



Organic chemistry

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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.



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



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

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



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-

H

ere 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 in series goes to: The chain which has the greatest number of side chains. a) substituents have **b**) The chain whose the lowestnumbers. 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.

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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-2one ("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).

CH4	methane	CH ₃ CH ₂ CH ₃	propane
CH ₃ CH ₃	ethane	CH ₃ [CH ₂] ₂ CH ₃	butane
CH ₃ [CH ₂] ₃ CH ₃	pentane	CH ₃ [CH ₂] ₄ CH3	hexane
CH ₃ [CH ₂] ₅ CH ₃	heptane	CH ₃ [CH ₂] ₆ CH3	octane
CH ₃ [CH ₂]7CH ₃	nonane	CH ₃ [CH ₂] ₈ CH ₃	decane

Synthesis

1- From alkenes (by catalytic hydrogenation).

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

ethylene ethane

2- From alkynes (by catalytic hydrogenation).

HC \equiv CH $\xrightarrow{2H_2/Pt}$ CH₃-CH₃ acetylene

3- From alkyl halides (RX).

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

 $\begin{array}{c} CH_{3}Br \xrightarrow{Zn/HCl} CH_{4} + HBr \\ methyl methane \\ bromide \end{array}$

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

4- From Wolff Kishner's reaction.

$$H_{3C} \xrightarrow{O} CH_{3} + N_{2}H_{4} \xrightarrow{KOH} CH_{3}CH_{2}CH_{3} + N_{2} + H_{2}O$$

acetone hydrazine propane

5- From organometalic reagents.

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

6- Hydrolysis of metal carbides.

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

aluminium carbide

Reactions

1- Halogenation.

$$CH_4 + X_2 \xrightarrow{light or} CH_3X + HX$$

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

$$methyl$$

$$hv = energy$$

2-Nitration.

$$CH_4 + HNO_3 \xrightarrow{\text{vapour phase}} CH_3NO_2 + H_2O$$

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).

 $CH_{3}CH_{2}-Br + KOH \xrightarrow{alcohol} CH_{2}=CH_{2} + KBr + H_{2}O$ ethyl bromide

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

3- From alcohols (via dehydration).

$$\begin{array}{c} \text{CH}_3\text{CH}_2\text{-OH} & \xrightarrow{\text{Conc. H}_2\text{SO}_4/180 \ ^{\text{o}}\text{C}} \\ \text{or Al}_2\text{O}_3/400 \ ^{\text{o}}\text{C} \end{array} \quad \text{CH}_2\text{=CH}_2 + \text{H}_2\text{O}_3\text{-C} \\ \end{array}$$

4- Dehalogenation of vicinal dihalides.

$$\begin{array}{ccc} CH_2 & -CH_2 & Zn \\ | & | \\ Br & Br \\ 1,2-dibromoethane \end{array} \rightarrow CH_2 = CH_2 + ZnBr_2$$

Reactions

1- Addition of hydrogen.

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

2- Addition of halogens.

$$CH_2 = CH_2 + Br_2 \longrightarrow CH_2 - CH_2$$
$$| \\Br Br$$

3- Addition of halogen acids.

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

4- Addition of water.

$$CH_{3}-CH=CH_{2} \xrightarrow{H^{+}} CH_{3} \xrightarrow{H} CH_{3} \xrightarrow{H} CH_{3}$$
propene
$$OH$$
propan-2-ol

C-Alkynes

Unsaturated hydrocarbons (contain triple bond).

Synthesis

From alkyl halides.

Br Br

$$CH-CH$$
 $\xrightarrow{2 Zn}$ $HC \equiv CH + 2 ZnBr_2$
Br Br
 $1,1,2,2$ -
tetrabromoethane

 $\begin{array}{cccc} Br & Br \\ | & | \\ CH_2 - CH_2 & + \end{array} & 2KOH \xrightarrow{alco.} HC \equiv CH + 2KBr + 2H_2O \end{array}$

1,2-dibromoethane

$$CH_2 = CH \xrightarrow[]{H_2} CH \equiv CH$$

Br
bromoethylene

Reactions

1- Addition of hydrogen.

HC≡CH
$$\xrightarrow{2H_2/Cat.}$$
 CH₃-CH₃
HC≡CH $\xrightarrow{H_2/Pd}$ CH₂=CH₂

2- Addition of bromine.

3- Addition of hydrogen cyanide (HCN).

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

4- Addition of HBr.



<u>Halogen derivatives of saturated hydrocarbons</u> (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.

 $\begin{array}{cccc} CH_3 - CH_2Br & CH_3 - CH_2 - CH_2Cl & CH_3 - CH_2I \\ bromoethane & 1-chloropropane & CH_3 \end{array}$

-iodo-2-methylpropane

primary alkyl halide

 $\begin{array}{ccc} CH_3 - CH - CH_3 & CH_3 - CH - CH_2 CH_3 \\ & & | \\ Br & Br \\ \end{array}$

2-bromopropane 2-bromobutane

secondary alkyl halide



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 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

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

3- From alcohols.

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

4- Addition of hydrogen halides to alkenes.

$$H_{3}C - C \equiv CH \xrightarrow{HCl} CH_{3} - \overset{Cl}{C} = CH_{2} + CH_{3} - CH_{2} - CH_{2}CH_{2}$$

propyne 2-chloroprop-1-ene 1-chloropropane

Reactions

Nucleophilic substitution.

RX + NaOH → ROH (alcohols) + NaX RX + NaR → R-R (alkanes) + NaX RX + KI → RI (alkyl halides) + KX RX + NaOR → ROR (ethers) + NaX sodium alkoxide

<u>Alcohols</u>

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 ₃ OH			
n-propanol	CH ₃ CH ₂ CH ₂ OH			
iso-propanol	CH ₃ CH(OH)CH ₃			
t-butanol	(CH ₃) ₃ COH			

Synthesis

1- From alkyl halides by hydrolysis.

RX + NaOH ----> ROH (alcohols) + NaX

2- From aldehydes and ketones.



3- From ethers.

 $\begin{array}{c} C_2H_5OC_2H_5 \\ \text{diethyl ether} \end{array} \xrightarrow{H_2O} 2C_2H_5OH \\ pressure \end{array}$

4- From alkenes.

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

Reactions

1- Reaction with halogen acids.

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

2- Dehydration.

$$CH_{3}CH_{2}-OH \xrightarrow{Conc. H_{2}SO_{4}/180 \ ^{o}C} CH_{2}=CH_{2} + H_{2}O$$
or Al_{2}O_{3}/400 \ ^{o}C

3- Esterification.

$$CH_3CH_2OH + CH_3COOH \underbrace{conc. H_2SO_4}_{ethyl acetate} CH_3COOC_2H_5 + H_2O$$

4-Reaction with ammonium.

ROH + ROH
$$\xrightarrow{\text{pressure}}$$
 (R)₂NH + H₂O
secondary
amines
(R)₂NH + ROH $\xrightarrow{\text{pressure}}$ R₃N + H₂O
tertiary

amines

5- Reaction with phosphorus pentasulphide (P_2S_5) .

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

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" (CH₃–CH₂–O–CH₂–CH₃).

Synthesis

1- From alkyl halides (Williamson Synthesis).

$$RX + NaOR \longrightarrow ROR$$
 (ethers) + NaX

2- By dehydration of alcohols.

$$2C_{2}H_{5}OH \xrightarrow{H_{2}SO_{4}} C_{2}H_{5}OC_{2}H_{5}$$

diethyl ether

Reactions

1- Cleavage by halogen acids.

ROR + HX
$$\xrightarrow{\text{conc.}}$$
 RX + ROH
(CH₃CH₂)₂O + HI $\xrightarrow{\text{high temp.}}$ CH₃CH₂I + CH₃CH₂OH
(CH₃CH₂)₂O + 2HI (conc.) $\xrightarrow{\text{high temp.}}$ 2CH₃CH₂I + H₂O

2- Reaction with phosphorus pentasulphide P₂S₅.

0000

$$5C_2H_5OC_2H_5 + P_2S_5 \xrightarrow{\Delta} 5C_2H_5SC_2H_5 + P_2O_5$$

diethylthioether

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.

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

perchloro diethyl ether

5- Reaction with carbon monoxide

$$C_2H_5OC_2H_5 \xrightarrow{CO} C_2H_5COOC_2H_5$$

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 → RSH + KX Thioalcohols or thiols

CH₃Br \xrightarrow{Mg} CH₃MgBr $\xrightarrow{S_8, H^+}$ CH₃SH Grignard methanethiol reagent

2- From alcohols.

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

Reactions

1- With sodium.

2 C ₂ H ₅ SH	+	2Na>	2 C ₂ H ₅ SNa
ethanethiol			sodium
			ethanethiolate

2- Reaction with lead acetate.

 $2RSH + (CH_{3}COO)_{2}Pb \longrightarrow (RS)_{2}Pb \downarrow + 2 CH_{3}COOH$ lead acetate lead mercaptide

3- Reaction with alumina/zinc sulphide.

 $2 \text{ CH}_{3}\text{CH}_{2}\text{SH} \xrightarrow{\text{Al}_{2}\text{O}_{3}} \text{(CH}_{3}\text{CH}_{2})_{2}\text{S} + \text{H}_{2}\text{S}$ $\xrightarrow{\text{ZnS/300 °C}} \text{diethylthioether}$

4- Reaction with alkenes.

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

5- Formation of thioethers

$$CH_{3}SH + CH_{3}ONa \longrightarrow CH_{3}SNa \xrightarrow{CH_{3}Br} CH_{3}SCH_{3}$$
sodium
dimethylthioether
methanethiolate

6- Oxidation by iodine

 $2CH_3SH \xrightarrow{I_2} CH_3SSCH_3$ disulfide

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 K₂S).

RX + KSR ----> RSR + KX potassium thioethers alkanethiolate

2- From ethers (via reaction with P₂S₅).

 $5 \text{ ROR} + P_2 S_5 \longrightarrow 5 \text{ RSR} + P_2 O_5$

Reactions

1- Desulphurization.

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

2- Oxidation.

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

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.

$$\begin{array}{c} \text{RCH}_2\text{OH} & \xrightarrow{\text{Cu/325 °C}} & \text{RCHO} \\ \hline & -\text{H}_2 & \text{aldehydes} \end{array}$$

2- From acid derivatives (from acetyl chlorides).

 $CH_{3}COCI \xrightarrow{H_{2}/Pd} CH_{3}CHO + HCI$ acetyl chloride acetaldehyde

3- From alkenes (by hydroformylation).

$$CH_{3}CH = CH_{2} + CO + H_{2} \longrightarrow CH_{3}CH_{2}CH_{2}CH_{0}$$
propene butyraldehyde

4- From nitriles

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

5- From geminal halide hydrolysis

$$\text{RCHCl}_2 \xrightarrow{\text{KOH}} \text{RCHOHCl} \longrightarrow \text{RCHO}$$

Reactions

1- Addition of hydrogen.

a- Reduction to alkanes (Clemensen reduction).

$$CH_{3}CHO \xrightarrow{Zn[Hg]/HCl} H_{3}C-CH_{3} + H_{2}O$$

2- Addition of hydrogen cyanide.

$$CH_{3}CHO + HCN \longrightarrow CH_{3}CH$$

$$CN$$

$$CN$$

$$acetaldehyde$$

$$cyanohydrine$$

3- Addition of hydrazine (H₂N-NH₂).

$$CH_{3}CHO + H_{2}NNH_{2} \longrightarrow CH_{3}CH=NNH_{2} + H_{2}O$$

acetaldehyde
hydrazone
$$-H_{2}O \bigvee CH_{3}CHO$$

$$CH_{3}CH=N-NCHCH_{3}$$

4- Oxidation with potassium dichromate K₂Cr₂O₇/conc H₂SO₄.

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 CH₃C(O)CH₃. 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.

(R)₂CHOH
$$\xrightarrow{\text{oxidtion}}$$
 (R)₂C=O
sec. alcohols $K_2Cr_2O_7/H_2SO_4$ ketones

b- Dehydrogenation.

$$(R)_2 CHOH \xrightarrow{Cu/325 \ ^{\circ}C} (R)_2 C=O$$

Reactions

1- Reduction to alkanes.



2- Addition of ammonia derivatives

a- With hydroxyl amine.

$$(CH_3)_2CO + H_2NOH \longrightarrow (CH_3)_2C=NOH$$

acetone
oxime

b- With hydrazine.

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

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-CO₂H, 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



prim. alcohols

2- From aldehydes by oxidation

RCHO
$$\xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7/\text{ conc H}_2\text{SO}_4}$$
 RCOOH

3- Hydrolysis of acid derivatives.

 $CH_3COCI + H_2O \longrightarrow CH_3COOH + HCI$

Reactions

1- Salt formation.

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

 $2 \text{ CH}_{3}\text{COOH} + 2\text{Na} \longrightarrow 2 \text{ CH}_{3}\text{COONa} + \text{H}_{2} \uparrow$ sodium
acetate $2 \text{ CH}_{3}\text{COOH} + \text{CuO} \longrightarrow (\text{CH}_{3}\text{COO})_{2}\text{Cu} + \text{H}_{2}\text{O}$ copper
acetate $C\text{H}_{3}\text{COOH} + \text{NaOH} \longrightarrow C\text{H}_{3}\text{COONa} + \text{H}_{2}\text{O}$ $C\text{H}_{3}\text{COOH} + \text{NaHCO}_{3} \longrightarrow C\text{H}_{3}\text{COONa} + C\text{O}_{2} + \text{H}_{2}\text{O}$

2- Esterification.

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

methyl acetate

3- Halogenation.

 $\begin{array}{cccc} CH_{3}COOH \xrightarrow{Cl_{2}/P} & ClCH_{2}COOH \xrightarrow{Cl_{2}/P} & Cl_{2}CHCOOH \xrightarrow{Cl_{2}/P} & Cl_{3}CCOOH \\ \hline monochloroacetic & dichloroacetic & trichloroacetic \\ acid & acid & acid \end{array}$

4- Oxidation (only formic acid).

HCOOH $\xrightarrow{\text{oxidn.}}$ CO₂ + H₂O formic acid

Reactions of carboxylic acid salts.

1- Silver salts.

2- Heating of ammonium salts.

 $\begin{array}{ccc} \text{RCOONH}_4 & \stackrel{\triangle}{\longrightarrow} & \text{RCONH}_2 + & \text{H}_2\text{O} \\ & \text{amide} \end{array}$

<u>B- Acid derivatives</u> 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.

 $CH_3CH_2OH + CH_3COOH - CH_2SO_4 + H_2O$ ethyl acetate

2- From acylhalides.

3- Carbonylation of alkenes and/or alcohols.

 $CH_3OH + CO + C_2H_4 \longrightarrow C_2H_5COOCH_3$ methyl propionate

> CH₃OH + CO → HCOOCH₃ methyl formate

4- Addition of carboxylic acid to alkenes.

 $C_2H_4 + CH_3CO_2H \longrightarrow CH_3CO_2C_2H_5$

Reactions

1- Ammonolysis.

 $CH_3COOC_2H_5 + NH_3 \longrightarrow CH_3CONH_2 + C_2H_5OH$ acetamide

2- Aminolysis.

 $CH_3COOC_2H_5 + CH_3NH_2 \longrightarrow CH_3CONHCH_3 + C_2H_5OH$ acetanilide

3- Transesterfication (with lower alcohols).

 $CH_3COOC_4H_9 + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + C_4H_9OH$ butyl acetate

<u>2- Acylchlorides</u>

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, CH₃COCl. Acyl chlorides are the most important subset of acyl halides.

Synthesis

1- From carboxylic acids.

2- From anhydrides.

 $(CH_3CO)_2O + HCl \longrightarrow CH_3COCl + CH_3COOH$ acetic anhydride acetyl chloride

Reactions

1- Hydrolysis to acid.

 $CH_3COCI + H_2O \longrightarrow CH_3COOH + HCI$

2- Alcoholysis to esters.

ROH + R'COCl → R'COOR + HCl

3- Synthesis of anhydrides

RCOCl + RCOONa - NaCl RCOOCOR anhydride

4- Formation of amides

$$\begin{array}{rcl} \text{RCOCl} + \text{NH}_3 & \xrightarrow{-\text{HCl}} & \text{RCONH}_2\\ & \text{amide} \end{array}$$

5- Reduction to aldehydes

$$RCOCI \xrightarrow{H_2} RCHO + HCI$$

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, (CH₃CO)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 → (RCO)₂O + NaCl anhydrides CH₃COCl + HCOONa → HCOOCOCH₃ sodium formate acetic formic anhydride

2- From carboxylic acids by dehydration.

 $CH_{3}COOH \xrightarrow{P_{2}O_{5}} CH_{3}COOCOCH_{3}$ acetic anhydride

Reactions

1- Hydrolysis to acids.

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

2-With alcohols

 $\begin{array}{rcl} \text{RCOOCOR} &+ & \text{R'OH} \longrightarrow & \text{RCOOR'} \\ & & \text{ester} \end{array}$

3- With ammonia

$$\begin{array}{rcl} \text{RCOOCOR} + \text{NH}_3 & \longrightarrow & \text{RCONH}_2 \\ & & \text{amide} \end{array}$$

4- Reduction

$$\begin{array}{ccc} \text{RCOOCOR} & \xrightarrow{\text{H}^+} & \text{RCH}_2\text{OH} \\ & & \text{alcohol} \end{array}$$

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 H₃C–CONH₂, benzamide C₆H₅–CONH₂, and dimethylformamide HCON(–CH₃)₂. Amides are qualified as primary, secondary, and tertiary according to whether the amine subgroup has the form –NH₂, –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.

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

2- Partial hydrolysis of nitriles.

$$\begin{array}{rcl} RC \equiv & N + H_2O & \xrightarrow{HCl} & RCONH_2\\ nitrile & \end{array}$$

Reactions

1- Dehydration to nitrils.

$$\operatorname{RCONH}_2 \xrightarrow{P_2O_5} \operatorname{RC} = N + H_2O$$

nitrile

2- Reduction to primary amines.

$$\frac{\text{Na/EtOH}}{(2H_2)} \rightarrow \text{RCH}_2\text{NH}_2 + H_2O$$
prim. amine
<u>Amines</u>

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 (NCIH₂). The substituent -NH₂ 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).

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

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

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

Reactions

1- Acylation.

$$RNH_{2} + RCOCI \longrightarrow RNHCOR + HCI$$
$$- HCI \downarrow RCOCI$$
$$RN(COR)_{2}$$

2- Oxidation.

a- Primary amines.

$$\operatorname{RCH}_{2}\operatorname{NH}_{2} \xrightarrow{\operatorname{KMnO}_{4}} \operatorname{RCH} \xrightarrow{\operatorname{HH}} \operatorname{RCHO}_{\operatorname{Imine}} \xrightarrow{\operatorname{H}^{+}} \operatorname{RCHO}_{\operatorname{Imine}}$$

b- Secondary amines.

$$R_2NH \xrightarrow{KMnO_4} R_2N \longrightarrow R_2N$$

c- Tertiary amines.

$$R_3N \xrightarrow{H_2O_2} R_3N \longrightarrow O$$

Amine oxide

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Aromatic compound

(Part 2)

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Aromatic compound

Aromatic compounds are organic <u>chemical compounds</u> that contain one or more <u>rings</u> with <u>pi electrons</u> delocalized all the way around them. In contrast to compounds that exhibit <u>aromaticity</u>, <u>aliphatic compounds</u> lack this delocalization. The term "aromatic" referred simply to the fact that many such compounds have a sweet or pleasant odour ; however, not all aromatic compounds have a sweet odour, and not all compounds with a sweet odour are aromatic compounds.

Aromatic hydrocarbons, or **arenes**, are aromatic organic compounds containing solely carbon and hydrogen atoms. The configuration of six carbon atoms in aromatic compounds is called a "benzene ring", after the simple aromatic compound <u>benzene</u>, or a <u>phenyl</u> group when part of a larger compound.

Hückel's rule

Not all aromatic compounds are benzene-based; aromaticity can also manifest in **heteroarenes**, which follow <u>Hückel's rule</u> (for monocyclic rings: when the number of its π electrons equals 4n + 2, where n = 0, 1, 2, 3, ...). In these compounds, at least one carbon atom is replaced by one of the <u>hetero</u> <u>atoms oxygen</u>, <u>nitrogen</u>, or <u>sulfur</u>.

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Benzene ring model

Benzene (also called **cyclohexatriene**) is an <u>organic chemical</u> <u>compound with</u> the <u>molecular</u> formula C_6H_6 . The benzene <u>molecule</u> is composed of six <u>carbon</u> atoms joined in a planar <u>ring</u> with one <u>hydrogen</u> atom attached to each. Because it contains only carbon and hydrogen atoms, benzene is classed as a <u>hydrocarbon</u>.

Benzene is a natural constituent of <u>crude oil</u> and is one of the elementary <u>petrochemicals</u>. Due to the cyclic continuous <u>pi</u> <u>bonds</u> between the carbon atoms, benzene is classed as an <u>aromatic hydrocarbon</u>. Benzene is a colorless and highly flammable liquid with a sweet smell.

General properties of aromatic hydrocarbons:

- 1. They display aromaticity
- 2. The carbon-hydrogen ratio is high
- They burn with a strong sooty yellow flame because of the high carbon–hydrogen ratio

4. They undergo electrophilic substitution

reactions and nucleophilic aromatic substitutions



1- By reaction of phenol with zinc dust



2- By reaction of sodium benzoate with soda lime



3- By passing acetylene in red hot tube



4- By boiling benzene sulphonic acid with water and HCl



Reaction of benzene ring :-

Addition reaction of benzene :-

Benzene undergoes certain addition reaction

1- Addition of hydrogen

When a mixture of benzene and hydrogen is passed over nickel catalyst form cyclohexane



2- addition of halogen

Benzene can add chlorine in the presence of ultraviolet light to give 1,2,3,4,5,6-hexachlorocyclohexan



Substitution reaction

1-Halogenation

Benzene react with CL-Br in absence of sun light in percent of

FeCl3 to form chlorobenzene or bromobenzene.



2- Nitration

Benzene react with conc. $HNO_3 \mbox{ and } \mbox{ conc. } H_2SO_4 \mbox{ to form nitrobenzene}$.



Mechanism of nitration :-



3- Sulphonation

Benzene react with conc. $\mathrm{H}_2\mathrm{SO}_4$ to form benzene sulphonic acid .



4-Friedil-craft alkylation:-

Benzene react with methyl chloride in presence of AlCl₃ anhydride.



5-friedil-craft acylation:-

Benzene react with acyl chloride in presence of AlCl₃ anhydride.



Toluene (alkylbenzene)

is a substituted aromatic hydrocarbon. It is a colorless, water-

insoluble liquid with the smell associated with paint thinners. It is a

mono-substituted <u>benzene</u> derivative, consisting of a <u>methyl</u>

group (CH₃) attached to a phenyl group. As such, its systematic

IUPAC name is **methylbenzene**. Toluene is predominantly used

as an industrial feedstock and a solvent.



Preparation of toluene

<u>1-</u> Friedil-craft alkylation:-

Benzene react with methyl chloride in presence of AlCl₃ anhydride.



2-The Wurtz–Fittig reaction:-

is the chemical reaction of aryl halides with alkyl

halides and sodium metal in the presence of dry ether to give

substituted aromatic compounds.



Mechanism :-





3- From Grignard reagents



Phenyl magnesium bromide Grignard reagent

Reaction of toluene :-A- Oxidation of the side chain

1- Oxidation by $KMNO_4$:- toluene oxidized by $kMno_4$ / H_2SO_4 to benzoic acid



2- Oxidation with MnO₂/H₂SO₄



3- Catalytic oxidation by air



Ethyl benzene or Phenyl ethane

B-Reaction in benzene ring

1- Reduction :-



2-Nitration



Preparation of T.N.T

Trinitrotoluene (more commonly known as **TNT**, more specifically **2,4,6-trinitrotoluene**, and by its preferred IUPAC name **2-Methyl-1,3,5-trinitrobenzene**, is a <u>chemical compound</u> with the formula $C_6H_2(NO_2)_3CH_3$. TNT is occasionally used as a <u>reagent</u> in <u>chemical</u> <u>synthesis</u>, but it is best known as an <u>explosive</u> <u>material</u> with convenient handling properties.

 $HNO_3 + H_2SO_4 \longrightarrow NO_2^+ + HSO_4^- + H_2O$



3- Reaction with H₂SO₄



o-Toluenesulphonic acid

 SO_3H *p*-Toluenesulphonic acid

CH₃

4- Friedel-Craft alkylation



o-Xylene



5- Reaction with halogens



C- Reaction of the side chain

1-Halogenation







Benzyl halides

Benzyl chloride

Benzyl chloride, or α -chlorotoluene, is an <u>organic</u>

<u>compound</u> with the <u>formula</u> $C_6H_5CH_2CI$. This colorless liquid is a reactive <u>organochlorine compound</u> that is a widely used chemical building block.

Synthesis and preparation :-

1-From toluene



Reactions

1-With aqueous NaOH



2- With potassium cyanide KCN



3- With ammonia NH₃



Benzal chloride Synthesis and preparation :-

1-From benzyl chloride



Reactions

1-With aq. Na₂CO₃



Benzotrichloride

Synthesis and preparation :-

1-From benzal chloride



Reactions

1-With aq. Na₂CO₃



Preparation of DDT

Dichlorodiphenyltrichloroethane, commonly known as DDT, is a

colorless, tasteless, and almost odorless crystalline chemical

compound an organochloride.



Aromatic nitro compounds Nitrobenzene

Nitrobenzene is an organic compound with the chemical

formula $C_6H_5NO_2$. It is a water-insoluble pale yellow oil with

an <u>almond</u>-like odor. It freezes to give greenish-yellow crystals. It

is produced on a large scale from <u>benzene</u> as a precursor

to <u>aniline</u>. In the laboratory, it is occasionally used as a <u>solvent</u>,

especially for <u>electrophilic</u> reagents.

Synthesis and preparation :-

1- From direct nitration of benzene



2- From diazonium salt



Reactions

Reduction to aniline



Aromatic amines Aniline

_aniline is the simplest <u>aromatic amine</u>. It is an industrially significant <u>commodity chemical</u>, as well as a versatile starting material for <u>fine chemical</u> synthesis. Its main use is in the manufacture of precursors to <u>polyurethane</u>, dyes, and other industrial chemicals. Like most volatile amines, it has the odor of rotten <u>fish</u>.

Synthesis and preparation :-

1-From benzamide



Reactions

1- With methanol



N-methylaniline N, N-dimethylaniline

2- Reaction with bromine



3- Reaction with acetyl chloride or acetic anhydride



4- Reaction with sulphoric acid



5- Boiling with water



sandmeyer reaction



[X = Cl, Br]

Aromatic diazonium salts

Synthesis and preparation :-

1-From aniline



Reactions 1- Boiling with water



2-With potassium iodide



3- With copper cyanide



4- With sodium nitrite and copper nitrite



Aromatic compound



Phenols

Phenol (also called carbolic acid) is an aromatic organic

<u>compound</u> with the molecular <u>formula</u> C_6H_5OH . It is a

white crystalline solid that is volatile. The molecule consists of

a <u>phenyl group</u> $(-C_6H_5)$ bonded to a <u>hydroxy group</u> (-OH).

Mildly acidic, it requires careful handling because it can

cause chemical burns.

Synthesis and preparation :-

1-From salicylic acid



2- With phosphorous pentachloride



3- With bromine



4-Alkylation



5-Nitration



6- Reduction



Aryl thiols

Thiophenol is an organosulfur compound with the formula

 C_6H_5SH , sometimes abbreviated as PhSH. This foul-smelling

colorless liquid is the simplest aromatic thiol.

Synthesis and preparation :-

From phenols



Reactions 1- With mild oxidizing agent



2- With strong KMnO₄



Aromatic alcohol

Benzyl alcohol is an aromatic alcohol with the formula

 $C_6H_5CH_2OH$. Benzyl alcohol is a colorless liquid with a mild

pleasant aromatic odor. It is a useful solvent due to its polarity, low

toxicity, and low vapor pressure. Benzyl alcohol has

moderate solubility in water .

Synthesis and preparation :-

From benzyl chloride



Reactions

1- Oxidation



2- Esterformation



Aromatic aldehyde

Benzaldehyde (C₆H₅CHO) is an <u>organic compound</u> consisting of a <u>benzene</u> ring with a <u>formyl</u> substituent. It is the simplest <u>aromatic aldehyde</u> and one of the most industrially useful. It is a colorless liquid with a characteristic <u>almond</u>-like <u>odor</u>. The primary component of <u>bitter almond</u> oil, benzaldehyde can be extracted from a number of other natural sources. Synthetic benzaldehyde is the flavoring agent in imitation almond extract, which is used to flavor cakes and other baked goods.

Synthesis and preparation :-

1- From benzyl chloride



2- From benzoyl chloride



Reactions

1-Oxidation



2- Cannizaro reaction



3- With hydrazine



4- With phenylhydrazine



5- With semicarbazide



6- With amines



Aromatic ketones

Acetophenone is the organic compound with

the formula $C_6H_5C(O)CH_3$ (also represented by the pseudoelement

symbols PhAc or BzMe). It is the simplest aromatic ketone. This

colorless, viscous liquid is a precursor to useful $\underline{\text{resins}}$ and

fragrances.

Synthesis and preparation :-

By the reaction of Grignar reagents benzonitrile



Reactions

1- With bromine





2- With hydrazine



3- With phenyl hydrazine



4- With hydrogen cyanide





Aromatic carboxylic acid

Benzoic acid is a white (or colorless) solid with the formula $C_6H_5CO_2H$. It is the simplest <u>aromatic carboxylic acid</u>. The name is derived from <u>gum benzoin</u>, which was for a long time its only source. Benzoic acid occurs naturally in many plants and serves as an intermediate in the biosynthesis of many <u>secondary</u> <u>metabolites</u>. Salts of benzoic acid are used as food preservatives. Benzoic acid is an important precursor for the industrial synthesis of many other organic substances. The salts and <u>esters</u> of benzoic acid are known as **benzoates**.
Synthesis and preparation :-

From toluene



Reactions 1- With NaOH



2- With Na₂CO₃



3- With lithium aluminium hydride



4- With ammonia



5- Ester formation



6-Nitration



Benzensulfonic acid

Benzenesulfonic acid (conjugate base benzenesulfonate) is an organosulfur compound with the formula $C_6H_6O_3S$. It is the simplest aromatic sulfonic acid. It forms white deliquescent sheet crystals or a white waxy solid that is soluble in water and ethanol, slightly soluble in benzene and insoluble in nonpolar solvents like diethyl ether. It is often stored in the form of alkali metal salts. Its aqueous solution is strongly acidic.

Synthesis and preparation :-

From benzene



<u>Reaction :-</u> 1-with NaOH



2- with HCl



Preparation of Saccharin

Saccharin is an <u>artificial sweetener</u> with effectively no <u>food</u> <u>energy</u>. It is about 550 times as sweet as <u>sucrose</u> but has a bitter or metallic <u>aftertaste</u>, especially at high concentrations. Saccharin is used to sweeten products such as drinks, candies, cookies, and medicines.



Reference

- 1- Reaction of aromatic compound book
- 2- Text book of organic chemistry