal; formaldehyde ethanal; acetaldehyde.

5. Carboxylic Acids: prefix: carboxy-; suffix: -oic acid (abbreviation: —COOH). A carboxylic acid can only be on carbon 1, so the “1” is generally omitted from the name. methanoic acid; formic acid ethanoic

acid; acetic acid (Note: Chemists traditionally use, and IUPAC accepts, the names "formic acid" and "acetic acid" in place of "methanoic acid" and "ethanoic acid".) Special case: When the chain numbering cannot include the carbon of the COOH, the suffix "carboxylic acid" is used. Salts of Carboxylic Acids are named with cation first, followed by the anion name of the carboxylic acid, where "ic acid" is replaced by "ate": acetic acid becomes acetate, butanoic acid becomes butanoate

6. Esters Esters are named as "organic salts" that is, the alkyl name comes first, followed by the name of the carboxylate anion. (common abbreviation: —COOR) "alkyl alkanoate" "alkanoate" "alkyl" carboxylate alkyl.

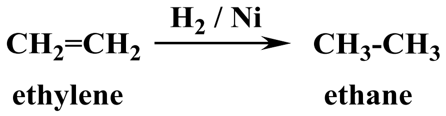
A- Alkanes

Alkanes are the family of saturated hydrocarbons, that is, molecules containing carbon and hydrogen connected by single bonds only. These molecules can be in continuous chains (called linear or acyclic).

CH_4	methane	$CH_3CH_2CH_3$	propane
CH_3CH_3	ethane	$CH_3[CH_2]_2CH_3$	butane
$CH_3[CH_2]_3CH_3$	pentane	$CH_3[CH_2]_4CH3$	hexane
$CH_3[CH_2]_5CH_3$	heptane	$CH_3[CH_2]_6CH3$	octane
$CH_3[CH_2]_7CH_3$	nonane	$CH_3[CH_2]_8CH_3$	decane

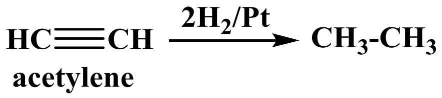
Synthesis

1- From alkenes (by catalytic hydrogenation).



$$CH_2{=}CH_2 \xrightarrow{H_2\ /\ Ni} CH_3\text{-}CH_3$$

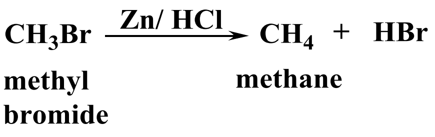
2- From alkynes (by catalytic hydrogenation).



$$HC{\equiv}CH \xrightarrow{2H_2/Pt} CH_3\text{-}CH_3$$

3- From alkyl halides (RX).

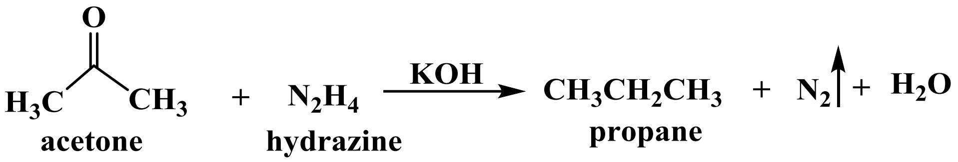
R= alkyl X= halogen= F, Cl, Br, I



$$CH_3Br \xrightarrow{Zn/\ HCl} CH_4 + HBr$$

$$2CH_3Br + 2Na \longrightarrow CH_3\text{-}CH_3 + 2NaBr \text{ (Wurtz reaction)}$$

4- From Wolff Kishner's reaction.



5- From organometalic reagents.

$$CH_3Li + H_2O \longrightarrow CH_4 + LiOH$$

methyl lithium

6- Hydrolysis of metal carbides.

$$Al_4C_3 + 12H_2O \longrightarrow 3CH_4 + 4\,Al(OH)_3$$

aluminium
carbide

<u>Reactions</u>

1- Halogenation.

$$CH_4 + X_2 \xrightarrow[250\text{-}400^oC]{\text{light or}} CH_3X + HX$$

$$CH_4 \xrightarrow{Cl_2/\,hv} CH_3Cl \xrightarrow{Cl_2} CH_2Cl_2 \xrightarrow{Cl_2} CHCl_3 \xrightarrow{Cl_2} CCl_4$$

methyl
chloride

hv= energy

2- Nitration.

$$CH_4 + HNO_3 \xrightarrow[150\text{-}475\ ^oC]{\text{vapour phase}} CH_3NO_2 + H_2O$$

nitromethane

3- Oxidation.

$$CH_4 + O_2 \longrightarrow CO_2 + 2H_2O$$

B- Alkenes

Unsaturated hydrocarbons (contain double bonds).

Synthesis

1- From alkynes (*via* catalytic hydrogenation).

$$HC\equiv CH \xrightarrow{H_2/Pd} CH_2{=}CH_2$$

2- From alkyl halides (*via* dehydrohalogenation).

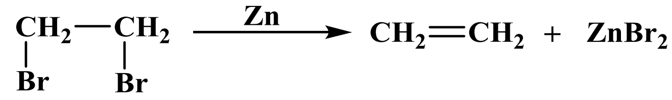
$$\underset{\text{ethyl bromide}}{CH_3CH_2\text{-}Br} + KOH \xrightarrow[\triangle]{\text{alcohol}} CH_2{=}CH_2 + KBr + H_2O$$

$$CH_3{-}CH_2Br \xrightarrow[CH_3OH]{CH_3ONa} CH_2{=}CH_2 + NaBr$$

3- From alcohols (*via* dehydration).

$$\underset{\text{ethanol}}{CH_3CH_2\text{-}OH} \xrightarrow[\text{or } Al_2O_3/400\ ^oC]{\text{Conc. } H_2SO_4/180\ ^oC} CH_2{=}CH_2 + H_2O$$

4- Dehalogenation of vicinal dihalides.



$$\underset{Br}{CH_2}{-}\underset{Br}{CH_2} \xrightarrow{Zn} CH_2{=}CH_2 + ZnBr_2$$

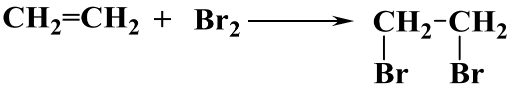
1,2-dibromoethane

Reactions

1- Addition of hydrogen.

$$CH_2{=}CH_2 + H_2 \longrightarrow CH_3{-}CH_3$$

2- Addition of halogens.

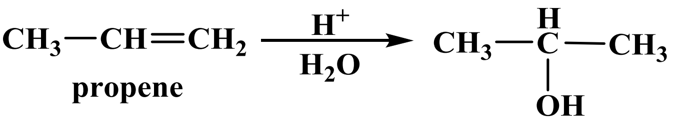


$$CH_2{=}CH_2 + Br_2 \longrightarrow \underset{Br}{CH_2}{-}\underset{Br}{CH_2}$$

3- Addition of halogen acids.

$$CH_2{=}CH_2 + HBr \longrightarrow CH_3{-}CH_2Br$$

4- Addition of water.



$$CH_3{-}CH{=}CH_2 \xrightarrow[H_2O]{H^+} CH_3{-}\underset{OH}{\overset{H}{C}}{-}CH_3$$

propene

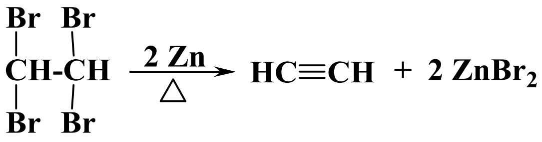
propan-2-ol

C-Alkynes

Unsaturated hydrocarbons (contain triple bond).

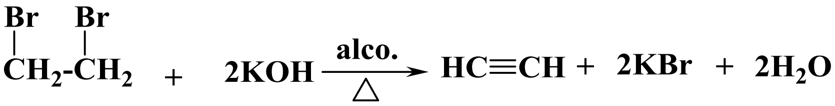
Synthesis

From alkyl halides.



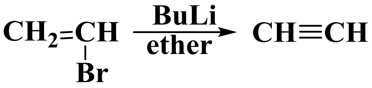
$$\overset{Br}{\underset{Br}{CH}}-\overset{Br}{\underset{Br}{CH}} \xrightarrow[\triangle]{2\ Zn} HC\equiv CH + 2\ ZnBr_2$$

1,1,2,2-tetrabromoethane



$$\overset{Br}{CH_2}-\overset{Br}{CH_2} + 2KOH \xrightarrow[\triangle]{alco.} HC\equiv CH + 2KBr + 2H_2O$$

1,2-dibromoethane



$$CH_2=\underset{Br}{CH} \xrightarrow[ether]{BuLi} CH\equiv CH$$

bromoethylene

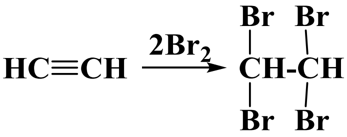
Reactions

1- Addition of hydrogen.

$$HC\equiv CH \xrightarrow{2H_2/Cat.} CH_3-CH_3$$

$$HC\equiv CH \xrightarrow{H_2/Pd} CH_2=CH_2$$

2- Addition of bromine.



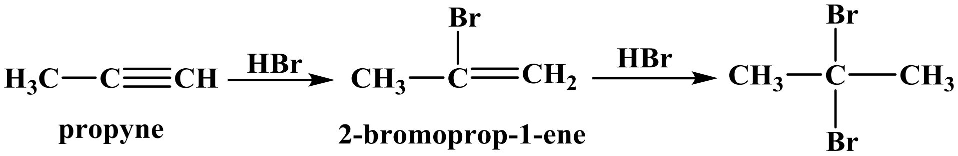
$$HC\equiv CH \xrightarrow{2Br_2} \overset{Br}{\underset{Br}{CH}}-\overset{Br}{\underset{Br}{CH}}$$

3- Addition of hydrogen cyanide (HCN).

$$HC\equiv CH \xrightarrow{HCN} CH_2=CHCN$$

vinyl cyanide

4- Addition of HBr.



$$H_3C{-}C{\equiv}CH \xrightarrow{HBr} CH_3{-}\overset{\overset{\large Br}{|}}{C}{=}CH_2 \xrightarrow{HBr} CH_3{-}\underset{\underset{\large Br}{|}}{\overset{\overset{\large Br}{|}}{C}}{-}CH_3$$

propyne **2-bromoprop-1-ene** **2,2-dibromopropane**

Halogen derivatives of saturated hydrocarbons

(Alkyl halides)

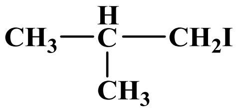
Alkyl halides are also known as haloalkanes. Alkyl halides are compounds in which one or more hydrogen atoms in an alkane have been replaced by halogen atoms (fluorine, chlorine, bromine or iodine). Alkyl halides can be classified as primary, secondary, or tertiary.

CH_3-CH_2Br

bromoethane

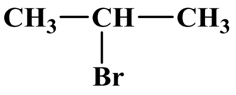
$CH_3-CH_2-CH_2Cl$

1-chloropropane

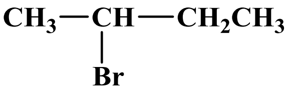

$CH_3-\underset{CH_3}{\overset{H}{C}}-CH_2I$

1-iodo-2-methylpropane

primary alkyl halide

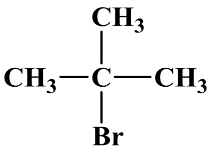

$CH_3-\underset{Br}{CH}-CH_3$

2-bromopropane

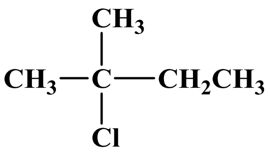

$CH_3-\underset{Br}{CH}-CH_2CH_3$

2-bromobutane

secondary alkyl halide


$CH_3-\underset{Br}{\overset{CH_3}{C}}-CH_3$

2-bromo-2-methylpropane

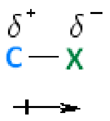

$CH_3-\underset{Cl}{\overset{CH_3}{C}}-CH_2CH_3$

2-chloro-2-methylbutane

tertiary alkyl halide

With respect to electronegativity, halogens are more electronegative than carbons. This results in a carbon-halogen bond that is polarized. As shown in the image below, carbon atom has a partial positive charge, while the halogen has a partial negative charge.

The Polar C-X Bond



The following image shows the relationships between bond length, bond strength, and molecular size. As we progress down the periodic table from fluorine to iodine, molecular size increases. As a result, we also see an increase

in bond length. Conversely, as molecular size increases and we get longer bonds, the strength of those bonds decreases.

Bond length	C-F < C-Cl < C-Br < C-I
Bond strength	C-I < C-Br < C-Cl < C-F
Molecular size	F < Cl < Br < I

Synthesis

1- From alkanes.

$$RH + X_2 \xrightarrow{hv} RX + HX$$

2- From alkenes.

i) *Via* addition of halogen acids

$$CH_2{=}CH_2 + HX \longrightarrow CH_3{-}CH_2X$$

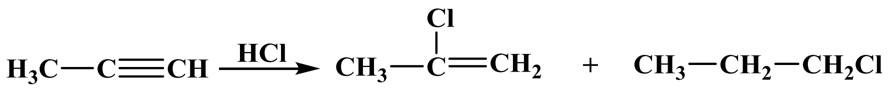
ii) *Via* addition of halogen

$$CH_2{=}CH_2 + X_2 \longrightarrow CH_2X{-}CH_2X \text{ (vicinal dihalides)}$$

3- From alcohols.

$$CH_3CH_2OH + HBr\text{ (conc.)} \longrightarrow CH_3CH_2Br + H_2O$$

4- Addition of hydrogen halides to alkenes.



$$H_3C{-}C{\equiv}CH \xrightarrow{HCl} CH_3{-}\overset{Cl}{\overset{|}{C}}{=}CH_2 + CH_3{-}CH_2{-}CH_2Cl$$

propyne 2-chloroprop-1-ene 1-chloropropane

Reactions

Nucleophilic substitution.

$$RX + NaOH \longrightarrow ROH \text{ (alcohols)} + NaX$$

$$RX + NaR \longrightarrow R{-}R \text{ (alkanes)} + NaX$$

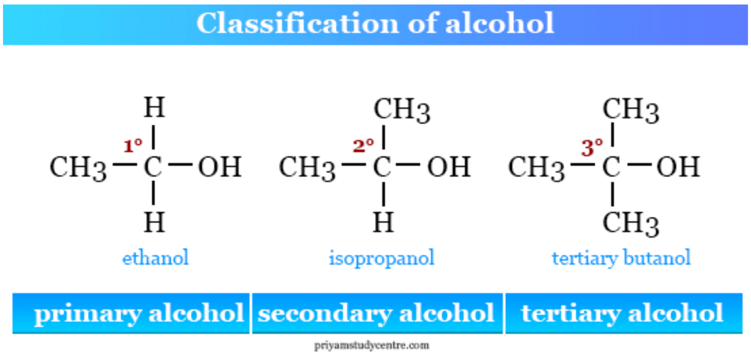
$$RX + KI \longrightarrow RI \text{ (alkyl halides)} + KX$$

$$RX + NaOR \longrightarrow ROR \text{ (ethers)} + NaX$$

sodium alkoxide

Alcohols

Aliphatic alcohols are organic chemical compounds. They are flammable liquids and are highly soluble in water and many organic solvents. Highly volatile liquids, they are stable in water under typical use conditions.



-Types of aliphatic alcohol

1- Methanol, ethanol, propanol, isopropyl alcohol, butanol, isobutanol, etc are examples of monohydric alcohols because these contain only one hydroxyl group.

2- Ethylene glycol, trimethylene glycol, pentamethylene glycol, isobutene glycol are dihydric types of aliphatic alcohols. These chemicals contain two alcoholic groups.

3- The only important trihydric aliphatic organic compound is glycerol or propane-1-2-2-triol because these contain three alcoholic groups. Glycerol occurs in almost all animals and vegetable oils.

4- D-sorbitol, D-mannitol, and dulcitol are the polyhydric aliphatic

alcohols that occur naturally contain more than three hydroxyl groups.

Examples of alcohol

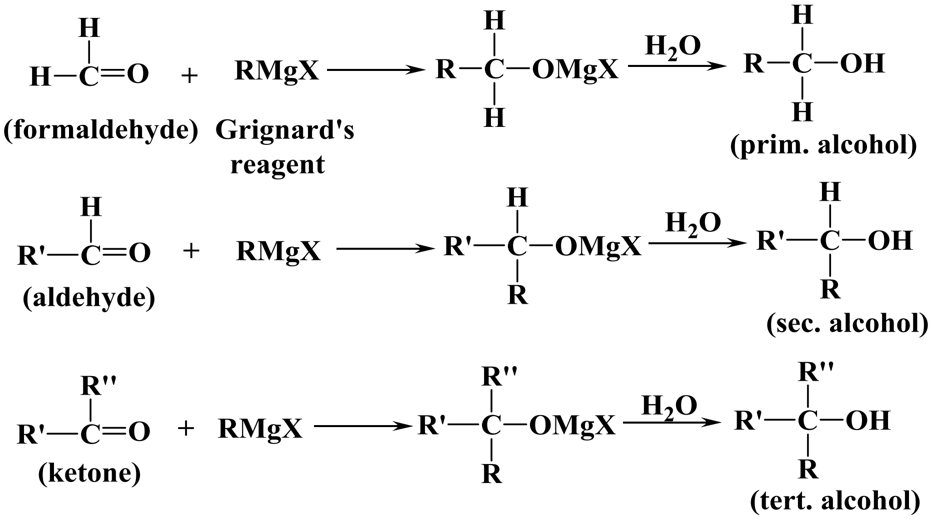
Names	Formula
methanol	CH_3OH
n-propanol	$CH_3CH_2CH_2OH$
iso-propanol	$CH_3CH(OH)CH_3$
t-butanol	$(CH_3)_3COH$

Synthesis

1- From alkyl halides by hydrolysis.

$$RX + NaOH \longrightarrow ROH \text{ (alcohols)} + NaX$$

2- From aldehydes and ketones.



$$\underset{\text{(formaldehyde)}}{H-\overset{H}{C}=O} + \underset{\text{Grignard's reagent}}{RMgX} \longrightarrow R-\overset{H}{\underset{H}{C}}-OMgX \xrightarrow{H_2O} \underset{\text{(prim. alcohol)}}{R-\overset{H}{\underset{H}{C}}-OH}$$

$$\underset{\text{(aldehyde)}}{R'-\overset{H}{C}=O} + RMgX \longrightarrow R'-\overset{H}{\underset{R}{C}}-OMgX \xrightarrow{H_2O} \underset{\text{(sec. alcohol)}}{R'-\overset{H}{\underset{R}{C}}-OH}$$

$$\underset{\text{(ketone)}}{R'-\overset{R''}{C}=O} + RMgX \longrightarrow R'-\overset{R''}{\underset{R}{C}}-OMgX \xrightarrow{H_2O} \underset{\text{(tert. alcohol)}}{R'-\overset{R''}{\underset{R}{C}}-OH}$$

3- From ethers.

$$\underset{\text{diethyl ether}}{C_2H_5OC_2H_5} \xrightarrow[\text{dil. } H_2SO_4 \text{ pressure}]{H_2O} 2C_2H_5OH$$

4- From alkenes.

$$CH_2{=}CH_2 \xrightarrow[H_2SO_4 \atop \triangle]{H_2O} CH_3{-}CH_2OH$$

Reactions

1- Reaction with halogen acids.

$$CH_3CH_2OH + HBr\ (conc.) \longrightarrow CH_3CH_2Br + H_2O$$

2- Dehydration.

$$CH_3CH_2\text{-}OH \xrightarrow[or\ Al_2O_3/400\ ^oC]{Conc.\ H_2SO_4/180\ ^oC} CH_2{=}CH_2 + H_2O$$

3- Esterification.

$$CH_3CH_2OH + CH_3COOH \xrightleftharpoons{conc.\ H_2SO_4} \underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

4-Reaction with ammonium.

$$ROH + NH_3 \xrightarrow{pressure} \underset{\text{primary amines}}{RNH_2} + H_2O$$

$$ROH + ROH \xrightarrow{pressure} \underset{\text{secondary amines}}{(R)_2NH} + H_2O$$

$$(R)_2NH + ROH \xrightarrow{pressure} \underset{\text{tertiary amines}}{R_3N} + H_2O$$

5- Reaction with phosphorus pentasulphide (P_2S_5).

$$5ROH + P_2S_5 \longrightarrow \underset{\text{thiol}}{5RSH} + P_2O_5$$

Ethers

Ethers are a class of organic compounds that contain an ether group - an oxygen atom connected to two alkyl or aryl groups. They have the general formula R–O–R′, where R and R′ represent the alkyl or aryl groups. Ethers can again be classified into two varieties: if the alkyl groups are the same on both sides of the oxygen atom, then it is simple or symmetrical ether, whereas if they are different, the ethers are called mixed or unsymmetrical ethers. A typical example of the first group is the solvent and anaesthetic diethyl ether, commonly referred to simply as "ether" (CH_3–CH_2–O–CH_2–CH_3).

Synthesis

1- From alkyl halides (Williamson Synthesis).

$$RX + NaOR \longrightarrow ROR\ (\text{ethers}) + NaX$$

2- By dehydration of alcohols.

$$2C_2H_5OH \xrightarrow[-\,H_2O]{H_2SO_4} \underset{\text{diethyl ether}}{C_2H_5OC_2H_5}$$

Reactions

1- Cleavage by halogen acids.

$$ROR + HX \xrightarrow[\text{high temp.}]{\text{conc.}} RX + ROH$$

$$(CH_3CH_2)_2O + HI \xrightarrow{\text{high temp.}} CH_3CH_2I + CH_3CH_2OH$$

$$(CH_3CH_2)_2O + 2HI\ (\text{conc.}) \xrightarrow{\text{high temp.}} 2CH_3CH_2I + H_2O$$

2- Reaction with phosphorus pentasulphide P_2S_5.

$$5C_2H_5OC_2H_5 + P_2S_5 \xrightarrow{\triangle} \underset{\text{diethylthioether}}{5C_2H_5SC_2H_5} + P_2O_5$$

3- Oxidation.

$$C_2H_5OC_2H_5 \xrightarrow{6O_2} 4CO_2 + 5H_2O$$

4- Halogenation.

a- In dark gives the substituted ether.

$$C_2H_5OC_2H_5 \xrightarrow{Cl_2,\ dark} CH_3CHClOCHClCH_3$$

1,1'- dichloro diethyl ether

b- In sunlight it substitutes all hydrogen atoms present.

$$C_2H_5OC_2H_5 \xrightarrow{Cl_2,\ sunlight} C_2Cl_5OC_2Cl_5$$

perchloro diethyl ether

5- Reaction with carbon monoxide

$$C_2H_5OC_2H_5 \xrightarrow[P,\ \triangle]{CO} C_2H_5COOC_2H_5$$

ethyl propionate

Thioalcohols

A thiol or thiol derivative is any organosulfur compound of the form R−SH, where R represents an alkyl or other organic substituent. The –SH functional group itself is referred to as either a thiol group or a sulfhydryl group, or a sulfanyl group. Thiols are the sulfur analogue of alcohols (that is, sulfur takes the place of oxygen in the hydroxyl group of an alcohol). Thiols are sometimes referred to as mercaptans.

Synthesis

1- From alkyl halides.

$$RX + KSH \longrightarrow \underset{\text{Thioalcohols or thiols}}{RSH} + KX$$

$$CH_3Br \xrightarrow{Mg} \underset{\text{Grignard reagent}}{CH_3MgBr} \xrightarrow{S_8,\ H^+} \underset{\text{methanethiol}}{CH_3SH}$$

2- From alcohols.

$$5ROH + P_2S_5 \longrightarrow 5RSH + P_2O_5$$

Reactions

1- With sodium.

$$\underset{\text{ethanethiol}}{2\ C_2H_5SH} + 2Na \longrightarrow \underset{\text{sodium ethanethiolate}}{2\ C_2H_5SNa}$$

2- Reaction with lead acetate.

$$2RSH + \underset{\text{lead acetate}}{(CH_3COO)_2Pb} \longrightarrow \underset{\text{lead mercaptide}}{(RS)_2Pb\downarrow} + 2\ CH_3COOH$$

3- Reaction with alumina/zinc sulphide.

$$2\ CH_3CH_2SH \xrightarrow[ZnS/300\ ^oC]{Al_2O_3} \underset{\text{diethylthioether}}{(CH_3CH_2)_2S} + H_2S$$

4- Reaction with alkenes.

$$CH_3SH + RHC{=}CH_2 \longrightarrow RH_2C{-}CH_2SCH_3$$

5- Formation of thioethers

$$CH_3SH + CH_3ONa \longrightarrow \underset{\text{sodium methanethiolate}}{CH_3SNa} \xrightarrow{CH_3Br} \underset{\text{dimethylthioether}}{CH_3SCH_3}$$

6- Oxidation by iodine

$$2CH_3SH \xrightarrow{I_2} \underset{\text{disulfide}}{CH_3SSCH_3}$$

Thioethers

(Alkyl sulphides)

An organic sulfide or thioether is a functional group in organosulfur chemistry with the connectivity C–S–C as shown on right. Like many other sulfur-containing compounds, volatile sulfides have foul odors. A sulfide is similar to an ether except that it contains a sulfur atom in place of the oxygen. The grouping of oxygen and sulfur in the periodic table suggests that the chemical properties of ethers and sulfides are somewhat similar.

Synthesis

1- From alkyl halides (*via* heating with K_2S).

$$RX + \underset{\text{potassium alkanethiolate}}{KSR} \longrightarrow \underset{\text{thioethers}}{RSR} + KX$$

2- From ethers (*via* reaction with P_2S_5).

$$5\,ROR + P_2S_5 \longrightarrow 5\,RSR + P_2O_5$$

Reactions

1- Desulphurization.

$$(CH_3CH_2)_2S + H_2 \xrightarrow{Ni} 2\,CH_3CH_3 + NiS$$

2- Oxidation.

$$(C_2H_5)_2S \xrightarrow{H_2O_2} \underset{\text{diethylsulphoxide}}{(C_2H_5)_2S{=}O} \xrightarrow{H_2O} \underset{\text{diethylsulphone}}{(C_2H_5)_2SO_2}$$

Aldehydes and ketones

Aliphatic aldehydes and ketones are essential building blocks for the synthesis of more complex organic compounds e.g. formaldehyde, acetaldehyde, and acetone.

A- Aldehydes

Chemically, an aldehyde is a compound containing a functional group with the structure -CHO, consisting of a carbonyl center (a carbon double-bonded to oxygen) with the carbon atom also bonded to hydrogen and to any generic alkyl or side chain R group. The functional group itself (i.e. without the "R" side chain) is known as an aldehyde or formyl group. Aldehydes, which are generally created by removing hydrogen from an alcohol, are common in organic chemistry; the most well-known is formaldehyde. As they are frequently strongly scented, many fragrances are or contain aldehydes.

Synthesis

1- *Via* dehydrogenation of alcohols.

$$\underset{\text{prim. alcohols}}{RCH_2OH} \xrightarrow[-\ H_2]{Cu/325\ ^{o}C} \underset{\text{aldehydes}}{RCHO}$$

2- From acid derivatives (from acetyl chlorides).

$$\underset{\text{acetyl chloride}}{CH_3COCl} \xrightarrow{H_2/Pd} \underset{\text{acetaldehyde}}{CH_3CHO} + HCl$$

3- From alkenes (by hydroformylation).

$$\underset{\text{propene}}{CH_3CH{=}CH_2} + CO + H_2 \longrightarrow \underset{\text{butyraldehyde}}{CH_3CH_2CH_2CHO}$$

4- From nitriles

$$RC{\equiv}N \xrightarrow[SnCl_2]{HCl} RCHO + NH_4Cl$$

5- From geminal halide hydrolysis

$$RCHCl_2 \xrightarrow{KOH} RCHOHCl \longrightarrow RCHO$$

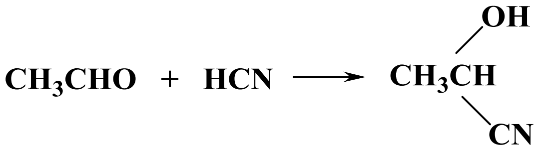
Reactions

1- Addition of hydrogen.

a- Reduction to alkanes (Clemensen reduction).

$$CH_3CHO \xrightarrow{Zn[Hg]/HCl} H_3C{-}CH_3 + H_2O$$

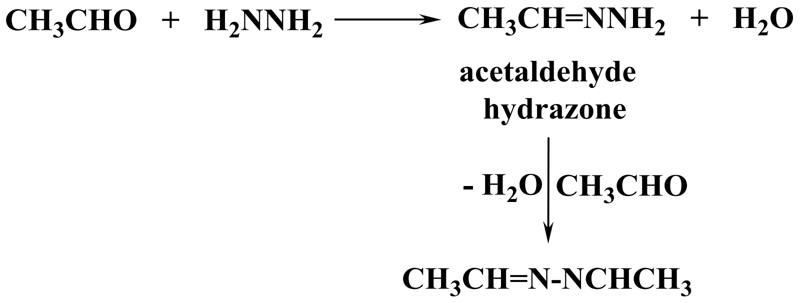
2- Addition of hydrogen cyanide.



$$CH_3CHO + HCN \longrightarrow CH_3CH(OH)(CN)$$

acetaldehyde
cyanohydrine

3- Addition of hydrazine ($H_2N\text{-}NH_2$).



$$CH_3CHO + H_2NNH_2 \longrightarrow CH_3CH{=}NNH_2 + H_2O$$

acetaldehyde
hydrazone

$$\xrightarrow[-\,H_2O]{CH_3CHO} CH_3CH{=}N\text{-}NCHCH_3$$

4- Oxidation with potassium dichromate $K_2Cr_2O_7$/conc H_2SO_4.

$$RCHO \xrightarrow{K_2Cr_2O_7/\text{ conc } H_2SO_4} RCOOH$$

carboxylic acid

B- Ketones

In chemistry, a ketone is a functional group with the structure $R_2C{=}O$, where R can be a variety of carbon-containing substituents. Ketones contain a carbonyl group (a carbon-oxygen double bond). The simplest ketone is acetone (R = R' = methyl), with the formula $CH_3C(O)CH_3$. Many ketones are of great importance in biology and in industry. Examples include many sugars (ketoses), many steroids (e.g., testosterone), and the solvent acetone.

Synthesis

From alcohols by

a- Oxidation.

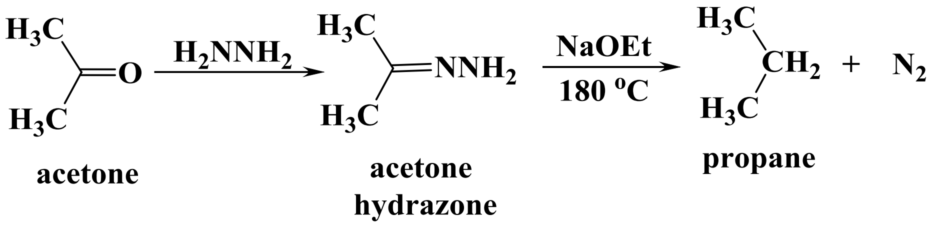
$$\underset{\text{sec. alcohols}}{(R)_2CHOH} \xrightarrow[K_2Cr_2O_7/H_2SO_4]{\text{oxidtion}} \underset{\text{ketones}}{(R)_2C{=}O}$$

b- Dehydrogenation.

$$(R)_2CHOH \xrightarrow[-\,H_2]{Cu/325\ ^{o}C} (R)_2C{=}O$$

Reactions

1- Reduction to alkanes.



2- Addition of ammonia derivatives

a- With hydroxyl amine.

$$(CH_3)_2CO + H_2NOH \longrightarrow \underset{\text{acetone oxime}}{(CH_3)_2C{=}NOH}$$

b- With hydrazine.

$$(CH_3)_2CO \quad + \quad H_2NNH_2 \longrightarrow \underset{\substack{\text{acetone}\\ \text{hydrazone}}}{(CH_3)_2C{=}NNH_2} \xrightarrow{(CH_3)_2CO} \underset{\text{azine}}{(CH_3)_2C{=}NNC{=}(CH_3)_2}$$

Carboxylic acids and their derivatives

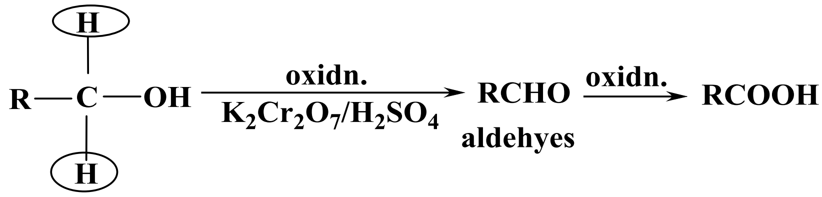
A- Carboxylic acids

A carboxylic acid is an organic acid that contains a carboxyl group (C(=O)OH) attached to an R-group. The general formula of a carboxylic acid is R−COOH or R−CO_2H, with R referring to the alkyl, alkenyl, aryl, or other group. Carboxylic acids occur widely. Important examples include the amino acids and fatty acids.

Deprotonation of a carboxylic acid gives a carboxylate anion COO^-.

Synthesis

1- From primary alcohols by oxidation



$$R-CH_2-OH \xrightarrow[K_2Cr_2O_7/H_2SO_4]{oxidn.} RCHO \xrightarrow{oxidn.} RCOOH$$

prim. alcohols

aldehyes

2- From aldehydes by oxidation

$$RCHO \xrightarrow{K_2Cr_2O_7/\text{ conc } H_2SO_4} RCOOH$$

3- Hydrolysis of acid derivatives.

$$CH_3COCl + H_2O \longrightarrow CH_3COOH + HCl$$

Reactions

1- Salt formation.

Acids react with metals, metal oxides, hydroxides, carbonates to form salts of carboxylic acids.

$$2\,CH_3COOH + 2Na \longrightarrow 2\,CH_3COONa + H_2\uparrow$$

sodium acetate

$$2\,CH_3COOH + CuO \longrightarrow (CH_3COO)_2Cu + H_2O$$

copper acetate

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

$$CH_3COOH + NaHCO_3 \longrightarrow CH_3COONa + CO_2 + H_2O$$

2- Esterification.

$$CH_3COOH + CH_3OH \longrightarrow CH_3COOCH_3 + H_2O$$

methyl acetate

3- Halogenation.

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

monochloroacetic acid   dichloroacetic   trichloroacetic acid

4- Oxidation (only formic acid).

$$HCOOH \xrightarrow{oxidn.} CO_2 + H_2O$$

formic acid

Reactions of carboxylic acid salts.

1- Silver salts.

$$RX + R'COOAg \longrightarrow R'COOR + AgX$$

esters

2- Heating of ammonium salts.

$$RCOONH_4 \xrightarrow{\triangle} RCONH_2 + H_2O$$

amide

B- Acid derivatives

1- Esters

An ester is a chemical compound derived from an acid (organic or inorganic) in which at least one –OH hydroxyl group is replaced by an –O–alkyl (alkoxy) group, as in the substitution reaction of a carboxylic acid and an alcohol.

Synthesis

1- From acids.

$$CH_3CH_2OH + CH_3COOH \xleftrightarrow{\text{conc. } H_2SO_4} \underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

2- From acylhalides.

$$ROH + \underset{\text{acid chloride}}{R'COCl} \longrightarrow \underset{\text{esters}}{R'COOR} + HCl$$

3- Carbonylation of alkenes and/or alcohols.

$$CH_3OH + CO + C_2H_4 \longrightarrow \underset{\text{methyl propionate}}{C_2H_5COOCH_3}$$

$$CH_3OH + CO \longrightarrow \underset{\text{methyl formate}}{HCOOCH_3}$$

4- Addition of carboxylic acid to alkenes.

$$C_2H_4 + CH_3CO_2H \longrightarrow CH_3CO_2C_2H_5$$

Reactions

1- Ammonolysis.

$$CH_3COOC_2H_5 + NH_3 \longrightarrow \underset{\text{acetamide}}{CH_3CONH_2} + C_2H_5OH$$

2- Aminolysis.

$$CH_3COOC_2H_5 + CH_3NH_2 \longrightarrow \underset{\text{acetanilide}}{CH_3CONHCH_3} + C_2H_5OH$$

3- Transesterfication (with lower alcohols).

$$\underset{\textbf{butyl acetate}}{CH_3COOC_4H_9} + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + C_4H_9OH$$

2- Acylchlorides

In organic chemistry, an acyl chloride (or acid chloride) is an organic compound with the functional group -COCl. Their formula is usually written RCOCl, where R is a side chain. They are reactive derivatives of carboxylic acids. A specific example of an acyl chloride is acetyl chloride, CH_3COCl. Acyl chlorides are the most important subset of acyl halides.

Synthesis

1- From carboxylic acids.

$$\mathbf{CH_3COOH + \underset{\text{phosphorus pentachloride}}{PCl_5} \longrightarrow CH_3COCl + \underset{\text{phosphorus oxychloride}}{POCl_3} + HCl}$$

$$\mathbf{\underset{\text{propionic acid}}{CH_3CH_2COOH} + \underset{\text{phosgene}}{COCl_2} \longrightarrow \underset{\text{propionyl chloride}}{CH_3CH_2COCl} + HCl + CO_2}$$

$$\mathbf{CH_3COOH + \underset{\text{sulfurous dichloride or thionyl chloride}}{SOCl_2} \longrightarrow \underset{\text{acetyl chloride}}{CH_3COCl} + HCl + SO_2\uparrow}$$

2- From anhydrides.

$$\mathbf{\underset{\text{acetic anhydride}}{(CH_3CO)_2O} + HCl \longrightarrow \underset{\text{acetyl chloride}}{CH_3COCl} + CH_3COOH}$$

Reactions

1- Hydrolysis to acid.

$$\mathbf{CH_3COCl + H_2O \longrightarrow CH_3COOH + HCl}$$

2- Alcoholysis to esters.

$$\mathbf{ROH + R'COCl \longrightarrow R'COOR + HCl}$$

3- Synthesis of anhydrides

$$\mathbf{RCOCl + RCOONa \xrightarrow{-\,NaCl} \underset{\text{anhydride}}{RCOOCOR}}$$

4- Formation of amides

$$RCOCl + NH_3 \xrightarrow{-\ HCl} \underset{\text{amide}}{RCONH_2}$$

5- Reduction to aldehydes

$$RCOCl \xrightarrow[Pd\text{-}BaSO_4]{H_2} RCHO + HCl$$

3-Anhydrides

An acid anhydride is a compound that has two acyl groups bonded to the same oxygen atom. A common type of organic acid anhydride is a carboxylic anhydride, where the parent acid is a carboxylic acid, the formula of the anhydride being $(RC(O))_2O$. Symmetrical acid anhydrides of this type are named by replacing the word acid in the name of the parent carboxylic acid by the word anhydride. Thus, $(CH_3CO)_2O$ is called acetic anhydride. Mixed (or unsymmetrical) acid anhydrides, such as acetic formic anhydride, are known, whereby reaction occurs between two different carboxylic acids. Nomenclature of unsymmetrical acid anhydrides list the names of both of the reacted carboxylic acids before the word "anhydride" (for example, the dehydration reaction between benzoic acid and propanoic acid would yield "benzoic propanoic anhydride").

Synthesis

1- From acyl halides.

$$RCOCl + RCOONa \longrightarrow \underset{\text{anhydrides}}{(RCO)_2O} + NaCl$$

$$CH_3COCl + \underset{\text{sodium formate}}{HCOONa} \longrightarrow \underset{\text{acetic formic anhydride}}{HCOOCOCH_3}$$

2- From carboxylic acids by dehydration.

$$CH_3COOH \xrightarrow{P_2O_5} \underset{\text{acetic anhydride}}{CH_3COOCOCH_3}$$

Reactions

1- Hydrolysis to acids.

$$RCOOCOR + H_2O \xrightarrow{\triangle} 2\ RCOOH$$

2- With alcohols

$$RCOOCOR + R'OH \longrightarrow \underset{\text{ester}}{RCOOR'}$$

3- With ammonia

$$RCOOCOR + NH_3 \longrightarrow \underset{\text{amide}}{RCONH_2}$$

4- Reduction

$$RCOOCOR \xrightarrow{H^+} \underset{\text{alcohol}}{RCH_2OH}$$

4- Amides

In organic chemistry, an amide also known as an organic amide or a carboxamide, is a compound with the general formula RC(=O)NR′R″, where R, R', and R″ represent organic groups or hydrogen atoms. It can be viewed as a derivative of a carboxylic acid RC(=O)OH with the hydroxyl group –OH replaced by an amine group –NR′R″; or, equivalently, an acyl (alkanoyl) group RC(=O)– joined to an amine group. Common examples of amides are acetamide $H_3C–CONH_2$, benzamide $C_6H_5–CONH_2$, and dimethylformamide $HCON(–CH_3)_2$. Amides are qualified as primary, secondary, and tertiary according to whether the amine subgroup has the form $–NH_2$, –NHR, or –NRR', where R and R' are groups other than hydrogen. The core –C(=O)N= of amides is called the amide group (specifically, carboxamide group).

Synthesis

1- From ammonium salts by pyrolysis.

$$\mathbf{RCOONH_4 \xrightarrow{\triangle} RCONH_2 + H_2O}$$

2- Partial hydrolysis of nitriles.

$$\mathbf{\underset{nitrile}{RC{\equiv}N} + H_2O \xrightarrow{HCl} RCONH_2}$$

Reactions

1- Dehydration to nitrils.

$$\mathbf{RCONH_2 \xrightarrow{P_2O_5} \underset{nitrile}{RC{\equiv}N} + H_2O}$$

2- Reduction to primary amines.

$$\mathbf{RCONH_2 \xrightarrow[(2H_2)]{Na/EtOH} \underset{prim.\ amine}{RCH_2NH_2} + H_2O}$$

Amines

In organic chemistry, amines are compounds and functional groups that contain a basic nitrogen atom with a lone pair. Amines are formally derivatives of ammonia, wherein one or more hydrogen atoms have been replaced by a substituent such as an alkyl or aryl group (these may respectively be called alkylamines and arylamines; amines in which both types of substituent are attached to one nitrogen atom may be called alkylarylamines). Important amines include amino acids, biogenic amines, trimethylamine, and aniline; Inorganic derivatives of ammonia are also called amines, such as monochloramine ($NClH_2$). The substituent $-NH_2$ is called an amino group. Compounds with a nitrogen atom attached to a carbonyl group, thus having the structure R–CO–NR′R″, are called amides and have different chemical properties from amines.

Synthesis

Synthesis of primary, secondary and tertiary amines from alcohols (mixture).

$$\mathrm{ROH} + \mathrm{NH_3} \xrightarrow{\text{pressure}} \mathrm{RNH_2} + \mathrm{H_2O}$$

$$\mathrm{ROH} + \mathrm{RNH_2} \xrightarrow{\text{pressure}} \mathrm{R_2NH} + \mathrm{H_2O}$$

$$\mathrm{ROH} + \mathrm{R_2NH} \xrightarrow{\text{pressure}} \mathrm{R_3N} + \mathrm{H_2O}$$

Reactions

1- Acylation.

$$\begin{tikzcd}
\mathrm{RNH_2} + \mathrm{RCOCl} \arrow[r] & \mathrm{RNHCOR} \arrow[d, "\mathrm{-\,HCl}"', "\mathrm{RCOCl}"] & + \ \mathrm{HCl} \\
& \mathrm{RN(COR)_2} &
\end{tikzcd}$$

2- Oxidation.

a- Primary amines.

$$RCH_2NH_2 \xrightarrow{KMnO_4} \underset{\text{Imine}}{RCH{=}NH} \xrightarrow{H^+} RCHO$$

b- Secondary amines.

$$R_2NH \xrightarrow{KMnO_4} R_2N-NR_2$$

c- Tertiary amines.

$$R_3N \xrightarrow{H_2O_2} \underset{\text{Amine oxide}}{R_3N \rightarrow O}$$

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