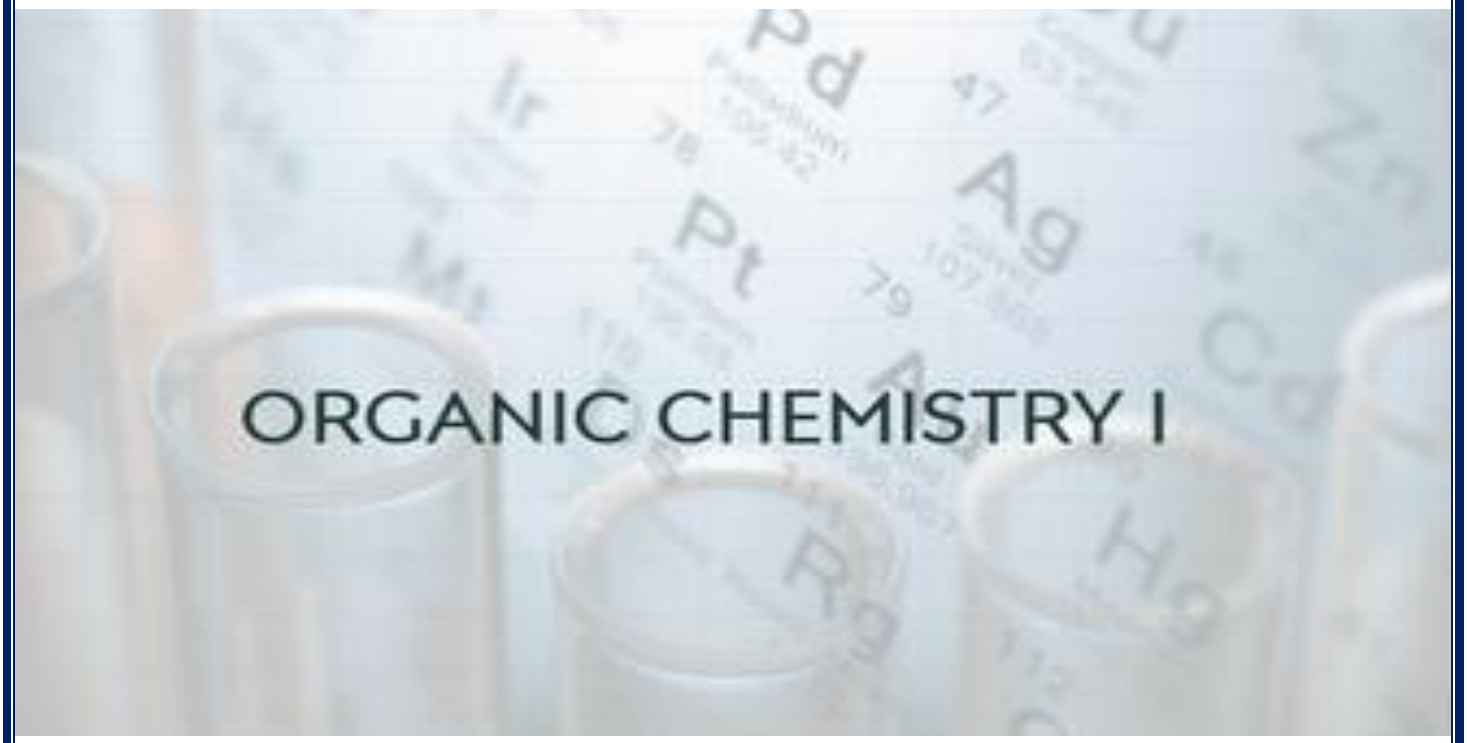
Echahid Hamma Lakhdar University – El Oued

Faculty of Technology

Department : Process and Petrochemical Engineering

ORGANIC CHEMISTRY – COURSES AND EXERCISES

2nd year process engineering and petrochemical industries



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University year: 2025/2026

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CHAPTER III: ISOMERISM AND STEREOISOMERISM

PREFACE

Organic chemistry is a field of chemistry devoted to the study of molecules that contain carbon. This includes the analysis of their structures, properties, compositions, reactions, and methods of synthesis. It serves as the foundation of biochemistry, which focuses on the study of naturally occurring molecules and their interactions. Organic chemistry has numerous applications in the industrial world such as in materials, dyes, and pharmaceuticals giving it a major economic significance.

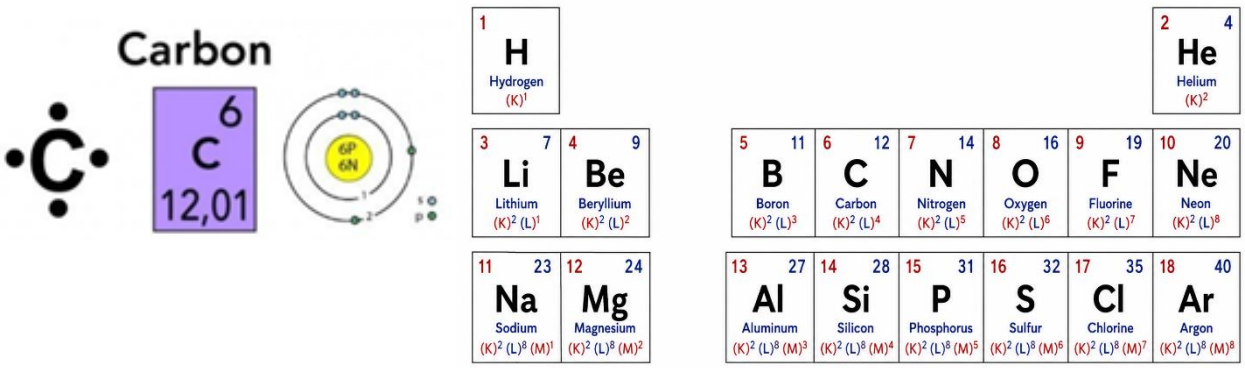
The writing of this course, dedicated to organic chemistry, aims to introduce the basic concepts of general organic chemistry. This manual is intended for 2nd year process engineering and petrochemical industries students in the chemical track. It will also be of interest to students in other fields such as process engineering, the petrochemical industry, biology, and pharmacy. Using this manual does not require in-depth prior knowledge of organic chemistry. This course is structured into five chapters:

1. ***GENERALITIES***
2. ***CLASSIFICATION OF ORGANIC FUNCTIONS***
3. ***ISOMERISM AND STEREOISOMERISM***
4. ***ELECTRONIC STRUCTURES OF MOLECULES***
5. ***REACTIONS AND THEIR MECHANISMS***

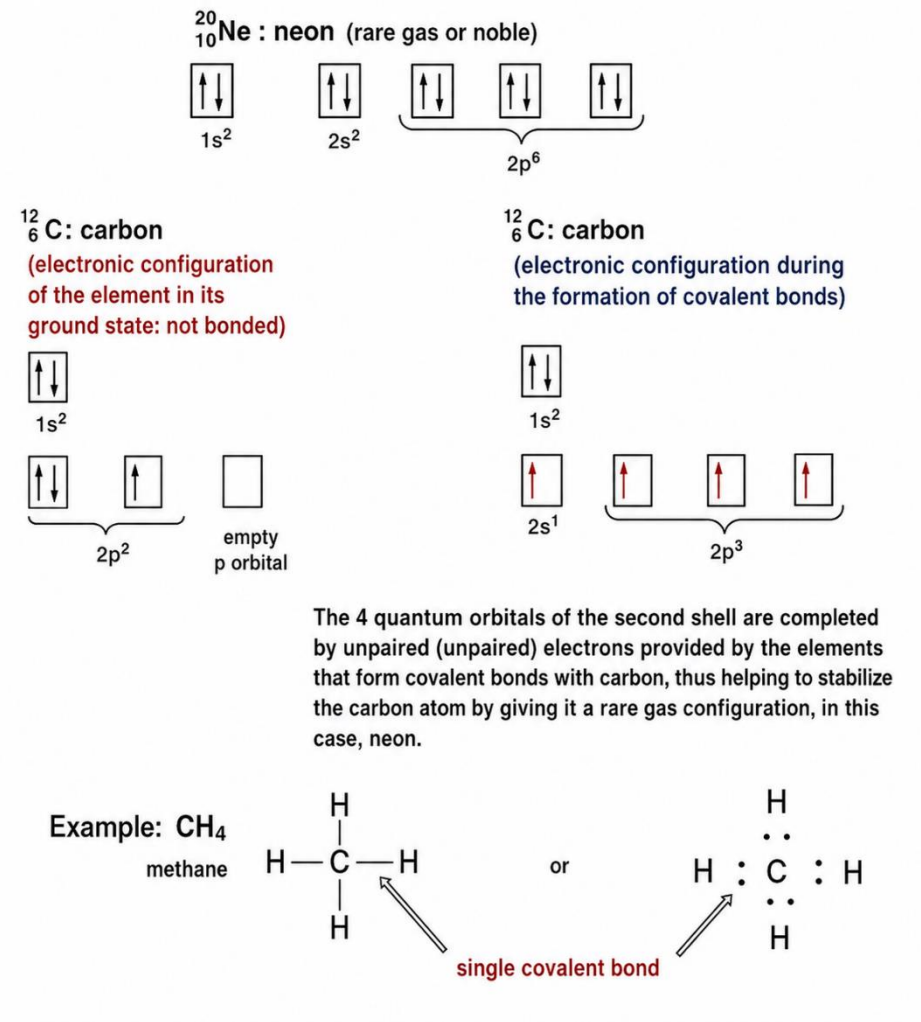
Chapter I: GENERALITIES

I. The carbon atom

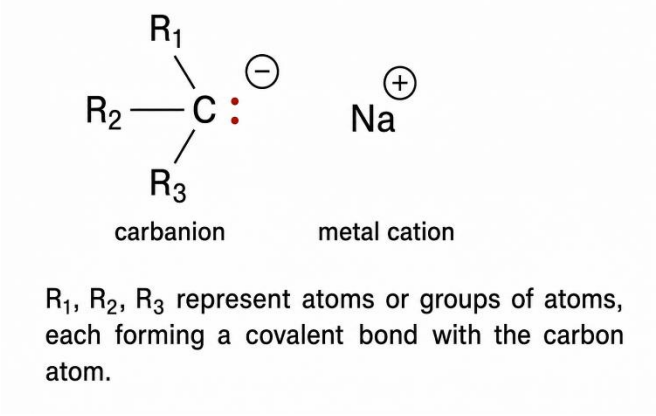
The element "carbon" is located in the middle of the second period of the Mendeleyev table between boron (B) and nitrogen (N).



Carbon belongs to the 4th family of elements. Its atomic number (Z) is 6, and its electronic configuration is: $1\ s^2\ 2\ s^2\ 2\ p^2$



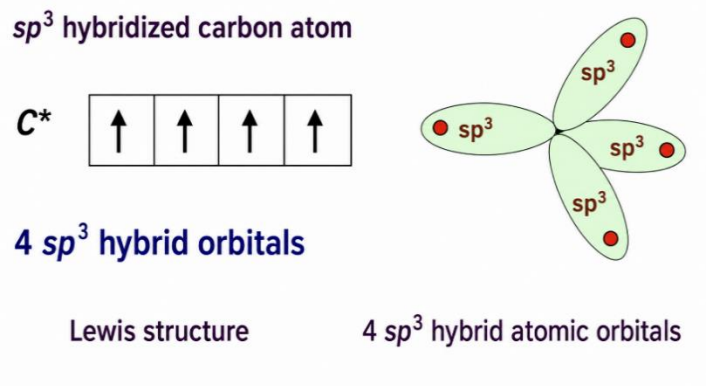
A covalent bond, symbolized by a line, results from the sharing of a single electron by each atom making up the bond; these two electrons define the bonding doublet. Carbon can form ionic bonds with alkali metals (Na, K and Li).



R_1, R_2, R_3 represent atoms or groups of atoms, each forming a covalent bond with the carbon atom.

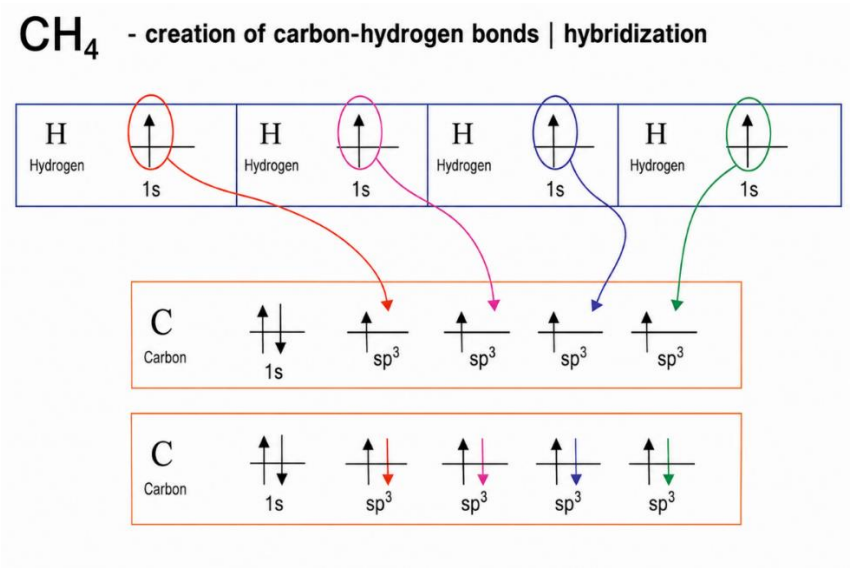
I.1The sp3

If a carbon atom forms 4 σ-single bonds with other atoms, it is in the "sp^3" hybridized state. The four axes of symmetry of these hybridized carbon orbitals form equal dihedral angles of 109° 28'. The carbon nucleus is at the center of the representation.



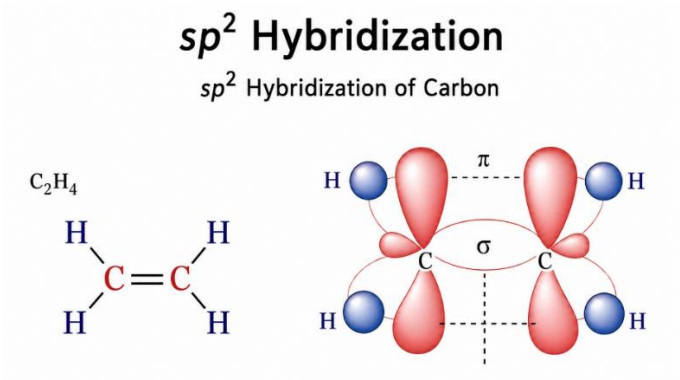
This type of hybridization is that of the carbon in CH_4 methane: 4 equivalent σ-bonds are formed by overlapping the 4 "sp^3" hybridized orbitals of the carbon with the 4 "s".

The 4 spherical "s" orbitals of 4 hydrogen atoms forming a tetrahedral system. The 4spherical "s" orbitals of 4 hydrogen atoms form a tetrahedral system. This carbon hybridization is found in all alkanes with the general formula C_nH_{2n+2}, such as ethane C_2H_6, propane C_3H_8 , butane C_4H_{10} , etc.



I.2 sp2 hybridization

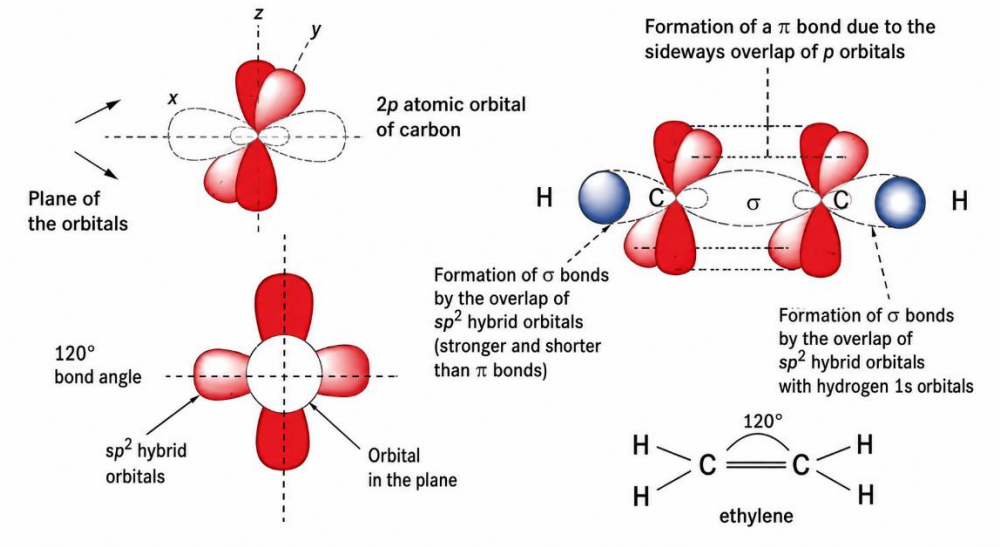
In this type of carbon atomic orbital hybridization, only one "p" orbital in layer 2 remains pure. The other 3 orbitals are hybridized "sp^2" from the "s" orbital and the two remaining "p" orbitals. 8 The 3 "sp^2" hybridized orbitals are equivalent, with coplanar axes of symmetryand 120° angles between them. The pure "p" orbital lies on either side of this plane, and its axis is perpendicular to it.



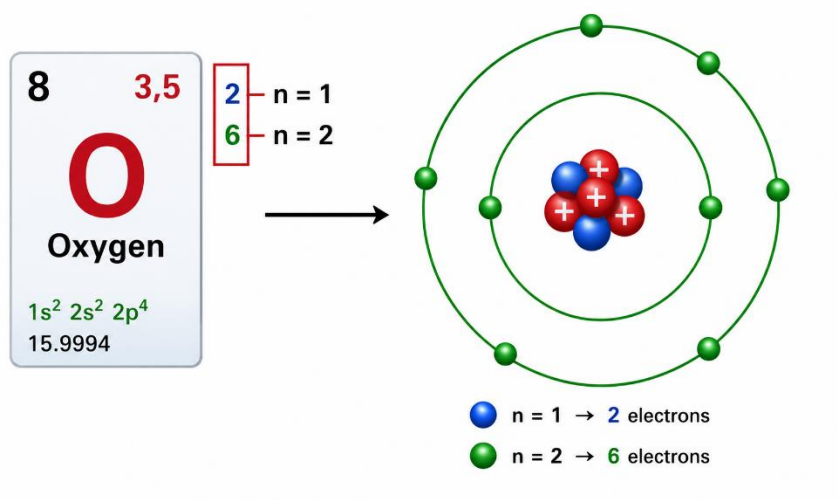
Double bonds represent electron-dense regions of the molecule.

I.3 Sp hybridization

When carbon is in the sp-hybridized state, two pure p-orbitals are accompanied by two equivalent sp-hybridized orbitals, formed from the s-orbital and the third p-orbital in carbon layer 2. - The axes of the two "sp" orbitals are collinear. - The axes of the two pure "p" orbitals are perpendicular to each other and to the common axis of the hybridized "sp" orbitals.



II. The oxygen atom (electronic configuration and bond types)

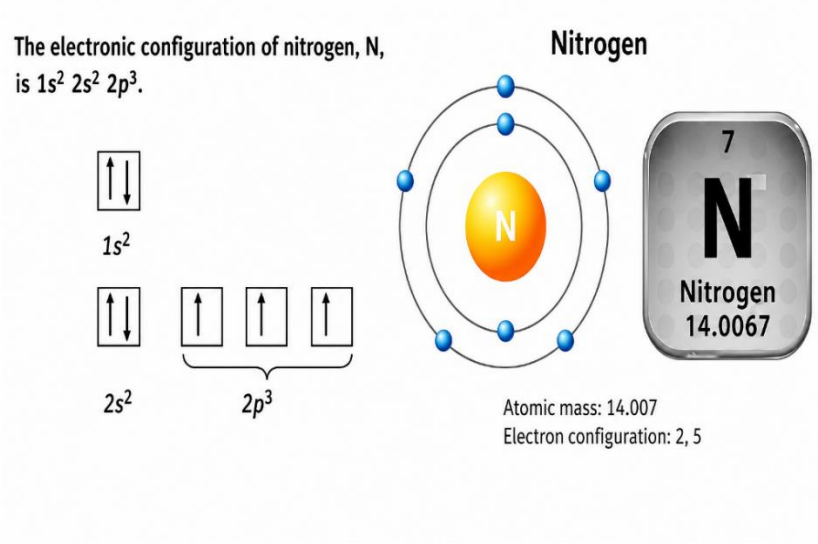


When oxygen forms a double bond, as in the >C=O carbonyl group, it is in a state of "sp2 - type" hybridization (like the accompanying carbon), and there are 3 hybridized orbitals, two of which each contain a pair of electrons and the third a single electron; they are accompaniedby a "p" orbital.

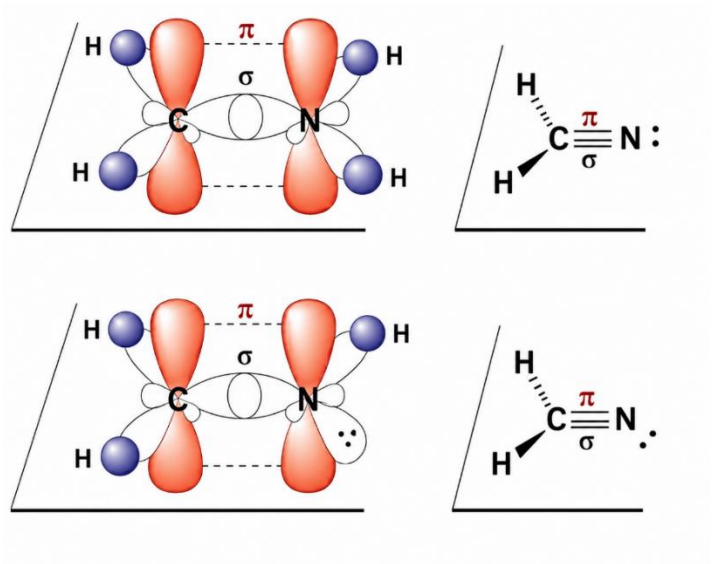
A "pure" orbital whose axis is perpendicular to the plane defined by the three axes of the "hybridized" orbitals.

"As in formaldehyde.

III. The nitrogen atom (electronic configuration and bond types)



When nitrogen forms a double bond and a single bond, as in imines >C=N-R', oximes >C=N-OH..., it is in the "sp^2-type" hybridization state: two of the three hybridized orbitals each contain a single electron, and the third, a pair of electrons.



Chapter Ⅱ：CLASSIFICATION OF ORGANIC FUNCTIONS

Generalities

Organic chemistry is the chemistry of compounds made up of carbon atoms. There are also other organic compounds containing different atoms called heteroatoms (such as oxygen (O), nitrogen (N) and halogen (Cl)). Some metals are also found in organic molecules.

1. **Formulae of organic compounds**

1.1 Gross formula A

Every organic compound has a gross formula, e.g. CxHyOz, but the same gross formula usually corresponds to several so-called isomers. The gross formula is insufficient to define a compound, as it does not specify how the atoms are linked together.

1.2 Structural formula

The structural formula can be used to distinguish isomers. It gives the relative positions of atoms in molecules.

Example:

CH_3-CH_2-O-CH_2-CH_3 and CH_3-O-CH_2-CH_2-CH_3

Are two isomers with the same empirical formula $C_4H_{10}O$

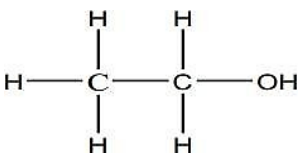
There are three types of developed formula.

1.2.1 The semi-developed formula:

Represents all the bonds in the structural formula except the one with the hydrogen atoms**.**

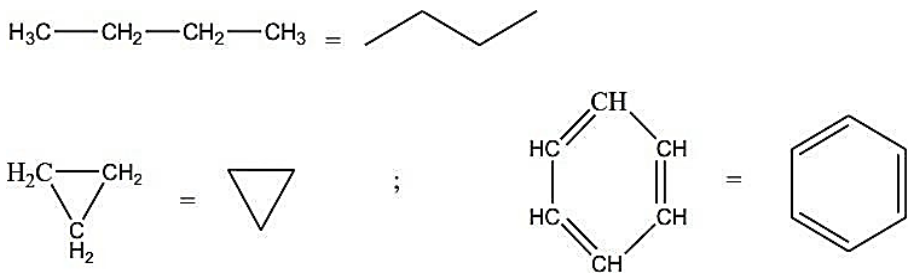
CH_3-CH_2-OH

1.2.2 The flat structural formula:



1.2.3 Topological formula:

Further simplification is possible, especially for cyclic chains: only the bonds between carbon atoms are shown.



Organic chemistry nomenclature is used to:

a) Find the name of a molecule knowing its structure.

b) Find the structure of a molecule knowing the name.

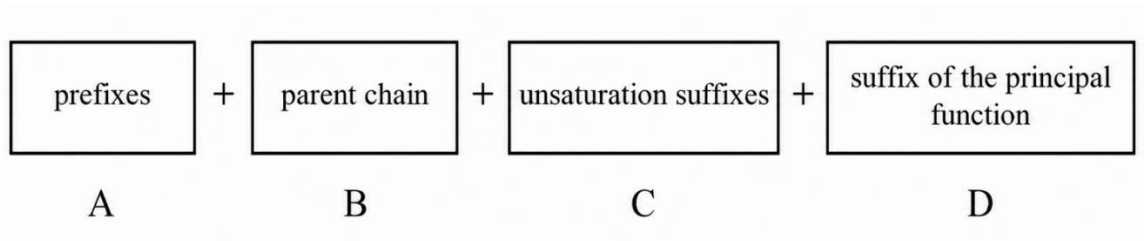
II.1 Acyclic aliphatic hydrocarbons

II.1.1 Acyclic saturated hydrocarbons (H.C):

Hydrocarbons are compounds made up of carbon and hydrogen atoms.
Alkanes have the general formula $\mathbf{C_nH_{2n+2}}$

To name a compound or product, we apply the systematic nomenclature recommended by **IUPAC** (International Union of Pure and Applied Chemistry).

To name an aliphatic hydrocarbon, proceed as follows: the name of the hydrocarbon is designated by the prefix corresponding to the number of carbons in the chain, followed by the ending **ane**.



According to Table **1** below

Table 1: Prefix corresponding to the number of carbons

Number of C	**Prefix**	**Number of C**	**Prefix**
1	Meth	**8**	Oct
2	Eth	**9**	Non
3	Prop	**10**	Dec
4	But	**11**	Undec
5	Pent	**12**	Dodec
6	Hex	**13**	Tridec
7	Hept		

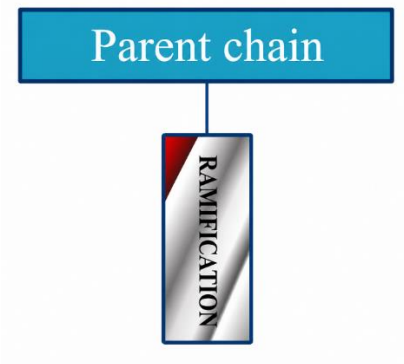
Example:

CH_3-CH_2-CH_2-CH_3 with empirical formula **C_4H_{10}** 4 carbons: prefix but: **butane.**

II.1.2 Branched saturated hydrocarbons (alkyl)

Branching is a substituent (or radical) attached to the main chain. As shown in the following diagram:

A radical takes an yle ending

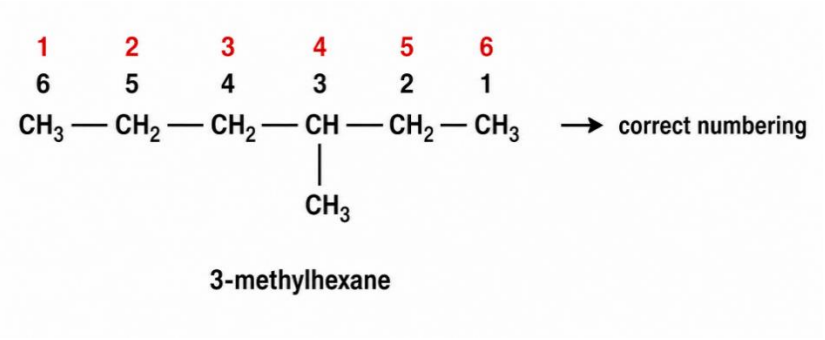


Example: CH_3-CH_2- → **ethyl.**

a) Channel numbering

The main chain is the one with the highest number of carbon atoms. The indices indicating the location of the radicals should be as small as possible.

Example:



- In the name, substituents do not take an **e**, the ending is **yl**, and they are placed before the main group.

- If there are several substituent groups, they are placed in aliphatic order (without multiplying prefixes).
- If the same group occurs several times in the molecule, a multiplying prefix is used (see Table 2).

Table 2: Multiplier prefixes.

Nb. of identical substituents	Prefix
2	Di
3	Tri
4	Tetra

b) Clues and signs

General rules for all compounds:

position clues are placed immediately before the part of the noun to which they refer.

Indices are linked to the function by a dash (-).

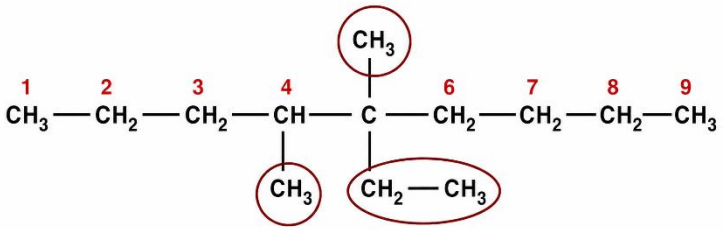
If there are several clues to the same part, they are separated by a comma (,).

Example: what is the most correct nomenclature, using IUPAC rules, for naming the following molecule?

Numbering from left to right

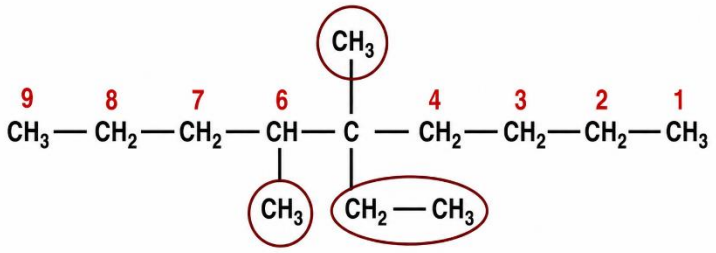
Sum= 5 + 4 + 5 = 14

Numbering from right to left



5-ethyl-4,5-dimethylnonane

Answer: the most correct name is **the first one** because it corresponds to the sum of the most **smaller.**

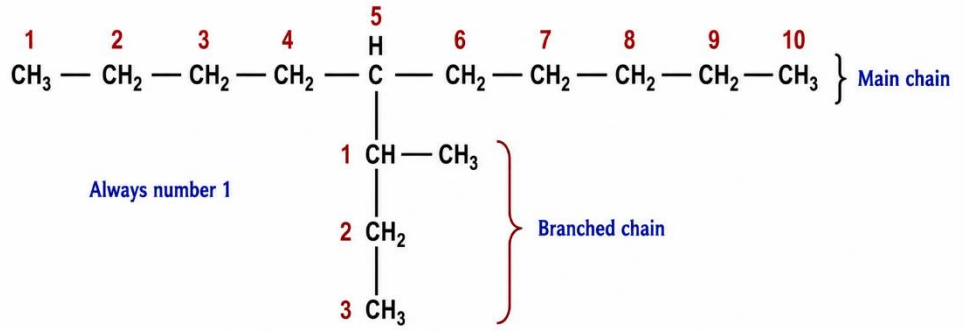


5-ethyl-5,6-dimethylnonane

Sum = 5 + 5 + 6 = 16

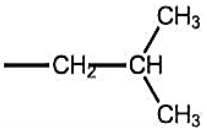
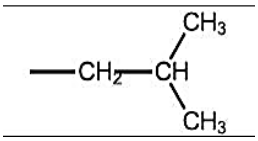
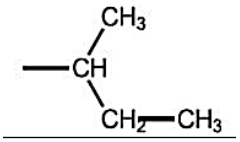
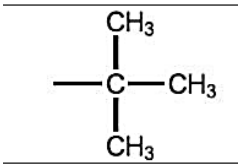
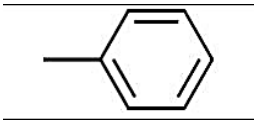
c) Multiple ramifications

- Side chains are numbered from the carbon bonded to the main chain.
- If necessary, the name of the secondary channel is enclosed in brackets.



5-(1-methylpropyl) decane

Some branched alkyl groups have specific names (see Table 3).

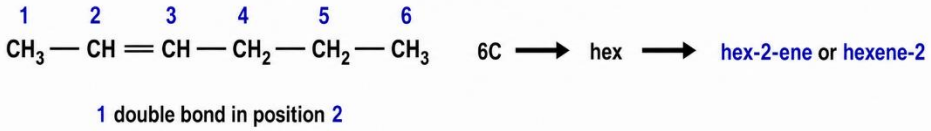
Group Name	**Formula / Structure**	**Abbreviation**
methyl group	$-CH_3$	_-Me
ethyl group	$-CH_2CH_3$	-Et
propyl group	$-CH_2CH_2CH_3$	_-Pr
isopropyl group		-iPr
butyl group (or n-butyl)	$-CH_2CH_2CH_2CH_3$	-Bu (or -nBu)
isobutyl group		-iBu
sec-butyl group		-sBu
tert-butyl group		-tBu
phenyl group		-Ph

II-.2 Acyclic unsaturated hydrocarbons

II.2.1 Hydrocarbons with double bonds: alkenes

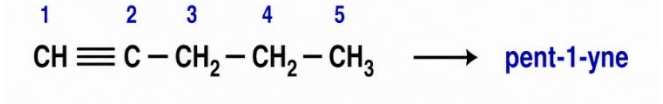
The name of an unsaturated hydrocarbon with a double bond is formed by the prefix of the saturated hydrocarbon. The ending **ane** becomes **ène**. If there are several double bonds:

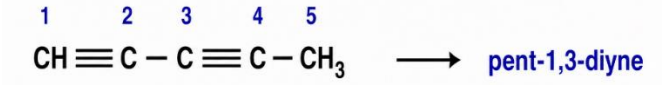
Number of double bonds	Termination
2	diene
3	triene

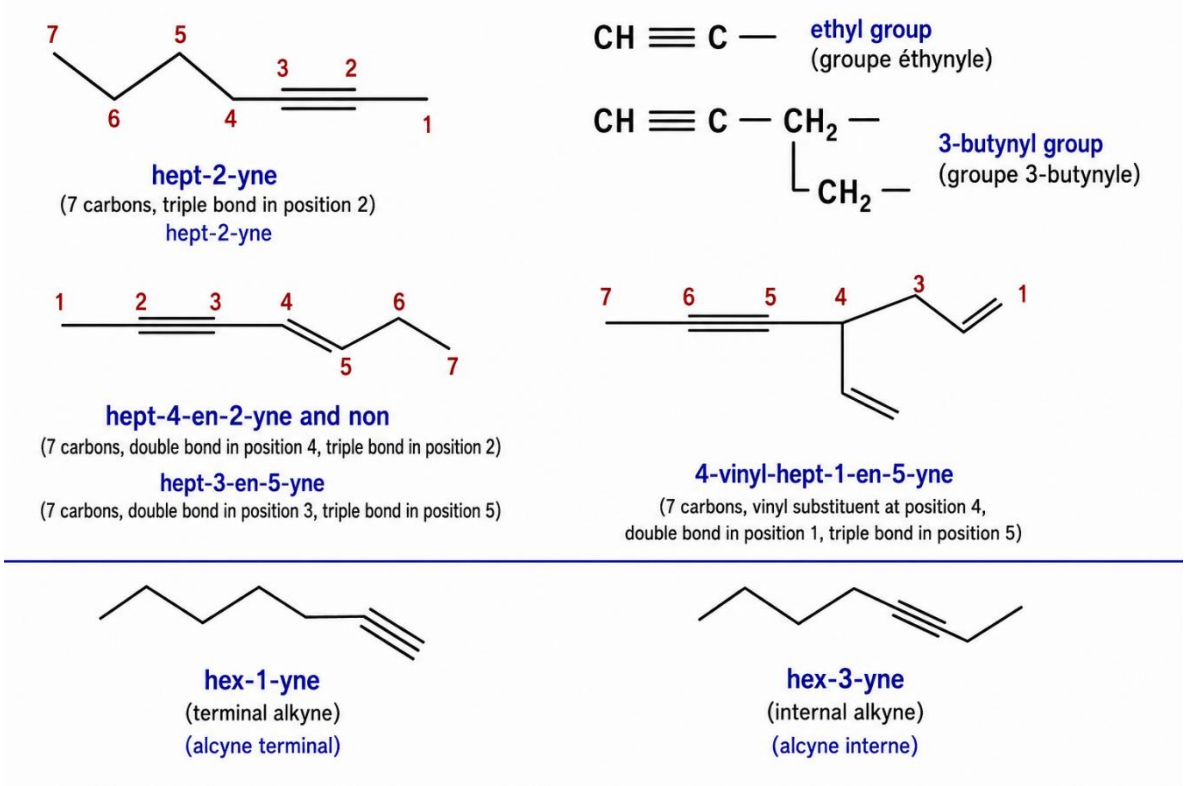


II.2.2 Hydrocarbons with triple bonds: alkynes

The name o f an unsaturated hydrocarbon with a triple bond is formed by the prefix of the saturated hydrocarbon. The ending **ane** becomes **yne**.

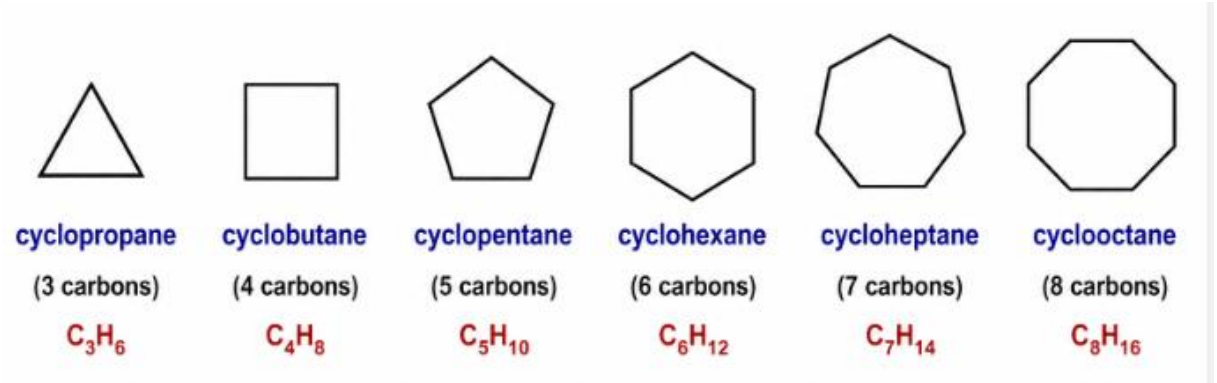




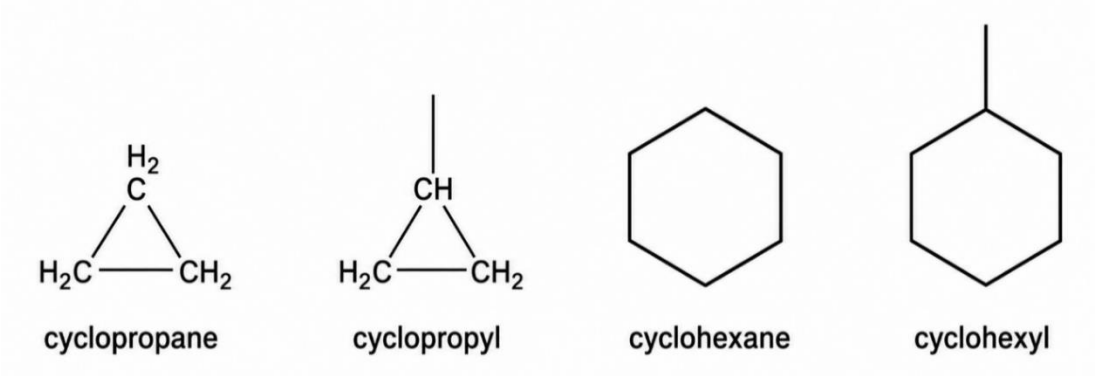


II.2.3 Saturated and unsaturated monocyclic hydrocarbons

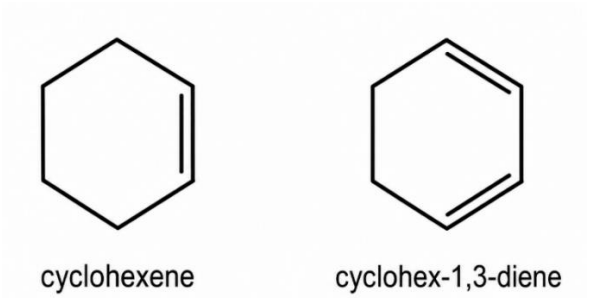
Cyclic alkanes are simply designated by the prefix "cyclo" followed by the name of the linear alkane corresponding to the number of carbons in the ring: cyclopropane, cyclobutane, cyclohexane, cycloheptane...



II.2.4 Unsaturated monocyclic hydrocarbons



II.2.5 Saturated monocyclic hydrocarbons

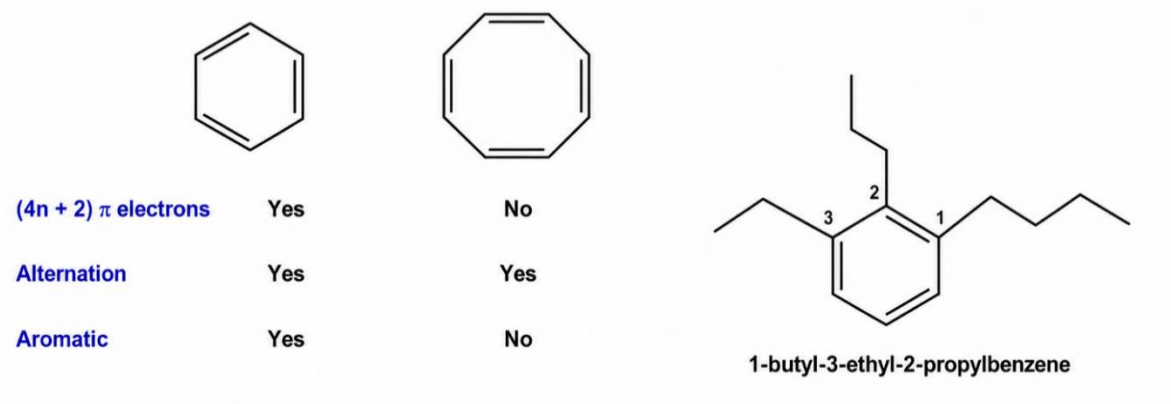


II.2.6 Aromatic monocyclic hydrocarbons

A mono- or polycyclic compound is aromatic when:

- It has alternating double bonds
- It contains (4n+2) electrons, n being an integer.

Example



II. Chemical functions

These are the atoms or groups of atoms that characterize a family of organic compounds and determine all its properties and reactivities.

- determining the name of a functionalized molecule

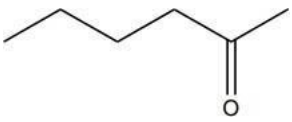
1. Determine the main function: suffix
2. Determining the basic structure: chain or cycle
3. Number
4. Naming substituents
5. Assemble the names of the substituents in alphabetical order - The various functional groups are listed in Table 3 in order of priority.

- The main group is chosen from the top of Table 3. It is designated by the corresponding suffix.
- All other groups are designated by prefixes.

Example

Main function: ketone, one terminal. Main chain: the one bearing the main function,

6 Carbon: hex. Numbering: 2



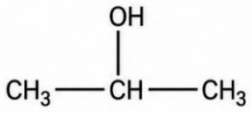
Name: hexan-2-one

II.1 Alcohols

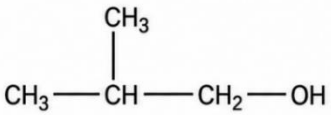
An alcohol is any compound in which the -OH group is the main group, provided it is not carried by a carbon belonging to the ring of an aromatic compound. Alcohols are named by adding the suffix "ol".

Example:

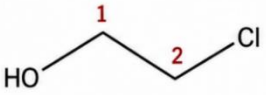
- **If the principal functional group is an alcohol: suffix = -ol**



propan-2-ol



2-methylpropan-1-ol



2-chloroethan-1-ol

- **If the group is secondary: prefix = hydroxy-**

6-hydroxyhexanoic acid

III.2 R-O-R' ethers

They are considered derivatives of alcohols, in which the hydroxyl proton of the -OH is replaced by an **-R'** group. - Ethers are not a priority group and are always designated by the prefix: oxy-

- The longest chain is the main group R. - The remaining radical, R′, is derived from the corresponding alcohol.

methoxyethane

Principal functional group: alcohol ⇒ -ol

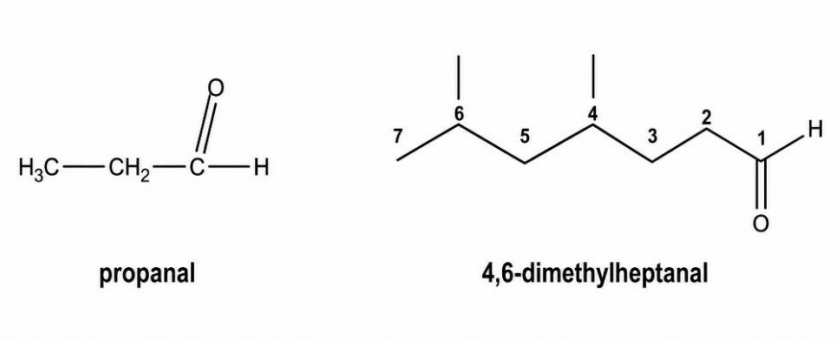
Secondary functional group: ether ⇒ oxy-

⇒ 2-ethoxyethanol

III.3 Aldehydes

When the -CH=O group is the main group of a compound and is not carried by a ring, the aldehyde is named by replacing the final "**e**" of the corresponding hydrocarbon with "al".

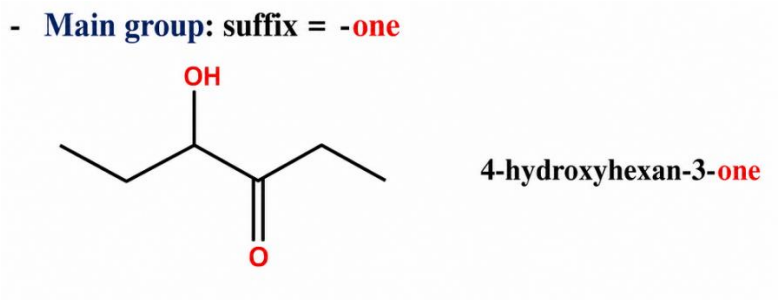
Example:



III.4 Ketones

The name of an acyclic ketone is formed by adding the suffix "one" to the name of the corresponding hydrocarbon. The numbering of the main chain is chosen so that the sum of the indices of the carbon atoms bearing a doubly bonded oxygen is as low as possible.

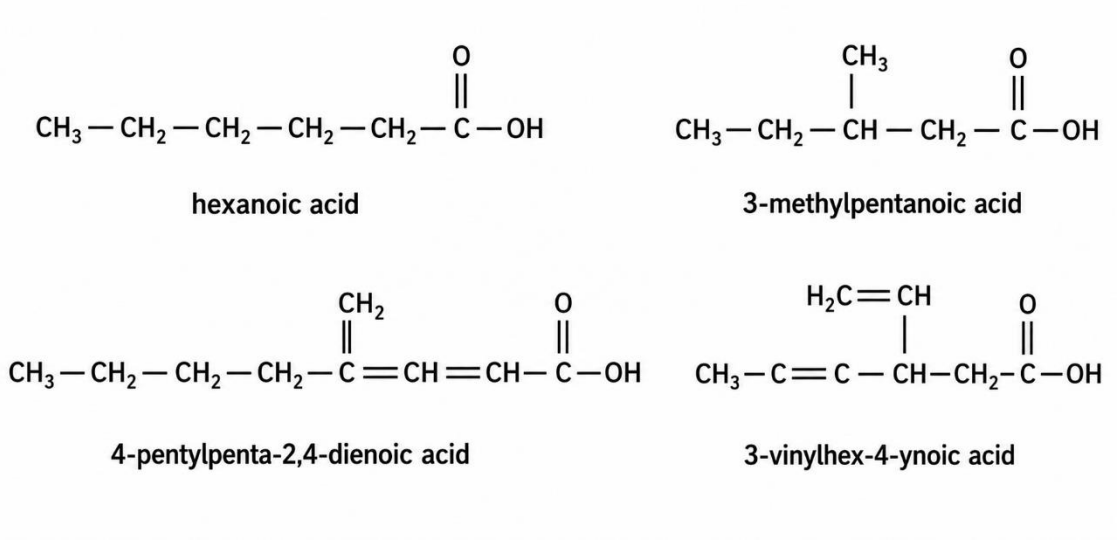
Examples:



III.5 Carboxylic acids

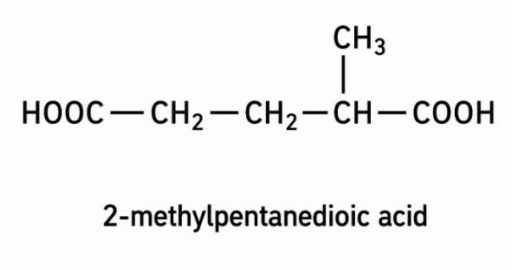
The acid is named by replacing the final "**e**" in the corresponding hydrocarbon name with "oic" and preceding the resulting name with the word acid. The main chain of the hydrocarbon is chosen so that it contains the -COOH group, then according to the usual criteria. The carbon atom of the -COOH **group (functional carbon) always bears the number 1.**

Example:



When two -COOH groups are the main groups in a compound (diacid), the acid is named by replacing the final "e" in the name of the corresponding hydrocarbon with "**dioic**" andpreceding the resulting name with the word acid. The main chain of the hydrocarbon is theone containing the -COOH groups. The carbon atom of one of the -COOH groups is numbered 1, the choice being made according to the usual criteria (chain, then set of substituent indices).

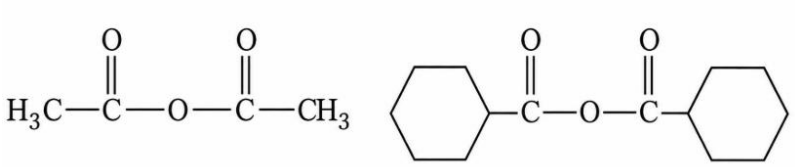
Example: 2-methylpentendoic acid



III.6 Acid anhydrides

Symmetrical anhydrides of unsubstituted monocarboxylic acids are named by replacing the word **acid** with the word anhydride.

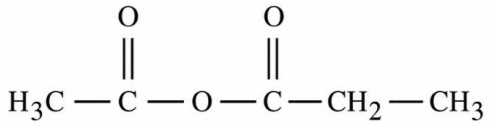
Examples:



Ethanoic anhydride
(acetic anhydride)

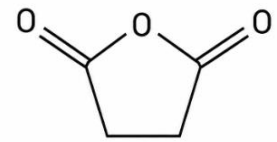
Cyclohexane carboxylic anhydride

Mixed anhydrides (different substituents) are named by following the word anhydride with the names of the two acids, without the word acid, separated by a hyphen and listed in alphabetical order.



Ethanoic – propanoic anhydride
(acetic – propionic anhydride)

Like symmetrical anhydrides, cyclic anhydrides are named a f t e r t h e corresponding diacid.



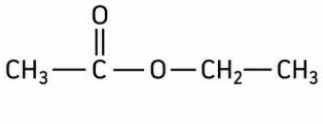
Butanedioic anhydride
(succinic anhydride)

Butenedioic anhydride
(maleic anhydride)

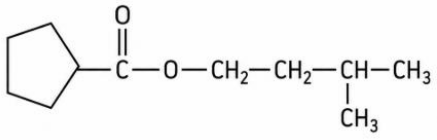
III.7 Esters

Esters are named by replacing the "**ique**" in the acid name with the "**ate**" (alkyl alkanoate).

Example

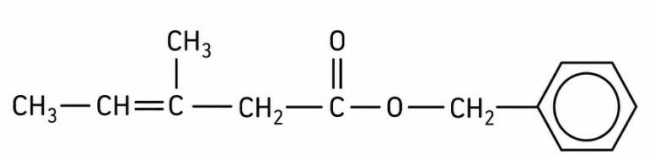


Ethyl ethanoate
(ethyl acetate)



3-methylbutyl cyclopentane carboxylate

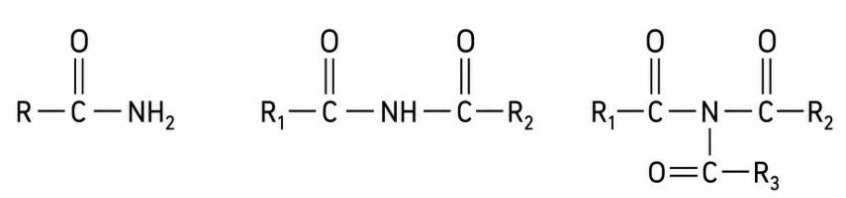
If the main chain contains groups or unsaturations, it is numbered starting from the functional carbon.



3-methylpent-3-enoate de benzyle
(3-methylpent-3-enoate of benzyl)

III.8 Amides

Amides are compounds containing one, two or three alkyl groups R-CO- linked to a nitrogen atom.

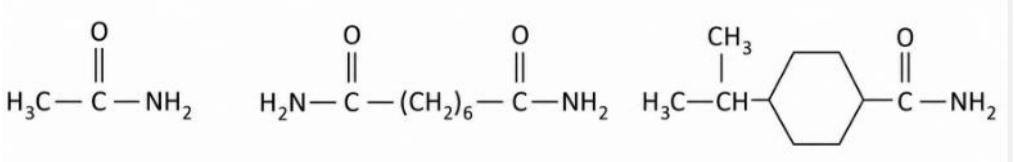


Primary amide Secondary amide Tertiary amide

R_1, R_2 and R_3 may be identical or different

Primary amides derived from an organic acid by replacing the -OH group with - NH_2 are named from the acid name by deleting the word acid and replacing the "ique" or "oïque" ending of the acid name with amide, or by replacing the carboxylic ending with carboxamide.

Example:



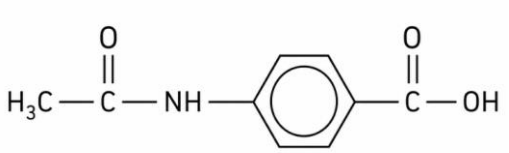
Ethanamide
(acetamide)

Octanediamide

4-isopropylcyclohexane
carboxamide

When the amide function is not the main one, the R-CO-NH- and R-CO-NR'- groups derived from the amide name are called amido.

Example:



4-acetamidobenzoic acid

III.9 Nitriles

Compounds in which the **-C≡N** group is the main moiety are called nitriles. When acyclic, these compounds are named by adding the suffix "nitrile" to the name of the corresponding hydrocarbon. The carbon atom bearing the nitrogen atom has the number 1.

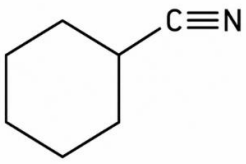
Example:

2-méthylpentanenitrile
(2-méthylpentanenitrile)

2-méthylpent-3-ènenitrile
(2-méthylpent-3-ènenitrile)

R-C≡N compounds derived from an acid whose name ends in carboxylic are named from the name of the acid by deleting the word acid and replacing carboxylic with carbonitrile.

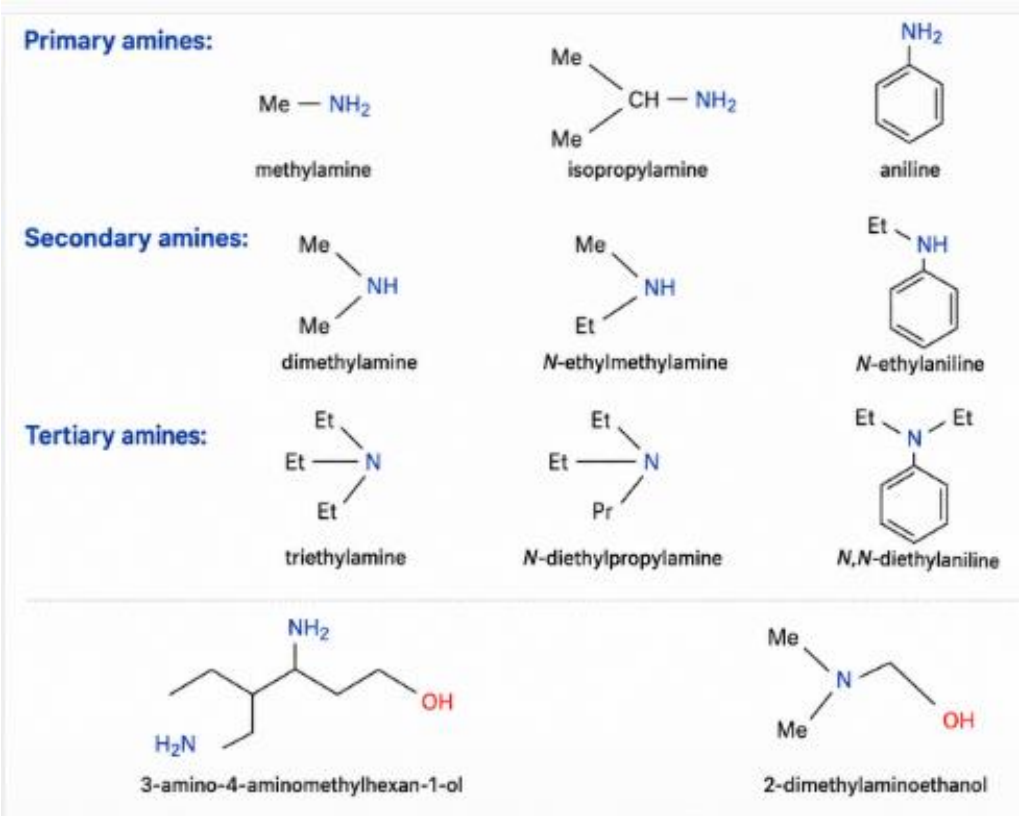
Example:



cyclohexane carbonitrile

III.10 Amines

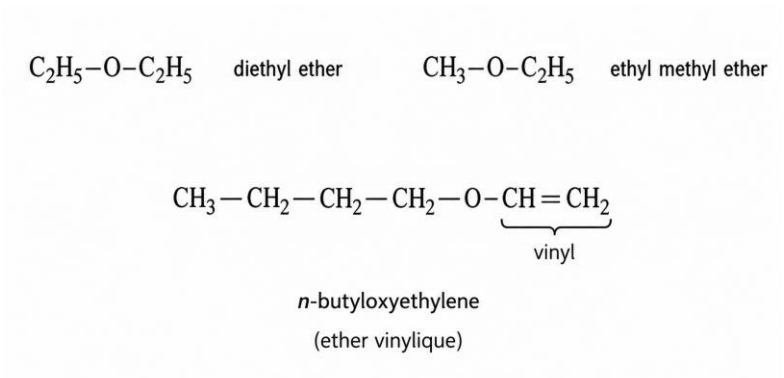
Compounds of the general formula NR1R2R3, in which the R groups are either a hydrogen atom or a group linked to the nitrogen atom by a carbon atom, are called amines.



III.11 Ether oxides

Any compound obtained from a hydrocarbon by replacing a methylene group (-CH2-) with an oxygen atom is called an ether oxide. The systematic name of the acyclic ether is obtained by preceding the name of the corresponding hydrocarbon with the prefix "oxa", preceded by the number of the replaced carbon atom and a hyphen. This prefix is arranged like the others, in alphabetical order.

Example:



III.12 Alkyl halides or halogen compounds

Halogenated derivatives of hydrocarbons are referred to as substituted hydrocarbons. These substituents (F: **fluoro**, Cl: **chloro**, Br: **bromo**, I: **iodo**) are always prefixed, with or without a multiplicative prefix.

Example:

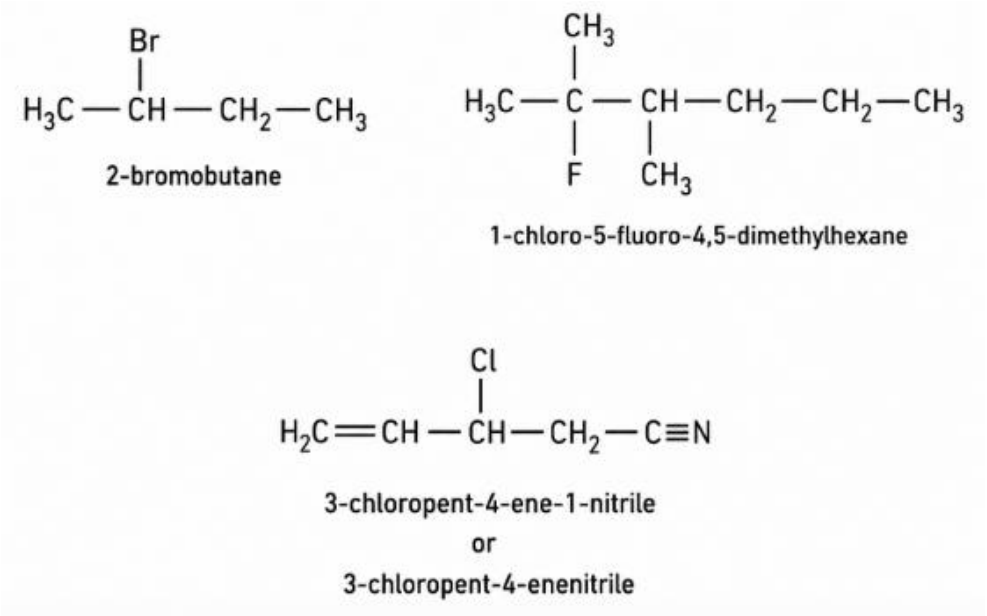


Table 3: Suffixes and prefixes used to designate some important functional groups. The groups in this table are listed in descending order of priority.

Class	Formula*	Prefix: Secondary group	Suffix: Principal group
Carboxylic acids	-COOH -(C)OOH	Carboxy-	carboxylic acid ...oic acid
Sulfonic acids	(-SO_3H)	Sulfo-	sulfonic acid
Acid anhydrides...	R-COOOC-R	-	acid anhydride
Esters	-COOR -(C)OOR	R-oxycarbonyl-	...carboxylate of R ...oate of R
Acyl halides	-CO-halogen -(C)O-halogen	Halogenoformyl-	...carbonyl halide ...oyl halide
Amides	(-CO-NH_2) (-(C)O-NH_2)	Carbamoyl-	-carboxamide -amide
Aldehydes	-CHO -(C)HO	Formyl- Oxo-	-carbaldehyde -al
Amidines	(-C(=NH)-NH2) (-(C)(=NH)-NH2)	Amidino-	-carboxamidine -amidine
Nitriles	(-CequivN) (-(C)equivN)	Cyano-	-carbonitrile -nitrile
Ketones		Oxo-	-one
Alcohols	-OH	Hydroxy-	-ol
Phenols	(phenyl)-OH	Hydroxy-	-
Thiols	-SH	Mercapto-	-thiol

Hydroperoxides	-O-OH	Hydroperoxy-	-
Amines	(-NH2)	Amino-	-amine
Imines	=NH	Imino-	-imine
Ethers	-OR	R-oxy-	-
Sulfides	-SR	R-thio-	-
Peroxides	-O-OR	R-dioxy-	-

Note: Carbon atoms (and phenyl) indicated in parentheses are included in the parent structure name and not in the suffix or prefix.

TD +Corrected series

TD Organic chemistry

1) Draw the structural formula of the following molecules:

a) $(CH_3)_2CHCH_2OH$

b) $Cl_2C=CCl_2$

c) $CH_3CCl_2CH_3$

d) $(CH_3)_2C(CH_2CH_3)_2$

2) Give the semi-developed formula or the name of the following products:

a) hexa-1,3-diène

b) hept-2-yne-4-ène

c) pentène

d) octa-1,3,5-trien-7-yne

e) 2-méthylbutane

f) 2-penta-1,3-diénylbutane

3) Draw the topological formula (zig-zag) of the molecules below:

a) $CH_3(C=CH_2)CH_2CH_3$

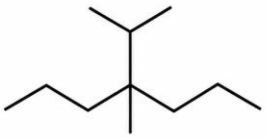
b) $CH_3C(CH_2CH_3)CH_2CH_3$

c) $CH_3CH_2CH=CHCH_2CH(CH_3)_2$

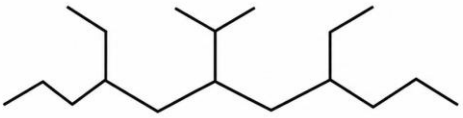
d) $(CH_3)_2CHCH_2CH(CH_3)_2$

4) Provide the systematic nomenclature for the following molecules.

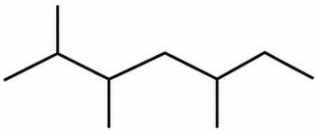
a)



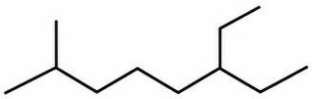
b)



c)



d)

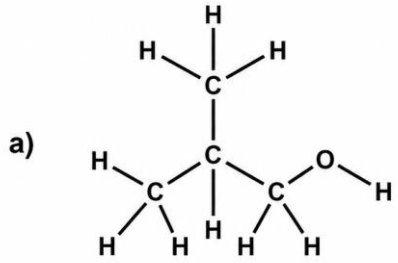


****Good luck****

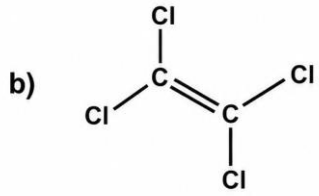
Answers

1)

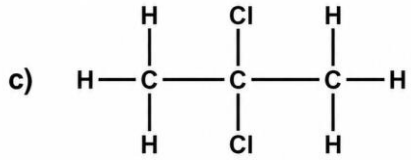
a)



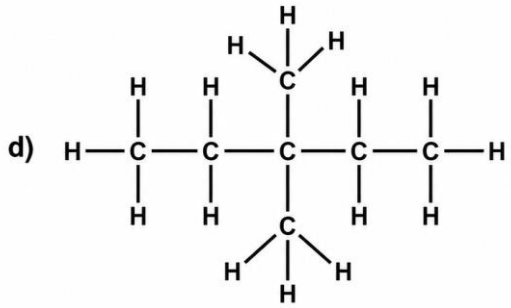
b)



c)



d)



2)

a) **hexa-1,3-diene**
Answer: $CH_2 = CH - CH = CH - CH_2 - CH_3$

b) **hept-2-yne-4-ene**
Answer: $CH_2 - C \equiv CH = CH - CH_2 - CH_3$

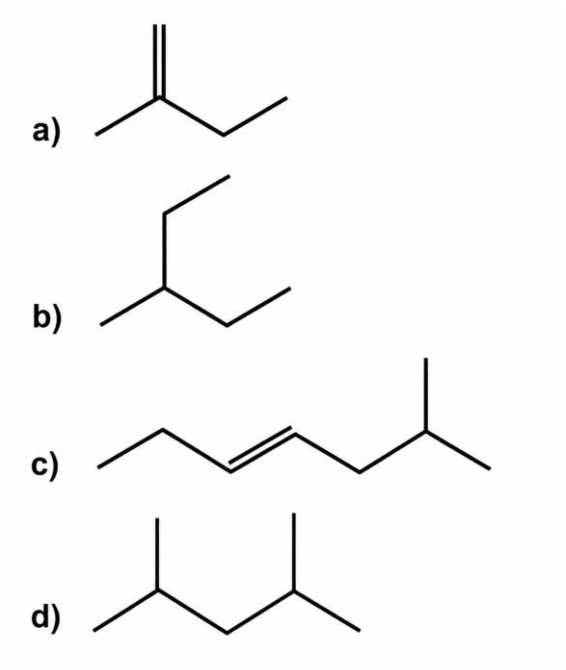
c) **pentene**
Answer: $CH_2 = CH - CH_2 - CH_2 - CH_3$

d) **octa-1,3,5-trien-7-yne**
Answer: $CH_2 = CH - CH = CH - CH = CH - C \equiv CH$

e) **Give a synonym for product (d):**
Answer: oct-1-yne-3,5,7-triene

f) **CH ≡ C – CH = CH – CH_2 – CH = CH – CH_3**
Answer: octa-1,2,5-trien-7-yne

3)



4)

a) 4-éthyl-2-méthylpentane.

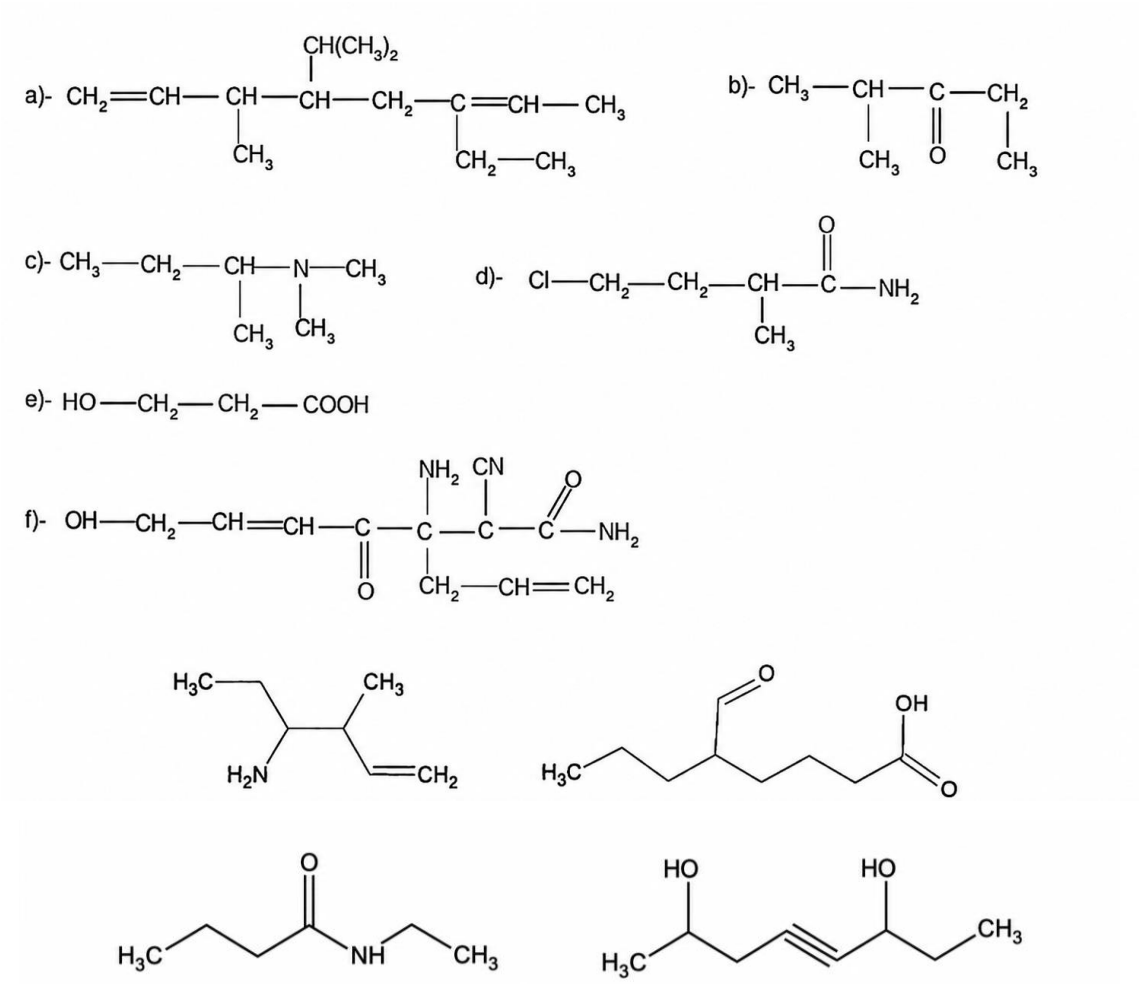
b) 5-éthyl-3-méthylheptane.

c) 3-isobutyl-5-isopropylheptane.

d) 4-(sec-butyl)-6-(tert-butyl)-3,5-diethyl-7-isopropyl-2-methylnonane

TD 01 Organic chemistry

a) Provide the systematic nomenclature according to the IUPAC rules for the following molecules.



b) Write the semi-developed formula corresponding to the following nouns:

1) Acide-5-cyclo pentyl-2-formyl hex-3-ènoique.

2) 2-bromo-5-hydroxy hept-3,5-diènal.

3) 3-amino-6-hydroxy-5-isopropyl-2-méthyl cyclohexanone.

4) 5-méthyl-3-(1,2-diméthyl propyle) hept-1-ène.

****Good luck****

✍ **Dr TABET.A**

Answers

a) -6-éthyl-4-isopropyl-3-méthyl octa-1,6-diène.

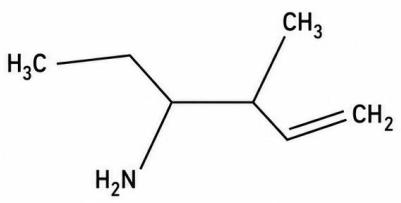
b) -4-méthyl pentan-3-one.

c) N, N- diméthyl-1-méthyl propanamine.

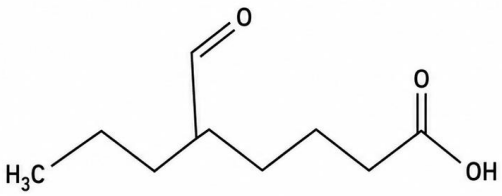
d) -1-amino-4-chloro-2-methyl butan-1-one.

e) 3-hydroxy propanoïque

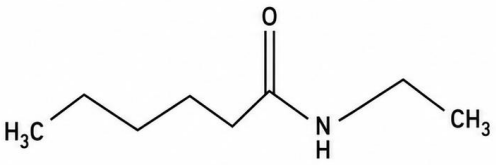
f) -3-allyl-3-amino-2-cyano-7-hydroxy-4-oxohept-5-énamide



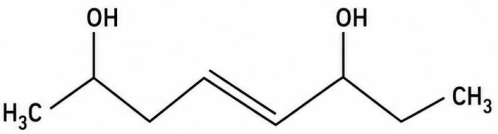
1-ethyl-2-methylbut-3-en-1-amine



5-formyloctanoic acid

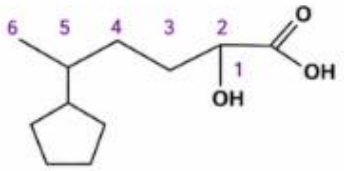


N-ethylbutanamide

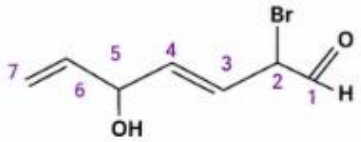


oct-4-ene-2,6-diol

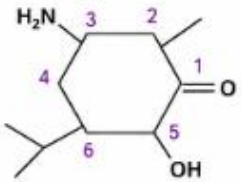
b)

1) 

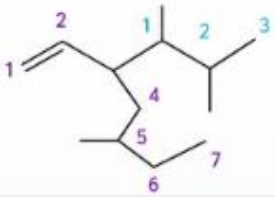
Acid- 5- cyclopentyl- 2- formyl hex- 3- enoic acid

2) 

2- bromo- 5- hydroxy hept- 3,5- dienal

3) 

3- amino- 6- hydroxy- 5- isopropyl- 2- methyl cyclohexanone

4) 

5- methyl- 3- (1,2- dimethyl propyl) hept- 1- ene

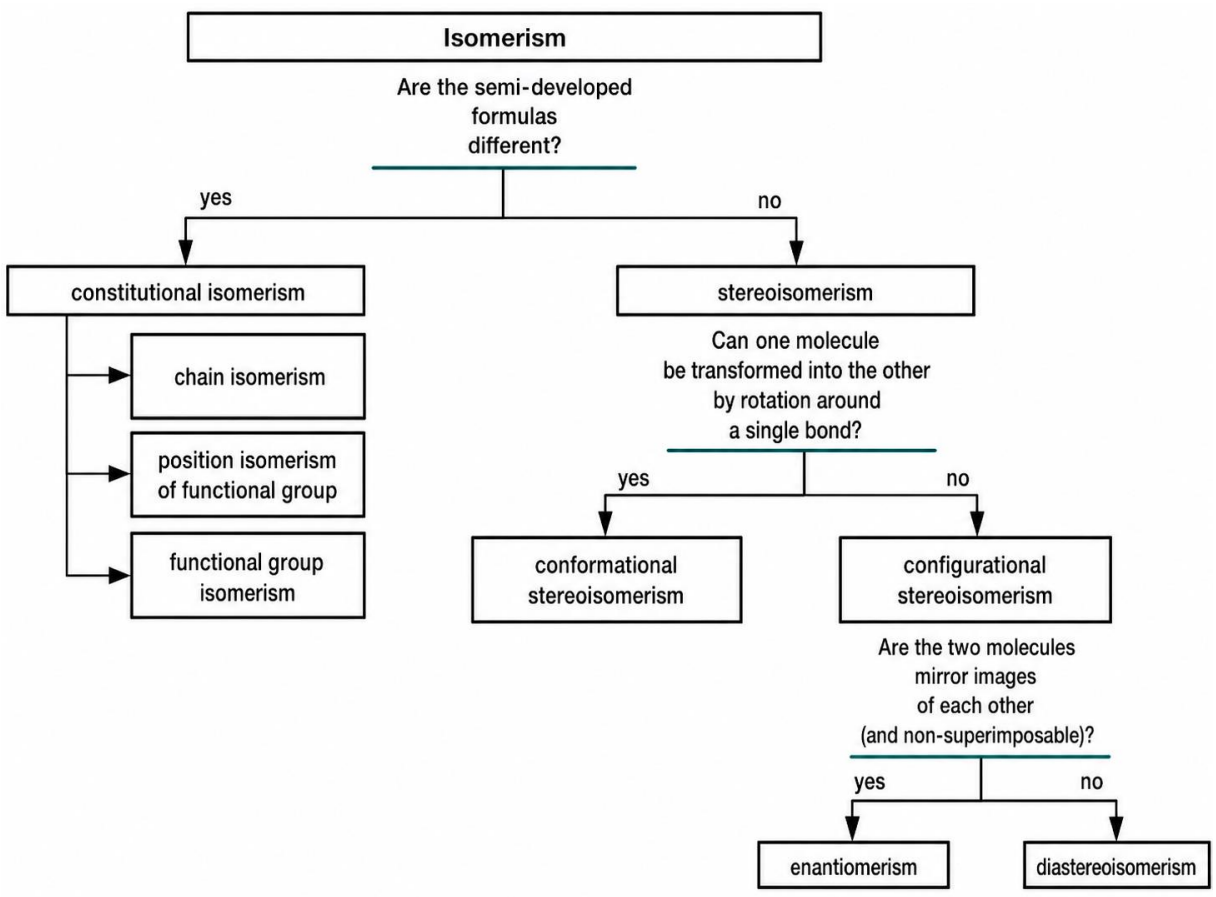
CHAPTER Ⅲ: ISOMERISM AND STEREOISOMERISM

1. **Classification of isomers and stereoisomers**

Isomers are chemical species of the same gross formula that differ in :

- The order or nature of bonds (constitutional isomerism)

- Or by the arrangement of atoms in space (stereoisomerism)



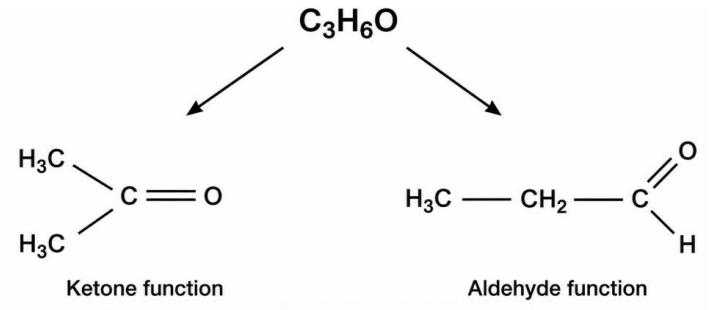
2. Flat isomerism or constitution isomerism

Two molecules with the same empirical formula but different planar structural formulae are called constitutional isomers. Isomers have different physical, chemical and biological properties. There are three types of isomerism:

2.1 **Functional isomerism:**

Functional isomers have different functional groups.

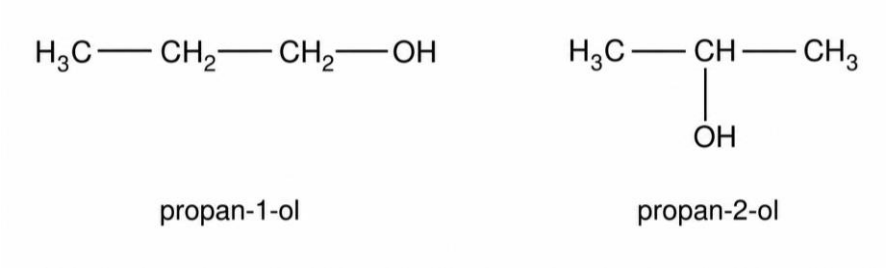
Example:



2.2 Positional isomerism:

Positional isomers have the same function, but the functional group or unsaturation is carried by different carbons in the carbon chain.

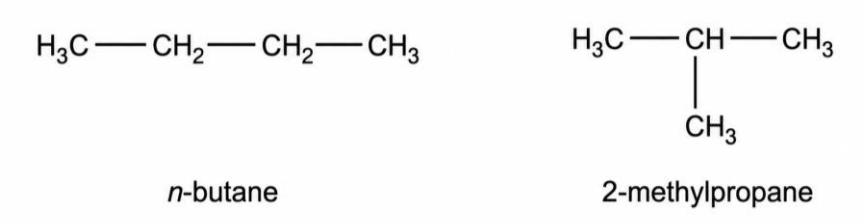
Example: C_3H_8O



2.3 Skeleton or chain isomerism:

The sequence of atoms on the carbon skeleton is different.

Example: C_4H_{10}



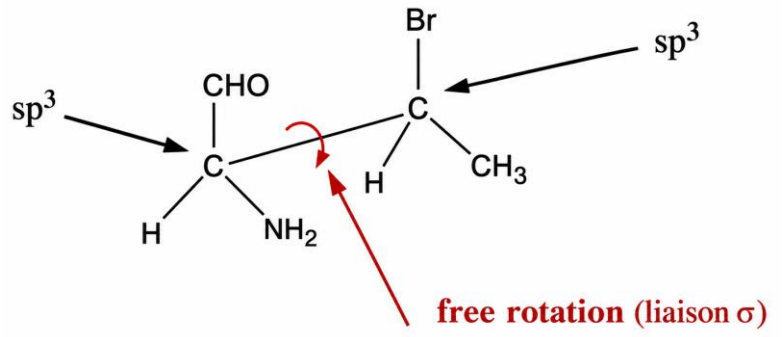
3. Stereoisomerics

These are isomers that have the same planar structural formula, but differ in the spatial arrangement (geometric arrangement) of their atoms.

3.1 Conventional representation of organic molecules

A representation in space of stereoisomers requires the introduction of a mode of representation in space.

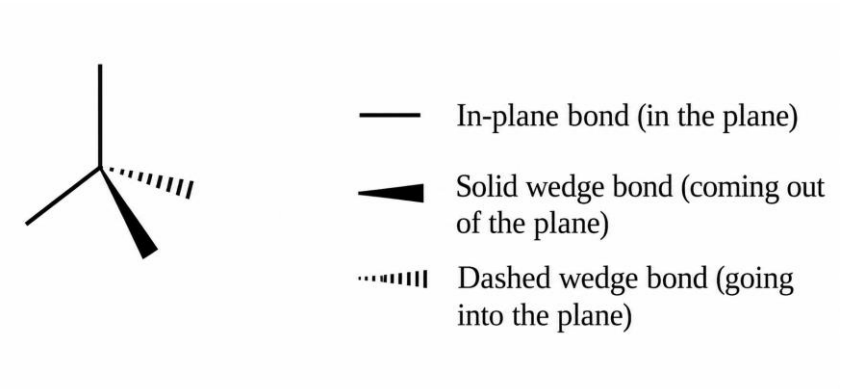
3.1.1 Perspective representation (or cavalier perspective)



Perspective representation is mainly used for cyclic molecules.

3.1.2 Projective representation or Cram convention

It consists in representing a link by convention

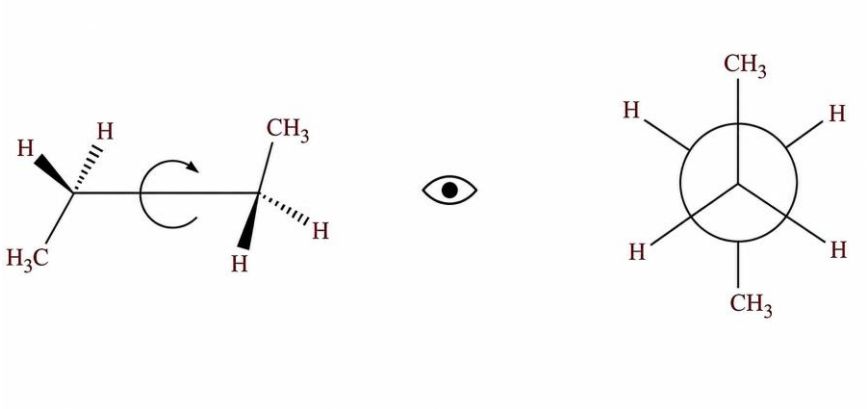


3.1.3 Newman projection

In the Newman representation, the molecule is viewed along the axis of a C-C single bond between two neighboring carbon atoms. The bonds emanating from the two atoms are projected onto a plane perpendicular to the bond axis under study.

- The bonds of the nearest atom (to the observer) are represented by segments starting from the same point, forming angles of 120°.

- The second carbon (furthest from the observer), eclipsed by the first, is represented by a circle. The bonds of this atom are represented by segments stopping at the periphery of the circle.

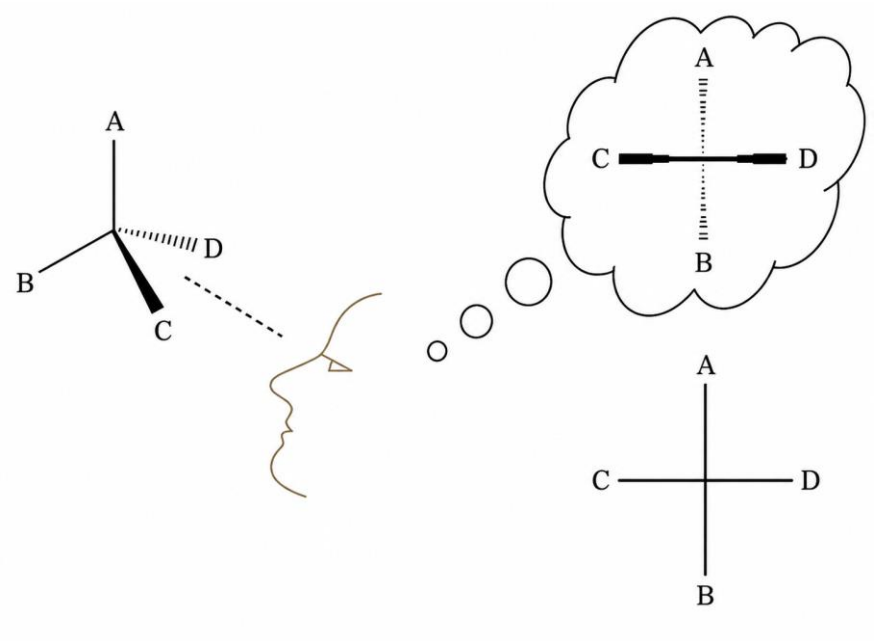


This Newman projection of an organic compound makes it possible to study its different conformations through several rotations around a single C-C bond.

3.1.4 Fisher projection

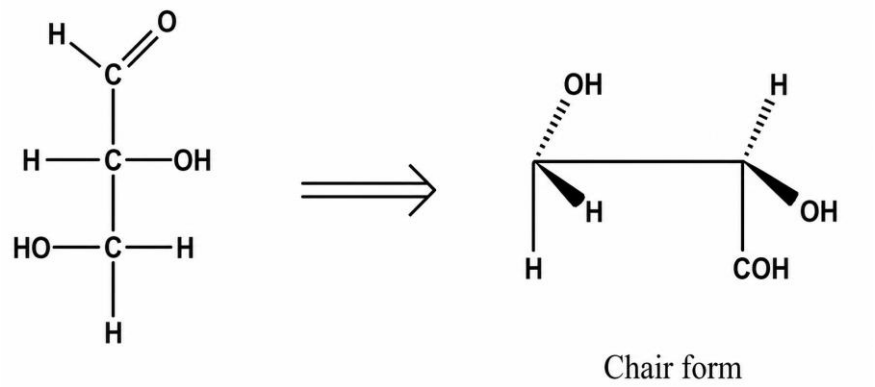
In Fisher projection, links are represented by vertical and horizontal solid lines, according to the following conventions:

- Vertical lines represent connections behind the figure plane.
- The horizontal lines represent the connections in front of the figure plane.
- The longest carbon chain is placed vertically and numbered from top to bottom.
- The weakest link (most often associated with the most oxidic carbon) is placed at the top.



This representation is mainly used in biochemistry to represent sugars and amino acids.

Example: Fisher and cavalier representation of a triose.



3.2 Configurational isomers:

These are molecules with the same composition and the same atomic bonds, but they differ in the way the atoms making up the molecule are arranged in space. They are therefore different molecules that can be isolated, and it is not possible to switch from one isomer to another without breaking at least one bond. There are two types of configuration isomerism

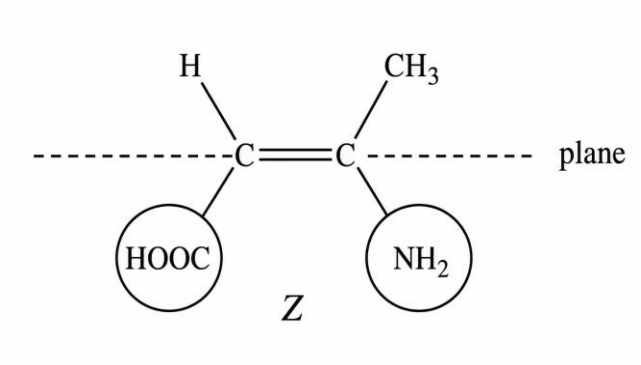
- Geometric isomerism (Z/ E) or (cis/ trans)
- Optical isomerism (S/ R)

3.3 Geometric isomerism or (Z/E) isomerism

This is a special case of possible isomerism in a molecule with a double bond between the two carbons linked to different chemical atoms or groups. This double bond prevents free rotation. They are therefore diastereoisomers (Z/ E) with different physicochemical properties (such as boiling temperature).

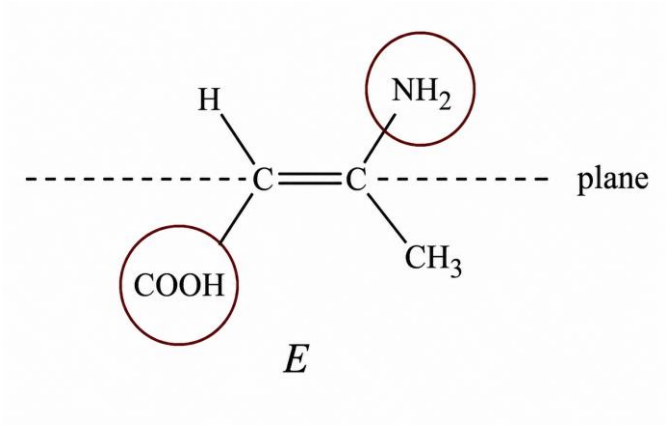
3.3.1 Z configuration :

Characterizes diastereomers whose priority groups are on the same side of the plane formed by the double bond. Z (German Zusammen means "together")



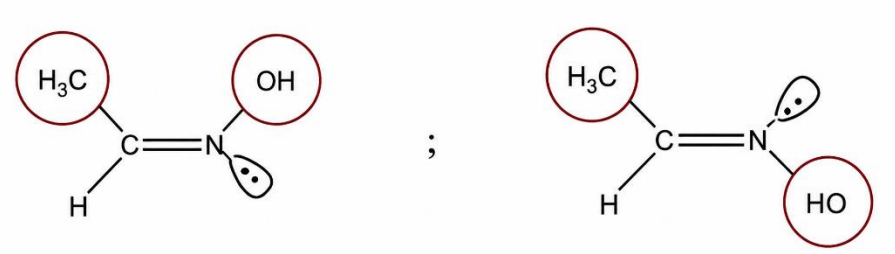
3.3.2 E configuration:

Characterizes diastereomers whose priority groups are on the opposite side of the plane formed by the double bond (E comes from the German entgegen meaning "opposite").



NB: It should be noted, however, that theold nomenclature (cis, trans) and the new one (Z, E) do not necessarily coincide.

- In the case of compounds with a double bond between a carbon atom and a nitrogen atom (imines and oximes), they are therefore considered as geometric isomers. However, the non-bonding nitrogen doublet is ranked as the last priority.



(syn) Ethanal oxime (anti) Ethanal oxime

3.4 CIP priority rules (Cahn, Inglod and Prelog):

The method of prioritizing substituents is based on the CIP rules (Cahn, Ingold and Prelog)

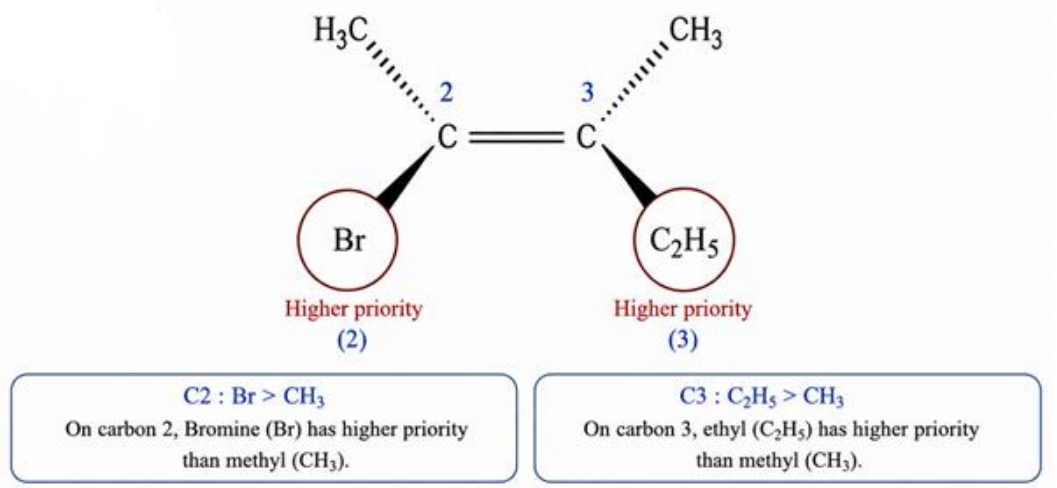
✓ **Rule 1**: the higher the atomic number Z of the Sp^2 carbon atom, the higher the priority of the substituent.

I53 > Br35 > Cl17 > F9 >O8 >N7 > C6 >H1 > : (doubletfree)

✓ **Rule 2**: if two atoms with the same atomic number occur at the same isomerism center, we look at the other atoms to which they are bonded, and rule 1 applies.

Applies $-OCH_3$ > -OH; $-CH_2CH_3$ > $-CH_3$; -NHR > NH

Example:



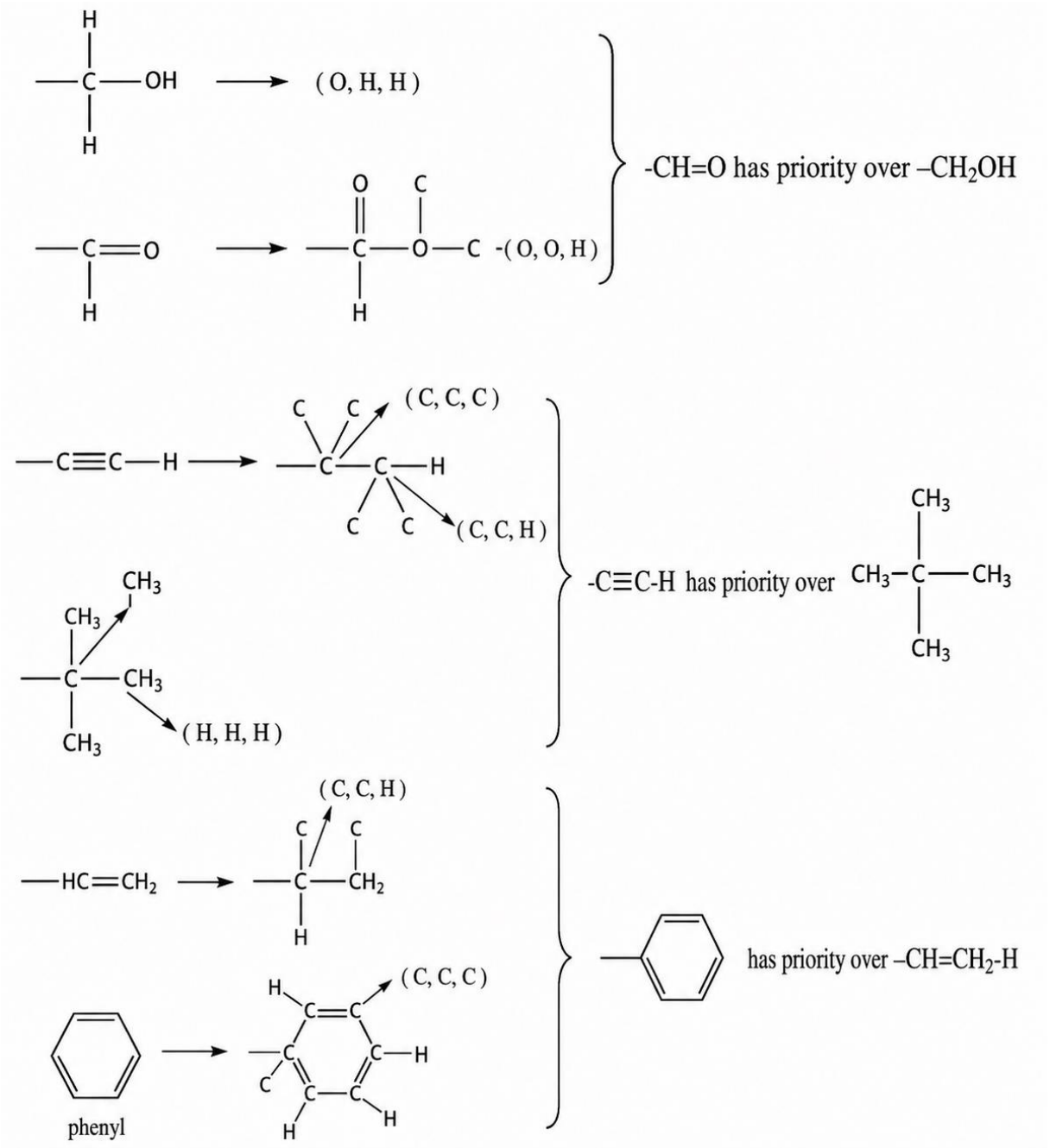
✓

Rule 3: if a carbon carries a doubly (or triply) bonded atom, the latter intervenes for two (or three) times.

Example: -COOH ≡ -C(O_3)-H > -CHO > CH_2OH

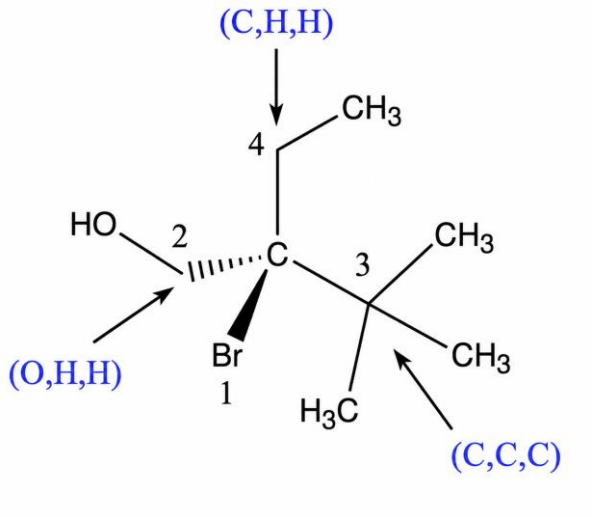
-C≡N > -C-NH2 -C=A: A is doubled, i.e. linked to two atoms of the same kind.

-C≡A: A is tripled, i.e. with three atoms of the same kind.



NB: Don't add up the atomic numbers of the atoms in a given position; only the largest Z "counts". So -CH_2OH, with a single O (Z=8) in second position, would take precedence over -$C(CH_3)_3$, which has three Cs (Z=6) in the same position.

Example:

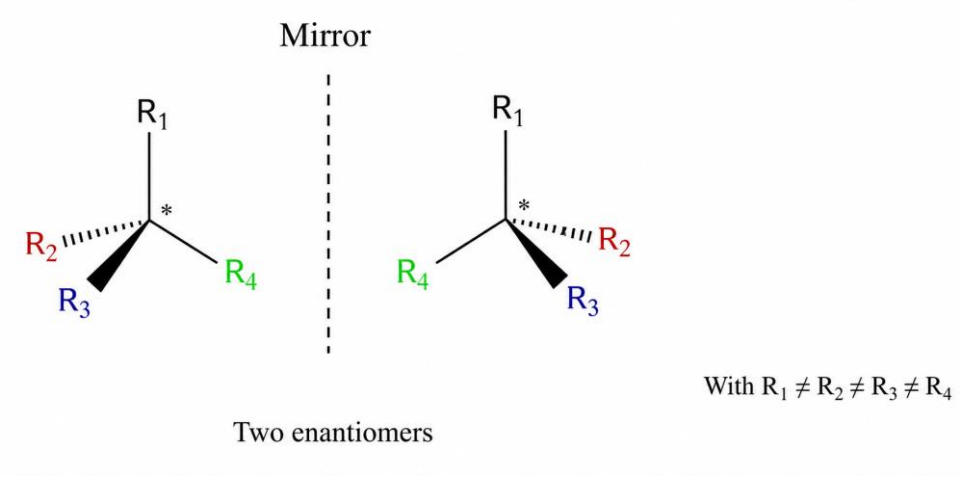


3.5 Optical isomerism and enantiomers

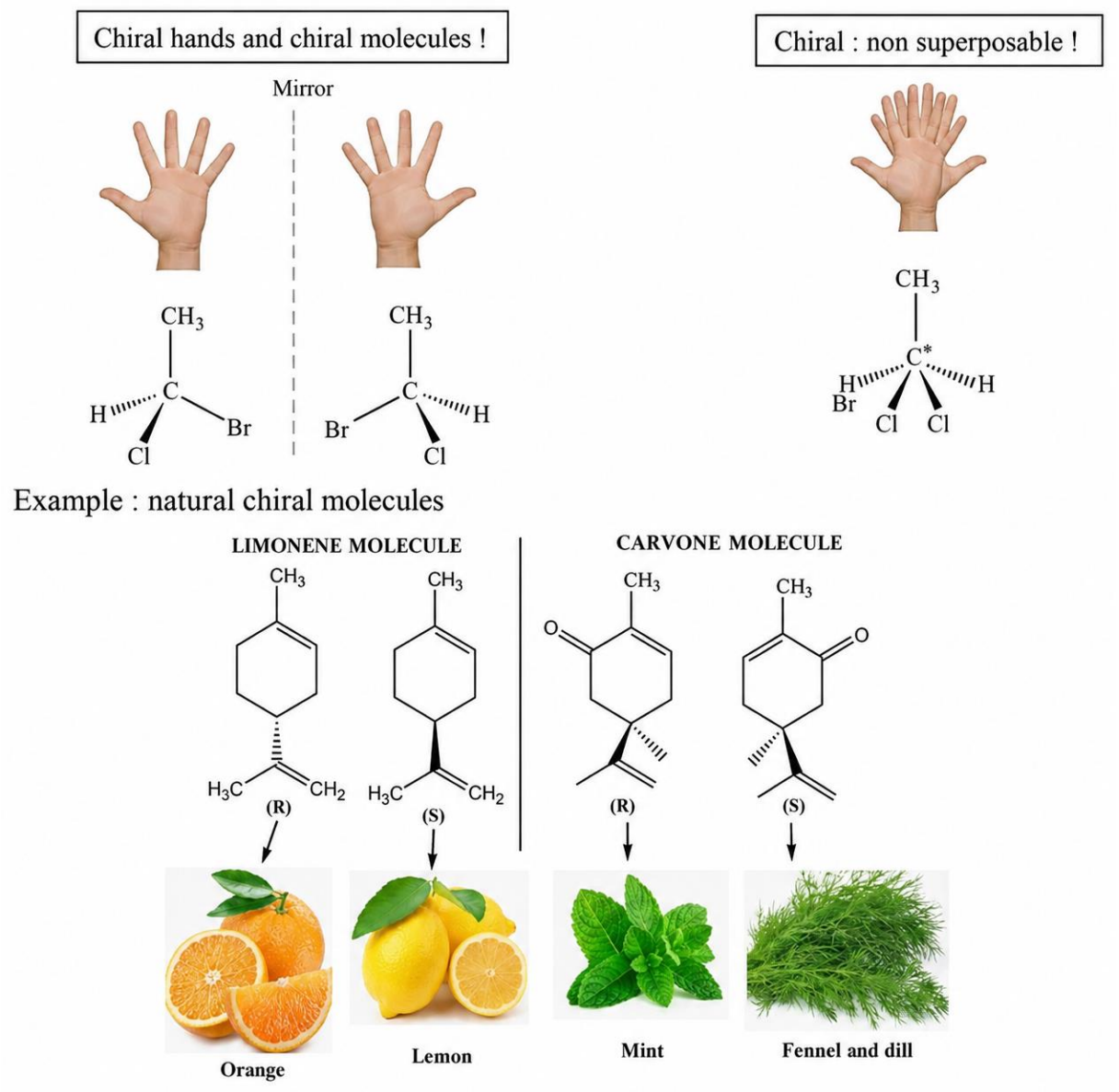
3.5.1 Definition of chirality criteria:

A molecule is said to be chiral if and only if it cannot be superimposed on its image in a plane mirror. It's a molecule with a single asymmetric carbon, denoted C* (Sp^3 tetrahedral carbon with four substituents, all different).

Example:



Two chiral molecules present two structures with different physicochemical properties, two configurations known as enantiomers. The word chirality comes from the Greek "cheir" meaning hand.



3.5.2 Determining absolute R or S configurations

Assigning an R or S configuration to a C* can only be done on a three-dimensional representation (Cram, Fisher, etc.) and not on a structural formula.

The steps :

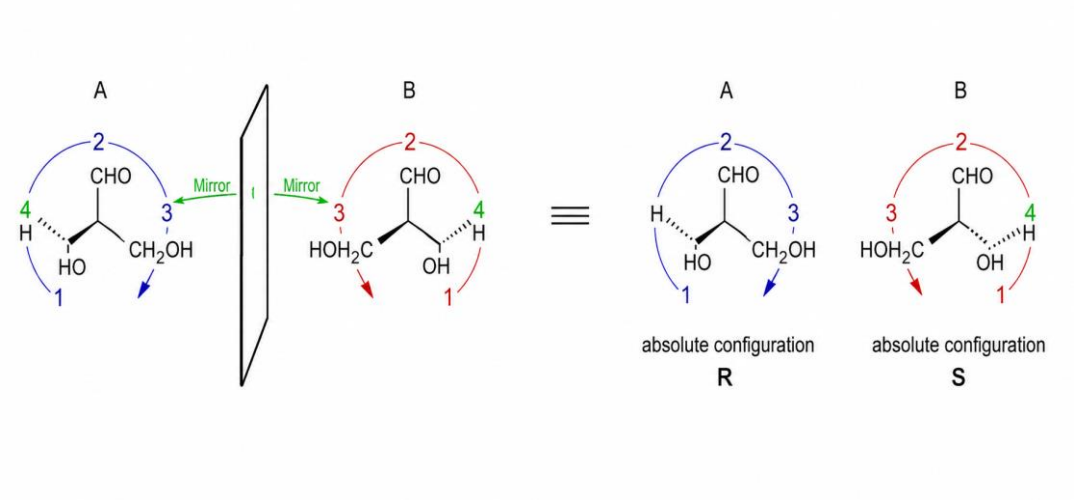
- Assign an order of priority to the four entities around the C* (from 1 to 4) according to Cahn, Ingold and Prelog (C.I.P.) rules.
- Newman projection of C* along the * C 4 axis (priority 4 substituent)
- Determine the direction of travel: 1 2 3, then assign the R/S configuration:

- Clockwise: **R** (**Rectus = straight**).
- Counter-clockwise: **S** (**Sinister = left**).

Note: Depending on the position of priority 4 in Cram's representation, it is more or less easy to obtain Newman's projection along the * C 4 axis.

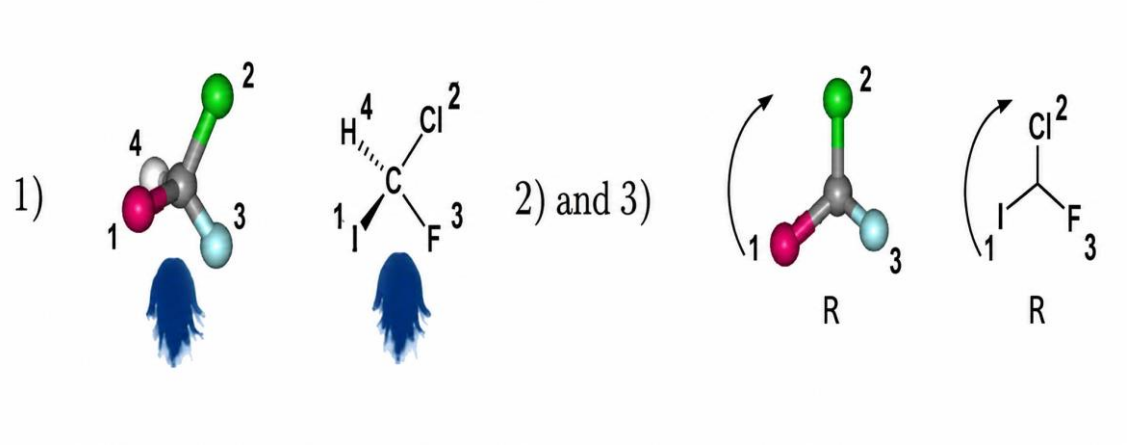
- ✓ If the Priority 4 entity is behind: follow the previous steps.
- ✓ If priority 4 is forward: reverse direction of rotation.
- ✓ If priority 4 is in the plane: swap using the method (2/2 or 50/50), ensuring that priority 4 is behind (do not reverse the direction of rotation).

Example:



Example:

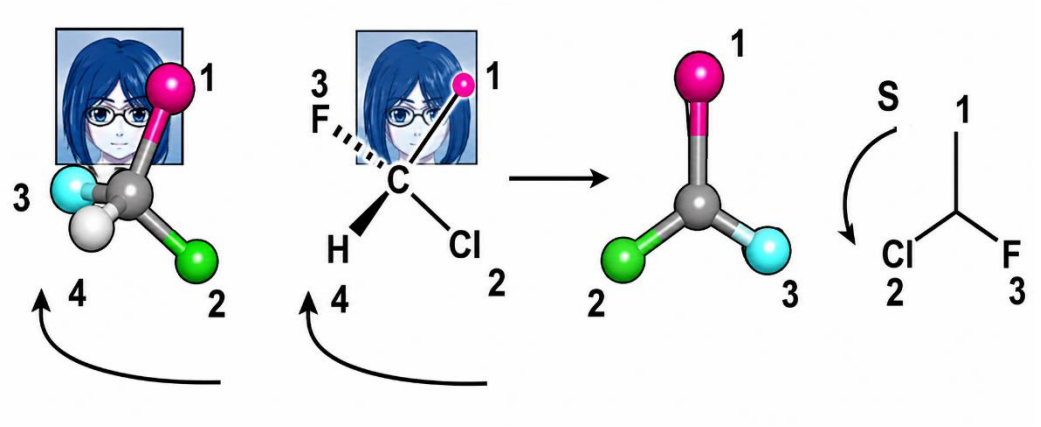
· Simplest case: Priority 4 at the rear: Carry out the 3 previous steps:



- **Case of priority 4 in front**

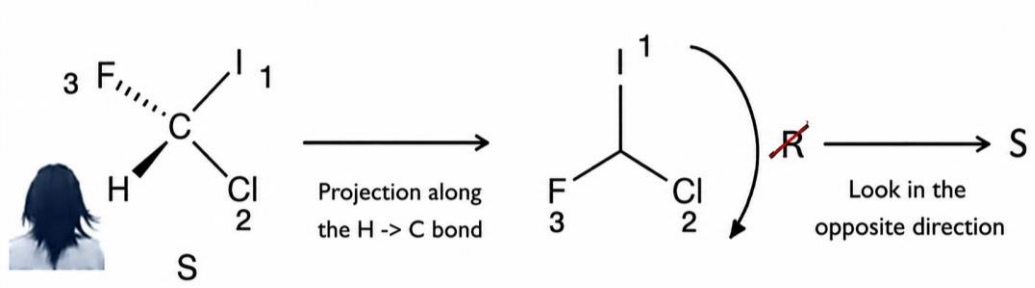
✓ **Method 1:**

The molecule can be flipped to place the group with **priority 4** toward the **back**.



✓ **Method 2:**

In this case, it may be useful to perform the projection in the **opposite direction**: **priority 4 → C***, and then **invert the order** of **1 → 2 → 3** obtained.



3.5.3 Molecules with several C* asymmetric carbons

In the general case, when a molecule has several asymmetrical C* carbons, two (2) possible configurations are envisaged for each. There may therefore be 2n stereoisomers.

$2C^* \rightarrow 2^2 = 4$

Among stereoisomers, we can distinguish between enantiomeric compounds (opposite rotatory power) and other diastereoisomers that can be considered as true geometric isomers, since they can have different physical and chemical properties.

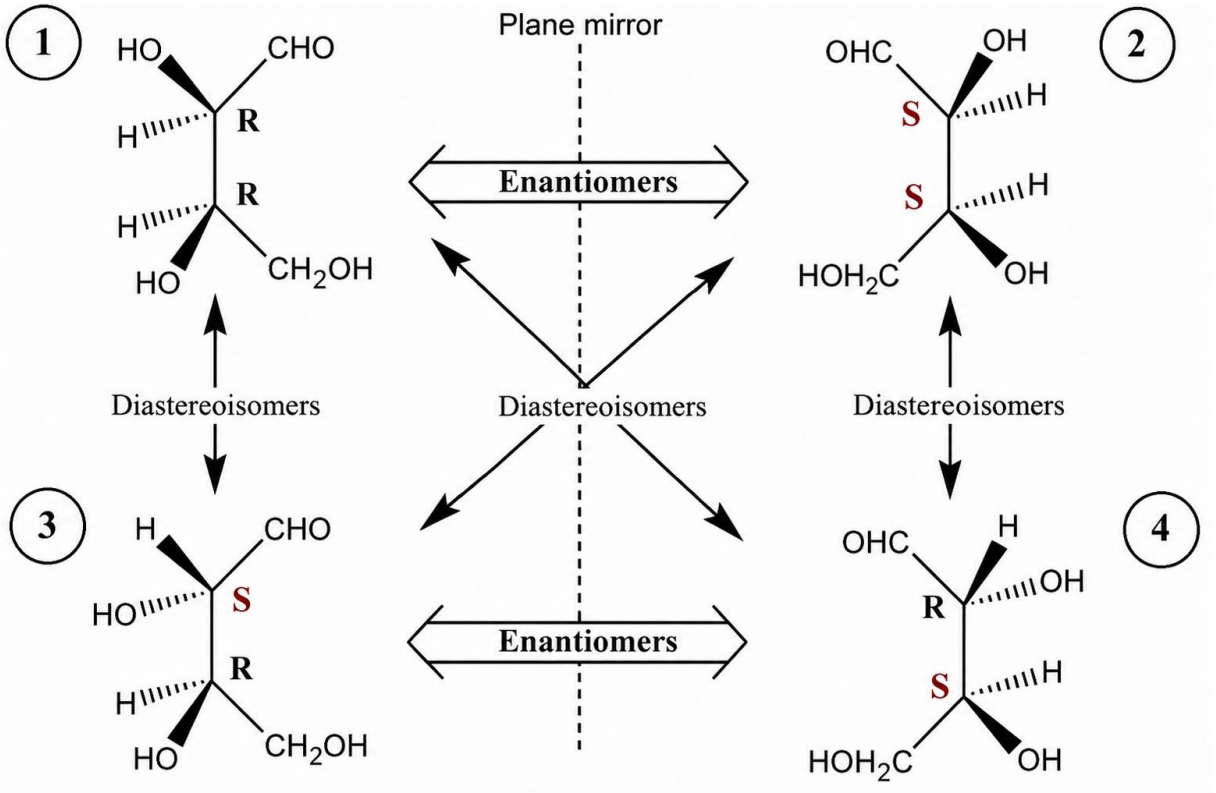
Such molecules are common in nature, particularly in natural compounds such as sugars and amino acids.

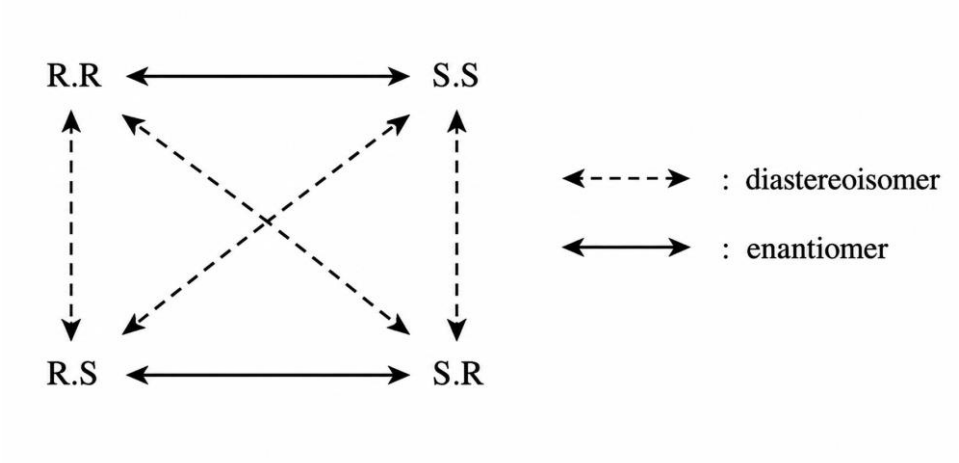
A molecule containing more than one asymmetric carbon **is not necessarily** chiral.

When a molecule has several asymmetric carbons, two configurations are expected:

→ **First case**: the asymmetric C* atoms do not have their three identical substituents ⇒ there are four stereoisomers {R, R; R, S; S, R; S, S}

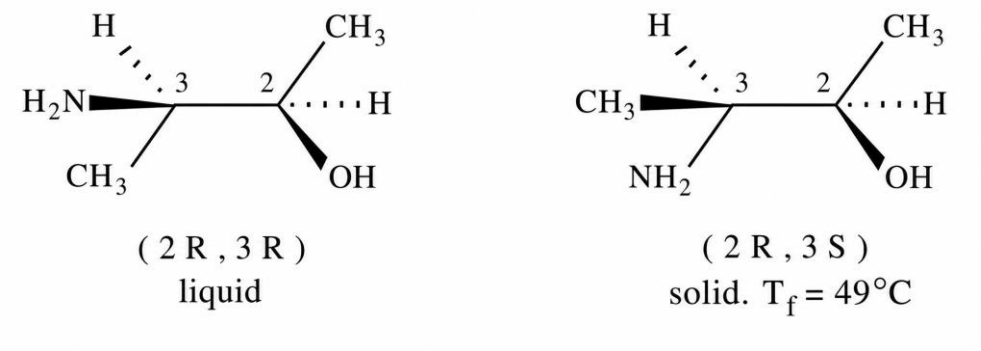
Example: 2,3,4-trihydroxybutanal (CH_2OH-CHOH-CHOH-CHO)





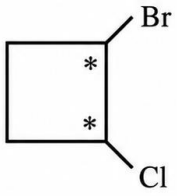
Note

Since diastereoisomers are not enantiomers, they must have remarkably different physical and chemical properties. Example: the (2R,3R) stereoisomer of 3-aminobutan-2-ol is a liquid, while its (2R,3S) diastereoisomer is a crystallized solid.

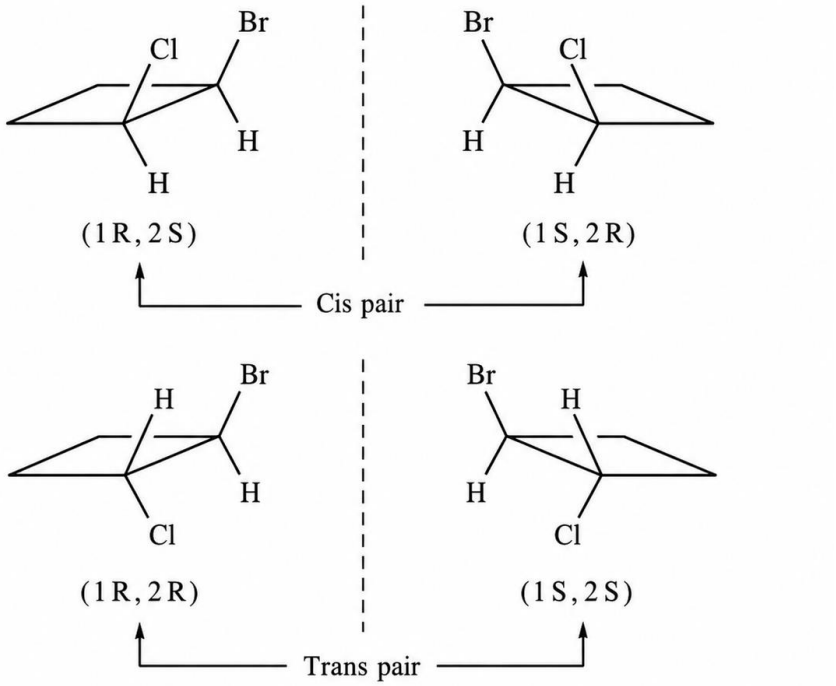


Cyclic molecules

Example: 1-bromo-2-chlorocyclobutane



There exist as 4 stereoisomers consisting of 2 pairs of enantiomers



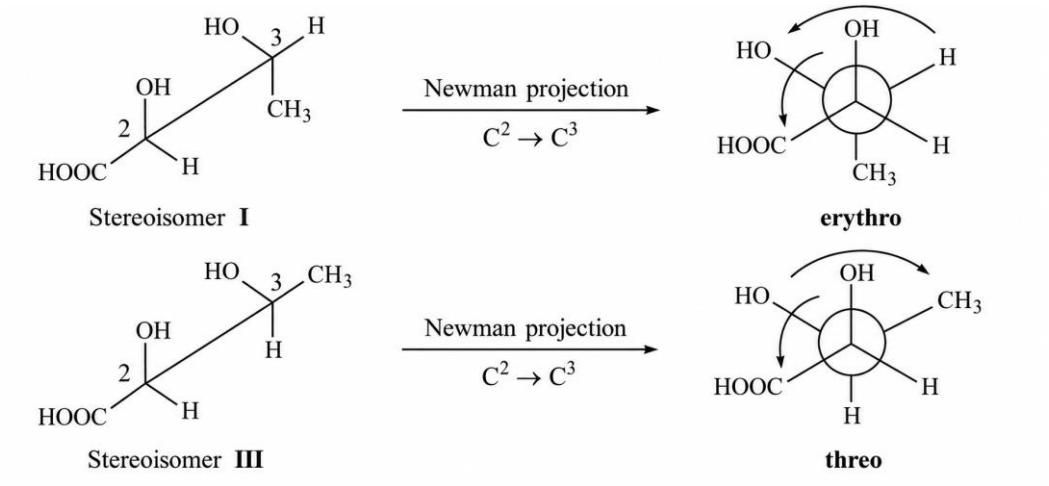
The fact that the molecule is cyclic doesn't change the number of possible configurations, and therefore the number of stereoisomers, but it does block rotation between the two asymmetric carbons.

3.5.4 Threo-erythro nomenclature :

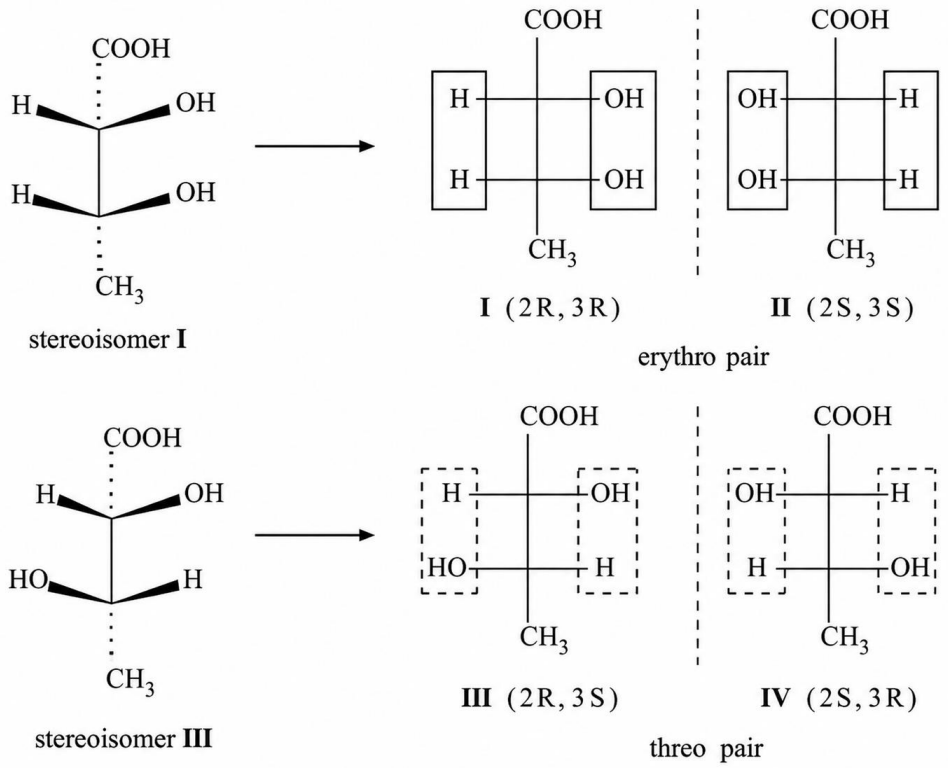
To designate diastereomers, chemists often use a special nomenclature which, although not part of the international nomenclature, is universally used.

- Newman projection Look at the molecule along the C*n → C*n+1 or n-1 axis, then project onto the sheet plane. The substituents on each C* are ranked in descending order according to the Cahn - Ingold - Prelog rules.

If the directions of rotation are identical on each C*, the compound is called erythro; if they are in opposite directions, the compound is called threo.

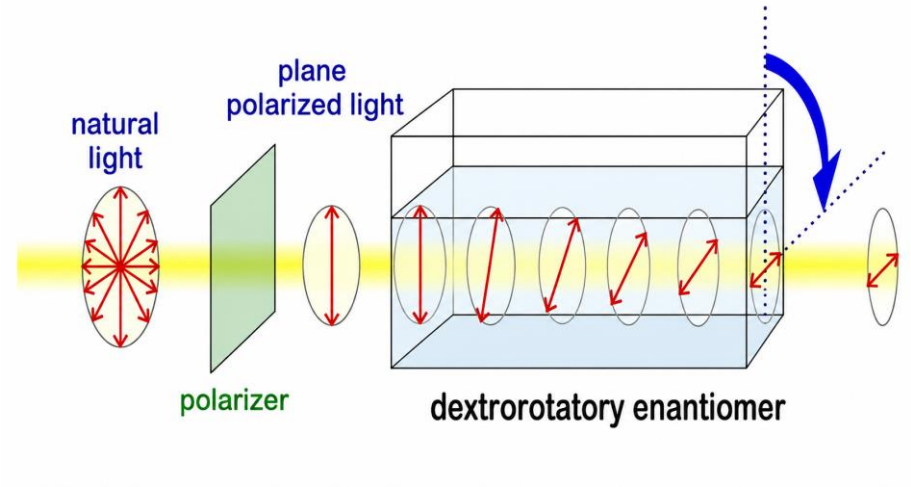


- Fischer projection When identical substituents are on the same side of the carbon chain, compounds are said to be **erythro**, whereas if they are on opposite sides of the carbon chain, they are said to be **threo**.



3.5.5 Optical activity

A chiral substance can deflect polarized light to the right (R) or left (S). A beam of unpolarized light is passed through a polarizer (see image below). The result is a polarized beam (vertical bidirectional arrow). This polarized light passes through an optically active chiral substance, changing the angle of the beam.



- ✓ If the enantiomer deflects the plane of polarized light to the right, it is called dextrorotatory (d) or (+) if $\alpha > 0$ (the angle of rotation turns to the right).
- ✓ If the enantiomer deflects the plane of the polarized light to the left, it is said to be levogyratory.

  (l) or (-) if $\alpha < 0$ (angle of rotation turns to the left).

A substance in a cell its rotation also depends on the wavelength used, the temperature and the solvent: generally the temperature is 20°C and the D line ($\lambda D = 589$ nm) emitted by a sodium vapor lamp.

Specific rotatory power

$$[\alpha]_{\lambda}^{T} = \frac{\alpha}{l\,C}$$

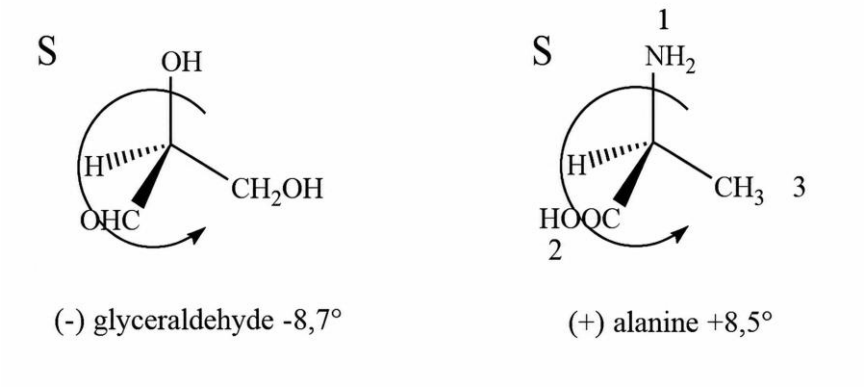
α: angle in degrees ;

l: cell length in cm ;

C: mass concentration in g.cm-3.

The presence of two enantiomers in equimolar quantities gives an $\alpha = 0$. They have opposite rotatory powers (±). The mixture is said to be racemic (optically inactive).

Note: Consider the (-) glyceraldehyde with S configuration and the (+) alanine with S configuration: we see that the R or S configuration is not linked to the sign of the deviation is (+8.5°), (-) glyceraldehyde the deviation is -8.7°.

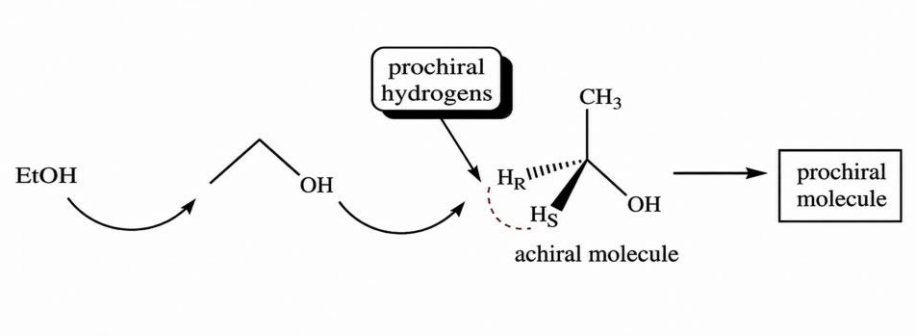


3.6 Prochirality

Prochiral molecules are achiral molecules that can be converted into chiral molecules in a single step.

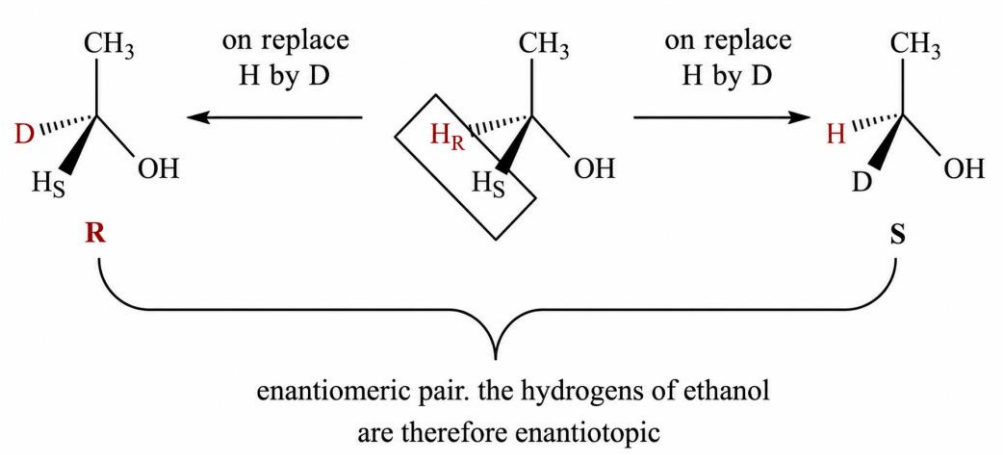
The prochiral faces of a planar trigonal atom (Sp2 hybrid) can give a chiral center by addition reaction on either face. This step may be substitution or addition of an atom or group of atoms.

Example:



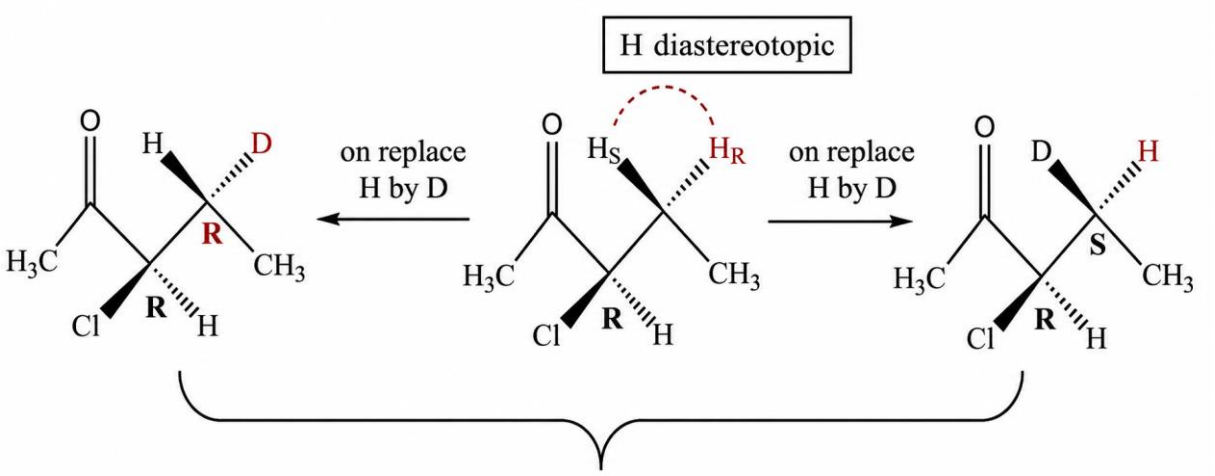
Substitution of one of the prochiral hydrogens into a tetrahedral Sp3 carbon, for example, by a heavy H (2H isotope, Deuterium) gives rise to a new chiral center. This molecule is called prochiral. If substitution by a Deuterium gives the **S** configuration, the substituted **H** is said to be **pro-S** and vice versa.

3.6.1 Proxy atoms / enantiotopy :



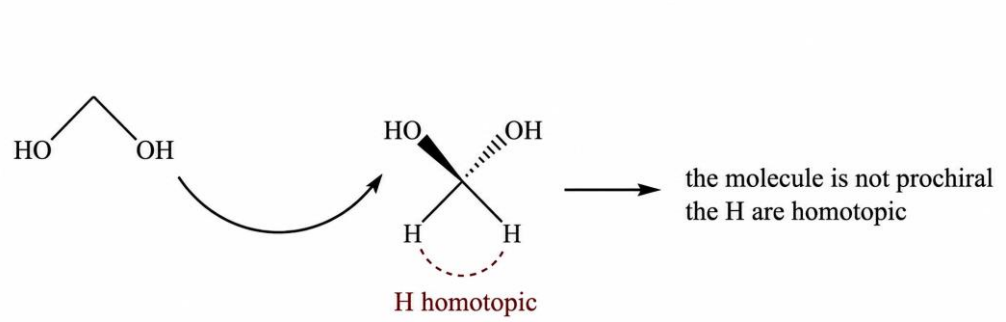
enantiomeric pair. the hydrogens of ethanol
are therefore enantiotopic

3.6.2 Proxy atoms / diastereotopy



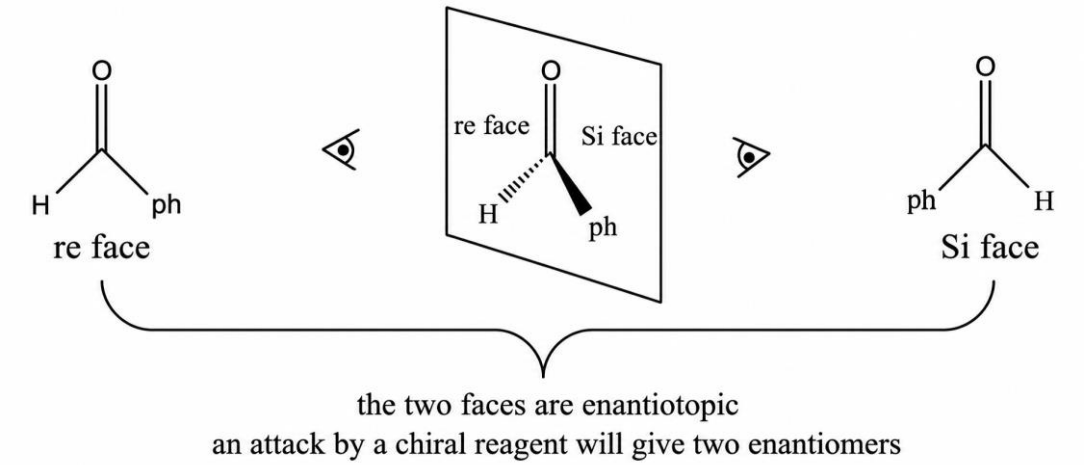
in a diastereomeric pair {R,R and R,S}, the H are diastereotopic

3.6.3 Non-proximal atoms / homotopy



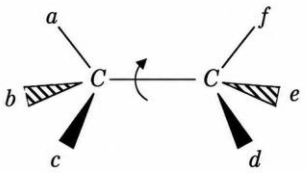
3.6.4 Prochiral faces and symmetry

Planar trigonal atoms (hybrid Sp^2) are not chiral, but can give a chiral center by an addition reaction on one of the faces if the atom contains three different substituents. These faces are designated by the terms re and si, where re is clockwise and si is anti-clockwise.

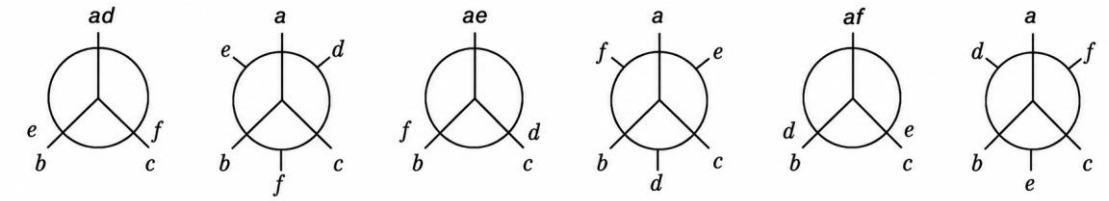


4. Conformational isomerism

Two conformers represent the same molecule in different spatial arrangements and energy states. The change from one conformation to another is made by simple rotation around a single bond (σ-bond), without breaking the bond. This transition requires just a few KJ and takes place rapidly at room temperature, with the same compound existing successively in different conformations in equilibrium with each other. Generally speaking, the different conformers of the same molecule do not constitute distinct chemical species. Indeed, the low energy barrier that separates them makes it impossible to separate them under ordinary conditions (25°C, 1 atm).



Newman Representations



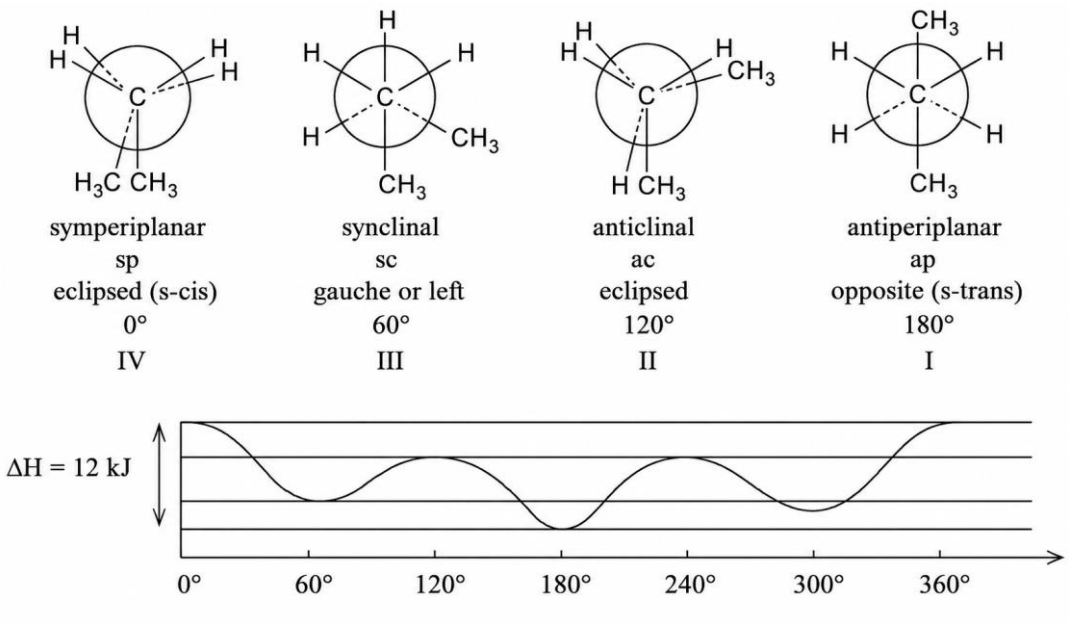
Around a Carbon-Carbon single bond, there is free rotation.

Depending on the different positions of the groups, we speak of conformations. These conformations are like snapshots of the molecule at particular points in time, the atoms being in perpetual rotation.

- Conformations 1, 3 and 5 are called **eclipsed** conformations.
- Conformations 2, 4 and 6 are called **staggered** conformations.

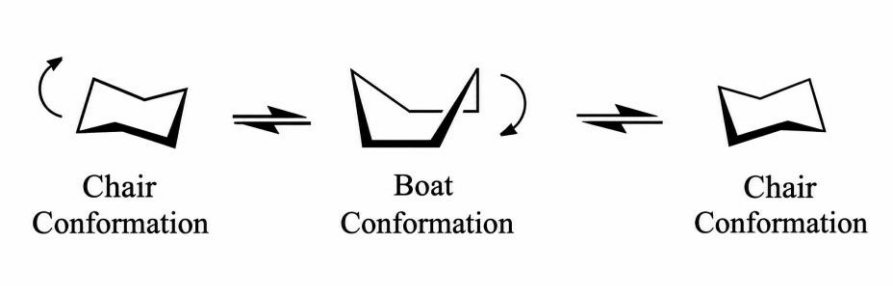
4.1 Conformational study of acyclic compounds (the case of butane)

There are four remarkable conformations:

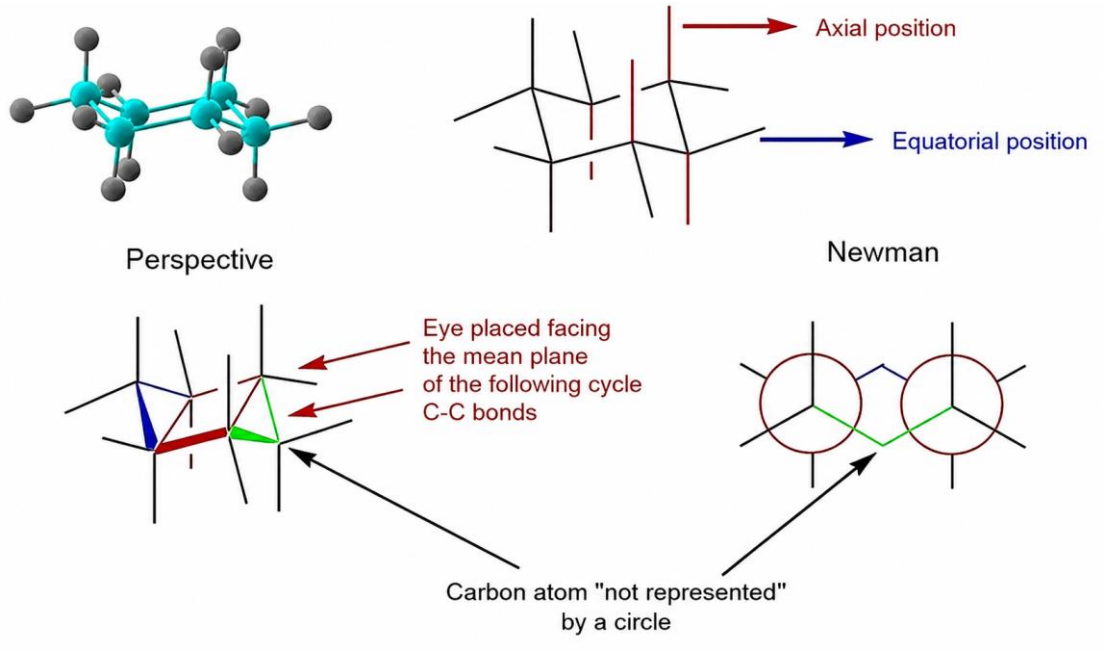


4.2 Conformational study of cyclic compounds (the case of cyclohexane)

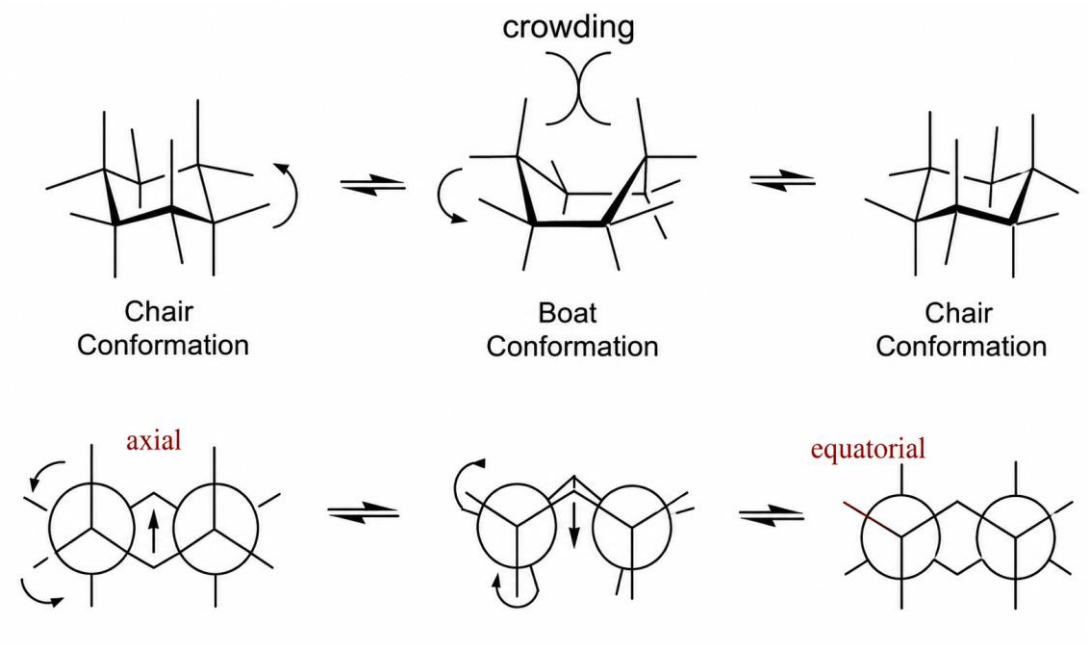
Cyclohexane exists in the chair and boat conformations.



It's essential to know that the hydrogens drawn vertically are the hydrogen atoms in the so- called axial position. The others, on the other hand, are in an equatorial position.



The transition of a cyclohexane into the **chair** conformation can be represented in Newman. to **boat** conformation:

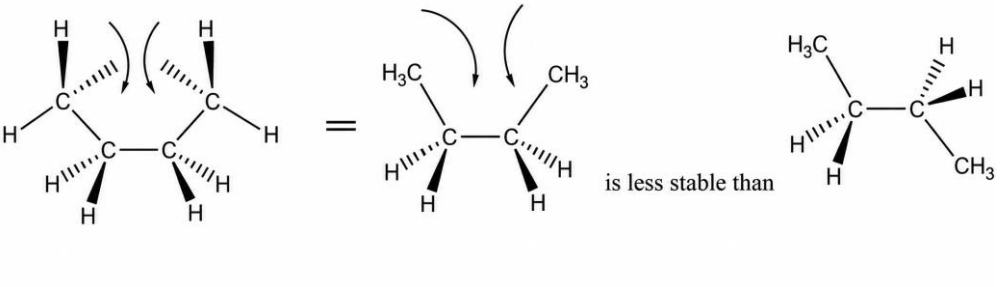


In the boat conformation, there is steric hindrance between the two extreme axial positions. The **boat** conformation is **less** stable than the **chair** conformation.

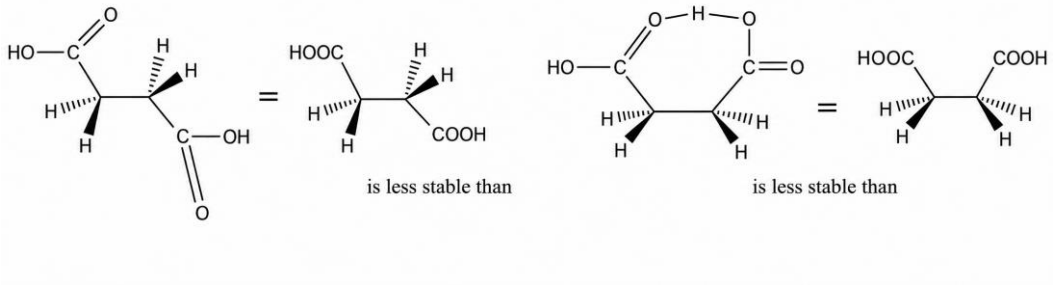
4-3- Stability and conformation

✓ The more stable a molecule, the lower its potential energy. Various intramolecular interactions are involved in the stability of a molecule:

✓ Steric hindrance: these are repulsive electrostatic and/or spatial interactions of unbound atoms or a group of atoms in the molecule. The more steric hindrance there is, the more the molecule is ≪ destabilized ≫



✓ Hydrogen bonds: these are interactions between an electronegative atom bonded to an H and another electronegative atom. These interactions stabilize molecules.



TD +Corrected series

TD 02 Organic chemistry

Exercise 01:

To write:

a)- C_3H_4 isomers

b) - two isomers of formula C_5H_6O each having one carbonyl group and two methyl groups;

c)- The isomers of C_4H_8Br giving their nomenclature names.

Exercise 02:

I. A hydrocarbon has a molar mass equal to 70 g/mole:

- Find its raw formula.
- Give the different isomers and name them.

II. Classify according to the rules of CAHN, INGOLD and PRELOG (conventions CIP) the substituents below by priority order

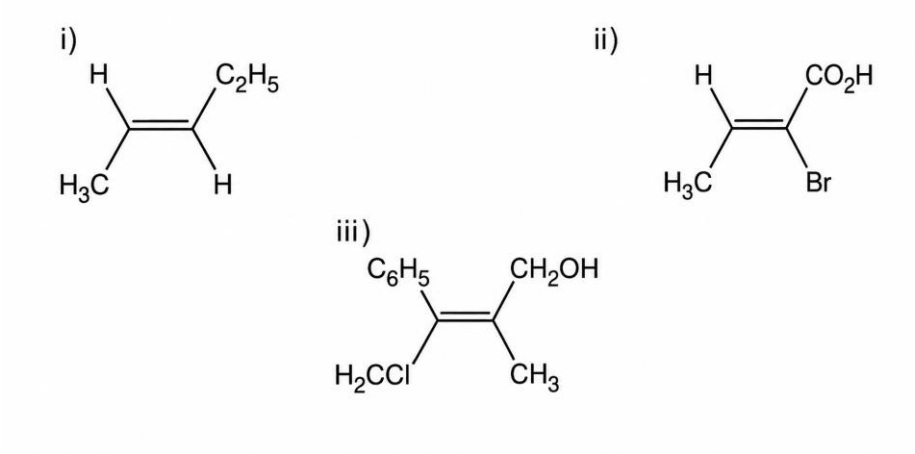
a)- $-CH_3$; $-CH_2-CH_3$; $-OH$; $-NH_2$

b)- $-COOH$; $-COOCH_3$; $-CH=CH_2$; $-C\equiv N$; $-CHO$

c)- $-C(CH_3)$; $-CCl_3$; $-CH_2-CH_2OH$; $-COCH_3$; $-CONH_2$; $-CH_2OH$

Exercise 03:

Using the nomenclature **R** and **S** to:



Exercise 04:

Represent the configurations of the following molecules by specifying the notations **Z. E** or **R. S** as well as the isomerism relationships between them.

a)-4-methylhepta-2.5-diène

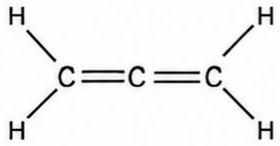
b)- 4-chloropent-2-éne.

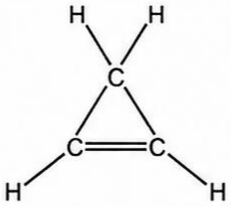
****Good luck****

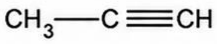
Answers

Exercice 01:

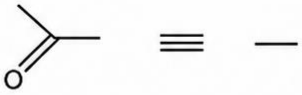
a)-



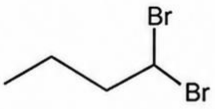




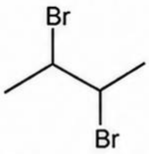
b)-



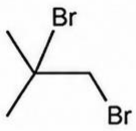
c)-



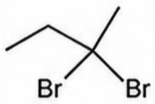
1,1-dibromo butane



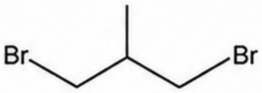
1,1-dibromo-2-methyl propane



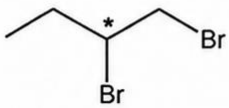
1,2-dibromo-2-methyl propane



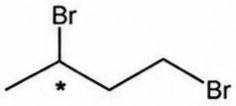
2,2-dibromo butane



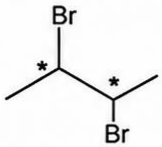
1,3-dibromo-2-methyl propane



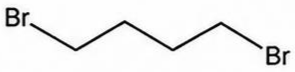
1,2-dibromo butane (2 enantiomers)



1,3-dibromo butane (2 enantiomers)



2,3-dibromo butane (1 meso + 2 enantiomers)



1,4-dibromo butane

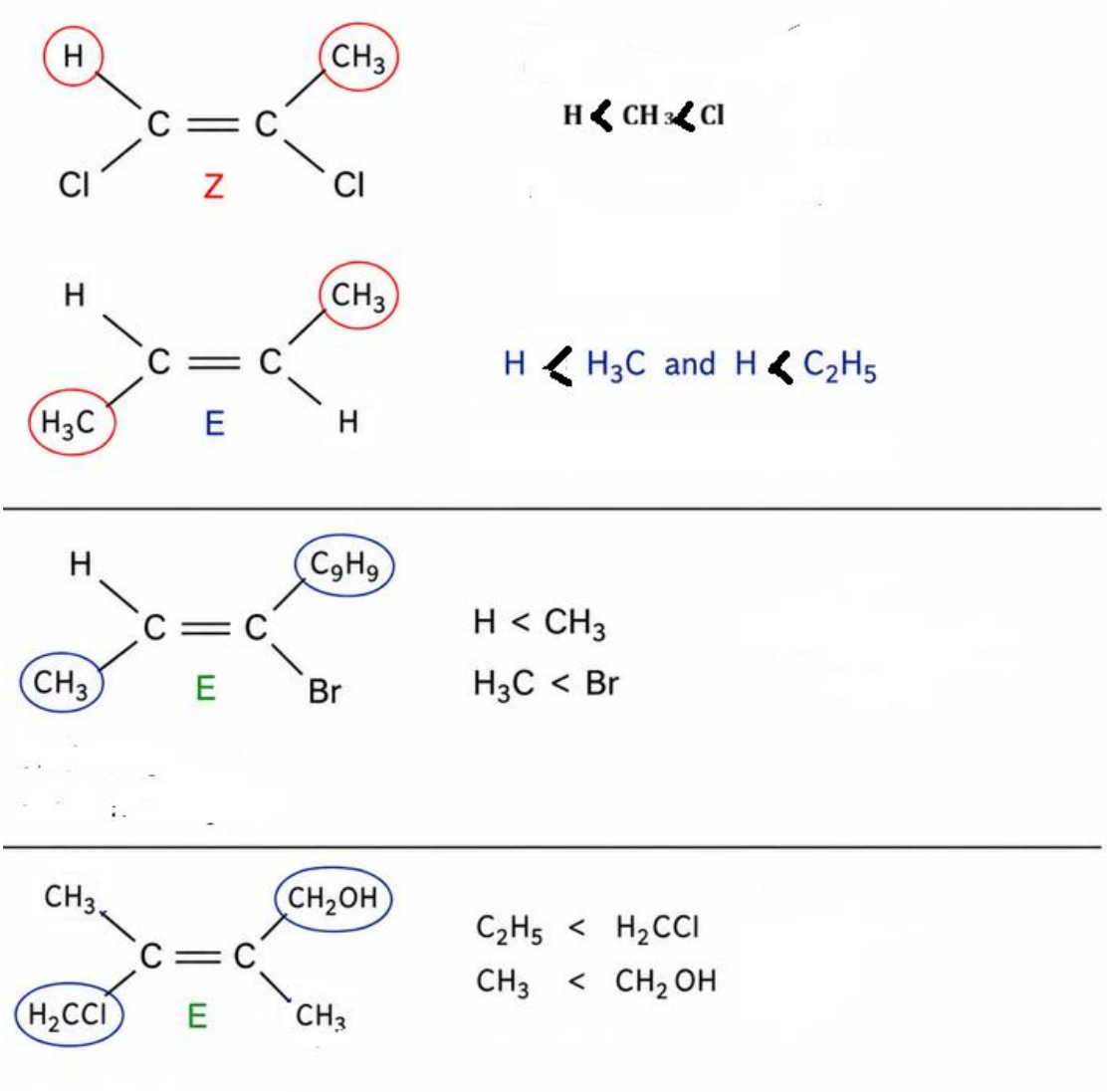
Exercice 02:

a)- -OH > – NH_2 > –CH_2-CH_3 > –CH_3

b)- -$COOCH_3$ > –COOH > –CHO > –C=N > –CH=CH_2

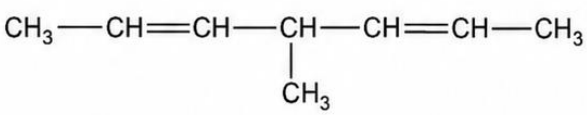
c)- –CCl_3 > –$CONH_2$ > –$COCH_3$ > –CH_2OH > –C $(CH_3)_3$ > –CH_2-CH_2OH

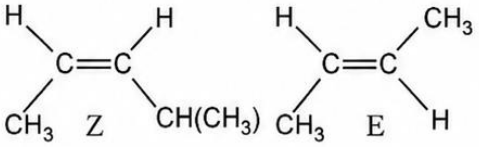
Exercice 03:


H
CH3
C
C
Cl
Z
Cl
H < CH3 < Cl
H
CH3
C
C
H3C
E
H
H < H3C and H < C2H5
H
C9H9
C
C
CH3
E
Br
H < CH3
H3C < Br
CH3
CH2OH
C
C
H2CCl
E
CH3
C2H5 < H2CCl
CH3 < CH2OH

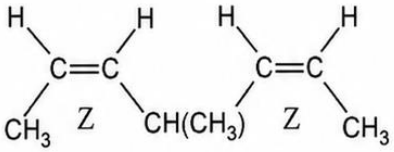
Exercice 04:

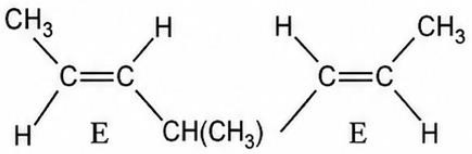
4-methylhepta-2,5-diene

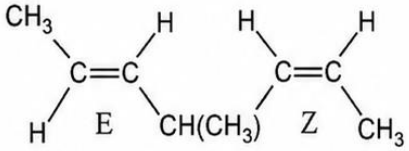




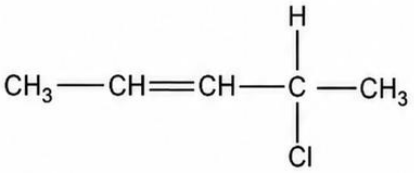
2 °C, 2° ⇔ 4 geometric stereoisomers.

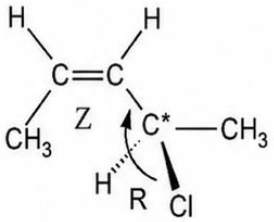


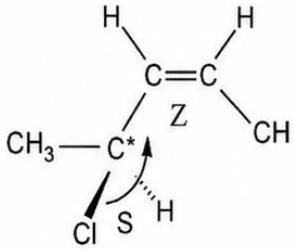


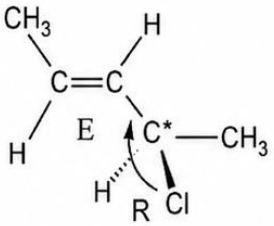


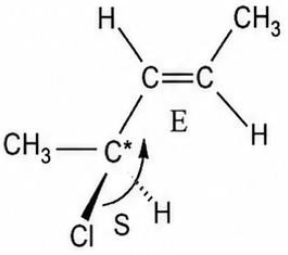
b)- 4-chloropent-2-ene.











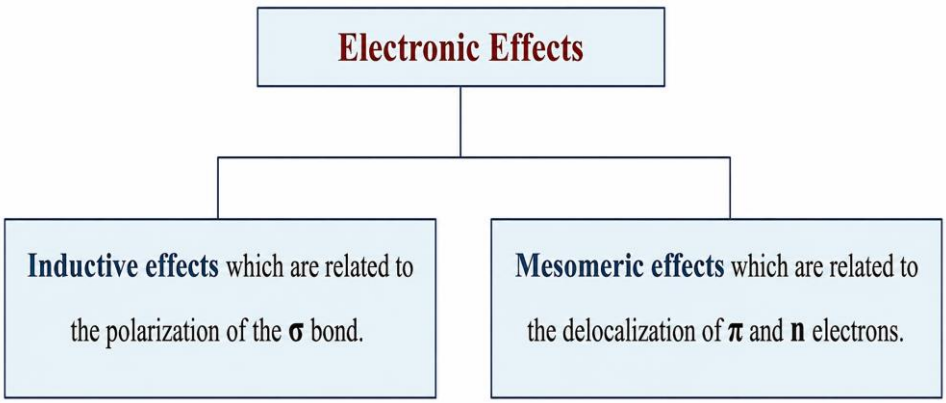
CHAPTER Ⅳ: ELECTRONIC STRUCTURES OF MOLECULES

I. Generalities

There are 2 types of electronic effects: **inductive effects**, which are due to the polarization of a σ- bond, and **mesomeric effects**, which are due to the delocalization of **π-electrons** and π-electrons.

n. Both effects can exist together in the same molecule.

In the case of the coexistence of 2 inductive and mesomeric effects of opposite signs, the mesomeric effect always prevails.



I.1 Physical properties of organic molecules Reminder :

a – Non-polar bond

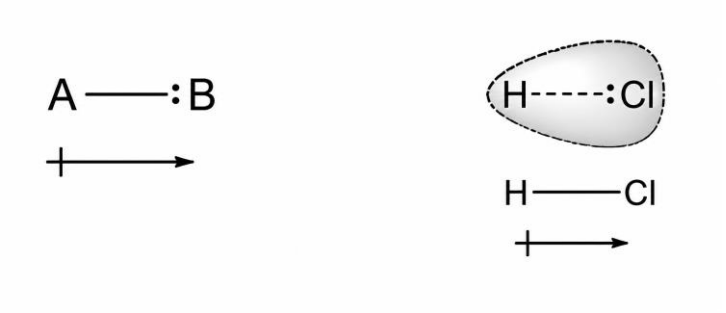
Symmetrical electronic cloud

❖ *If the two atoms in a covalent bond are identical, then:*

→ the bonding electron pair is shared equally between the two atoms.

→ **non-polar bond.**

b – Polar bond



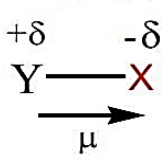
❖ *If the two atoms are different, then:*

→ The **more electronegative atom** attracts the bonding electrons toward itself.

→ The **electronic cloud** is no longer symmetrical.

→ The **bond becomes polarized.**

→ The **polarization** of the bond is characterized by its **dipole moment (μ):**



μ = δ × l (in Debye units)

where:

μ = dipole moment

δ = formal charge

l = bond length (in angströms, Å)

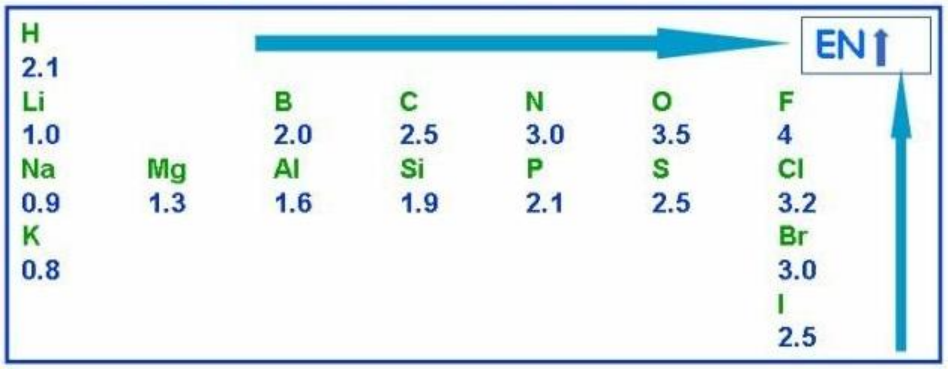
c- Electronegativity:

Electronegativity increases from left to right with the same period, and from bottom to top in the same column (see table below).

Relative electronegativities according to Pauling

Electronegativity, as defined by Pauling, measures the tendency of an atom in a molecule to attract the electronic cloud toward itself.

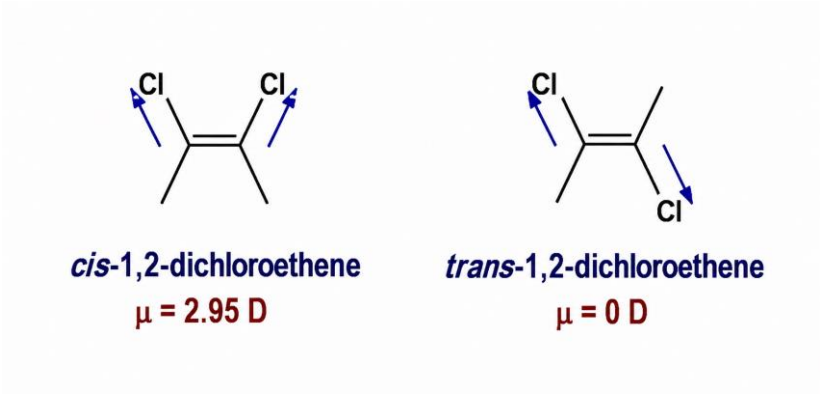
Relative electronegativities according to Pauling



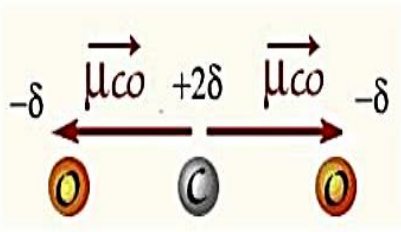
d – Vector composition model of dipole moments

In the case of a polyatomic molecule, the dipole moments are added as **vectors**.

A molecule can have polar bonds and still be globally nonpolar:



Thus, in the case of the **CO_2 molecule**, due to its linear and symmetrical geometry, the two C=O bond moments cancel each other out. The resulting dipole moment is therefore zero.

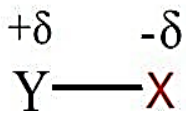


Note: Any molecule that possesses a center of symmetry has a zero dipole moment.

2 – Inductive Effect

The polarization of a bond induces a displacement of electrons along the bond — this is the **inductive effect**.

In other words, the inductive effect is the transmission of the polarity of a σ bond through neighboring groups of atoms.



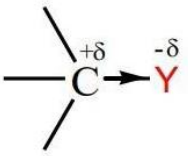
There are two types of inductive effect:

- Attractive inductive effect (-I)

- Inductive donor effect (+I)

2.1 – Electron-Withdrawing Inductive Effect (–I)

Elements with an electronegativity index higher than that of carbon exert an electron-withdrawing inductive effect, denoted (–I).

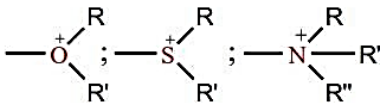


→ Electron-with drawing group (–I)

Y=

➤ **Halogens:** –F, –Cl, –Br, –I

➤ **Neutral or charged groups** such as **–OR, –SR, –NRR′**

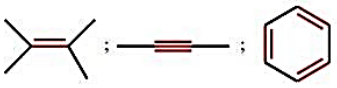


oxygen (O), **sulfur (S)**, or **nitrogen (N).**

➤ Neutral or charged groups containing **–NO, –NO₂, –SO₃H:**

These contain several heteroatoms and are strongly electron-withdrawing groups.

➤ Groups derived from alkenes, alkynes, or aromatic rings



➤ Groups consisting of a carbon atom bonded to one or more heteroatoms or halogens:

–CH_2X (halomethyl group),

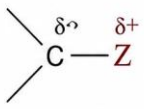
–CHX_2 (dihalomethyl group),

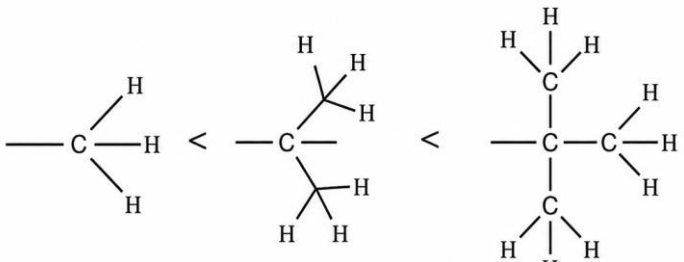
–CX_3 (trihalomethyl group),

–C≡N (cyano group).

I.2 Electro-donor inductive effect (+I)

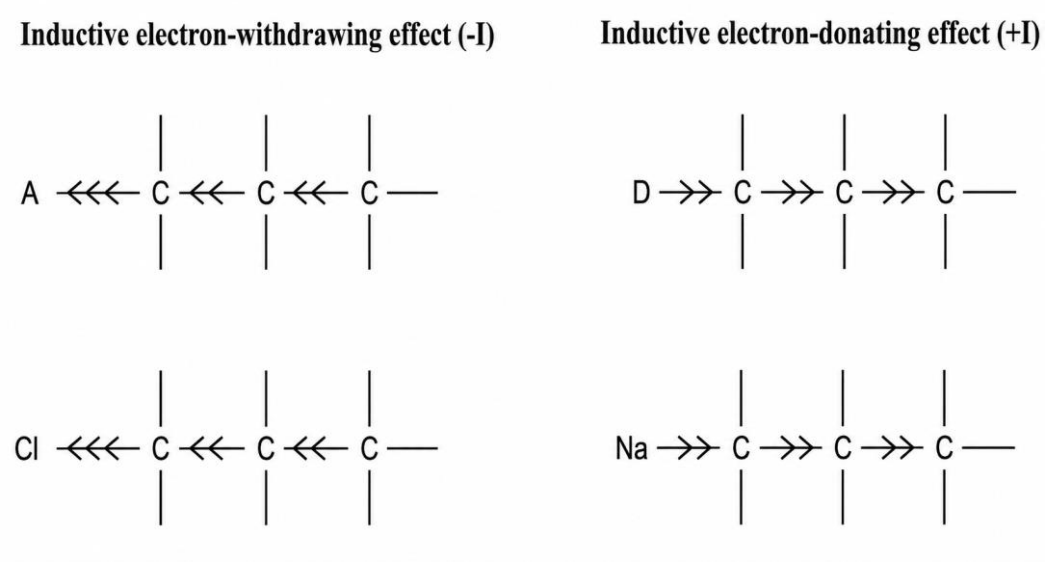
Elements with an electronegativity index lower than that of carbon exert an inductive donor effect noted (+I).

Z:  = an electron-withdrawing group

➢ Alkyl groups 

methyl isopropyl tert-butyl

➢ Metals Li, Na , K, MgX



2.3 Influence of the inductive effect

2.3.1 Acidity and basicity of compounds.

- **Acidity and basicity according to Brönsted.**

- Brönsted acidity expresses the ability of an entity to donate a proton (ion H+) to a basic reagent (water or a base), an acid is a compound capable of donating a proton.

The faster a proton is released, the stronger the acidity (acetic acid).

$$CH_3COOH \rightleftarrows CH_3COO^- + H^+ \quad // \quad CH_3CH_2OH \rightleftarrows CH_3CH_2O^- + H^+$$

Acetic acid — Ethanol

- Basicity reflects an entity's affinity for protons. A base is an electron-rich compound likely to capture a proton from an acidic reagent.

$$CH_3\ddot{N}H_2 + CH_3COOH \rightleftharpoons CH_3\overset{+}{N}H_3 + CH_3COO^-$$

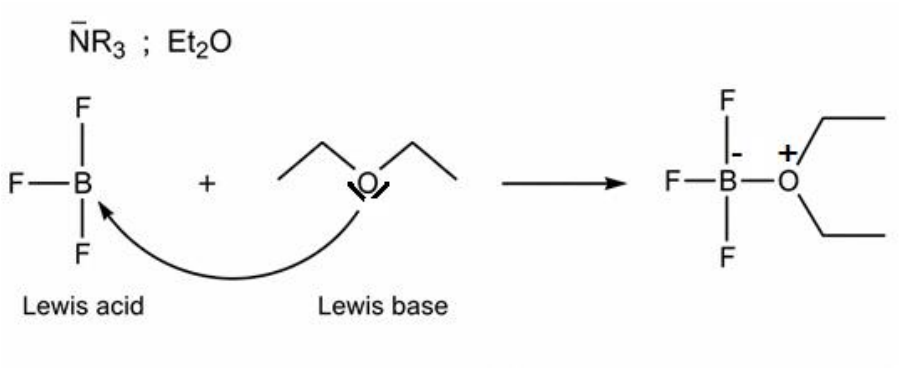
- **Lewis acidity and basicity**

A Lewis acid is a species containing an atom with an empty electron square that can interact with a free electron doublet.

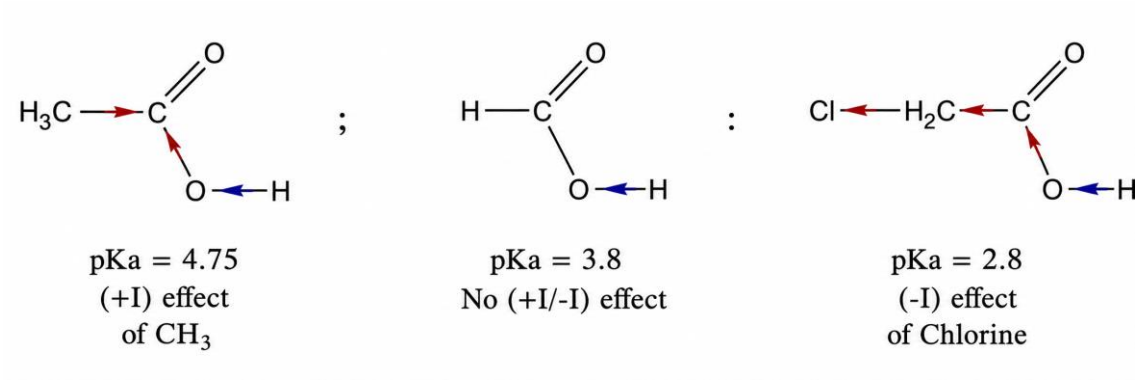
Exemple:

$\square BF_3$; $\square AlF_3$; $\square AlCl_3$

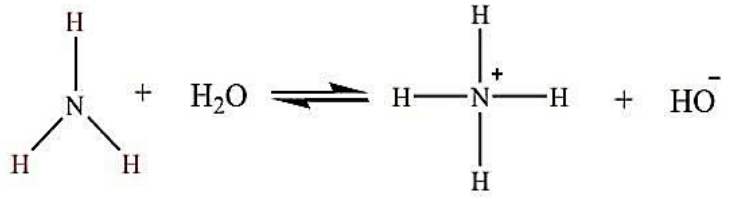
- A Lewis base is a species with a free doublet that can coordinate with a Lewis acid.

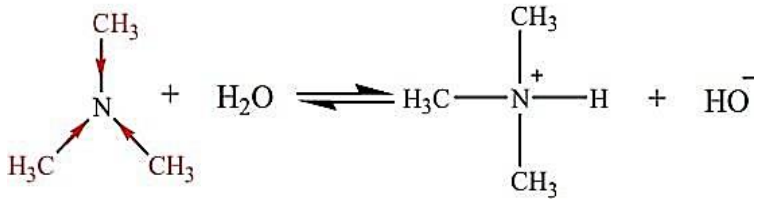


- **The inductive effect influences the acidity of the compounds.**



Groups with an inductive effect (-I) make the H more acidic (more easily removed by a base), so the carboxylic acid containing the chlorine is more acidic.



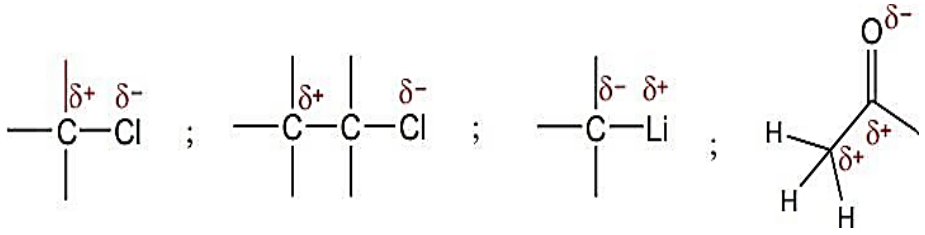


The inductive effect influences the basicity of compounds

In the case of amines, alkyl groups make the amine more basic than H (enrichment of the non- binding nitrogen doublet and/or stabilization by the inductive **+I** effect of ammonium).

- **Reactivity**

Polarization and its extension by the inductive effect play an important role in reactivity. They are responsible for the existence of electron-rich (δ +, nucleophilic center) and electron-poor (δ -, electrophilic center) sites.

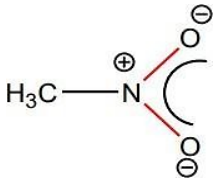


3.1 Mesomerism and resonance

In organic chemistry, we often encounter molecules that are correctly described by several **Lewis** Structures.

These two structures differ only in the location of the π or n electrons (free doublet). You can switch from one formula to the other simply by moving these electrons.

- These two Lewis representations are equivalent and are called resonance structures or mesomeric forms.
- The hybrid resonance form is the real form of all these structures (the others are imaginary).



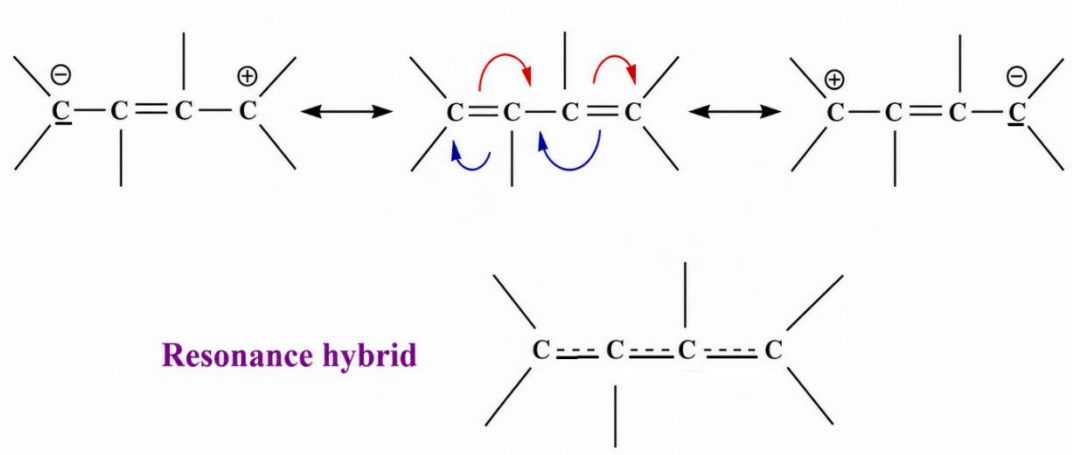
Mesomerism, or the mesomer effect, describes the delocalization of π, free electron doublets n and charges in conjugated molecules.

Note: conjugation is the alternation between double and single bonds in unsaturated molecules.

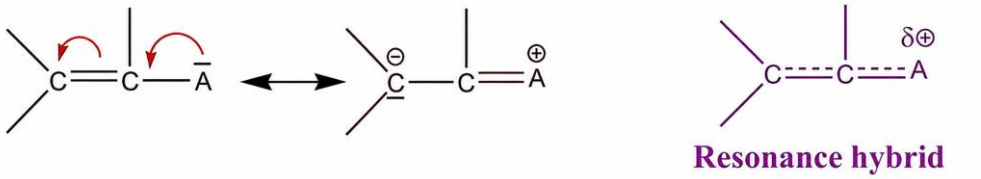
3.2 Mesomerism of unsaturated systems

The main conjugate systems

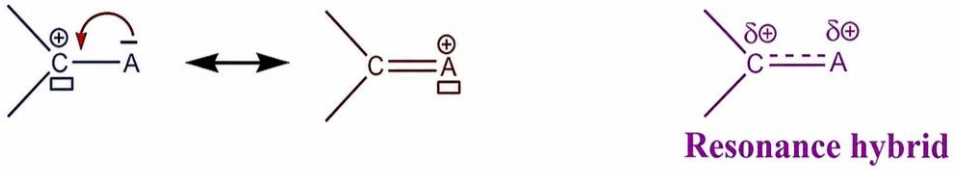
- **Electrons π**



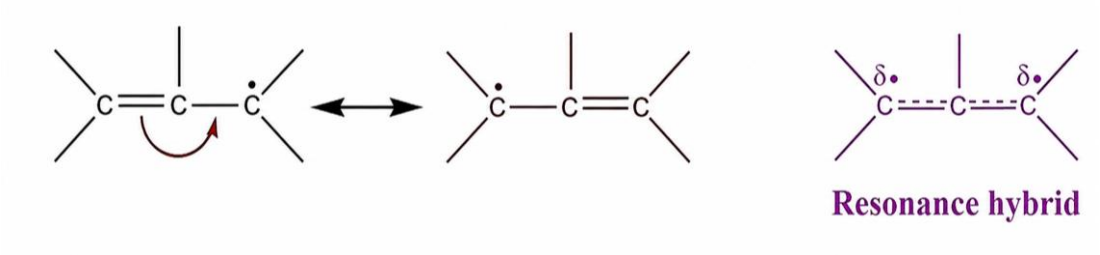
- **Electron π and electron n**



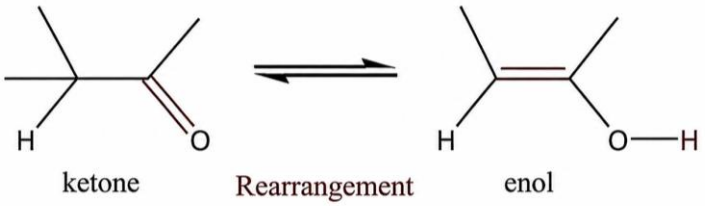
- **Electron n and electronic vacancy (vacant orbital)**



- **Electron π and unpaired electron (single electron)**



- **Tautomerism:** Unlike resonance, tautomerism is an equilibrium between two isomers that have their own distinct existence..



3.3 Aromaticity Hückel's rule :

A molecule is aromatic if it is :

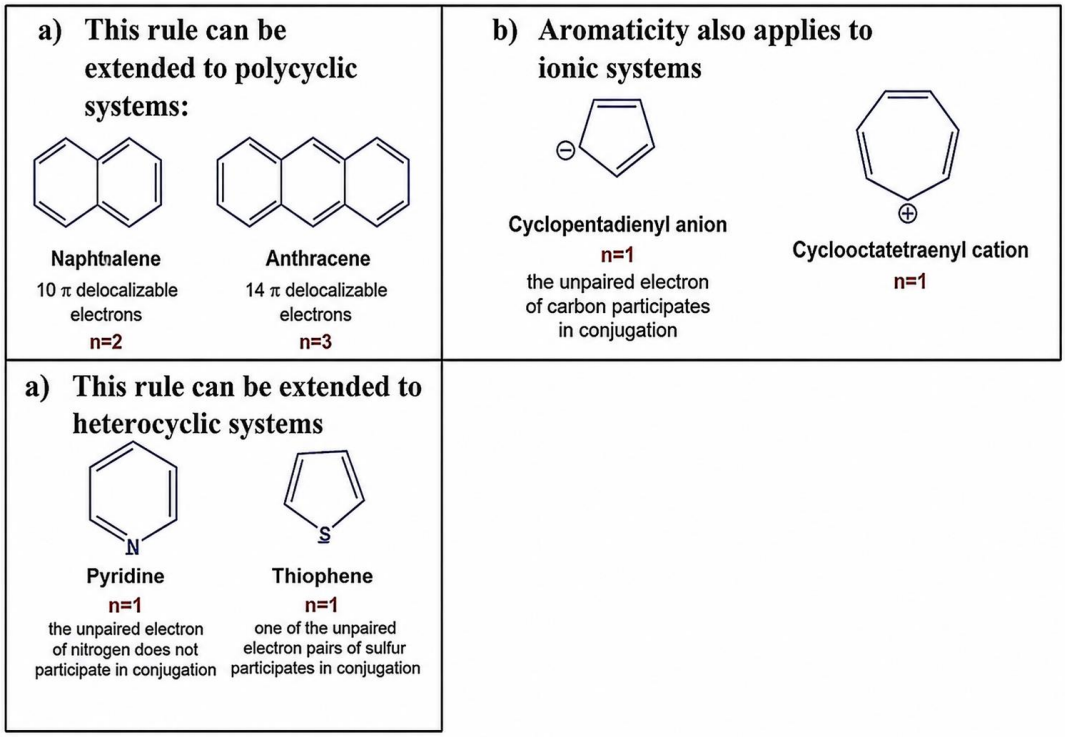
- cyclic.

- plane

- fully conjugated.

- it has (4n+2) delocalizable π electrons (n integer 0, 1, 2, 3...).

Planar cyclic molecules with (4n+2) □ electrons. These molecules are highly stable due to the delocalization of □ electrons. These molecules are therefore reactive. Aromaticity is a concept that can be applied to other cyclic molecules that do not necessarily have a benzene ring:



- **Mesomer effect**

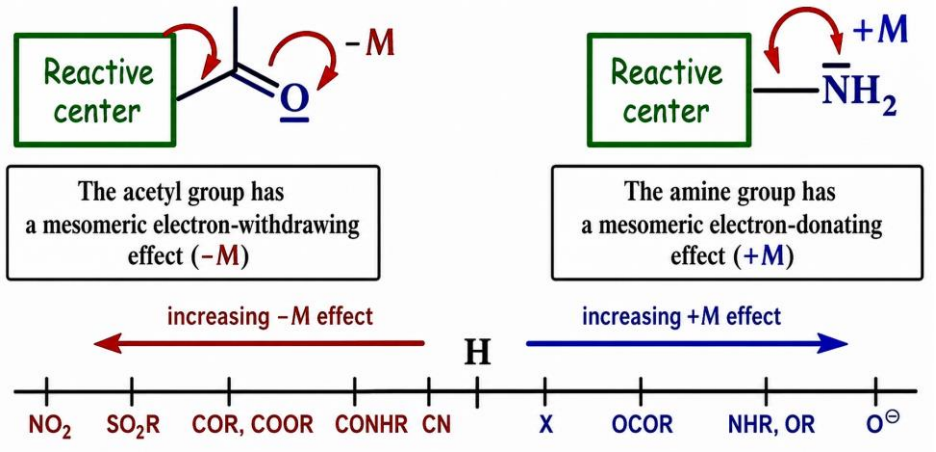
The displacement of π-bonding or non-bonding (n) electron doublets creates electron-rich or electron-poor sites within the molecule.

The mesomeric effect concerns :

- The π
- Free electron doublets
- Expenses.

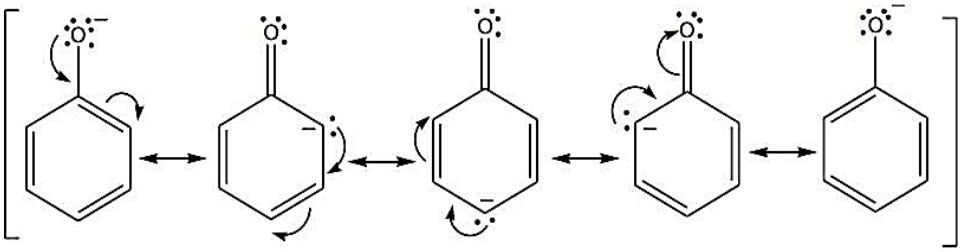
There are two types of mesomeric effects. Electron donor effects (+M) and electron attractor effects (-M).

➢ **Classification of mesomeric effects**

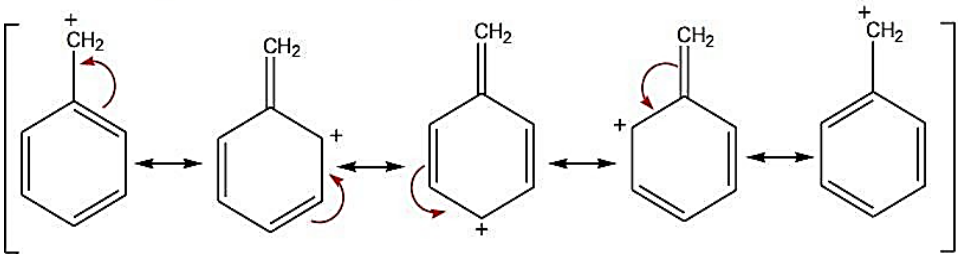


Writing mesomeric forms

a) Example of the phenolate ion

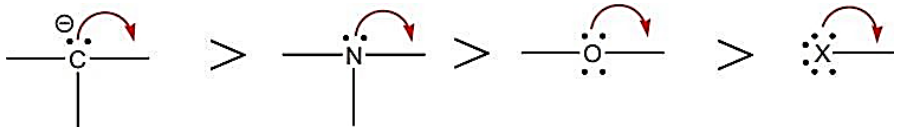


b) Example of the benzyl cation.

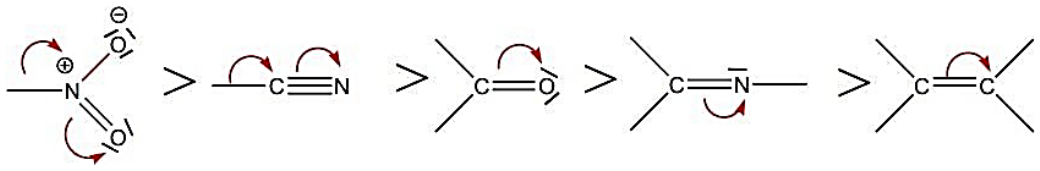


Classification of substituents with a mesomeric effect:

3.4.1 Mesomeric electro-donor effect (+M):



3.4.2 Electro-attractive mesomer effect (-M) :



TD +Corrected series

TD 04 Organic chemistry

Exercice 01

Using the periodic classification of the elements, indicate which element is the most important electronegative between:

a) oxygène and fluor

b) oxygène and phosphore

c) azote and aluminium

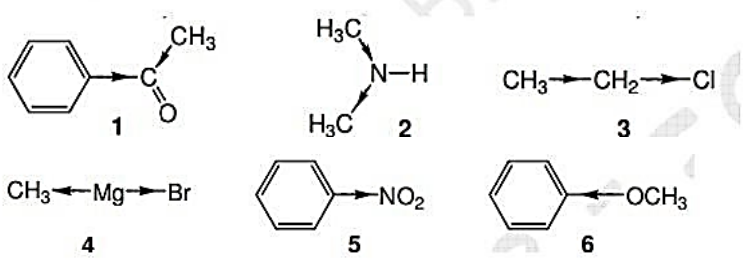
d) carbone and sodium

e) carbone and magnésium

f) carbone and lithium

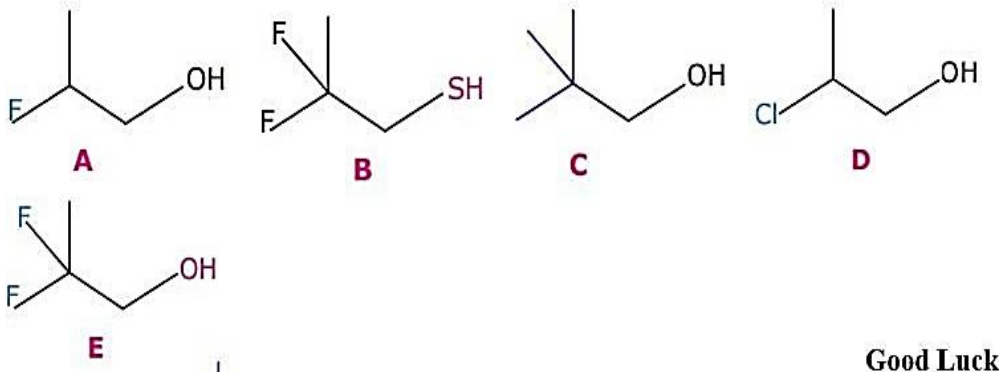
Exercice 02

Indicate the structures in which covalent bonds are polarized correctly:



Exercice 03

Rank molecules in order of decreasing acidity:



Good Luck

Corrected type

Exercice 01

The most electronegative element:

a) F > O b) O > P

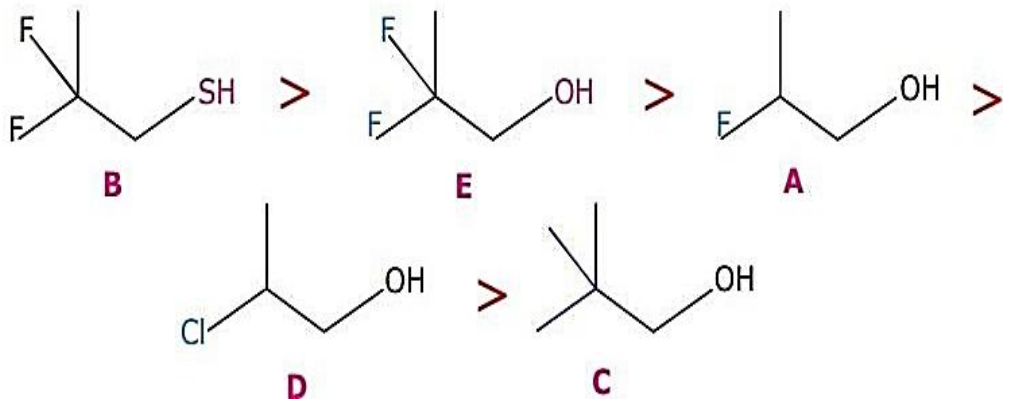
c) N > Al d) C > Na

e) C > Mg f) C > Li

Exercice 02

Structures in which covalent bonds are polarized correctly: 1, 3, 4, and 5.

Exercice 03



• Molecules **B** and **E** carry the same substituent groups **F**; the acidity depends only on the alcohol function **(OH)** and the thiol function **(SH)**: the **S–H bond** is weaker than the **O–H bond** because $\mathbf{d_s–H > d_o–H}$ (internuclear distances).
Therefore: **B** is more acidic than **E**.

• The influence of fluorine and chlorine is characterized by an **electron-withdrawing inductive effect (-I)**. Fluorine is more electronegative than chlorine, thus more electron-withdrawing; this effect weakens the **O–H bond** (by increasing the bond polarity), making it more acidic: **A** is more acidic than **D**.

• When the number of electron-withdrawing groups increases, the **inductive electron-withdrawing effect** increases: **E** is more acidic than **A**.

• Molecule **C** carries three **CH_3 (+I)** donor groups; it is the least acidic.

B > E > A > D > C

TD 05 Organic chemistry

Exercice 01

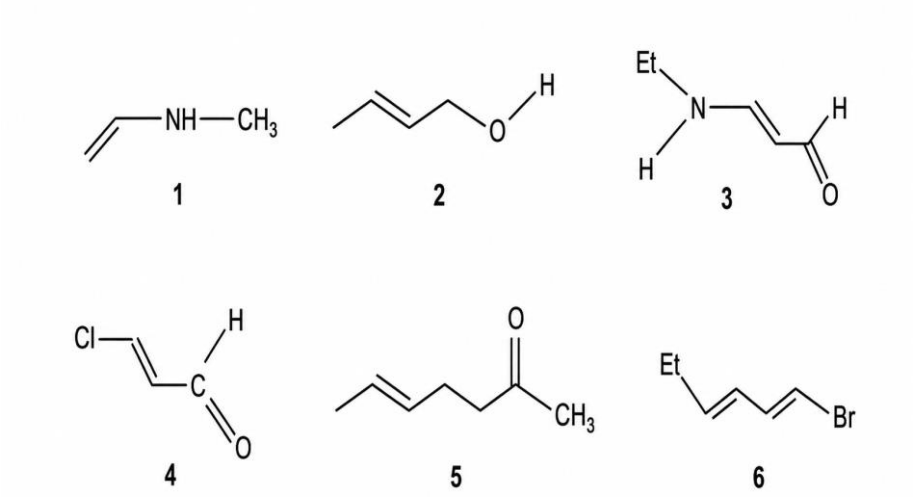
The strength of the acidic character of a compound is due to the greater or lesser ease with which the hydrogen of the functional group can separate from the molecule, in the form of a proton, following ionization of the O-H bond. thus the compound AH is all the more acidic as its conjugate base A is stabilized. On this basis, classify the following different compounds in order of increasing acidity:

1. CF_3-COOH , CH_3-COOH , CH_3-CH_2-COOH , HCOOH , CH_2F-COOH

2. CH_3-CH_2OH-$(CH_3)_2CHCH_2OH$, $(CH_3)_3COH$, $ClCH_2CH_2OH$,Cl_2CHCH_2OH, Cl_2CHCH_2SH

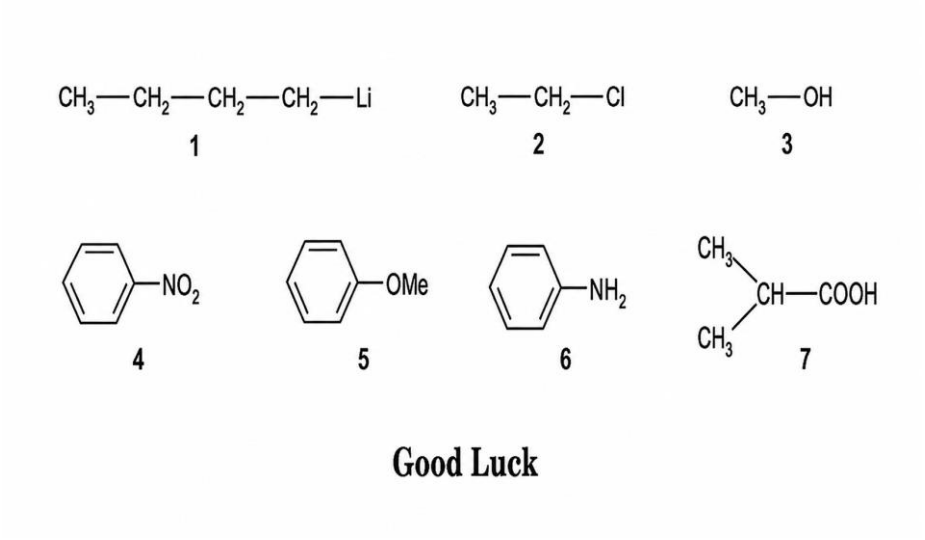
Exercice 02

In the list of 9 compounds below, indicate which molecules present a system or conjugated structure (e) that can lead to electron delocalization by mesomerism. When this is the case, we will write the resonance form (or mesomeric form) in which the relocation is maximum



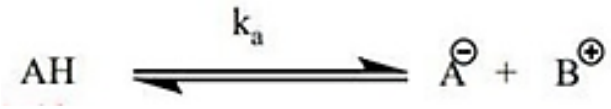
Exercice 03

Indicate for each of the following molecules the direction of the inductive effect (+I, -I) and possibly mesomeric (+M, -M) induced by atoms or groups of atoms underlined:



Corrected Type

Exercise 01



The equilibrium constant, Ka, is defined by **pKa = –log Ka**

Reaction: (Acid / Conjugate base)

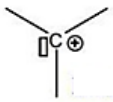
i) The smaller pKa, the larger Ka (higher concentration of H^+). The dissociation of A–H is effective → the acid is strong.

ii) The larger pKa, the smaller Ka (lower concentration of H^+). The dissociation of A–H is weak → the acid is weak.

Lewis Theory:

Every acid is a molecule having a vacant orbital (an electronic deficiency).

Examples BF_3 and $AlCl_3$ → Mineral acids;



$H^{\oplus}$ → Reaction intermediate.

Every base is a molecule having a filled free orbital (non-bonding pair). Thus, any molecule capable of donating a pair of electrons (or accepting a proton) is a Lewis base.

Analysis of the strength of acids and bases:

The stronger the acid, the more polarized the A–H bond is, and the more stable the conjugate base "A^-" becomes.

On Mendeleev's periodic table:

1 – For the same period:

Basicity: $C^- > N^- > O^- > F^-$

When electronegativity increases, the charge is better stabilized.

Acidity: CH < NH < OH < HF

pKa values: 44 → 35 → 16 → 3.2

As electronegativity increases, the polarity of the A–H bond also increases, making the dissociation of A–H easier.

2 – For the same group (column):

Basicity: $F^- > Cl^- > Br^- > I^-$ and $O^{2-} > S^{2-} > Se^{2-}$

When the atomic size increases, the charge is better stabilized.

Acidity: F–H < Cl–H < Br–H < I–H

pKa: 3.2, –2.2, –4.7, –5.2

When the atomic size increases, the polarizability of the bond also increases.

3 – Influence of the inductive effect on acidity

i) Donating inductive effect (+I)

RCOOH | R = H | R = CH_3 | R = $CH_3CH_2CH_2$

pKa | 3.75 | 4.76 | 4.82

RCOOH	R = H	R = CH_3	R = CH_3CH_2CH2
pk_a	3,75	4,76	4,82

Alkyl groups (R), being electron-donating (+I effect), decrease the polarity of the O–H bond, thus stabilizing the bond and reducing acidity.

iii) Mesomeric effect

Rsonance forms increase the polarity of the O–H bond; the bond becomes destabilized, and acidity increases. The charge becomes delocalized, the electron density on oxygen decreases, the conjugate base is stabilized, and acidity increases.

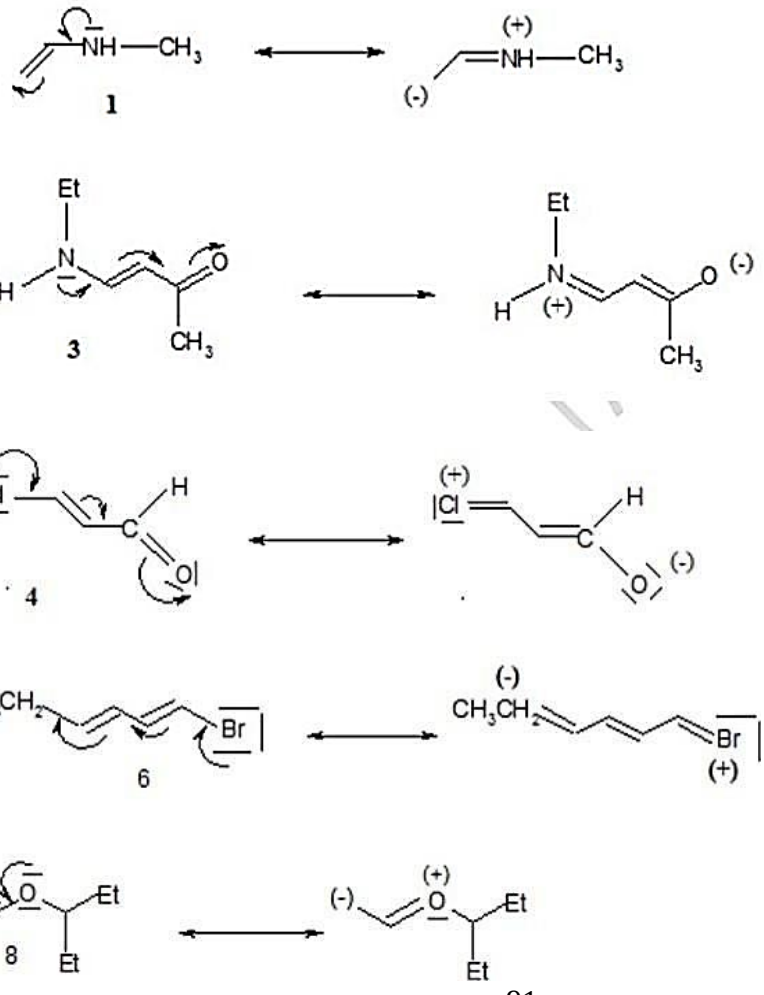
- The greater the number of electronegative atoms, the higher the acidity.
- The inductive effect decreases rapidly with the number of C–C bonds.

Exercice 02

Answer:

Molecules **1, 3, 4, 6** and **8** exhibit a conjugated system and can lead, by delocalization of either a non-bonding lone pair or a double bond, to a mesomeric (resonance) effect.

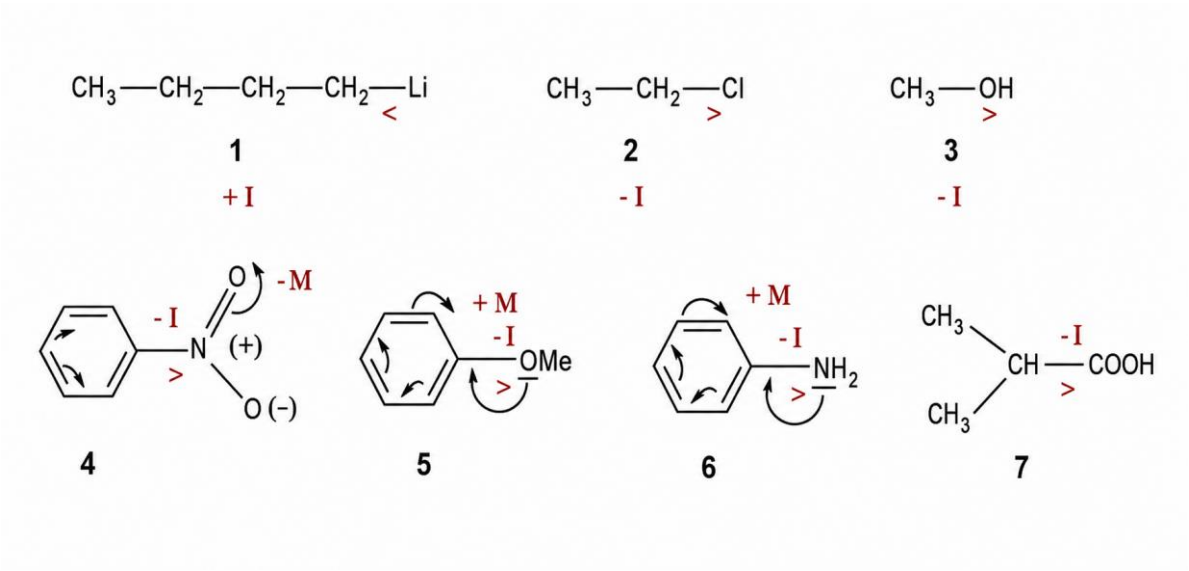
The resonance form (mesomeric form) in which delocalization is maximal is written on the right for each of these five compounds.



Exercise 03

Answer:

Direction of the **inductive effect** (+I, –I) and, where appropriate, the **mesomeric effect** (+M, –M) of the atoms or groups of atoms **underlined** in the considered molecules:



Chapter V: REACTIONS AND THER MECHANISMS

I- Definition

A ***mechanism*** is the actual process by which a reaction takes place:

- Which bonds are broken, in what order;
- How many steps are involved;
- The relative rate of each step, etc.

A detailed study of the sequence of steps which are involved in the conversion of reactants into product(s) is known as ***reaction mechanism***.

In order to state a mechanism completely, we should have to specify the *position of all atoms*, including those in *solvent molecules*, and the *energy of the system*, at every point in the process

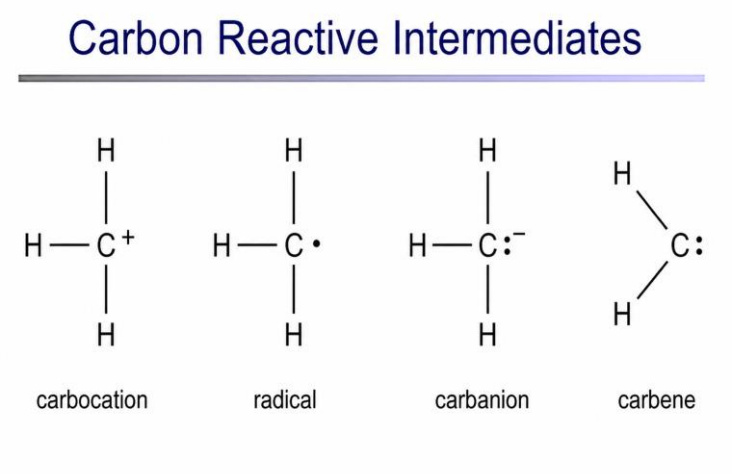
Chemical reaction: Substrate + reagent

There are two main types of reaction: product

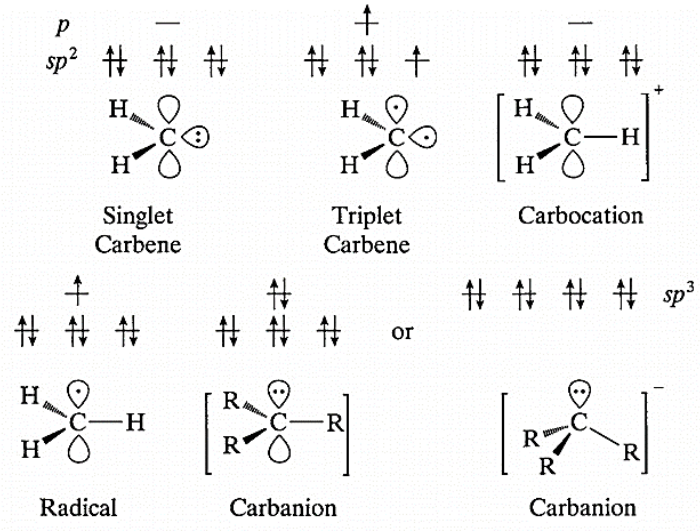
1. Synthetic reaction: a simple molecule is reacted with reagents to obtain a complex molecule.
2. Degradation reaction; the opposite of synthesis.

I-1- Reactive intermediate

There are four types of organic species; very short-lived and exist only as intermediates that are quickly converted to more stable molecules



- **nitrenes** (*nitrogen analogs of carbenes*)

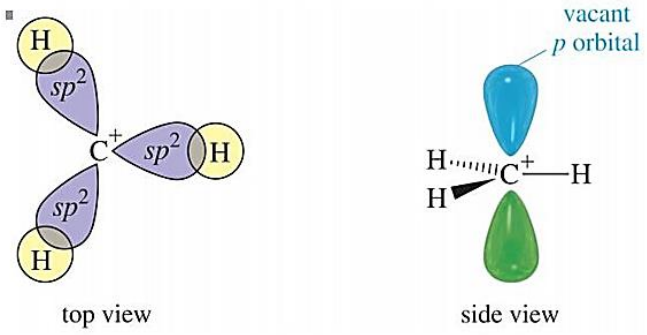


- **Carbocation**

- **Carbocation Structure**

✓ Carbon has 6 electrons, positively charged.

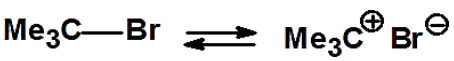
✓ Carbon is sp^2 hybridized with vacant *p* orbital



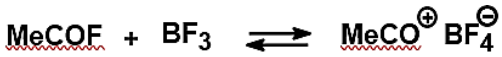
- **Methods of Forming Carbocation**

A) Heterolytic fission of neutral species

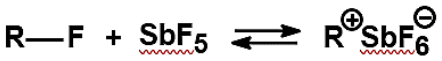
- Simple ionization; the electron pair remains with departing group, which is called leaving group and tertiary butyl group carries positive charge.



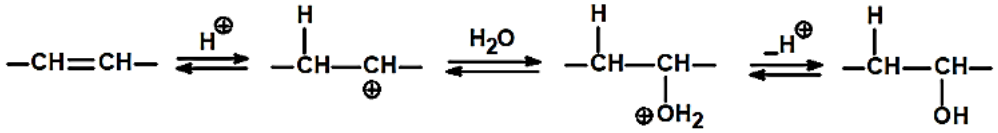
- Ionization may also be induced by Lewis acids, e.g. BF_3, $AlCl_3$ to yield in this case an acyl cation.



- With antimony pentaflouride (SbF_5) as a Lewis acid, with either liquid SO_2 or excess SbF_5 as solvent,

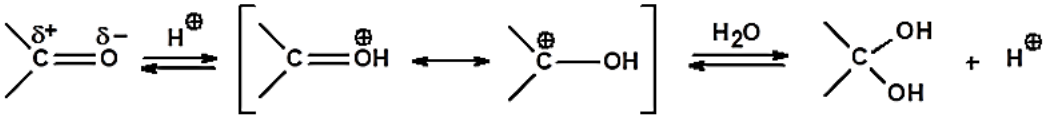


B) Addition of cations to neutral species



He most common cation is H^+, adding to unsaturated linkages, i.e. protonation, in for example the acid-catalyzed hydration of alkenes:

- Protonation can also occur on oxygen in a carbon-oxygen double bond



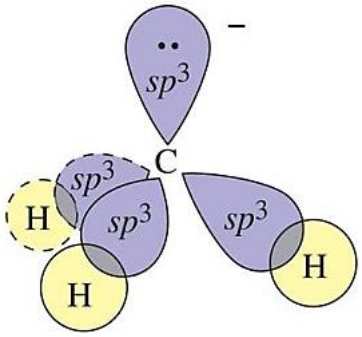
- **Carbanion**

- **Carbanion Structure**

✓ Eight electrons on carbon: 6 bonding plus one lone pair.

✓ Carbon has a negative charge.

✓ Destabilized by alkyl substituents.

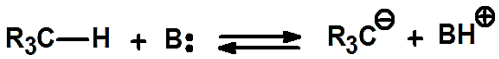


methyl anion

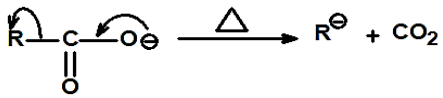
✓ Carbanion possess an unshared pair of electrons and is therefore a base.

✓ Carbanion can be formed by:

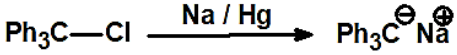
- Removal of a proton



- Removal of CO_2 from decarboxylation of RCO_2^-



- Removal of Cl from Ph_3C-Cl



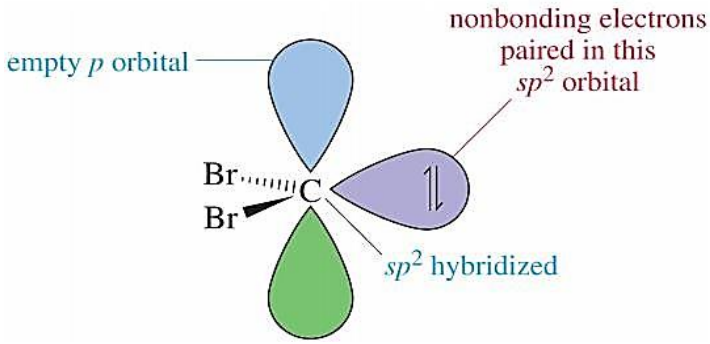
o **Carbenes and nitrenes**

• **Carbenes structure**

✓ elecarbon is neutral

✓ Vacant p orbital, so can be electrophilic

✓ Lone pair of ctrons, so can be nucleophilic



- **Free radicals**

- **Free radical Structure**

✓ Electron-deficient

✓ Stabilized by alkyl substituents.

✓ Order of stability: $3^o > 2^o > 1^o$.

Radicals are species that contain one or more unpaired electrons.

Many radicals are produced by homolytic cleavage of bonds.

$$Cl_2 \xrightarrow{h\nu} 2Cl^{\cdot}$$

Hydrogen abstraction; many radicals can remove hydrogen atoms from organic molecules to form carbon radicals.

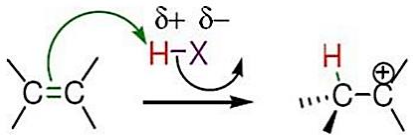
$$F^{\cdot} + CH_4 \longrightarrow HF + {}^{\cdot}CH_3$$

II- Types of organic reactions

II-1- Addition reaction

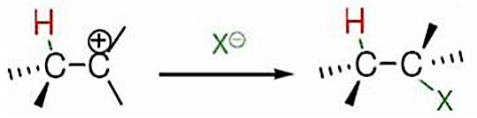
A- Hydrohalogenation reactions on alcenes

- **Reaction mechanism**: The various hydrohalic acids HX (hydrochloric, hydrobromic or hydroiodic) are added to alkenes to give monohalogenated derivatives.

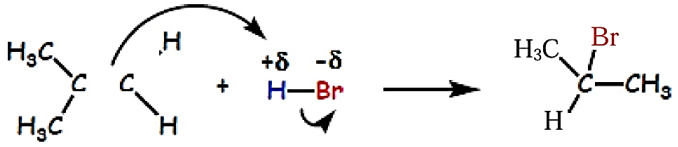


- ✓ **Stage 1**: The electrophile H^+ reacts on the π electrons of the double bond to form an intermediate carbocation (C^+)

- ✓ **Stage 2**:The halide ion then attacks the carbocation to finally form the halogenated molecule



Example



Product majority

Regioselectivity and Stereoselectivity :

• The hydrohalogenation of an asymmetric alkene obeys Markovnikov's rule: the proton attaches itself to the least substituted carbon (the most hydrogenated) so as to form the most stable carbocation: the inductive donor effects of the methyls stabilise the carbocation.) The reaction is regioselective.

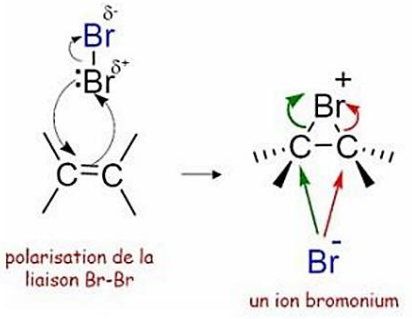
• All possible stereoisomers are obtained. The reaction is non- stereoselective.

• The same configuration isomers are obtained from (Z)-3,4- dimethylhex-3-ene: the reaction is non-stereospecific.

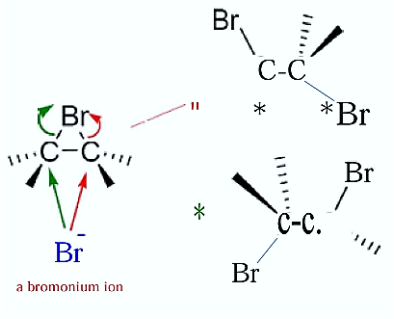
B-Dihalogenic reactions to alcenes

Reaction mechanism: When a dihalogen X_2 (Cl_2, Br_2, I_2) is close to the field of π electrons of a double bond, it polarises, which explains the appearance of an electrophilic end of the halogen molecule.

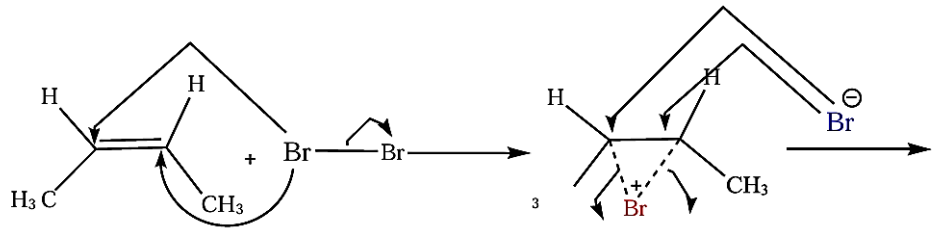
- ✓ **Stage 1**: The bromine atom (X^+) forms a halonium bridge on the substrate (bromonium) over the C-C



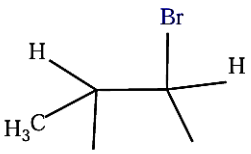
- ✓ **Stage 2**: The halide (X^-) released attacks the reaction intermediate anti, generating a dihalogenated (dibrominated) compound.



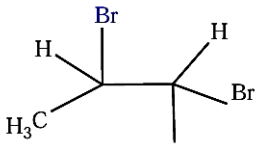
The nucleophilic alcene attacks the dibromine molecule and displaces a bromide anion, this happens in a single step and gives the intermediate reagent, a bromonium ion The nucleophilic bromide anion attacks the opposite side of a of the carbon atoms attached to the bromine and forms a new sigma bond, leaving the electrons common to the other bromine atom. The bromide anion can attack each carbon with equal ease, so two products are formed as a 50/50 racemic mixture.



but-2-ene dibrome Bromonium ion

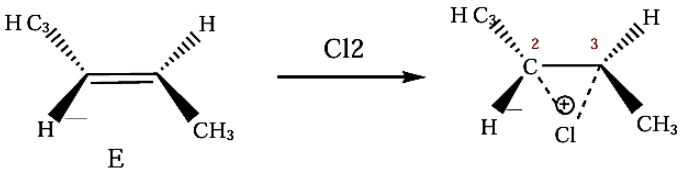


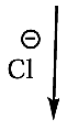
2,3-dibromo butane



2,3-dibromo butane

The addition of halogens is **stereospecific** because the bromide ion can only attack the bromonium ion from the rear Consequently, the addition of a dihalogen to any alkene is an anti (trans) addition: the two parts of the reagent attach to either side of the double bond.

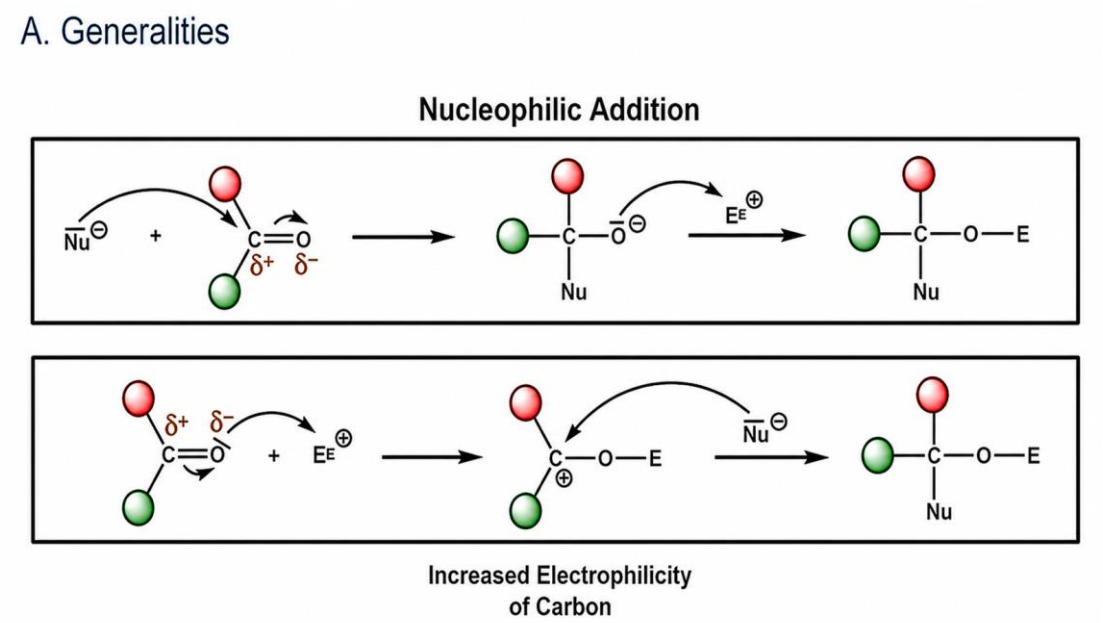




(A) attack on carbon 3 (B) attack on carbon 2 RS

SR

c) Addition to C=O carbonyls

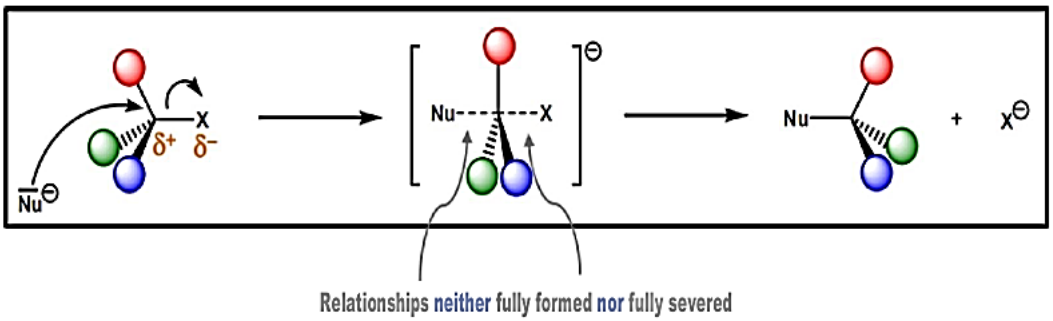


II-2- Substitution reaction

A- Bimolecular nucleophilic substitutions SN2

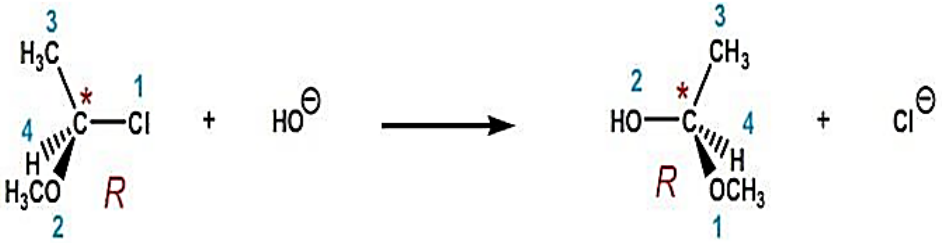
Mechanism

P 2 molecules of reactant are involved in this mechanism in a single elementary act: bimolecular reaction (SNt).



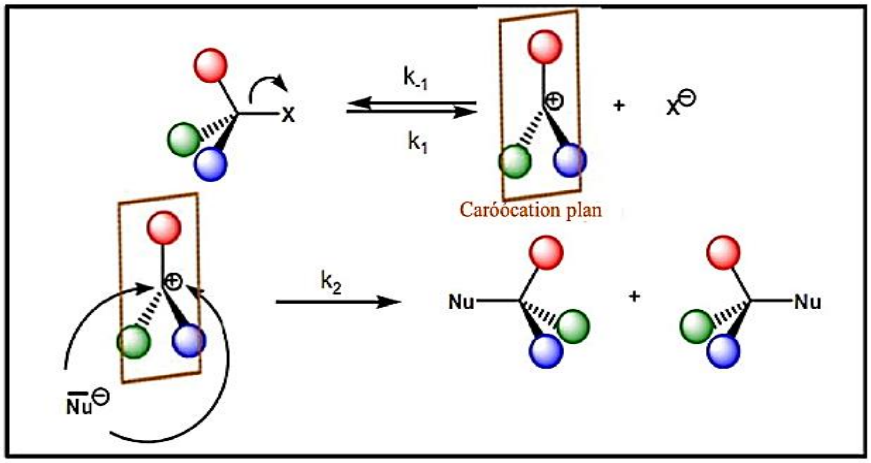
Stereochemistry

Walden inversion may involve reversing the configuration of the asymmetrical centre on which the readmission takes place, but this is not compulsory.



B- Molecular nucleophilic substitutions SN1

Mechanism

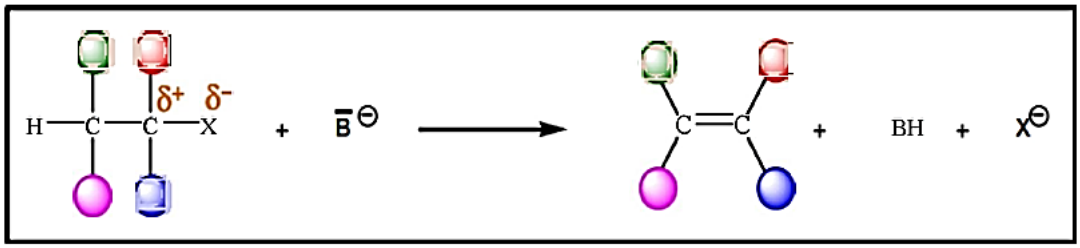


Influence of various parameters

Type of reactions	S 1_N	S 2_N
Mechanism	•2 steps •a first, kinetically limiting, monomolecular stage (departure of the nucleofuge), •a second, more bimolecular stage rapid (attack of the nucleophile on the reaction intermediate).	•1 bimolecular step: attack of the nucleophile synchronous with the departure of the nucleofuge (leaving group).
Intermediate	cation, usually carbocation.	no intermediary (one-step mechanism, we can just try to describe a "transition state")
Stereochemistry	Racemic mixture, no stereoselectivity.	Reversal of relative configuration ("*Walden inversion*"), enantiospecific reaction
Reaction speed	v=k*[R-GP] (order 1)	v=k*[R-GP][NU:] (order 2)
Influence of the radical	RIII-GP >> RII-GP > RI-GP (stabilisation of the intermediate (by inductive effects...))	RI-GP > RII-GP >> RIII-GP (destabilisation of the transition state by steric hindrance)
Influence of the nucleophile	The rate is not influenced by the nucleophile.	Speed increases as • its concentration • its nucleophilicity and decreases when it is too large.
Influence of solvent polarity	protic solvents (water, methanol, etc.) promote the SN1 process by facilitating the formation of carbocation by the establishment of hydrogen bonds	aprotic polar solvents (acetone, DMSO, etc.) promote the SN2 process by solvating the cation associated with the nucleophile

II-3- Elimination reaction

A- Elimination reactions (E1)

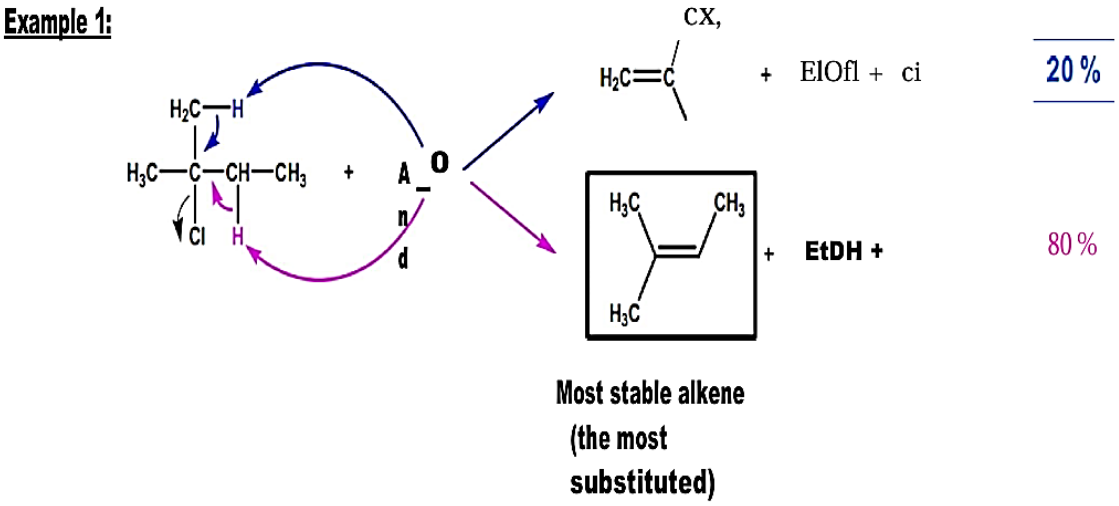


Nucleofuge (X) eliminated at the same time as an H carried by the C next to C-X, in the presence of a base (B-).

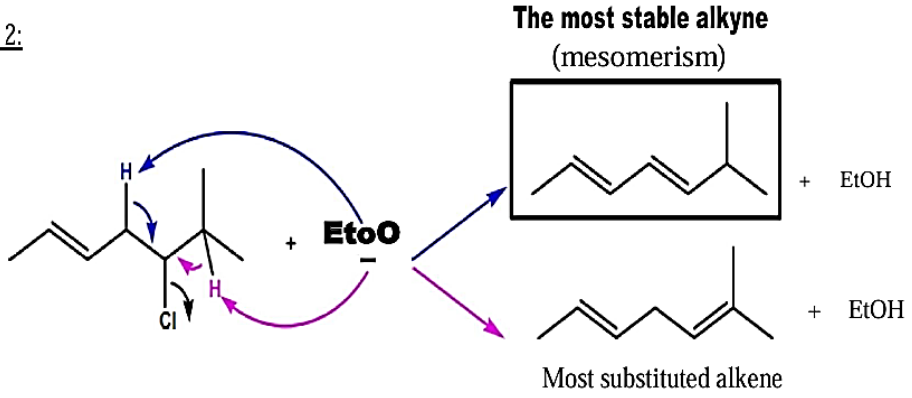
There are 2 limiting mechanisms:

- Eliminations of order 1 (E)
- Eliminations of order 2 (E)

Example 1:

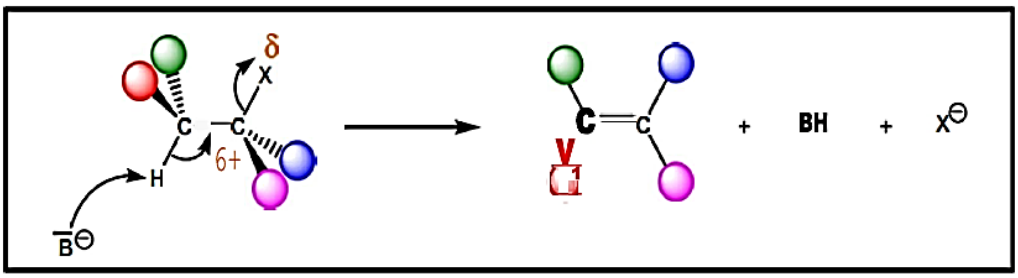


Example 2:



B- Bimoleculary Eliminations E2

A. Mechanism



Free rotation autouf Je *la* C-C bond but E, does not liev c u in this pafticuliar conformation |H and X

Type of reaction	SN, / E1	SNt / E2
Mechanism	2 steps V= k[RX] order 1	1 step y= k[RX][Nu] order 2 V= k[RX][B]: order 2
Intermediate	Carbocation	State of transition
Stereochemistry	Non-stereospecific : Naked attack on 2 sides of the plane Free rotation around C-C SN, : Racemic mixture E1: 2 alkenes Z and E	stereospecific û Nu dorsal attack Walden inversion H and X anticoplanar SN_ : Reversal of configuration. 1 single enantiomer E, : 1 single alkene

Influence of the substrate	CCIII > > II > I **(stabilisation of the intermediary)**	SN_ : Substrate I > II > > III **(destabilisation of the transition state by steric hindrance)** **E, : the higher the class, the faster the reaction**
Influence of the Nucleophile	**SN: weak nucleophile.** **E, weak base diluted and bad Nude**	**SN: : good nucleophile.** **E, : concentrated strong base and bad Nu**
Influence of the solvent	polar protic solvents facilitating the formation of carbocation by hydrogen bonding	aprotic polar solvents which solvate the cation associated with the nucleophile

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References Bibliographic

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Summary

Summary

Organic chemistry is the branch of chemistry that focuses on the study of carbon-containing compounds, including their structures, properties, compositions, reactions, and methods of synthesis. It provides the foundation for biochemistry and has extensive applications in various industrial sectors such as pharmaceuticals, materials, dyes, polymers, and petrochemical industries. This course introduces the fundamental concepts of organic chemistry and is intended for second-year students in Process Engineering and Petrochemical Industries, as well as students in related scientific disciplines. It requires no advanced prior knowledge and is organized into five chapters covering the basics of organic chemistry, functional group classification, isomerism, electronic structures, and reaction mechanisms.

Keywords: Organic chemistry ; Carbon compounds ; Functional groups ; Isomerism; Stereoisomerism; Electronic structure; Organic reactions; Reaction mechanisms; Biochemistry; Petrochemical industry

الملـــخـــص

تُعـد الكيميـاء العضـوية أحـد الفـروع الأساسـية للكيميـاء، وتهـتم بدراسـة المركبـات التـي تحتـوي علـى عنصـر الكربـون، مـن حيـث بنيتهـا وتركيبهـا وخواصـها الفيزيائيـة والكيميائيـة، إضـافة إلـى تفاعلاتهـا وطـرق تحضـيرها. كمـا تُشـكل الأسـاس الـذي تقـوم عليـه الكيميـاء الحيويـة، والتـي تُعنـى بدراسـة الجزيئـات الحيويـة وتفاعلاتهـا داخـل الكائنـات الحيـة. وتكتسـب الكيميـاء العضـوية أهميـة كبيـرة بفضـل تطبيقاتهـا الواسـعة فـي العديـد مـن المجـالات الصـناعية، مثـل الصـناعات الدوائيـة، والبتروكيميائيـة، وصناعة المواد والأصباغ والبوليمرات، مما يمنحها مكانة علمية واقتصادية بارزة.

يهـدف هـذا المقـرر إلـى تقـديم المبـادئ الأساسـية للكيميـاء العضـوية لطلبـة السـنة الثانيـة فـي تخصصـات هندسـة الطرائـق والصـناعات البتروكيميائيـة، كمـا يمكـن أن يسـتفيد منـه طلبـة تخصصـات أخـرى مثـل الكيميـاء، والبيولوجيـا، والصـيدلة. ولا يتطلـب المقـرر معرفـة متقدمـة مسـبقة فـي الكيميـاء العضـوية، إذ يبـدأ بالمفـاهيم الأساسـية ثـم يتـدرج إلـى الموضـوعات الأكثـر تخصصًـا. ويتكـون المقـرر مـن خمسـة فصـول رئيسـية تشـمل: المبـادئ العامـة للكيميـاء العضـوية، وتصـنيف الوظـائف العضـوية، والتماكـب والتماكب الفراغي، والبنية الإلكترونية للجزيئات، وآليات التفاعلات العضوية.

الكلمـــات المفتاحيـــة: الكيميـــاء العضـــوية، المركبـــات العضـــوية، الكربـــون، الوظـــائف العضـــوية، التماكـــب، التماكـــب الفراغـــي، البنيـــة الإلكترونيـــة، التفـــاعلات العضوية، آليات التفاعل، الكيمياء الحيوية، الصناعات البتروكيميائية.