Democratic and People's Republic of Algeria
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Faculty of Sciences
Department of Chemistry

Field: SM
Sector: Chemistry

Course Handout

Organic Chemistry 1

Carried out by:

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This handout is intended for students enrolled in 2nd year chemistry (SM)

Academic year: 2024/2025

Foreword

Organic chemistry is a field of chemistry that is devoted to the study of molecules containing carbon.

This handout of organic chemistry 1 course that I present, is intended not only for second-year students, specializing in chemistry in the field of the structure of matter, but also for all who must know the modern bases of this science. This course fits perfectly into the undergraduate programs in organic chemistry.

It is structured in five chapters:

- Chapter I: Reminder about Chemical Bonds.
- Chapter II: Systematic Nomenclature of Organic Compounds.
- Chapter III: Isomerism and Stereo-isomery.
- Chapter IV: Electronic Effects.
- Chapter V: Study of Reaction Mechanisms.

I hope that students will find in this course a good educational support capable of introducing them to the foundations of organic chemistry.

Summary

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I. Introduction

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Chapter I: Reminder About Chemical Bonds

I. Introduction:

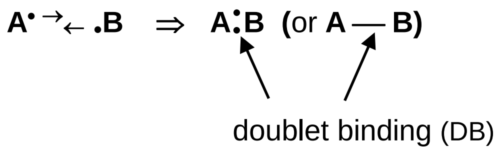
Atoms are sometimes found in the isolated state (Ex: noble gases, H at very high temperature), but this situation is very rare. Atoms are most often linked together by chemical bonds to form more stable organic structures. Bonds are formed by the electrons of their outer layers (valence electrons) in atoms. Two types of bonds are distinguished: **the covalent bond and the ionic bond**.

I.1. The covalent bond, Lewis model:

A covalent bond is a chemical bond in which two atoms share two electrons to form a doublet of binding electrons. This doublet can have two origins:

I.1.1. Covalent bond proper:

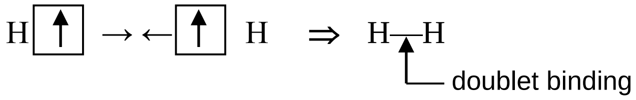
Each of the atoms A and B provides an odd electron from its external electron shell (valence electrons). Then the two electrons associate to form a common doublet or ***doublet binding*** to the two atoms. This can be schematized as follows:



χ (A) ≈ χ (B)
χ :electronegativity

Example : the molecule H_2

$_1H : 1s^1$
$_1H : 1s^1$



• Lewis representation of an atom or molecule:

The Lewis representation allows to schematize the state of the ***valence electrons*** of an atom, a molecule, or a mono or polyatomic ion.

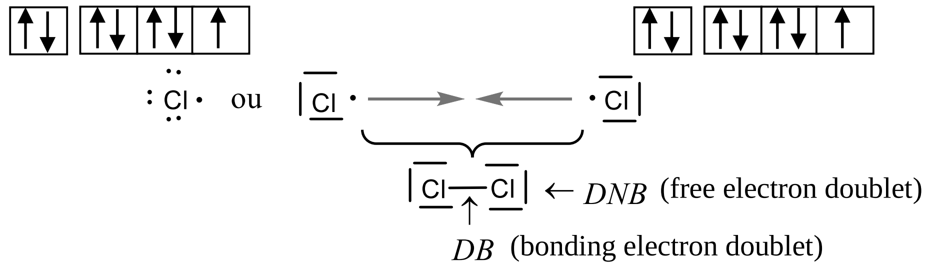
A single electron (single) of an atom or a monoatomic ion is represented by ***a dot***.

A pair of electrons (electron doublet) is represented by ***a line***, whether it is a covalent bond or a non-bonding doublet (free electron doublet).

Examples :

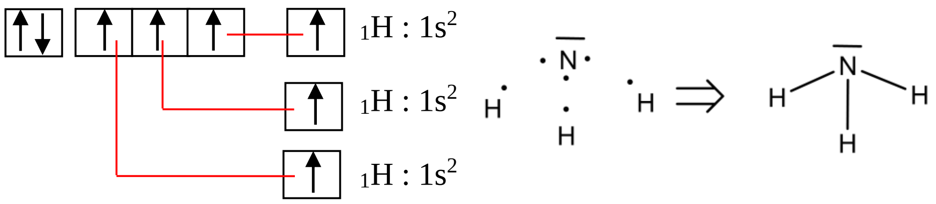
- formation of the Cl_2 molecule

$_{17}Cl : {}_{10}[Ne]\ 3s^2\ 3p^5$ $_{17}Cl : {}_{10}[Ne]\ 3s^2\ 3p^5$



- formation of ammonia NH_3 molecule

$_7N : 1s^2\ 2s^2\ 2p^3$



I.1.2 The Covalent Bond of Coordination (Dative):

One of the two atoms (the **donor**) provides a free electron doublet already formed in its outer shell. The other (the acceptor) receives this doublet in an empty box of its outer shell, as follows:

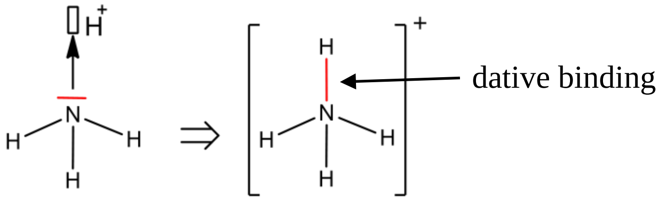
$$\mathbf{A}\ \square\!\leftarrow : \mathbf{B} \quad \Rightarrow \quad \mathbf{A} - \mathbf{B}$$

Example:

- formation of the ammonium ion NH_4^+ from NH_3 in the presence of an acid (H^+)

$_1H^+ : 1s^0$

□



Thus the NH_4^+ ion has three N-H bonds which already existed in ammonia NH_3 and which were formed by covalent bonds and one N-H bond which is formed by coordination.

I.2 The ionic bond:

If the two atoms **A** and **B** of the molecule **A-B** have a significant difference in electronegativity, the more electronegative element monopolizes (takes) an electron from the other less electronegative element. The molecule consists of two ions $\mathbf{A}^+$ and $\mathbf{B}^-$.

$$\mathbf{A}\bullet \curvearrowright \bullet\mathbf{B} \longrightarrow \mathbf{A}\ {:}\mathbf{B} \quad (\text{or} \quad \mathbf{A}^+\mathbf{B}^-$$

There is no longer a sharing of electrons between the two atoms that form the bond, but a transfer of electrons from one atom to another. It’s the ionic bond.

Example:

Formation of a pair of KCl ions (gaseous state). At a certain distance, there is a transfer of the electron from potassium to chlorine to give two charged species $K^{+}Cl^{-}$

➢ Concept of hydrogen bond.

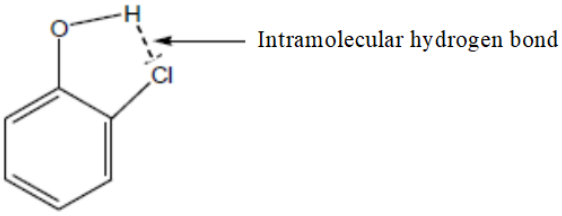
It is a low energy bond, it is made between a hydrogen atom and an electronegative atom having at least one free doublet such as halogens (F, Cl, Br, I) and heteroatoms (N, O, S).

The hydrogen bond can be ***intramolecular or intermolecular***, it is represented by dotted lines.

a) Intramolecular hydrogen bond

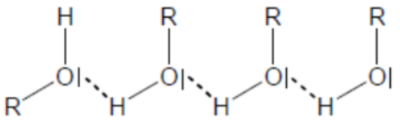
It is established in the same molecule. It is always forms to create a stable cycle.

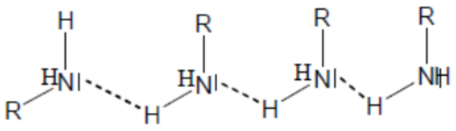
Example :

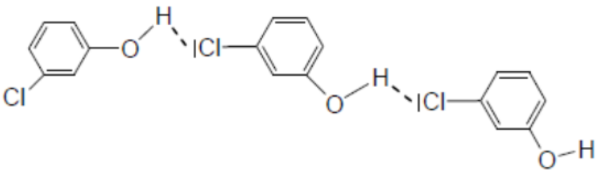


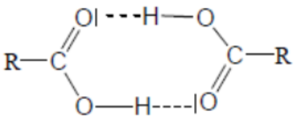
b) Intermolecular hydrogen bond

It is established between two molecules.



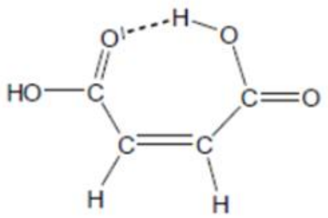




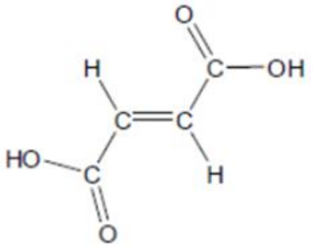


Hydrogen bonding can have an important influence on the physical and chemical properties of compounds. It can have effects on the melting points, boiling points, solubility, conformation, and acidity of molecules.

Example:



malic acid (cis) mp. = 131°C
Pka1 = 1,92, Pka2 = 6,23



Fumaric acid (trans) mp. = 287°C
Pka1 = 3,02, Pka2 = 4,38

I.4 Geometry of molecules: Gillespie theory

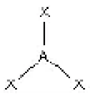
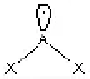
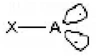
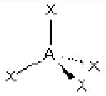
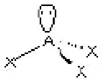
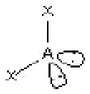
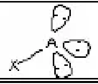
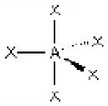
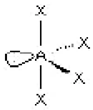
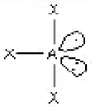
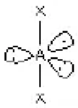
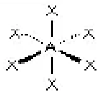
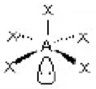
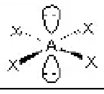
If a molecule is formed from a **central atom** to which all the others are directly linked, the orientation of the bonds from this central atom is sufficient to define the geometry of this molecule.

I.4.1 Gillespie rules (V.S.E.P.R. model):

The orientation of the bonds from an atom (i.e. the geometric shape of the molecules) can be predicted by applying Gillespie’s rules, based on the **V**alence **S**hell **E**lectron **P**airs **R**epulsion (V.S.E.P.R.) model. According to this theory, around a central atom **A**, we must consider both the number **n** of neighboring atoms **X** and the number **m** of free electron pairs **E** carried by **A**. The geometry of the molecule **AXnEm** around **A** depends on the sum **n + m**, so that the atoms **X** and the pairs **E** are the furthest from each other.

Examples of **AXnEm** type molecules are shown in Table I.1

Table I.1: Type and geometry of some **AXnEm**-shaped molecules

Total Domains	Generic Formula	Picture	Bonded Atoms	Lone Pairs	Molecular Shape	Electron Geometry	Example	Hybridi -zation	Bond Angles
1	AX		1	0	Linear	Linear	H_2	s	180
2	AX_2		2	0	Linear	Linear	CO_2	sp	180
	AXE		1	1	Linear	Linear	CN^-		
3	AX_3		3	0	Trigonal planar	Trigonal planar	$AlBr_3$	sp^2	120
	AX_2E		2	1	Bent	Trigonal planar	$SnCl_2$		
	AXE_2		1	2	Linear	Trigonal planar	O_2		
4	AX_4		4	0	Tetrahedral	Tetrahedral	$SiCl_4$	sp^3	109.5
	AX_3E		3	1	Trigonal pyramid	Tetrahedral	PH_3		
	AX_2E_2		2	2	Bent	Tetrahedral	$SeBr_2$		
	AXE_3		1	3	Linear	Tetrahedral	Cl_2		
5	AX_5		5	0	Trigonal bipyramid	Trigonal bipyramid	AsF_5	sp^3d	90 and 120
	AX_4E		4	1	See Saw	Trigonal bipyramid	SeH_4		
	AX_3E_2		3	2	T shape	Trigonal bipyramid	ICl_3		
	AX_2E_3		2	3	Linear	Trigonal bipyramid	BrF_2^-		
6	AX_6		6	0	Octahedral	Octahedral	$SeCl_6$	sp^3d^2	90
	AX_5E		5	1	Square pyramid	Octahedral	IF_5		
	AX_4E_2		4	2	Square planar	Octahedral	XeF_4		

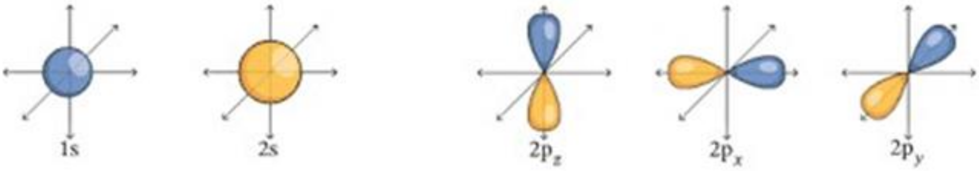
Notes
1. There are no stable AXE_4, AX_3E_3, AX_2E_4 or AXE_5 molecules.
2. All bonds are represented in this table as a line whether the bond is single, double, or triple.
3. Any atom bonded to the center atom counts as one domain, even if it is bonded by a double or triple bond. Count atoms and lone pairs to determine the number of domains, do not count bonds.
4. The number of bonded atoms plus lone pairs always adds up to the total number of domains.

I.5 Chemical bonding in the wave model:

We previously studied the types of bonds that unite atoms within a molecule. In light of the wave model of matter, each atom has atomic orbitals. Molecules also have orbitals, called molecular orbitals. We will study the mechanism that leads to the formation of these molecular orbitals. We will also see hybridization, that is to say the recombination of all empty orbitals in order to accommodate several electrons.

I.5.1 Atomic orbitals:

Atomic orbitals are mathematical functions that describe the location and wave behavior of an electron in an atom. The geometry of some 1s, 2s, and 2p orbitals (p_x, p_y, and p_z) is represented as follows.

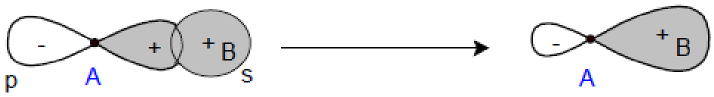


I.5.2 Overlapping of atomic orbitals, formation and nature of bonds:

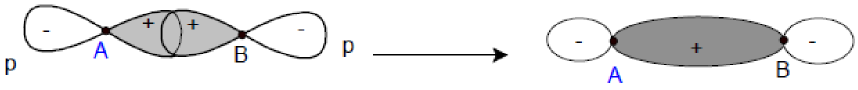
In the wave model of covalent bonding, the idea of sharing an electron pair introduced by Lewis is complemented by that of overlapping two atomic orbitals (AO), belonging to each of the two atoms that bind. These two AOs merge to give a molecular orbital (MO). There are two types of overlap:

- ✓ **Axial overlap:** This type of overlap concerns atomic orbitals of type s and p, and which leads to the formation of **sigma (σ)** type bonds.

Axial overlap type : *s-s*

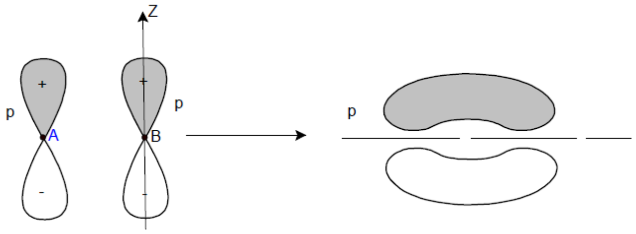


Axial overlap type : *s-p*



Axial overlap type : *p-p*

- ✓ **Lateral overlap:** This type of overlap only concerns p orbitals and leads to the formation of **pi (π)** type bonds.



Lateral overlap type : *p-p*

I.5.3 Hybridization theory:

Hybridization consists of mixing orbitals of an atom in order to form new hybrid orbitals that allow better qualitative description of the bonds between atoms. The resulting hybrid orbitals are very useful to explain the shape of the molecular orbitals of molecules.

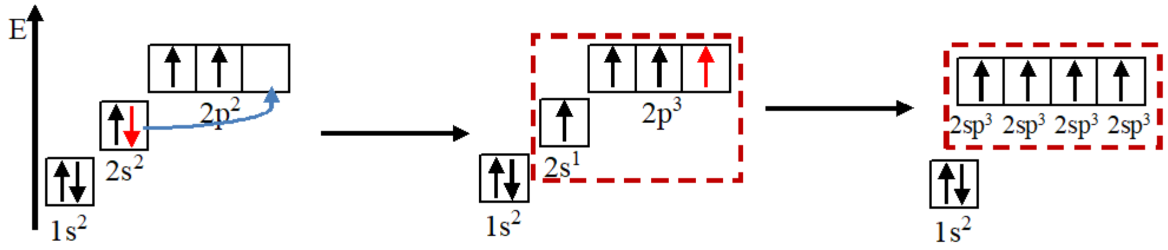
There are various types of hybridizations. Among the main ones we have: - *Tetragonal or tetrahedral hybridization* SP^3*; - Trigonal hybridization* SP^2*; - Digonal hybridization SP*

I.6 Carbon Hybridization:

I.6.1 Tetragonal Hybridization SP^3 :

The electronic configuration of carbon in the ground state is $1s^2$, $2s^2$, $2p^2$. (fig. a).

Carbon has 2 single electrons. It can only form 2 bonds. This electronic configuration does not explain the tetravalence of carbon (that is, the formation of 4 covalent bonds). It is therefore necessary to consider carbon in an excited state with the formation of hybrid orbitals.



C : Fondamental state (fig. a) ***C* : Excited state_*** (fig. b) *4 AO* ***Hybrid state*** (fig. c) *4 AO hybrids* sp^3 *of carbon*

<u>Excited state of carbon C:</u>* $1s^2$, $2s^1$, $2p^3$

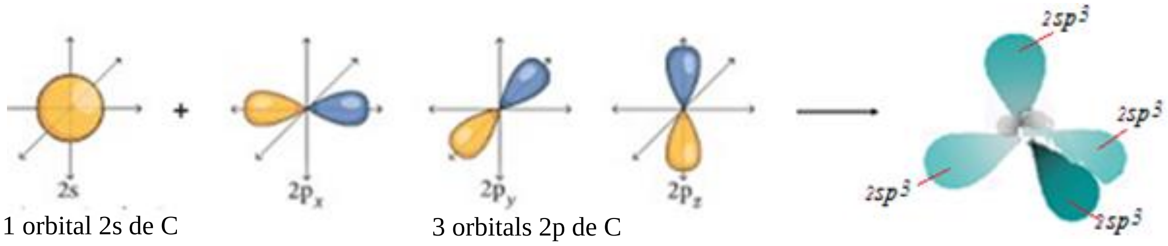
The hypothesis of the excited state of carbon allows to explain the formation of 4 covalent bonds, three of which are identical, which is in disagreement with the experiment (fig. b). According to the experiment the 4 C−H bonds are identical

<u>Hybrid state (hybridization</u> SP^3 *<u>):</u>*

To obtain 4 identical C−H bonds, we consider that carbon in its reaction state has 4 equivalent $2sp^3$ hybrid orbitals which are obtained by mixing the **2s atomic orbitals** with **3 orbitals 2p** (2px, 2py and 2pz). (fig. c)

We therefore obtain 4 identical hybrid orbitals capable of forming 4 σ bonds.

1 AO type s + 3 AO type p $\longrightarrow$ ***4AO identical hybrid orbitals sp³***



1 orbital 2s de C

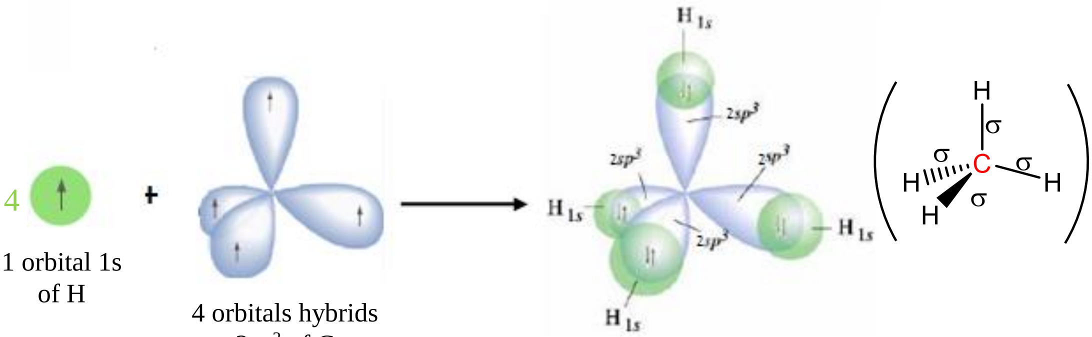
3 orbitals 2p de C

4 AO identical hybrid sp^3

The geometry of the 2sp^3 orbitals leads to the formulation of a tetrahedral and the angles between the orbitals are equal to 109.5°

- ✓ ***Example: methane (CH_4); sp^3 hybridization of carbon***

Formation of bonds in the CH_4 molecule



1 orbital 1s of H

4 orbitals hybrids 2sp^3 of C

Structure of the molecule CH_4 (4 σ bonds formed)

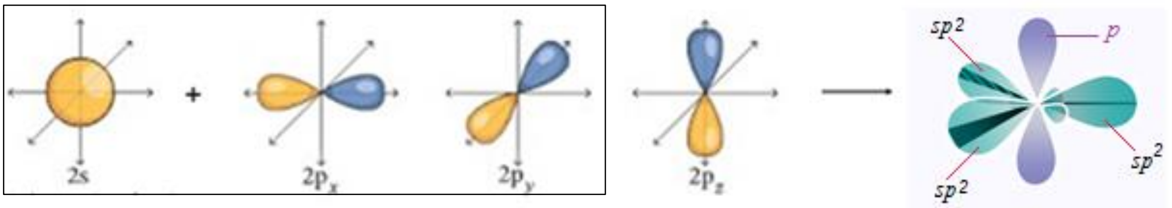
Recovery sp^3- s :

The s electrons of the 4 hydrogen atoms associate with the 4 sp3 electrons of carbon by axial overlap to give 4 σ molecular orbitals. Equivalence of the 4 bonds that point to the vertices of a tetrahedron.

I.6.2 sp^2 hybridization:

The sp^2 hybridization results from the linear combination of an **s orbital** with **2 p orbitals** of an atom (the AO s and p belonging to the same electron layer).

1 AO type s + 3 AO type p $\longrightarrow$ ***3 AO identical hybrid orbitals sp² + 1 AO type p pure***



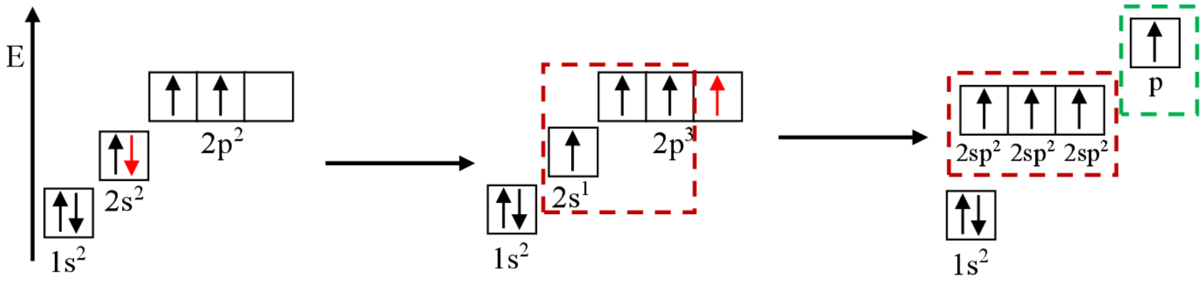
1 orbital 2s of C

3 orbitals 2p of C

triangular plan geometry

- ✓ ***Example: ethylene (C_2H_4); sp^2 hybridization of carbon***

Electronic configuration of C

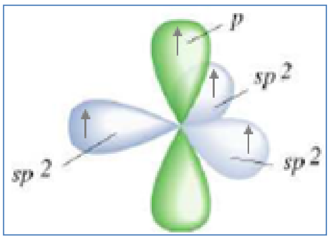


C : Fundamental state

C* : Excited state
3 AO

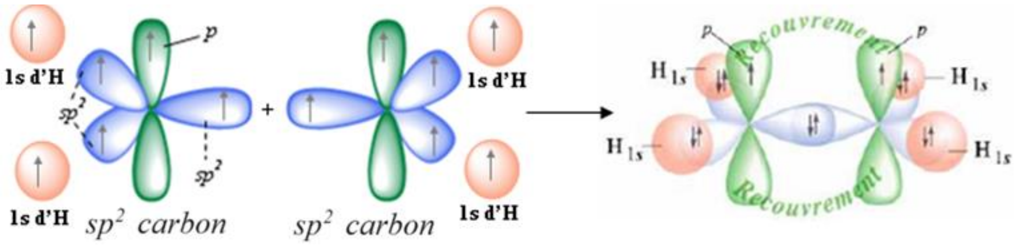
hybrid state
3 AO hybrids sp^2 +1 AO p non hybridized

sp^2 hybrid atomic orbitals of carbon:



We therefore obtain 3 identical sp^2 hybrid orbitals capable of forming 3 σ bonds and one a non-hybrid orbital P (pure).

Formation of bonds in the C_2H_4 molecule:



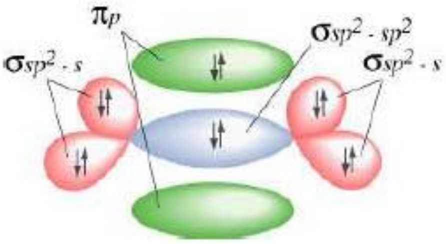
Sp^2 orbital overlap: - σ bond formed by overlap between 2 sp2 hybrid orbitals

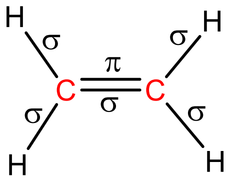
- σ bond with 1s electrons of hydrogen and sp2 electrons of carbon hybrid orbitals.

p orbital overlap:

The overlap of the p atomic orbitals, parallel non-hybridized of the two carbon atoms is carried out laterally. The bond formed is of type π. It contains two electrons of opposite sign.

Molecular orbitals of C_2H_4 .



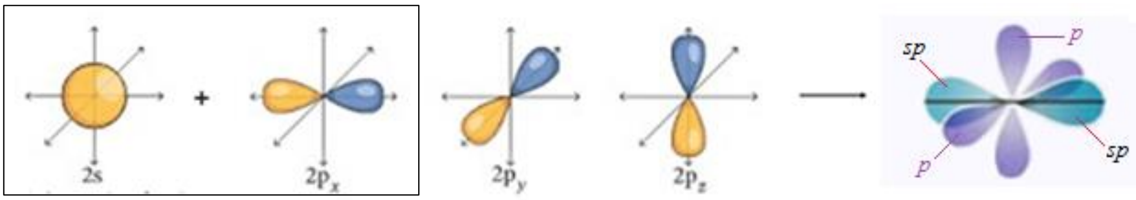


- Double bond (C = C) consisting of 1 σ bond and 1 π bond.
- $\sigma_{sp2-sp2}$ bond formed by overlap between 2 sp^2 hybrid orbitals
- π_p bond formed by lateral overlap of p orbitals parallel to each other.
- σ_{sp2-s} bond with *1s* electrons from hydrogen and *sp^2* electrons from hybrid orbitals.

I.6.3 SP hybridization:

SP hybridization results from the linear combination of an **s orbital** with a **p orbital** of an atom (the AO s and p belonging to the same electron shell). The other two p orbitals remain pure.

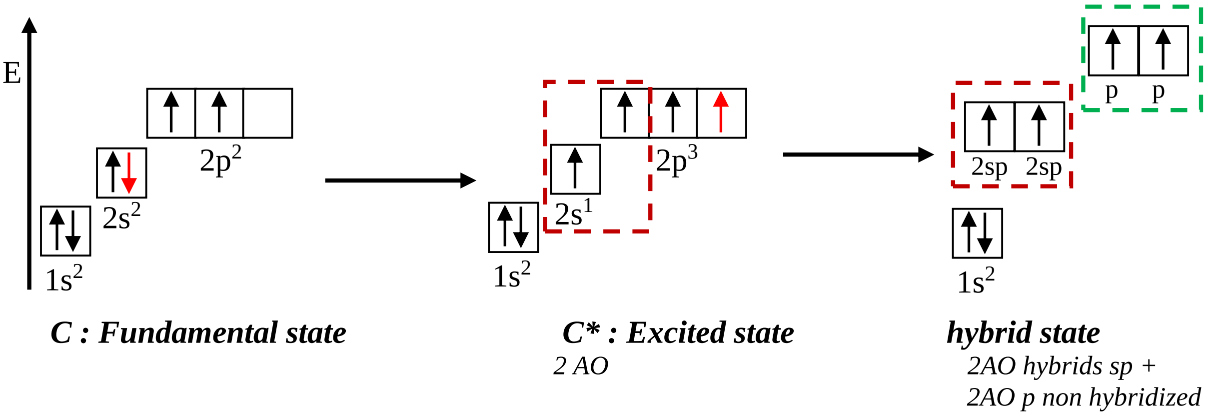
1 AO type s + 1 AO type p ⟶ 2 AO identical hybrid orbitals sp + 2 AO type p pure



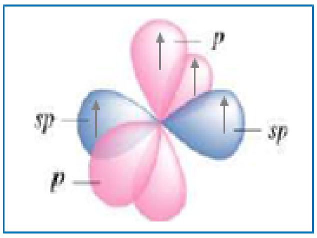
1 orbital 2s of C 3 orbitals 2p of C Linear geometry

- ✓ ***Example : ethylene (C_2H_2); sp hybridisation of carbon***

Electronic configuration of C



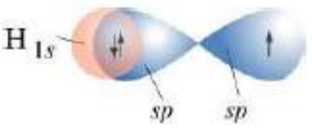
sp hybrid atomic orbitals:

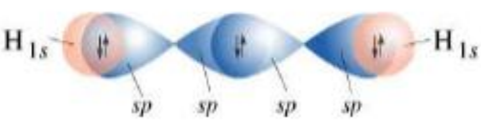


We therefore obtain 2 identical sp hybrid orbitals capable of forming 3 σ bonds and two non-hybrid p orbitals

Formation of bonds in the C_2H_2 molecule

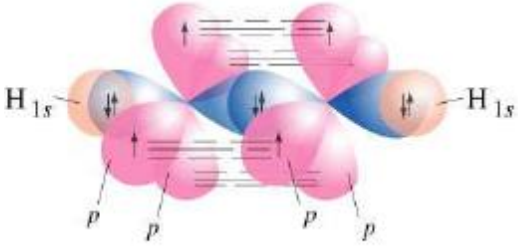
- *Overlap of sp orbitals*



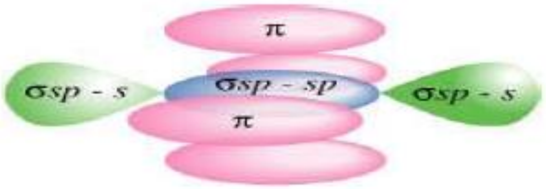


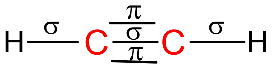
We have: Overlap *sp−s* *and* *Overlap sp−sp*

- *Overlap of sp and p orbitals*



Molecular orbitals of C_2H_2





C≡C triple bond consisting of one σ bond and two π bonds.

In conclusion, knowing the Lewis diagram of a molecule we can evaluate the state of hybridization of these atoms.

The degree of hybridization = ∑ bond σ + ∑ free electron pair n

∑ bond σ + ∑ free electron pair n	Hybridization state
4	SP^3
3	SP^2
2	SP

CHAPTER II: Systematic Nomenclature of Organic Compounds

Introduction:

An organic compound is a molecular entity made up of carbon and hydrogen atoms, to which are added, possibly, heteroatoms (oxygen, nitrogen, halogen, sulfur, etc.).

II. 1. Formulas of organic compounds:

Organic molecules can be represented in different ways, more or less detailed. There are four ways to write formulas: Raw formula, flat developed formula, semi-developed formula and simplified formula.

II.1.1. Raw formula:

Every organic compound has a corresponding a crude formula.

- If the compound is made up of 3 atoms C, H and O, the raw formula is CxHyOz
- If it is made up of 2 atoms C and H, the the raw formula is CxHy.

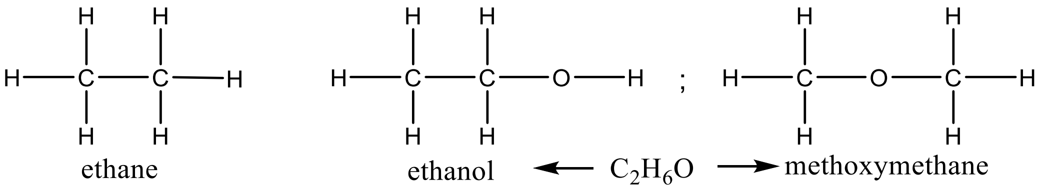
The crude formula of a molecule simply indicates the nature and number of the different atoms present, without indicating the sequence of these atoms in the molecule

Examples: C_2H_6 (ethane); C_2H_6O (ethanol or methoxymethane).

II.1.2. Developed formula (Lewis formulas):

The flat developed formula allows to distinguish the isomers. It shows all the bonds forming the molecule considered.

Examples :



The planar structural formulas represent the order of arrangement of these atoms in a molecule, but not their actual orientation in space.

II.1.3. Semi-developed formula:

In this writing, we show only the bonds between carbon atoms and atoms other than hydrogen, that is to say we eliminate the C-H, N-H and O-H bonds.

Examples:

$H_3C—CH_3$; $H_3C—CH_2—OH$; $H_3C—O—CH_2—CH_2—CH_3$

If we also eliminate the C-C, C-N, C-O bonds....., these formulas become compact formulas.

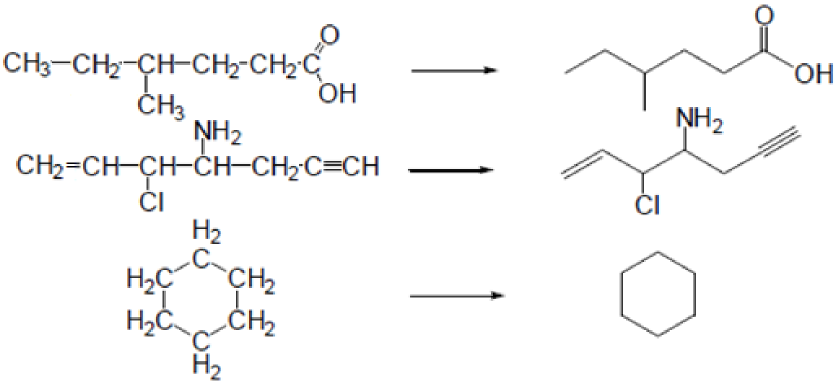
Examples: $CH_3CH_2CH_2CH_3$; CH_3CH_2OH; CH_3NHOH

Most of the time, we use semi-developed formulas.

II.1.4. Topological formula:

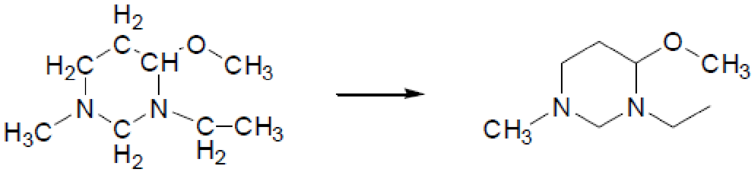
To simplify the writing of a developed formula, we can represent the main carbon chain and by eliminating the atoms of C, H and the bonds C-H.

Examples:



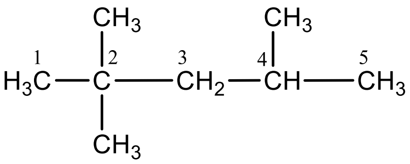
Note: If only one carbon atom is bonded to the heteroatom, it will be represented.

Example :



II.2 Classification of carbon atoms:

In the following molecule we have:



$$\overset{1}{H_3C}-\overset{CH_3}{\underset{CH_3}{\overset{2}{C}}}-\overset{3}{CH_2}-\overset{CH_3}{\overset{4}{CH}}-\overset{5}{CH_3}$$

- Carbons C_1 and C_5 are primary carbons, because they are linked to 1 carbon atom.
- C_3 is a secondary carbon, because it is linked to 2 carbon atoms.
- C_4 is a tertiary carbon, linked to 3 carbon atoms.
- C_2 is a quaternary carbon, linked to 4 carbon atoms.

II.3 Hydrocarbons:

These are molecules made up of carbon and hydrogen. There are two types of hydrocarbons.

II.3.1 aliphatic hydrocarbon:

They are open chain hydrocarbons (linear or branched). They are subdivided into three groups:

a) Alkanes: these are saturated hydrocarbons with the general formula C_nH_{2n+2}.

b) Alkenes (or olefins): these are unsaturated ethylenic hydrocarbons with the general formula C_nH_{2n}.

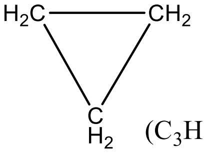
c) Alkynes: these are unsaturated acetylenic hydrocarbons with the general formula C_nH_{2n-2}.

II.3.2 Alicyclic hydrocarbon:

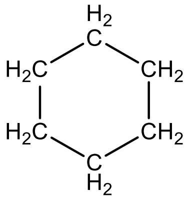
Are closed-chain (cyclic) hydrocarbons. They include:

a) Cyclanes: of general formula C_nH_{2n}. They are isomers of alkenes.

Example :



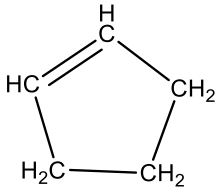
(C_3H_6)



(C_6H_{12})

b) Cyclenes (C_nH_{2n-2}): these are alkynes which have a double bond.

Example :

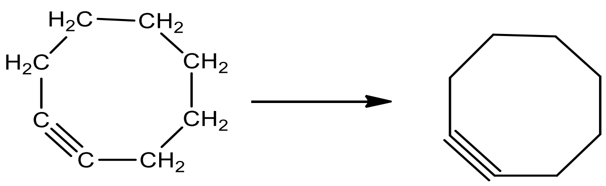


(C_5H_8)

c) Cyclins C_nH_{2n-2} ($n \geq 8$): contains a triple bond in the molecule.

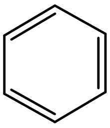
Example :

(C_8H_{12})

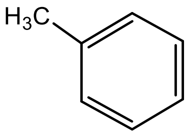


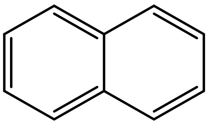
II.3.3 Aromatic hydrocarbon:

These are unsaturated hydrocarbons with one or more cycles. Most often, these cycles are of the benzene type.



benzene

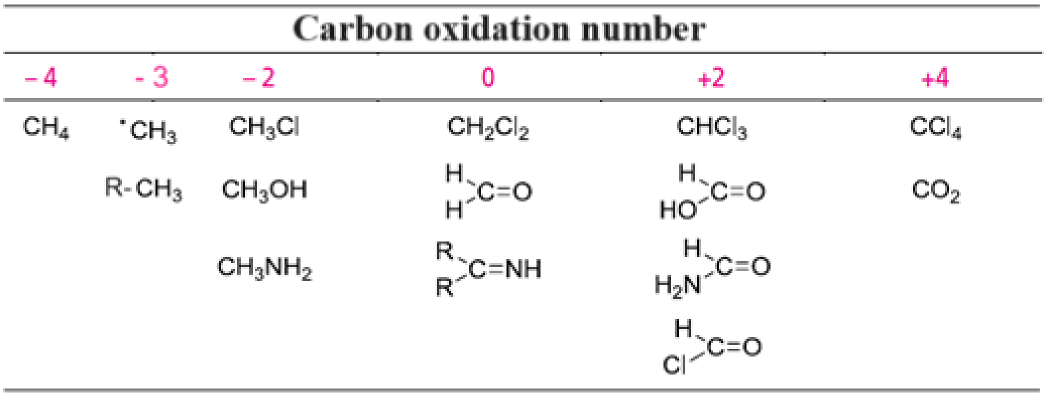




II.4 Chemical function and degree of oxidation:

- The chemical function is an atom or a group of atoms fixed on a carbon chain which presents a set of physicochemical properties.

- The degree of oxidation, in organic chemistry is the number of bonds exchanged by this carbon with atoms more electronegative than hydrogen. The following table summarizes the classification of some molecules according to the oxidation number of the carbon atom:



Carbon oxidation number					
- 4	- 3	- 2	0	+2	+4
CH_4	$^{\bullet}CH_3$	CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
	$R\text{-}CH_3$	CH_3OH	$\genfrac{}{}{0pt}{}{H}{H}C{=}O$	$\genfrac{}{}{0pt}{}{H}{HO}C{=}O$	CO_2
		CH_3NH_2	$\genfrac{}{}{0pt}{}{R}{R}C{=}NH$	$\genfrac{}{}{0pt}{}{H}{H_2N}C{=}O$	
				$\genfrac{}{}{0pt}{}{H}{Cl}C{=}O$	

Since hydrogen has an oxidation state of +1 in organic chemistry and –1 in metal hydrides, carbon in methane, CH_4, will therefore have an oxidation state of –4. On the other hand, in the radical $CH_3^{\bullet}$, carbon forms only three bonds with hydrogen and its oxidation state becomes -3.

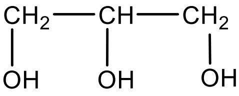
If we consider the molecule of methyl chloride, CH_3Cl, the carbon has an oxidation state of 2, because it "gains" 3 electrons by its bonds with three hydrogens, but "loses" one in its bond with chlorine, because Cl, more electronegative than carbon, has an oxidation state of –1.

If a carbon is bonded to another carbon, the two carbons are considered to neither lose nor gain an electron. Thus, in $R\text{-}CH_3$ where R represents a carbon group, the carbon of the methyl group has an oxidation number of –3 resulting from the bonds it forms with hydrogens alone.

II.5 Multiple and mixed functions (polyfunctional):

- The multiple function in a compound is a function grafted onto several carbons of a chain.

Example :

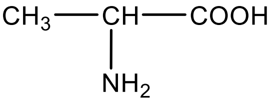


$$\underset{OH}{\underset{|}{CH_2}}-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH_2}}$$

same alcohol function
repeat 3 times

- The mixed (or polyfunctional) function of a compound is made up of several different functions grafted onto various carbons in a chain.

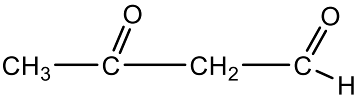
Example :



$$CH_3-\underset{NH_2}{\underset{|}{CH}}-COOH$$

2 different functions
(Acid + Amine)

;

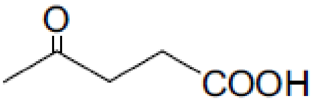


$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-H$$

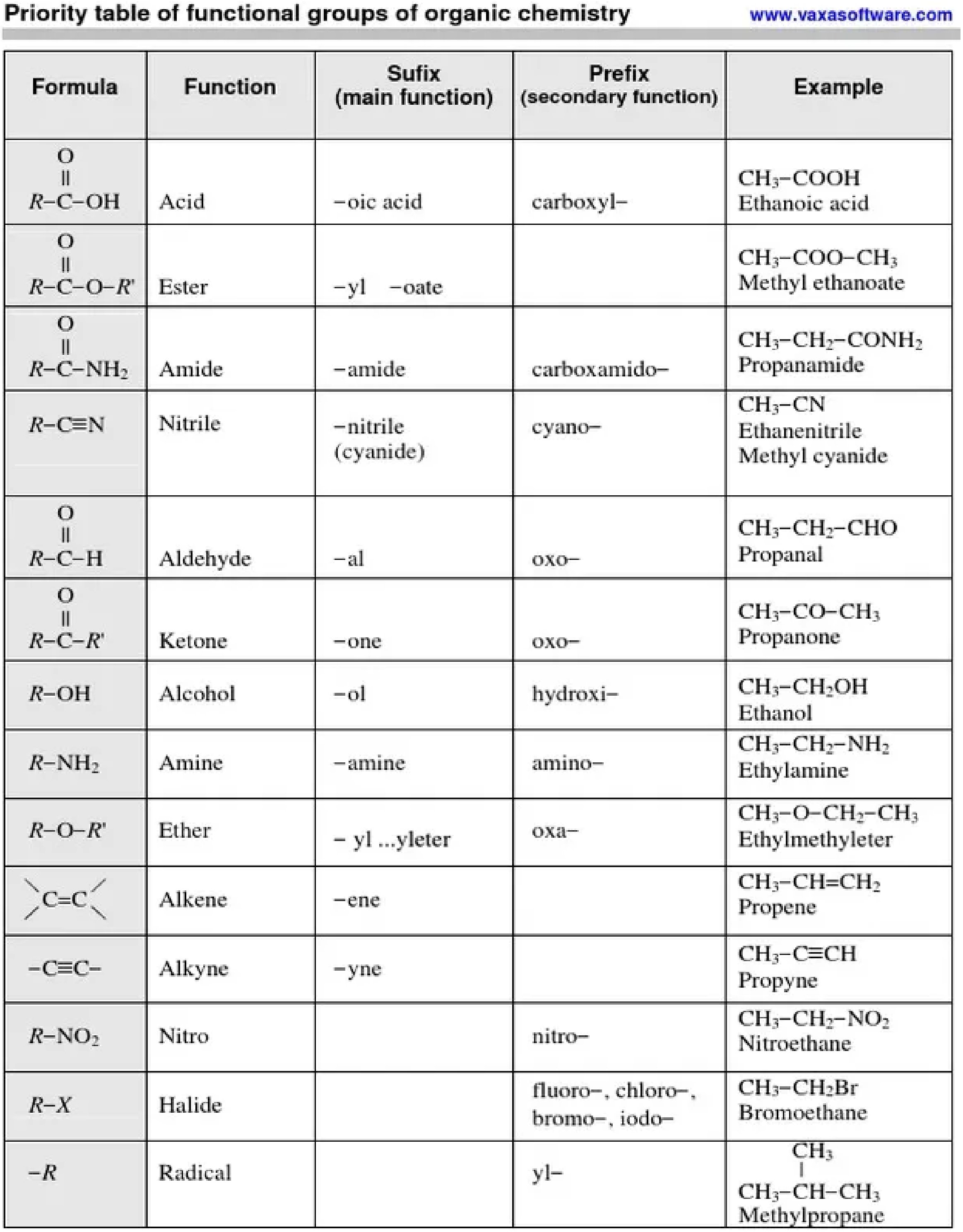
2 different functions
(ketone + Aldehyde)

II-6 Priority of chemical functions:

For a polyfunctional compound for example we have the following bifunctional molecule:



This molecule has two functions, acid and ketone. To see which of the functions has priority. A priority is established by the IUPAC (the international union of pure and applied chemistry) to name in an order the different chemical functions, partly based on the oxidation state of the carbon carrying the chemical function. Suffixes (termination) are associated with the main chemical functions and they are placed at the end of the name. As for the non-priority chemical functions in the molecule, they will be named by a prefix and placed with the substituents in front of the name of the chain.



Priority table of functional groups of organic chemistry www.vaxasoftware.com

Formula	Function	Sufix (main function)	Prefix (secondary function)	Example
$R-\overset{\overset{O}{\|}}{C}-OH$	Acid	−oic acid	carboxyl−	CH_3-COOH Ethanoic acid
$R-\overset{\overset{O}{\|}}{C}-O-R'$	Ester	−yl −oate		$CH_3-COO-CH_3$ Methyl ethanoate
$R-\overset{\overset{O}{\|}}{C}-NH_2$	Amide	−amide	carboxamido−	$CH_3-CH_2-CONH_2$ Propanamide
$R-C\equiv N$	Nitrile	−nitrile (cyanide)	cyano−	CH_3-CN Ethanenitrile Methyl cyanide
$R-\overset{\overset{O}{\|}}{C}-H$	Aldehyde	−al	oxo−	CH_3-CH_2-CHO Propanal
$R-\overset{\overset{O}{\|}}{C}-R'$	Ketone	−one	oxo−	$CH_3-CO-CH_3$ Propanone
$R-OH$	Alcohol	−ol	hydroxi−	CH_3-CH_2OH Ethanol
$R-NH_2$	Amine	−amine	amino−	$CH_3-CH_2-NH_2$ Ethylamine
$R-O-R'$	Ether	− yl ...yleter	oxa−	$CH_3-O-CH_2-CH_3$ Ethylmethyleter
$>C=C<$	Alkene	−ene		$CH_3-CH=CH_2$ Propene
$-C\equiv C-$	Alkyne	−yne		$CH_3-C\equiv CH$ Propyne
$R-NO_2$	Nitro		nitro−	$CH_3-CH_2-NO_2$ Nitroethane
$R-X$	Halide		fluoro−, chloro−, bromo−, iodo−	CH_3-CH_2Br Bromoethane
$-R$	Radical		yl−	$CH_3-\overset{\overset{CH_3}{\|}}{C}H-CH_3$ Methylpropane

II.7 Nomenclature of organic compounds:

To name compounds, it is necessary to know the rules adopted by IUPAC. The systematic name of an organic compound generally consists of three parts:

PREFIX----------FUNDAMENTAL STRUCTURAL UNIT------------SUFFIX

The Prefix part groups all the substituents listed in alphabetical order and each bearing the index of its location.

The Fundamental Structural Unit (FSU) part indicates the number of carbon atoms in the longest main chain and which contains the functional group (Suffix).

The Suffix part designates the main function present on the Fundamental Structural Unit.

II.7.1 Alkanes:

In this family the suffix is "ane". The simplest molecule consists of a carbon atom bonded to 4 hydrogen atoms. The name of this compound is methane. The following table gives the nomenclature of the first twelve alkanes and their radicals.

A radical or alkyl group (R= C_nH_{2n+1}) of an alkane is obtained by removing a hydrogen atom from a terminal carbon atom. The name of the group is obtained by replacing the ending "ane" of the corresponding alkane with "yl".

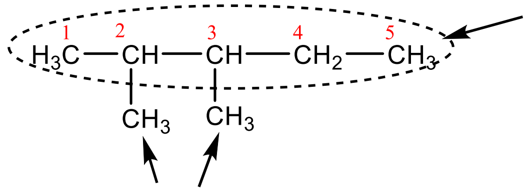
No. of C atoms	Name of alkane	Molecular formula	Name of alkyl group	Formula
1	Methane	CH_4	Methyl	$-CH_3$
2	Ethane	C_2H_6	Ethyl	$-C_2H_5$
3	Propane	C_3H_8	Propyl	$-C_3H_7$
4	Butane	C_4H_{10}	Butyl	$-C_4H_9$
5	Pentane	C_5H_{12}	Pentyl	$-C_5H_{11}$
6	Hexane	C_6H_{14}	Hexyl	$-C_6H_{13}$
7	Heptane	C_7H_{16}	Heptyl	$-C_7H_{15}$
8	Octane	C_8H_{18}	Octyl	$-C_8H_{17}$
9	Nonane	C_9H_{20}	Nonyl	$-C_9H_{19}$
10	Decane	$C_{10}H_{22}$	Decyl	$-C_{10}H_{21}$

- Rules for nomenclature of organic compounds:

(1) The atoms of the longest chain (main chain) are first numbered. The name of the compound is derived from that of the alkane.

(2) The ramifications on the longest carbon chain are considered substituents.

Example :

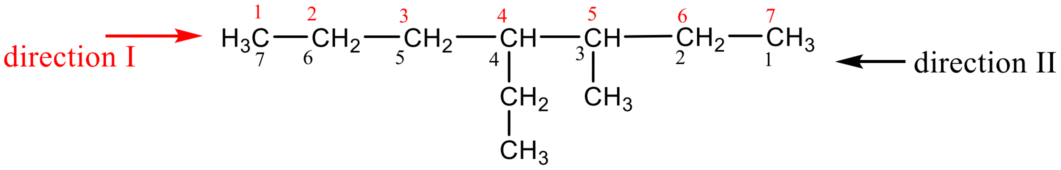


Longer chain (5 carbons ⇒ pentane derivative

substituting (radical)

(3) The main chain is numbered so that the first substituent is assigned the lowest possible index. The index corresponds to the number of the carbon in the main chain.

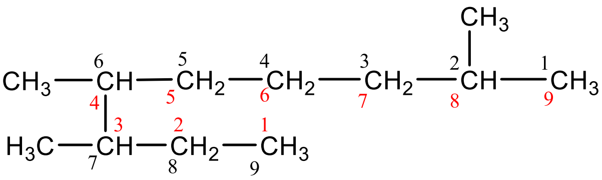
Example 1 :



- in direction I, the nomenclature is: 4-ethyl-5-methyl heptane. The index in direction II is 4.
- in direction II: 4-ethyl-3-methyl heptane. The index in direction II is 3.

we have 3<4 so the name of this compound is: 4-ethyl-3-methyl heptane.

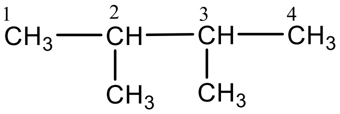
Example 2 :



2,6,7-trimethylnonane

(4) The identical substituents are derived from their prefix di, tri, tetra…..

Example :



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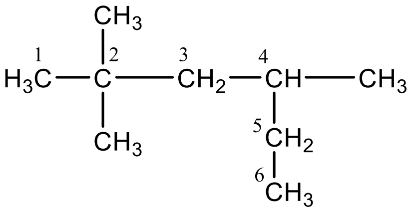


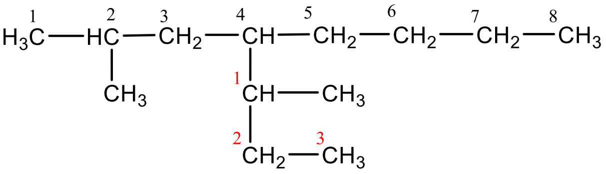
2,3-dimethylbutane

2,2,4-trimethylhexane

(5) When the radicals are branched the carbons of this radical are numbered and the name of the radical is given in parentheses.

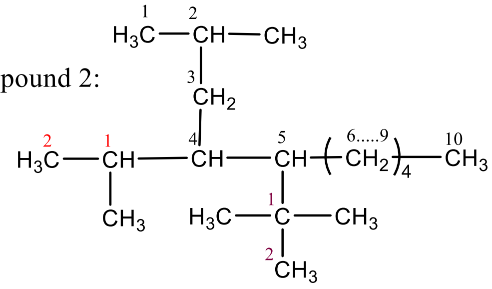
Example :

Compound 1:



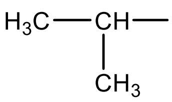
2-methyl-4-(1-methylpropyl)octane

Compound 2:



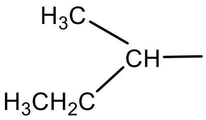
5-(1,1-dimethylethyl)-4-(1-methylethyl)-2-methyldecane

These names can be simplified if we use the radicals:

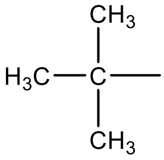


$$H_3C-\underset{\underset{\displaystyle CH_3}{|}}{CH}-$$

iso-propyl



sec-butyl



$$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-$$

tert-butyl

therefore the name of compound 1 will be: 4-(*sec*-butyl)-2-methyloctane

the name of compound 2 will be : 5-(*tert*-butyl)-4-isopropyl-2-methyldecane

II.7.2 Alkenes:

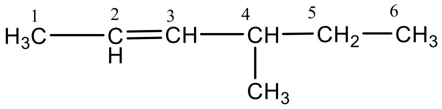
These are ethylenic hydrocarbons. The simplest molecule consists of two carbon atoms bonded to 2 hydrogen atoms. The name of this compound is ethene.

Rules:

(1) the suffix (termination) "ane" of the alkane replaced by "ene".

(2) the position of the C=C double bond which carries the smallest index imposes the direction of the numbering of the carbon chain.

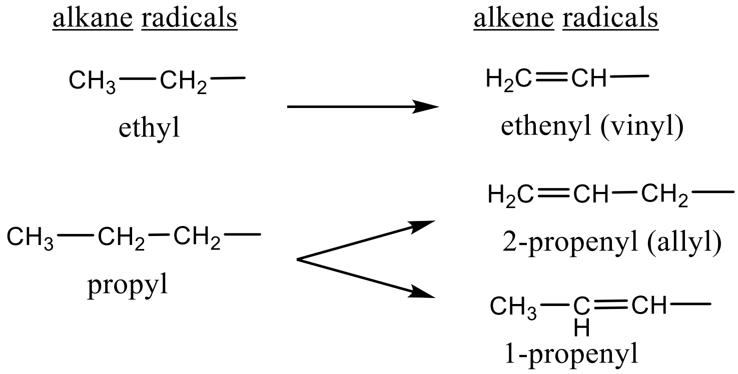
Exemple :



$$\overset{1}{H_3C}-\underset{H}{\overset{2}{C}}=\overset{3}{CH}-\underset{\underset{\displaystyle CH_3}{|}}{\overset{4}{CH}}-\overset{5}{CH_2}-\overset{6}{CH_3}$$

4-methylhex-2-ene

(3) in the case where the substituents contain C=C double bonds, the suffix "yl" of the alkane radicals is replaced by the suffix "enyl" of the alkene radicals.



II.7.3 Alkynes

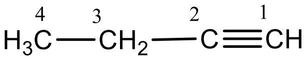
These are acetylenic hydrocarbons. The simplest molecule consists of two carbon atoms bonded to a hydrogen atom. The name of this compound is ethyne.

Rules:

(1) the ending "ane" of the alkane replaced by "yne".

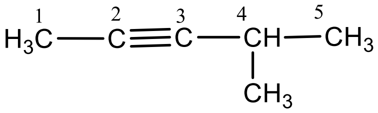
(2) the position of the triple bond C≡C which carries the lowest index imposes the direction of the numbering of the carbon chain.

Example :



$H_3C-CH_2-C\equiv CH$

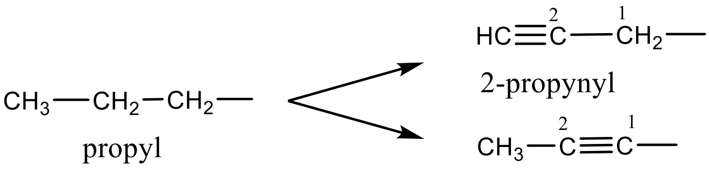
but-1-yne ;



$H_3C-C\equiv C-CH(CH_3)-CH_3$

4-methylpent-2-yne

(3) in the case where the substituents contain C≡C triple bonds, the suffix “yl” of the alkane radicals is replaced by the suffix “ynyl” of the alkyne radicals.



alkane radicals

alkyne radicals

$CH_3-CH_2-CH_2-$

propyl

$HC\equiv C-CH_2-$

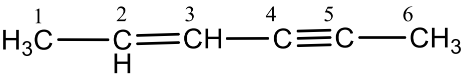
2-propynyl

$CH_3-C\equiv C-$

1-propynyl

(4) when the compound contains a C=C double bond and a C≡C triple bond, the double bond takes priority over the triple bond.

Example :



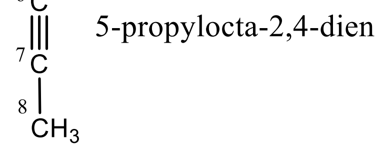
$H_3C-CH=CH-C\equiv C-CH_3$

hex-2-en-4-yne

(5) the order of priority of the carbon chains:

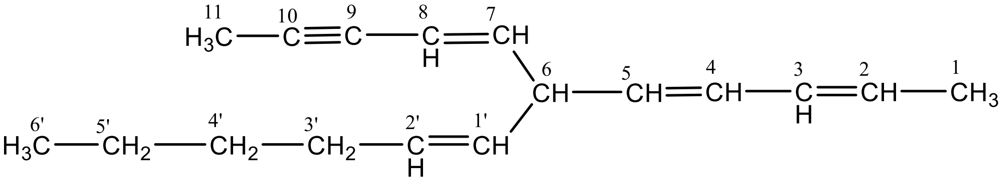
a) – the main chain contains the maximum number of double bonds and possibly the triple bond(s).

Example 1 :



5-propylocta-2,4-dien-6-yne

Example 2 :

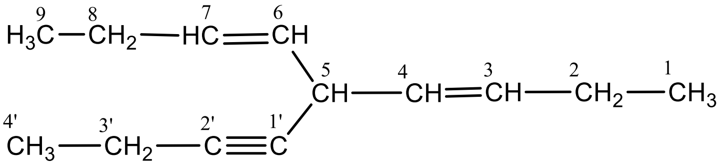


6-(1'-hexenyl)undeca-2,4,7-trien-9-yne

WARNING: in the case of unsaturated compounds, the main chain is not necessarily the longest but the one that contains the most unsaturations.

b) – the main chain contains the maximum number of double bonds.

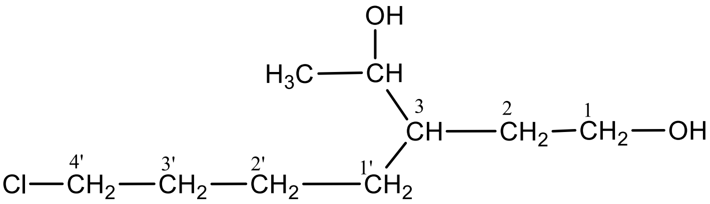
Example 1 :



5-(1-butynyl)nona-3,6-diène

c) the main chain contains the maximum number of substituents corresponding to the main group.

Example :

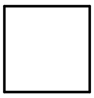


3-(4-chlorobutyl)pentan-1,4-diol

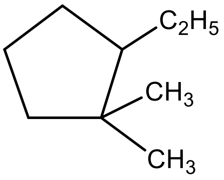
II.7.4 The Cyclanes, cyclenes and cyclynes :

Cyclanes are named by prefixing "cyclo" followed by the name of the linear alkane of the same number of C. The same thing for cyclenes and cyclynes.

Example :

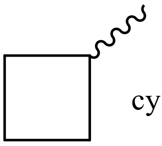


cyclobutane



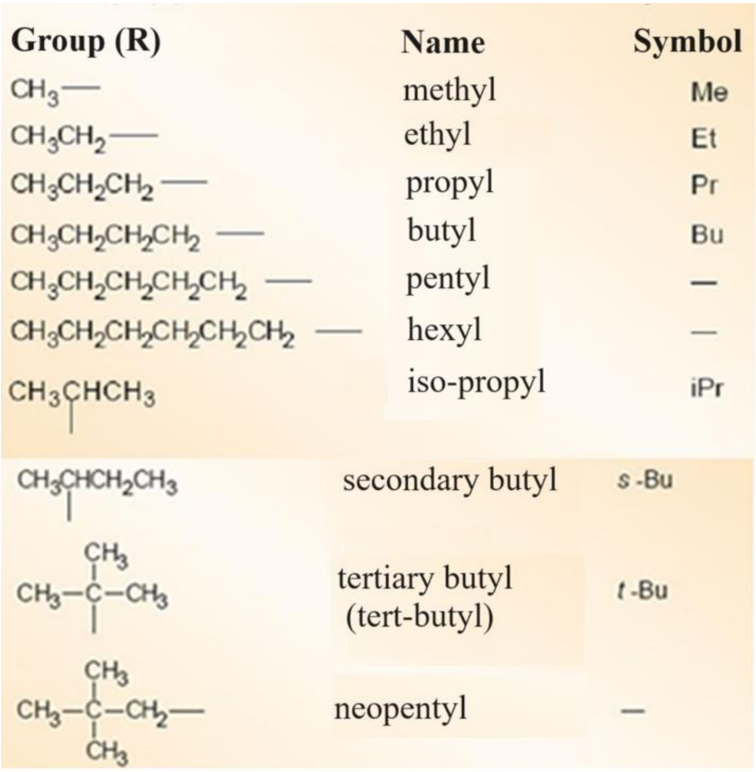
2-ethyl-1,1-dimethylcyclopentane

The cyclic chain radicals are named as follows:



Main radicals :

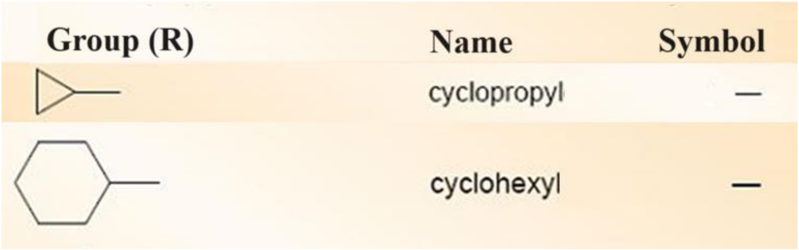
- Aliphatic series: 1) Alkyl radicals



Group (R)	Name	Symbol
$CH_3—$	methyl	Me
$CH_3CH_2—$	ethyl	Et
$CH_3CH_2CH_2—$	propyl	Pr
$CH_3CH_2CH_2CH_2—$	butyl	Bu
$CH_3CH_2CH_2CH_2CH_2—$	pentyl	—
$CH_3CH_2CH_2CH_2CH_2CH_2—$	hexyl	—
$CH_3\underset{\vert}{C}HCH_3$	iso-propyl	iPr
$CH_3\underset{\vert}{C}HCH_2CH_3$	secondary butyl	*s*-Bu
$CH_3-\overset{CH_3}{\underset{\vert}{C}}-CH_3$	tertiary butyl (tert-butyl)	*t*-Bu
$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2—$	neopentyl	—

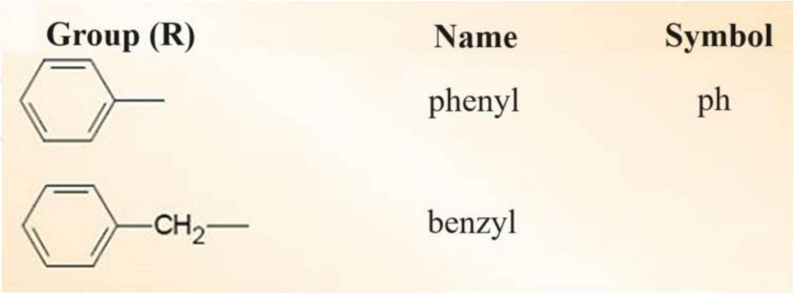
2) Cyclic series

- Cycloalkyl radicals



Group (R)	Name	Symbol
	cyclopropyl	—
	cyclohexyl	—

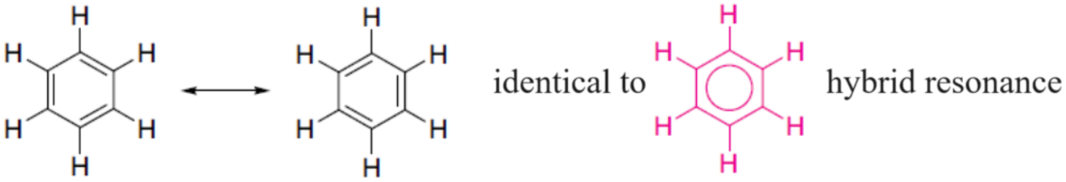
- Aryl radicals (Ar)



Group (R)	Name	Symbol
	phenyl	ph
$CH_2—$	benzyl	

II.7.5 Benzene hydrocarbons:

The series of these compounds contain one or more benzene nuclei. The simplest of these hydrocarbons is benzene C_6H_6.

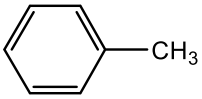


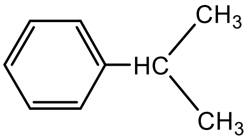
Substituted derivatives of benzene, formed by the replacement of one or more hydrogen atoms of the cycle by other atoms or groups of atoms.

- Monosubstituted derivatives of benzene:

In this case the benzene nucleus has only one substituent. To name it, we simply add the name of the substituent as a prefix to the word benzene.

Example :

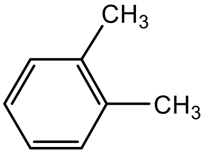

methylbenzene

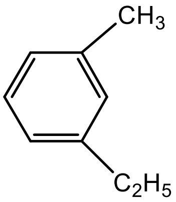

isopropylbenzene

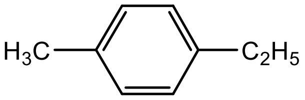
- Disubstituted benzene derivatives:

There are three possible arrangements for disubstituted benzene derivatives. The substituents can be adjacent, which is designated by the prefix 1,2- (or ortho- (o-)), positioned in 1,3- (prefix meta- (m-)), or in 1,4- (prefix para- (p-)). The substituents are listed in alphabetical order.

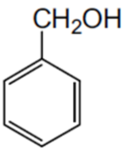
Example:

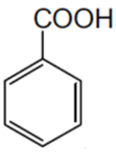

1,2-dimethylbenzene
or *o*-dimethylbenzene
ortho position

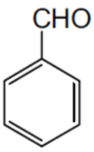

1,3-ethylmethylbenzene
or *m*-ethylmethylbenzene
meta position

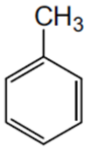

1,4-ethylmethylbenzene
ou *p*-ethylmethylbenzene
para position

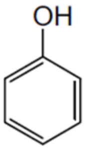
Many monosubstituted benzene derivatives have common names that are accepted by the IUPAC nomenclature.

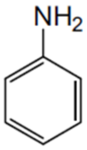

benzyl alcohol


benzoic acid


benzaldehyde


toluene

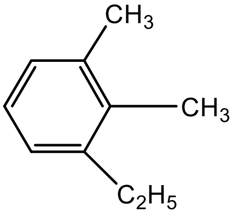

phenol


aniline

- Tri- and polysubstituted benzene derivatives:

When naming higher tri- and polysubstituted derivatives, the six carbons of the ring are numbered so as to have the smallest possible indices when listing the substituents.

Example :



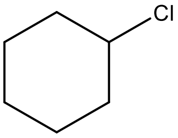
1-ethyl-2,3-dimethylbenzene

II.7.6 Halogenoalkanes R-X:

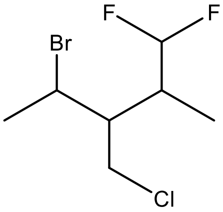
Halogenoalkanes or alkyl halides are compounds of formula R–X where X is a halogen atom F, Cl, Br or I.

In the IUPAC nomenclature, the halogen is considered as a substituent attached to the skeleton of the alkane. The name of this compound is that of the alkane followed by a fluoro, chloro, bromo or iodo prefix.

Example :



chlorocyclohexane



4-bromo-3-(1'-chloromethyl)-1,1-difluoro-2-methylpentane

II.6.7 The Alcohols R-OH:

A compound whose main group is the (-OH) group is called an alcohol, provided that the latter is carried by a saturated carbon atom.

Rules:

(1) The nomenclature of alcohols is very similar to the nomenclature of alkanes and is based on the same method. To name alcohols by replacing the terminal "e" of the alkane with the suffix "ol".

$$\textbf{Alkane} \longrightarrow \textbf{Alkanol}$$

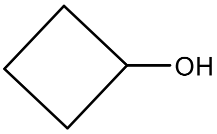
Example :

H_3C—OH

methanol

CH_3—CH_2—CH_2—OH

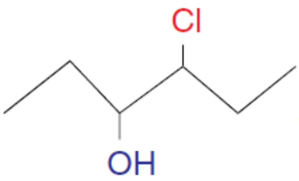
n-propan-1-ol
or n-propanol



cyclobutanol

(2) The presence of an OH group within a chain requires indicating the number of the carbon that carries it. It is still the lowest number that is retained.

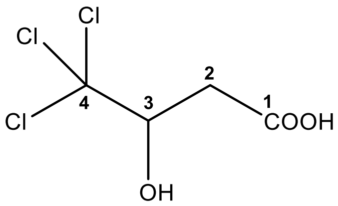
Example :



4-chlorohexan-3-ol

(3) In the case where the alcohol function is not a priority it is named by the prefix hydroxy.

Example :



4,4,4-trichloro-3-hydroxy butannoic acid
acide: priority function

(4) the radicals of alcohols (RO-) are called:

- Alkoxy for a group R containing 4 carbon atoms

Example: CH_3O- methoxy; C_2H_5O- ethoxy; C_3H_7O- propoxy; C_4H_9O- butoxy

- Alkyloxy for a group R containing at least 5 carbon atoms

Example: $C_5H_{11}O$- pentyloxy; ………

II.7.8 Ethers R-O-R′:

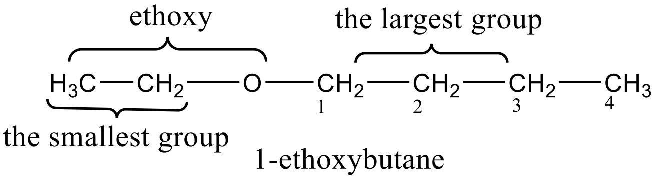
Ethers are organic compounds in which one oxygen atom is bonded to two alkyl groups or aryl groups. They are called alkoxyalkanes.

- IUPAC nomenclature

In IUPAC nomenclature, the larger alkyl (or aryl) group is used as the root name of the alkane and the smaller alkyl group is treated as an alkoxy radical on that alkane.

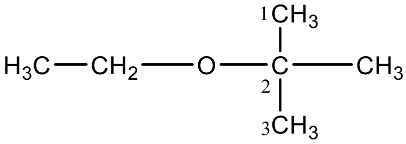
$$\textbf{Alkane} \longrightarrow \textbf{Alkoxyalkane}$$

Example :



$$\overbrace{\underbrace{H_3C-CH_2}_{\text{the smallest group}}-O}^{\text{ethoxy}}-\overbrace{\underset{1}{CH_2}-\underset{2}{CH_2}-\underset{3}{CH_2}}^{\text{the largest group}}-\underset{4}{CH_3}$$

1-ethoxybutane



$$H_3C-CH_2-O-\underset{{}_3CH_3}{\overset{{}_1CH_3}{\underset{2}{C}}}-CH_3$$

2-ethoxy-2-methylpropane

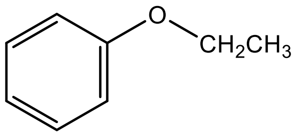
- Common Names

Common names for ethers are obtained by alphabetically naming the two groups attached to the oxygen followed by the word ether.

Example :

$CH_3OCH_2CH_3$
Ethyl methy ether

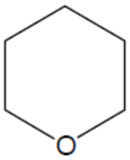
$CH_3CH_2OCH_2CH_3$
Diethyl ether



Ethyl phenyl ether

Note:

Cyclic ethers are named with the prefix "oxa" which indicates that a carbon in the ring has been replaced by an oxygen followed by the name of the cycloalkane.

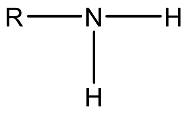


oxacyclohexane

Numbering begins with the heteroatom

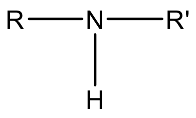
II.7.9 Amines:

An amine is an organic compound derived from ammonia NH_3 in which some hydrogens have been replaced by a carbon group. There are three classes of amines:



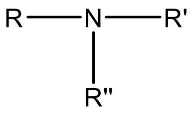
$R-\underset{\underset{H}{|}}{N}-H$

primary amine



$R-\underset{\underset{H}{|}}{N}-R'$

secondary amine



$R-\underset{\underset{R''}{|}}{N}-R'$

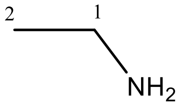
tertiary amine

to name the amines by replacing the terminal "e" of the alkane with the suffix "amine".

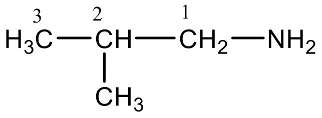
Alkane ⟶ **Alkanamine**

- Primary amines $R-NH_2$:

Example :

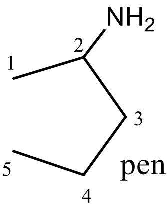


ethanamine
(or ethan-1-amine)



$\overset{3}{H_3C}-\underset{\underset{CH_3}{|}}{\overset{2}{CH}}-\overset{1}{CH_2}-NH_2$

2-methylpropan-1-amine



pentan-2-amine

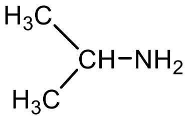
Primary amines are alkylamines, they can also be named as follows:

$H_3C—NH_2$

methylamine

$H_3C—CH_2—NH_2$

ethylamine



i-propylamine (*i*=*iso*)

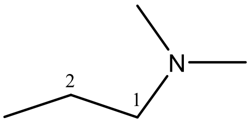
- Secondary and tertiary amines R-NH-R′ and R-N(R″)-R′:

In the case of secondary and tertiary amines the name of the amine is that of the largest chain of the alkyl

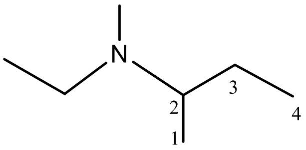
Example :

$H_3C—NH—C_2H_5$

N-methylethanamine
(or *N*-methylethan-1-amine)
(secondary amine)



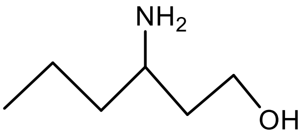
N,*N*-dimethylpropan-1-amine



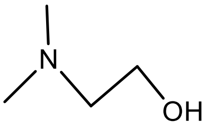
N-ethyl-*N*-methylbutan-2-amine

(tertiary amine)

If the amine function is not a priority it is named by the prefix amino.



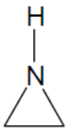
3-aminohexan-1-ol



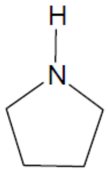
2-(*N,N*-dimethylamino)ethanol

- Cyclic amines

The nitrogen atom in the ring is indicated by the prefix: -aza



azacyclopropane (aziridine)



azacyclopentane (pyrrolidine)

II.7.10 Aldehydes RCHO:

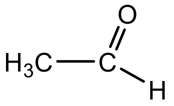
Compounds whose main group is the -CHO group are called aldehydes.

Aldehydes are alkanals derived from alkanes. The terminal "e" of the alkane is replaced by the suffix "al" of the aldehyde.

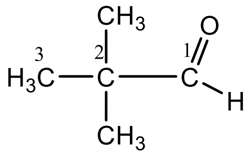
$$\textbf{Alkane} \longrightarrow \textbf{Alkanal}$$

When numbering the carbon chain, the functional carbon necessarily bears the number 1.

Example :



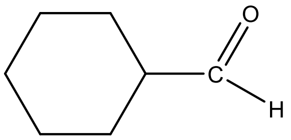
ethanal



2,2-dimethylpropanal

When the -CHO group is carried by a cycle, i.e. -CHO is replaced by H. the name of the aldehyde is obtained by adding the ending carbaldehyde to the name of the compound.

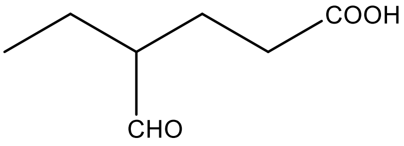
Example :



cyclohexanecarbaldehyde

If the aldehyde function is not a priority, it is designated by the prefix formyl.

Example :



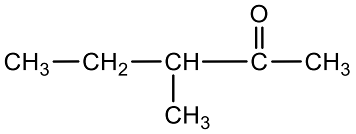
4-formylhexanoic acid

II.7.11 The Ketones RCOR′:

Compounds containing an oxygen atom doubly bonded to a single carbon atom, the latter being bonded to two carbon atoms, are called ketones.

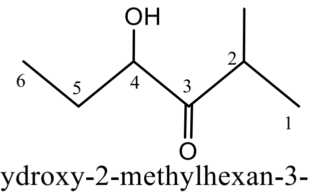
To name a ketone, refer to the rules for alkane nomenclature. The name of the ketone is the same as that of the corresponding alkane, replacing the terminal "e" of the alkane with the suffix "one", preceded by the position number of the functional carbon.

Example :



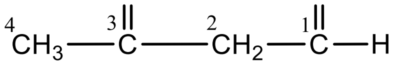
$CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-CH_3$

3-méthylpentan-2-one



4-hydroxy-2-methylhexan-3-one

If the ketone function is not a priority, it is named by the prefix oxo.



${}^{4}CH_3-{}^{3}\overset{O}{\overset{\|}{C}}-{}^{2}CH_2-{}^{1}\overset{O}{\overset{\|}{C}}-H$

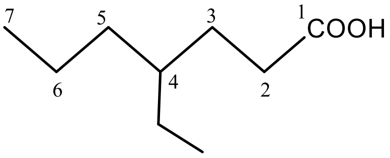
3-oxobutanal

II.7.11 Carboxylic acids RCOOH (alkanoic acids):

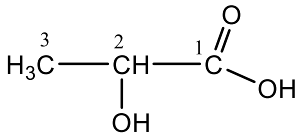
Compounds whose main group is the -COOH group are called Carboxylic acids.

The name of the compound is the name of the alkane corresponding to the carbon chain, terminated with the suffix **"oic"** and preceded by the word **Acid**. The carbon atom of the -COOH group always bears the number 1, as for aldehydes.

Example :

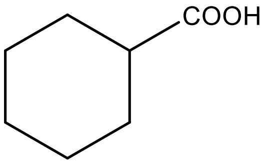


4-ethylheptanoic acid



2-hydroxypropanoic acid

When the -COOH group is carried by a cycle, that is to say -COOH is replaced by H. the name of the acid is obtained by adding the carboxylic termination to the name of the compound.

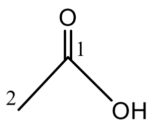


cyclohexanecarboxylic acid

II .7. 12 RCOOR′ esters:

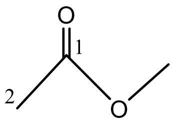
The ester results from the dehydration of a carboxylic acid RCOOH with an alcohol R′OH. They will be named by replacing the suffix **"oic"** of the acids from which they are derived with the suffix **"oate"** followed by the name of the R′ group present in the alcohol during the formation of the ester. The main chain is the one that carries the function derived from the acid.

Example :



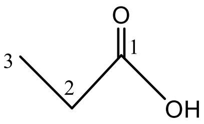
ethanoic acid

⟹



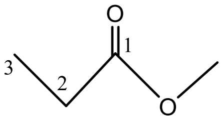
methyl ethanoate

;

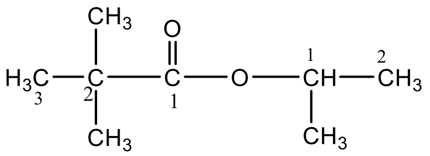


propanoic acid

⟹



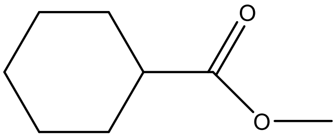
methyl propanoate



$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\overset{O}{||}}{C}-O-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

1-methylethyl 2,2-dimethylpropanoate
(or *i*-propyl 2,2-dimethylpropanoate)

When the -COOR′ group is carried by a cycle. The name of the ester is obtained by adding the carboxylate ending to the name of the compound.



methyl cyclohexanecarboxylate

II.7.13 Amides:

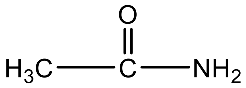
The amide function is derived from the carboxylic acid function by replacing the hydroxyl group -OH with - NH_2.

Amides are named by replacing the terminal "e" of the alkane with the suffix "amide".

Alkane ⟶ **Alkanamide**

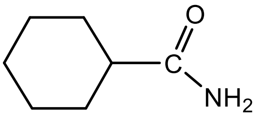
When the group -COOR′ is carried by a cycle. The name of the ester is obtained by adding the carboxamide ending to the name of the compound.

- Primary amide R-$CONH_2$:



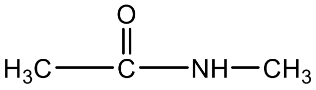
$H_3C-\overset{\overset{O}{\|}}{C}-NH_2$

ethanamide



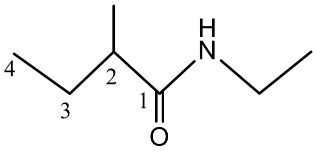
cyclohexanecarboxamide

- Secondary amide R-CON(R′)H :



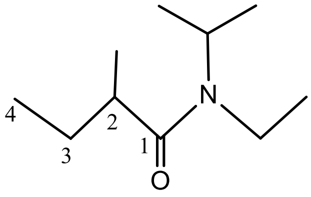
$H_3C-\overset{\overset{O}{\|}}{C}-NH-CH_3$

N-methylethanamide



N-ethyl-2-methylbutanamide

- Tertiary amide R-CON(R″) R′ :



N-ethyl-*N*-isopropyl-2-methylbutanamide

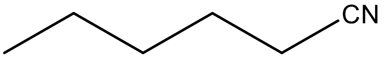
II.7.14 Nitriles (R-C≡N):

The nitriles carry the group -C≡N. Their name is made by adding the suffix **"nitrile"** to the name of the alkane from which they are derived (including the carbon of the function).

Example:

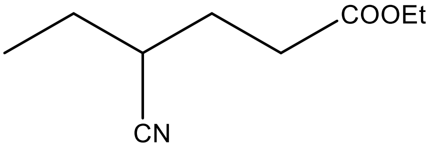
CH_3CN
ethanenitrile

C_2H_5CN
propanenitrile



hexanenitrile

If the nitrile function is not a priority, it is named by the prefix **cyano**.



ethyl 4-cyanohexanoate

CHAPTER III: Isomerism and Stereo-Isomery

III.1 Elemental analysis or microanalysis:

The aim of microanalysis is to obtain the chemical formula of the compound.

Let us assume a molecule with the chemical formula $C_xH_yN_zO_t$. The volume of carbon dioxide and the mass of water obtained during combustion provide access to the mass percentages of carbon and hydrogen. The percentage of nitrogen is measured by heating the product to be analyzed on copper oxide (Dumas method). Oxygen will often be measured by difference. We know that the atomic masses of carbon, hydrogen, nitrogen and oxygen are respectively 12, 1, 14 and 16, the expression of the molar mass of the compound to be analyzed will therefore be:

$$\boldsymbol{M = 12x + y + 14z + 16t}$$

The masses of the different elements being obviously proportional to the percentages we have the proportionalities:

$$\frac{12x}{\%C} = \frac{y}{\%H} = \frac{14z}{\%N} = \frac{16t}{\%O} = \frac{12x + y + 14z + 16t}{\%C + \%H + \%N + \%O} = \frac{M}{100\%}$$

$$x = \frac{M}{12}\,\frac{\%C}{100}, \text{etc.}$$

In this expression %C, %H, %N, %O respectively designate the mass percentages of carbon, hydrogen, nitrogen and oxygen. Note that the indices x, y, z, and t designating numbers of atoms, must necessarily have values close to an integer.

The molar masses remain to be determined.

Meyer's method. This method consists simply of measuring, when it is a gas or a vaporizable substance, the density (d) of the vapor or gas and determining the molar mass by the Avogadro relation **M = 29d.**

III.2 Concept of degree of unsaturation

Let us consider an aliphatic alkane. Its empirical formula is of the form C_nH_{2n+2}. Each time that two hydrogen atoms are removed from this alkane, we will say that we have an additional **degree of unsaturation**.

Thus, a compound with the empirical formula C_nH_{2n+2} will have zero degrees of unsaturation, a compound with the empirical formula C_nH_{2n} will have one degree of unsaturation, C_nH_{2n-2} will have two… An unsaturation corresponds to a **double bond** or a **cycle.**

How can we easily find this degree of unsaturation in the general case? If we consider a molecule with the empirical formula $C_cH_hN_nO_oX_x$ where c, h, n, o and x are obviously whole numbers, the degree of unsaturation i is given by the formula:

$$i = \frac{2c + 2 - h + n - x}{2}$$

An unsaturation can therefore correspond to:

- A double bond counts as one unsaturation
- A cycle counts as one unsaturation
- A triple bond counts as two unsaturations

Two unsaturations can correspond to:

- Two double bonds
- One triple bond
- One cycle and one double bond…

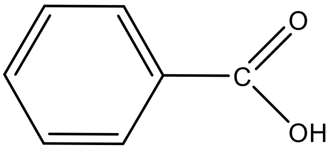
Examples :

So, by applying this formula, the compound with molecular formula C_2H_5Br will have zero unsaturation.

Unsaturation number of the molecule with molecular formula C_8H_6 is 6

Unsaturation number of the molecule with molecular formula $C_5H_{10}O$ is 1

Unsaturation number of the molecule shown below is 5



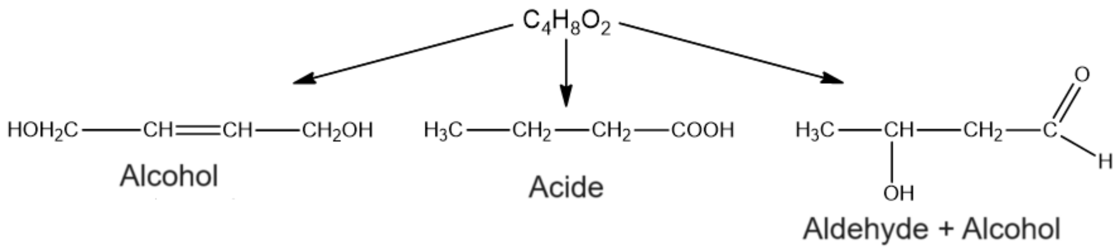
III.3 Planar isomerism:

Compounds that have the same molecular formula are called isomers if they differ in their physicochemical properties. It is said that between these compounds there is a relationship of isomerism. There are two types of planar isomerism: 1) constitutional isomerism, 2) tautomeric isomerism

III.4 Constitutional isomerism:

III.4.1 Functional isomerism:

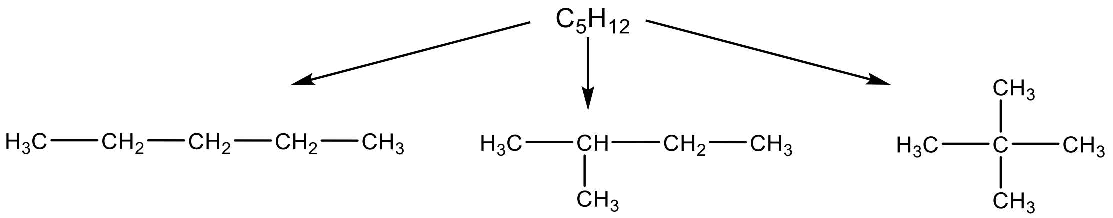
Functional isomers have the same molecular formula but the functional group is different.



For a gross formula $C_4H_8O_2$ we find three isomers

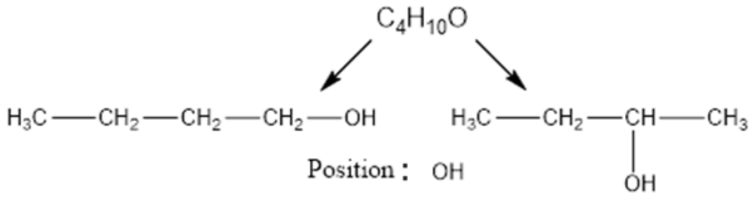
III.4.2 Skeletal isomerism

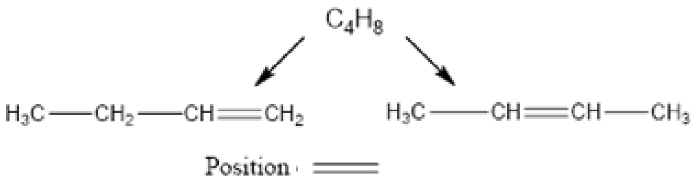
Skeletal (or chain) isomers have the same empirical formula but the sequence of carbon atoms is different.



III.4.3 Positional isomerism:

They have the same gross formula, they belong to the same function, but the functional group or the carbon-carbon multiple bond occupies different positions on the carbon chain.

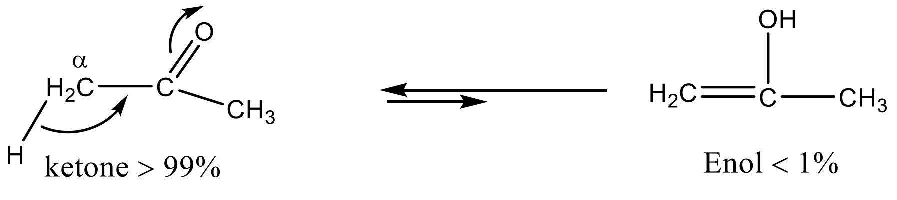




III.5 Tautomerism isomerism:

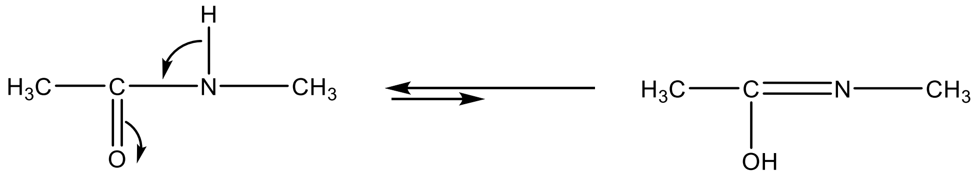
Tautomerism is the relationship that exists between two constitutional isomers that can be reversibly transformed into each other.

Example 1: - Keto-enolic tautomerism relationship:



So tautomerism is a migration of H from one atom to another.

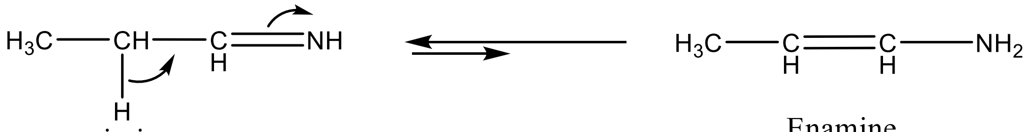
Example 2 : - tautomerism of amides



Amide

Iminoalcohol

Example 3 : - tautomerism of imines



imine

Enamine

III.6 Stereochemistry:

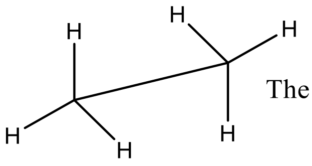
Stereochemistry studies the geometry of molecules in three-dimensional space. Some compounds may have the same gross formula, the same planar structural formula, and exhibit different properties. The study of these properties requires the representation of molecules in space.

III.7 Planar representation of spatial structures:

Several types of representations are used to draw three-dimensional molecules in the plane of the sheet, we distinguish: perspective representation, Cram's projective representation, Newman's representation and Fischer's projection.

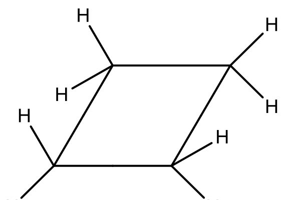
III.7.1 Perspective representation (cavalier):

The ethane molecule with the semi-developed formula $CH_3—CH_3$ is represented in perspective as follows:

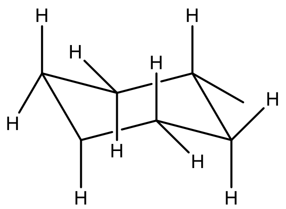


The C-C bond is seen in perspective

This representation is very useful for cyclic molecules:



Cyclobutane



Cyclohexane

III.7.2 Projective representation (Cram):

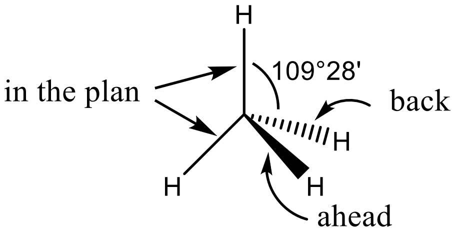
The Cram representation allows to specify the geometry of a molecule by showing the bonds in perspective.

The Cram representation is based on the following conditions:

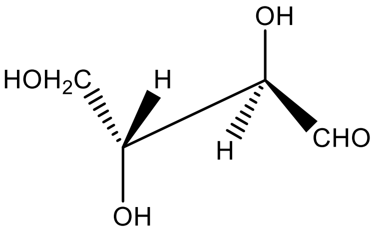
- Solid line ——— : Represents a bond located in the plane of the paper.
- Hatched triangle ıııl : Represents a bond oriented behind this plane.
- Solid triangle ◀ (or ◁) : Represents a bond oriented in front of this plane.

a) Representation of acyclic molecules

Example: methane CH_4

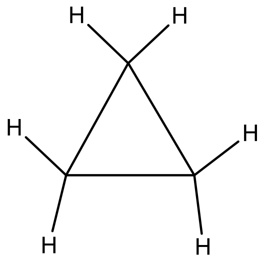


Example : $HOCH_2$-CH(OH)-CH(OH)-CHO

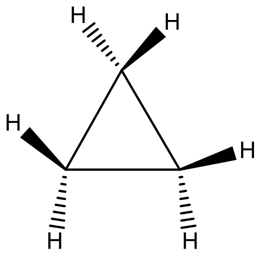


b) Representation of cyclic molecules :

Example: cyclopropane



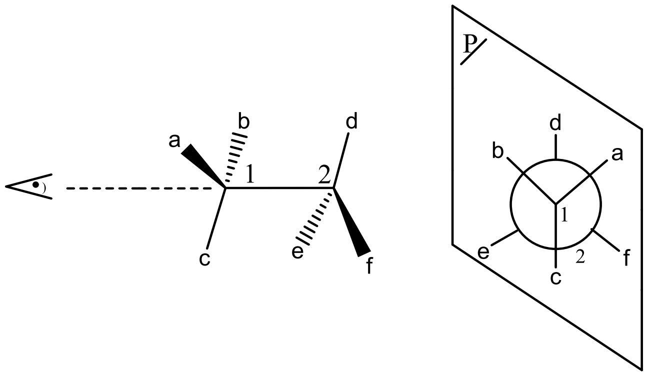
Perspective representation



Representation of Cram

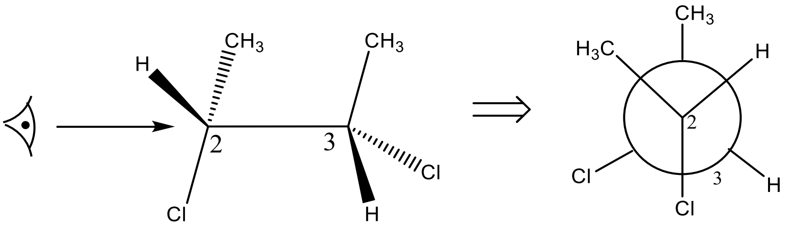
III.7.3. Newman's representation:

In Newman's representation, the molecule is viewed along the axis of a single C-C bond between two neighbouring carbon atoms. The bonds from the two atoms are projected on a plane perpendicular to the axis of the bond studied:



The C_1-C_2 bond is perpendicular to the P plane
The C_1 carbon is represented by a point
The C_2 carbon is represented by a circle

Example: 2,3-dichlorobutane



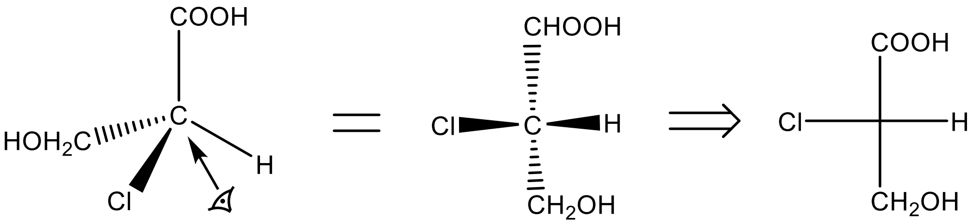
Representation of Newman

III.7.4. Fischer representation (or projection):

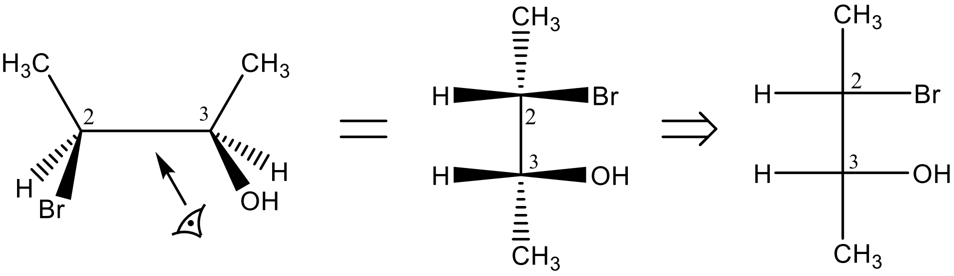
In Fischer projection, the observer must then position himself above the molecule so that:

- a vertical line corresponds to a bond in the plane or towards the rear.
- a horizontal line corresponds to a bond in front of the plane.
- represents the longest chain vertically, and the most oxidized function placed at the top of the chain.

<u>Example 1:</u>



<u>Example 2:</u> Case of two adjacent atoms.



III.8 Stereoisomerism:

When we consider a molecule in three-dimensional space, new cases of isomerism can appear. We then speak of **spatial isomerism** or **stereoisomerism**.

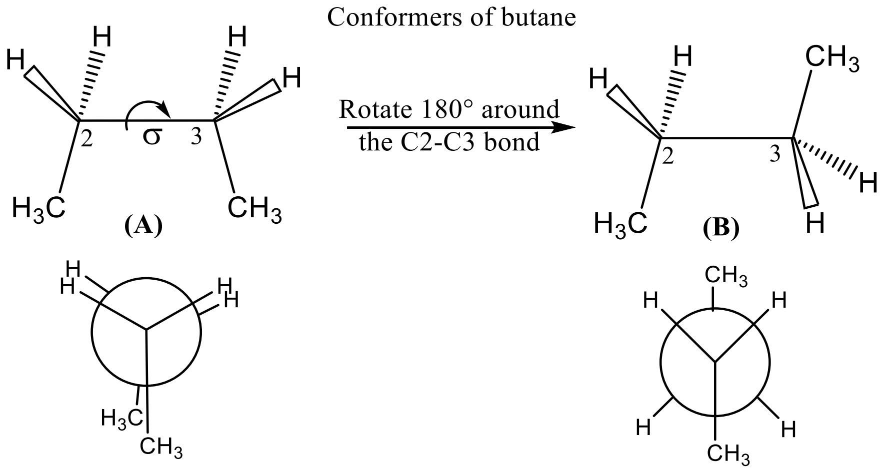
We call stereoisomers isomers that have the same planar developed formula but that differ in the spatial arrangement (geometric arrangement) of their atoms.

We can classify them into two categories: conformational stereoisomers (conformers) and configurational stereoisomers.

III.8.1 Conformational stereoisomers:

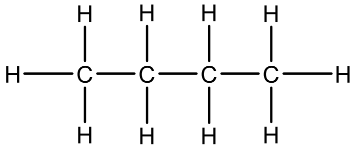
Molecules that can form various stereoisomers by simple rotation around their σ bonds are called "conformational stereoisomer molecules".

a) Conformer of butane represented in Cram and in Newman projection


Conformers of butane

(A): Eclipsed conformation (B): Starry conformation

The two structures correspond to the same structural formula:



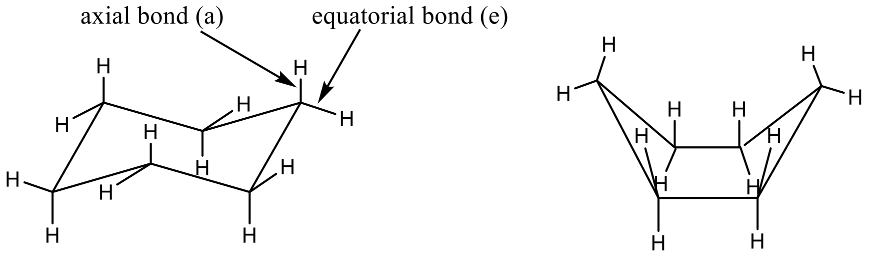
$$\begin{array}{ccccccccc} & & H & & H & & H & & H & \\ & & | & & | & & | & & | & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & \\ & & H & & H & & H & & H & \end{array}$$

a 180° rotation around the C2—C3 bond allows us to pass from molecule (A) to molecule (B). We will say that these forms (A) and (B) are conformational stereoisomers.

- Conformation (A) is called "eclipsed" and is less stable.
- Conformation (B) is called "star or offset" and is more stable.

b) Cyclohexane conformer

Cyclohexane can exist in 2 conformations, called chair form and boat form.



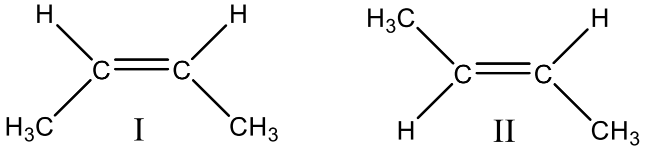
Chair form Boat form

The chair shape is more stable than the boat shape.

III.8.2 Configurational stereoisomers:

Gives the conformational isomers we pass from one conformation to another by simple rotation around the axis of the molecule. On the contrary, to pass from one configurational isomer to another, we must break and form at least one covalent bond.

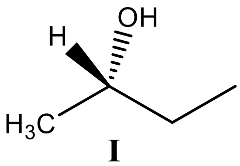
Example 1: but-2-ene. This compound can exist in two forms I and II



Configuration II is more stable than I

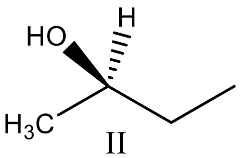
To obtain form II from form I, we must break the C1—C2, C2—H bonds and swap H and CH_3. In this case, the two structures I and II are configurational isomers, called geometric stereoisomers.

Example 2: 4-chlorobut-2-ol can exist in two forms I and II



I

and



II

Couples of configurational stereoisomers

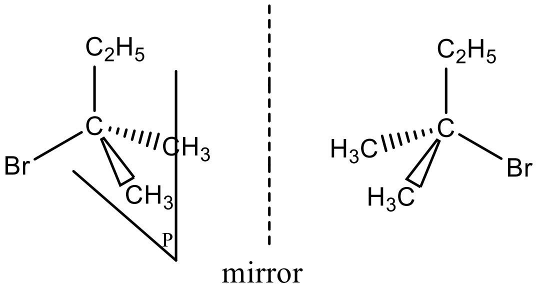
The two forms are called optical stereoisomers

III.9 Optical Isomerism:

III.9.1 Chirality – Enantiomer:

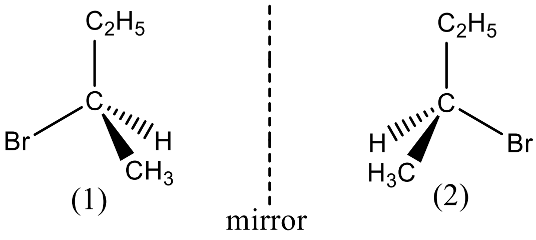
Any molecule that cannot be superimposed on its mirror image is chiral. Otherwise, it is achiral. This condition of chirality can be stated in a completely equivalent manner: An object (or molecule) is chiral if it does not have any element of symmetry (axis, plane, center).

Example 1: 2-bromo-2-methyl butane molecule



The molecule is superimposable to its image. (it contains a plane of symmetry P). So it is **achiral.**

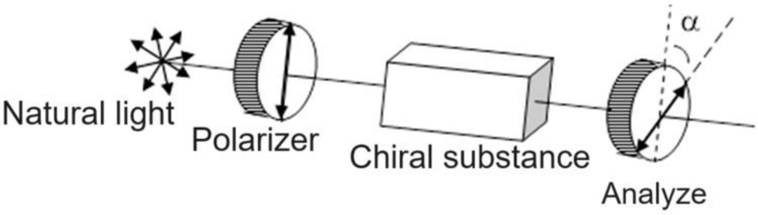
Example 2: 2-bromobutane



The molecule is not superimposable on its image (absence of symmetry elements). Therefore the molecule is **chiral**. The two forms (1) and (2) are **enantiomers** which belong to the **stereoisomers**. They are also called **optical isomers**.

III.9.2 Optical activity (OA):

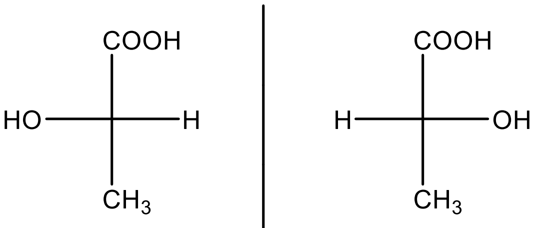
The chiral substance rotates the vibration plane of polarized light by an angle α.



Another definition: «For a compound to be optically active, it is sufficient that its molecule be chiral».

Example of lactic acid:

Lactic acid, a chiral compound, has two enantiomers



$[\alpha]_D = +3,33°$ $[\alpha]_D = -3,33°$

The (+) or (–) sign indicates the direction of rotation of the analyzer:

- ✓ The enantiomer that deflects the plane of polarized light to the right is called **dextrorotatory**, we denote it **(d)** or **(+)**;
- ✓ The one that deflects the plane to the left is called **levorotatory,** we denote it **(l)** or **(-)**;

So the two configurations are named:

I: (+)-lactic acid II: (–)-lactic acid

III.9.3 Asymmetric (or chirality) center:

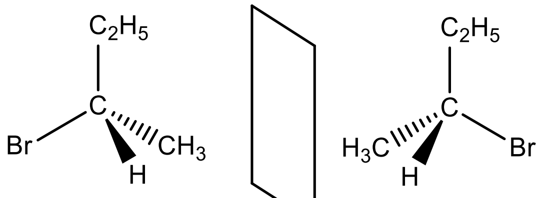
III.9.3.1 Asymmetric carbon:

The asymmetric carbon noted C* is a sp^3 hybridized carbon (tetrahedral) whose four substituents are all different.

III.9.3.2 Absolute configuration of an asymmetric carbon:

a) Definition of the absolute configuration:

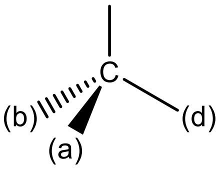
We have seen previously that for a chiral molecule (case of 2-bromobutane) containing an asymmetric carbon atom (C*), there are two different spatial arrangements of the substituents around this carbon (two enantiomers), each of these arrangements is called a **configuration**.



Configuration: (I) 2-bromobutane Configuration: (II) 2-bromobutane

b) R/S nomenclature of the asymmetric carbon:

If we follow the nomenclature established by the IUPAC, we obtain the same name for these two configurations (I) and (II) which is impossible. To solve this problem, three chemists R.S. Cahn, C.K. Ingold and V. Prelog, established a series of rules to designate the R/S configuration for each asymmetric carbon of the enantiomers.

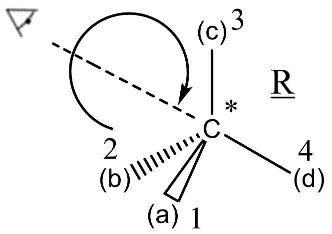


1) the substitutions are classified in decreasing order of the atomic numbers Z of the atoms. Either Z(a) > Z(b) > Z(c) > Z(d)

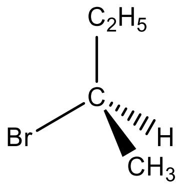
2) we look at the smallest substituent (d) through the asymmetric carbon.

3) we note the order of rotation of the sequence (a) → (b) → (c).

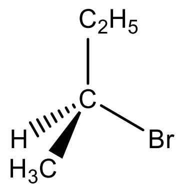
4) if this rotation is in the right direction (clockwise), the absolute configuration is R. if the opposite (left direction) the configuration is S.



Example 1: case of the 2-bromobutane molecule, the nomenclature of the two configurations is:

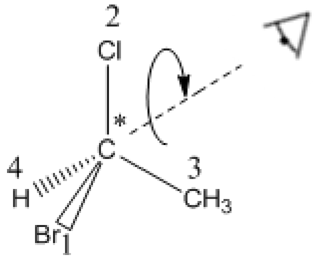


Configuration (I): R
(R)-2-bromobutane



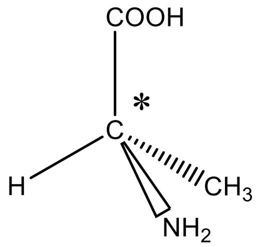
Configuration (II): S
(S)-2-bromobutane

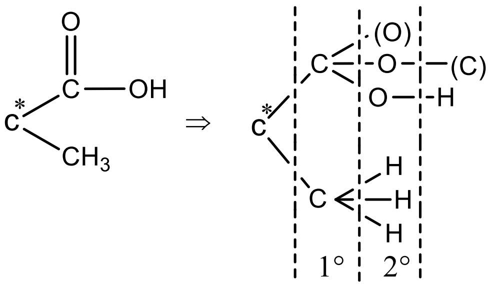
Example 2 : 1-Bromo-1-chloroethane   Br (Z=35) > Cl (Z=17) > C (Z=6) > H (Z=1)



(R)-bromo-1 chloro-1ethane

Example 3 : 2-Aminopropan-1-oic acid $CH_3CH(NH_2)COOH$



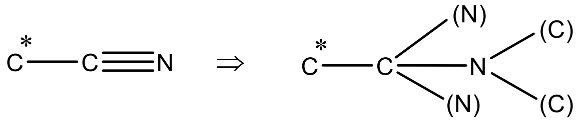


We have two identical atoms are linked to C*. In this case we consider the atoms in 2nd position.

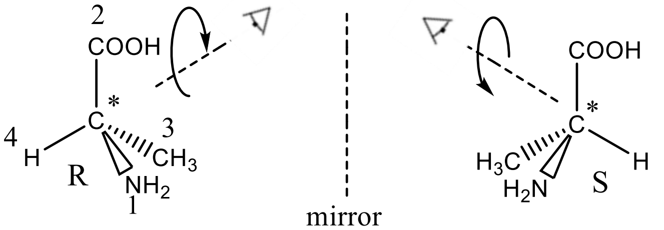
If the atom in 2nd position is linked by a double bond (=), we consider it open.

For a triple bond the same reasoning.

Remark :



Therefore, the classification of the substituents of 2-Aminopropan-1-oic acid is: $NH_2 > COOH > CH_3 > H$



(R)-2-Aminopropanoic acid (S)-2-Aminopropanoic acid

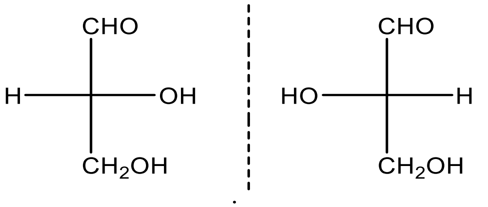
The two configurations R and S are enantiomers.

III.9.3.3 Fischer nomenclature D and L:

This nomenclature exists in ose compounds (sugars) and amino acids.

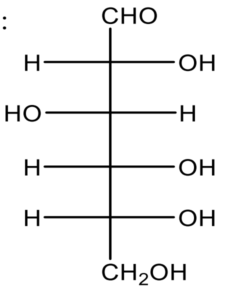
The rule: We look at the position of the last OH of the Fischer projection if it is on the right we have the **D** nomenclature if the OH is on the left we have the L nomenclature

Example 1 :



D-glyceraldehyde L-glyceraldehyde

Example 2 :



D (+)-glucose

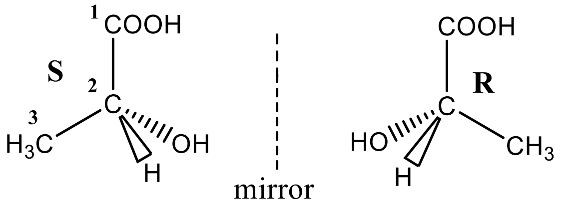
III.10 Configuration of some optically active compounds:

III.10.1 Molecule has a single asymmetric atom:

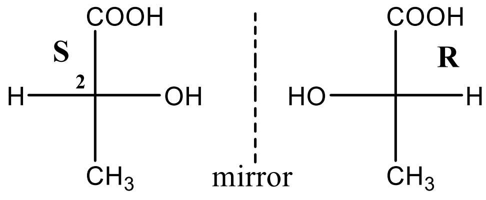
Example: Lactic acid molecule $CH_3–CHOH–COOH$

This molecule contains a single asymmetric carbon C* so we have 2 absolute configurations R and S for lactic acid.

- representation of Cram :

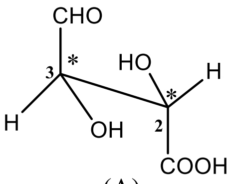


- representation of Fischier :

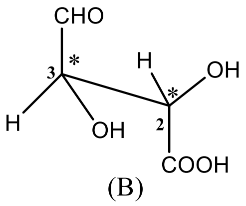


III.10.2 Molecule has two different asymmetric centers:

Let the molecule be: CHO–CHOH–CHOH–COOH. This compound can be present in two forms:

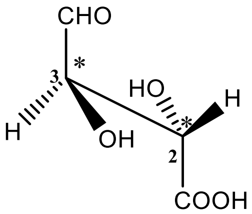


(A)

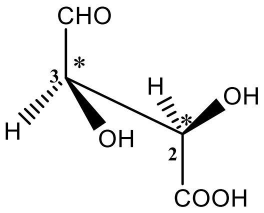


(B)

- Representation according to Cram :

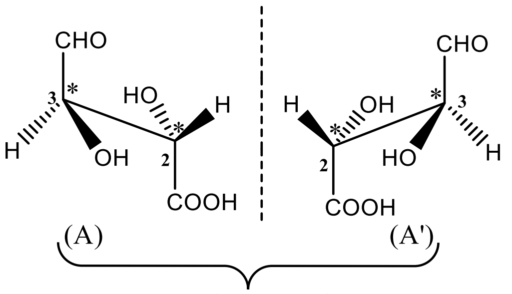


(A)



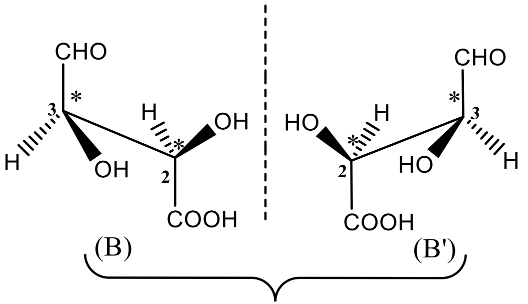
(B)

Absence of symmetry elements in (A) and (B), so we have two images of (A) and (B).



(A) (A')

enantiomer pair

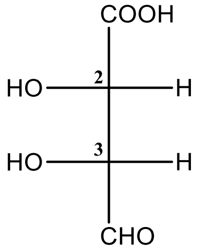


(B) (B')

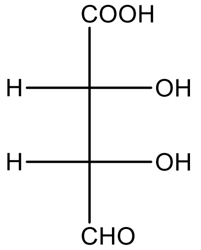
enantiomer pair

In all, we obtain two pairs of enantiomers, or four optically active stereoisoimers, so four different configurations.

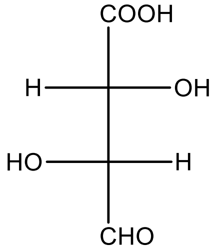
- In Fischer projection:



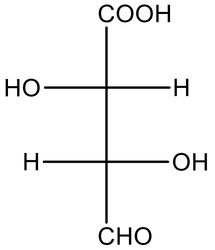
(A): 2S,3R



(A'): 2R,3S



(B): 2R,3R



(B'): 2S,3S

Conclusion :

- For a different center of symmetry $1C^*$ => $\begin{cases} \text{2stereoisomers, so 2 configurations OA} \\ \text{1pair of enantiomer} \end{cases}$

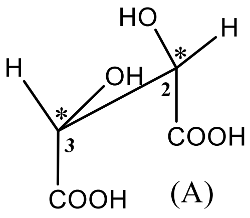
- For $2C^*$ => $\begin{cases} \text{4 stereoisomers, so 4 configurations OA} \\ \text{2 pairs of enantiomers} \end{cases}$

-For n C^* => $\begin{cases} 2^n \text{ stereoisomers, so } 2^n \text{ configurations OA} \\ \text{n pairs of enantiomers} \end{cases}$

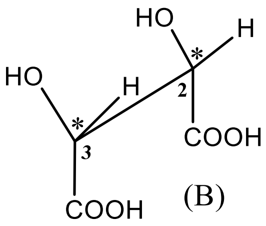
III.10.3 Molecule has two identical asymmetric centers:

Let the tartaric acid molecule: COOH – CH(HO) – CH(HO) – COOH

We distinguish two different forms.

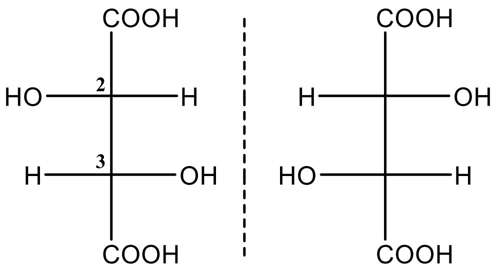


(A)



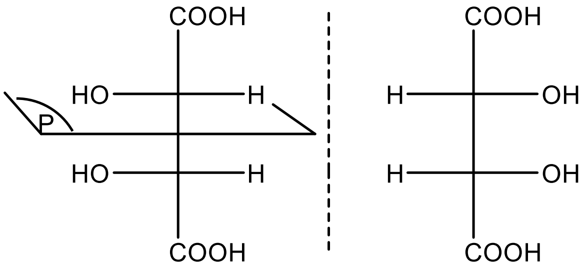
(B)

Representation of the images of (A) and (B)



(A): 2S,3S (A'): 2R,3R

enantiomer pair
(image A' is not superposable to A)



(B): 2S,3R (B'): 2R,3S

the image (B') is superposable to (B), rotated 180° on an axis C-C ⇒ (B') = (B).

The two representations B and **B'** are superimposable so they are identical. This is a single form called the ***meso form***. This is inactive on polarized light even if it contains 2 C* (it is ***achiral***) because of the presence of a plane of symmetry (the effect of the C* of R configuration on polarized light is compensated by the effect of the other C* of S configuration).

A meso compound is a stereoisomer that has a plane or center of symmetry. It is optically inactive because of the presence of a plane of symmetry that divides the molecule into two identical halves.

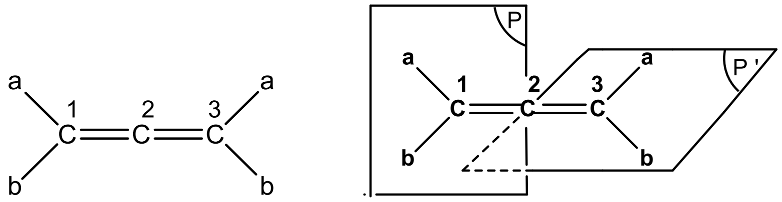
Conclusion :

For 2 centers of identical symmetry
$\begin{cases} \text{3 stereoisomers (A, A' and B) so} \\ \text{3 Configurations (A, A' OA and B no)} \\ \text{1 pair of enantiomer} \end{cases}$

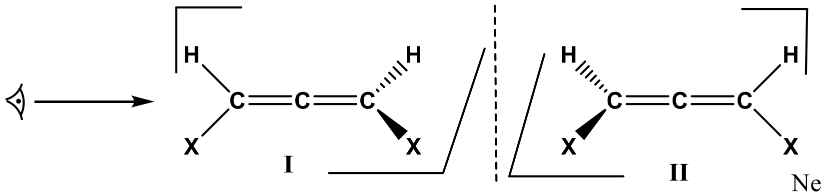
III.10.4. Optically active molecules without an asymmetric center:

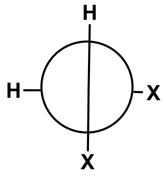
It is not mandatory to have an asymmetric carbon for there to be optical isomerism. Examples of molecules with neither a plane nor a center of symmetry and exhibiting optical isomerism.

- Allenic isomerism: Allenic molecules contain two double bonds carried by the same carbon atom. The substituents of the extreme atoms are located in perpendicular P and P' planes.



Example :





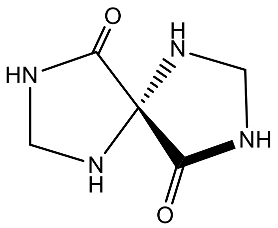
Newman projection of molecule I

Pair of two enantiomers for allenics : no asymmetrical centers

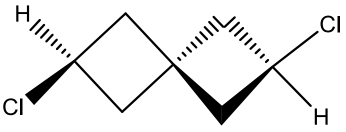
Both forms I and II are optically active

- Spiranic isomerism:

Example: the two molecules (A) and (B) do not contain an asymmetric center, but can give two optically active enantiomers.



;



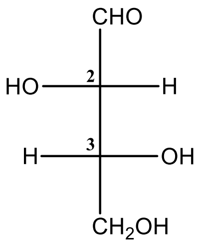
III.11 Diastereoisomerism:

These are optical stereoisomers that are not enantiomers ((are not images). Diastereoisomerism can be due to either:

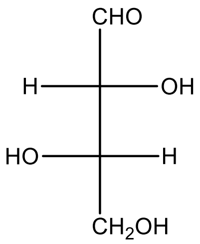
- Existence of several asymmetric carbons.
- Presence of a double bond

III.11.1 Diastereoisomerism comprising two asymmetric carbons:

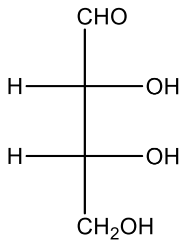
Example: the tetrose molecule CHO–CH(OH)–CH(OH)–CH_2OH



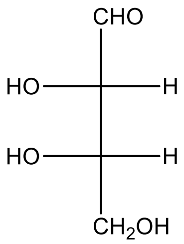
(A): 2S,3S



(B): 2R,3R



(C): 2R,3S



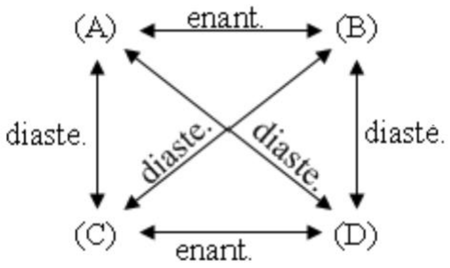
(D): 2S,3R

(A) and (B) } Are 2 pairs of enantiomers
(C) and(D)

(A) and (C) } Are 2 pairs of diastereoisomers
(A) and (D)

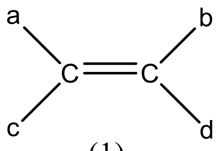
(B) and (C) } Are 2 pairs of diastereoisomers
(B) and (D)

So we have: 2 pairs of enantiomers and 4 pairs of diastereoisomers

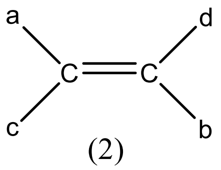


III.11.2 Diastereoisomers with a double bond:

a) Ethylene isomerism:



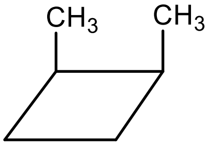
(1)



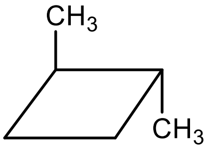
(2)

Molecules (1) and (2) are not images of each other in a mirror, therefore not enantiomers. They are diastereoisomers.

b) **Cyclic isomer**: Molecules I and II are diastereoisomers



I



II

III.12 Cis–trans or Z-E geometric isomerism:

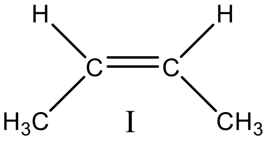
III.12.1 Geometric isomerism for alkenes:

The presence of a double bond C=C (ethylenic), C=N (imine) or N=N (diazonium) prevents the rotation of the two atoms relative to each other. Therefore, if each of these two atoms carries two different substituents, two different spatial structures that cannot be superimposed can be distinguished. These two structures are called geometric isomers.

III.12.2 Cis-trans isomerism

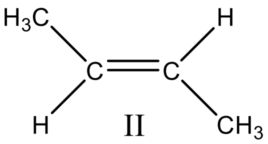
Cis-trans isomerism only applies if the substituents on the sp^2 carbons are identical.

Example 1: But-2-ene exists in two geometric isomers I and II (diastereoisomers).



I

Cis configuration



II

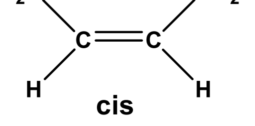
Trans configuration

The trans configuration is more stable than cis

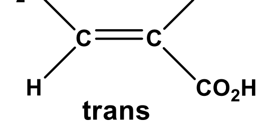
- Structure I: in which the 2 $-CH_3$ groups are on the same side of C=C. the configuration is Cis.
- Structure II: in which the 2 $-CH_3$ groups are on either side of C=C. the configuration is Trans.

Finally, due to the eclipsed interactions between the groups in the cis position, a trans compound will generally be more stable than a cis compound.

Example 2: The compound 1,4-diacid but-2-ene $HO_2C-CH=CH-CO_2H$, has two geometric isomers.

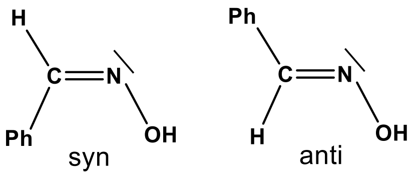


cis

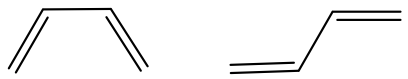


trans

Example 3: geometric isomerism in oximes and dienes.


syn anti

oximes

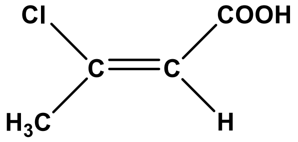

s-cis s-trans

diènes

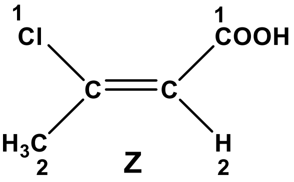
The of n free doublet of nitrogen plays the role of a substituent and is always classified last.

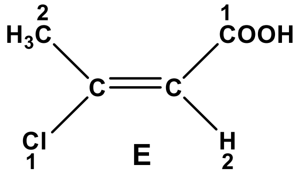
III.12.3 Z-E Isomerism:

The previous nomenclatures may present certain ambiguities as on the molecule below:



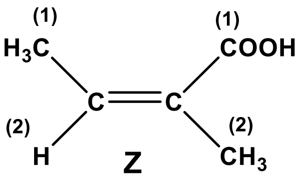
To remove this indetermination we define a new nomenclature Z and E. For this the substituents linked to each of the sp^2 carbons are numbered separately according to the rules of priorities of Cahn, Ingold and Prelog seen previously. The following two cases can then arise:



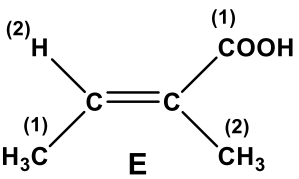


If the two priority groups are in the same half-plane limited by the double bond the diastereoisomer will be called **Z** (*Zusammen*), otherwise it will be called **E** (*Entgegen*).

Another example: 2-methylbut-2-enoic acid



(Z)-2-methylbut-2-enoic acid



(E)-2-methylbut-2-enoic acid

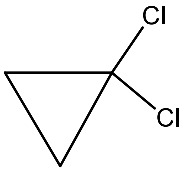
III.13 Cis-trans geometric isomerism for cycloalkanes:

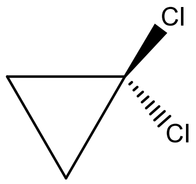
Cis-trans diastereoisomerism is used in cyclic compounds that carry two identical R substituents. It is based on the relative position of the two substituents:

- If the two substituents are on the same side of a plane defined by the cycle; this is the **"Cis"** isomer.
- If the two substituents are on either side of the cycle plane; this is the **"Trans"** isomer.

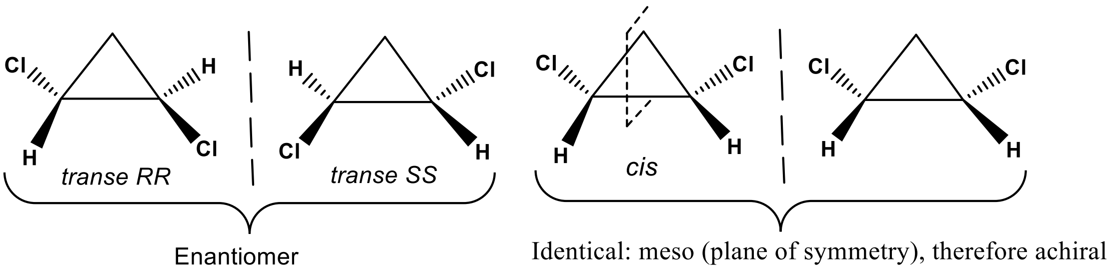
III.13.1 Case of dichlorocyclopropane:

Example 1: 1,1-dichlorocyclopropane. This compound has neither optical isomer nor geometric isomer so it exists in a single stereoisomeric form:





Example 2: 1,2-dichlorocyclopropane. The chlorines can be on either side of the cycle plane, we will then have a trans compound or on the same side we will say that we have a cis compound.



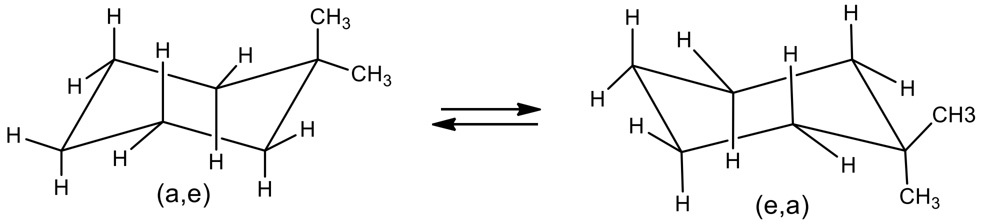
The *cis* compound, which is actually a *meso* compound, has a plane of symmetry; it is therefore optically inactive. On the other hand, the trans compound, which does not have any plane of symmetry, is optically active and can split into its two enantiomers RR and SS.

So this molecule has two types of isomerism:

- Geometric isomerism: cis and trans
- and Optical isomerism: 2 identical C*, so we will have 3 stereoisomers at most.

III.13.2 Case of dimethylcyclohexane:

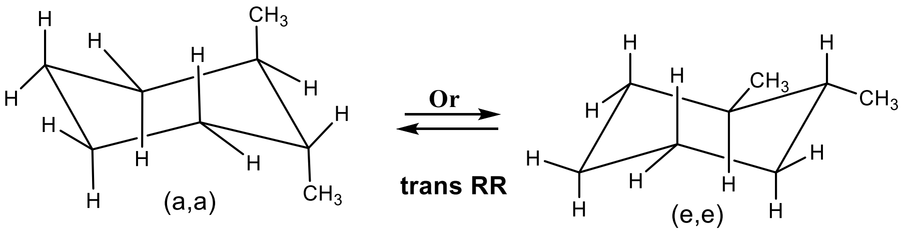
Example 1: 1,1-Dimethylcyclohexane, No optical or geometric isomerism.

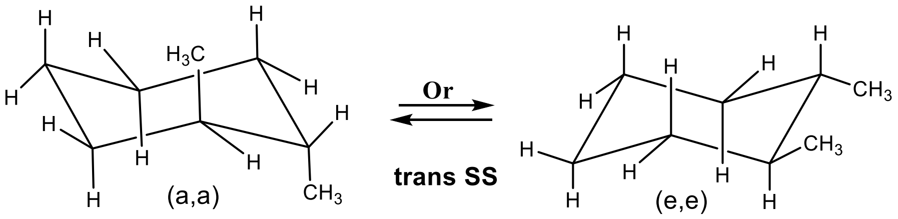


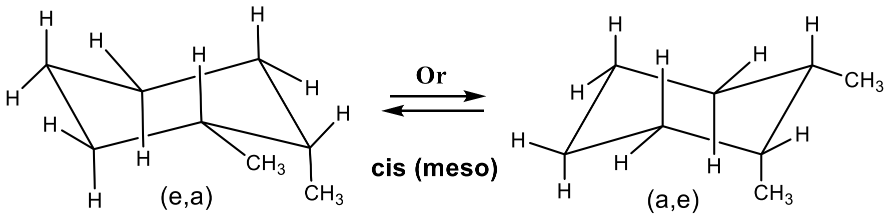
Example 2: 1,2-dimethylcyclohexane. This compound has optical isomerism and exists as two geometric isomers *cis* and *trans*.

- Trans will be axial-axial or equatorial-equatorial
- and cis axial-equatorial or equatorial-axial.

Each has two asymmetric carbons and only the trans is optically active. Cis 1,2-dimethylcyclohexane is a meso, it is optically inactive on polarized light.





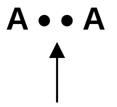


Chapter IV: Electronic Effects

(Inductive Effect and Mesomeric Effect)

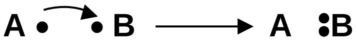
IV.1 Polarization of sigma bonds σ:

The distribution of a covalent bond of two atoms is symmetrical if the two atoms are identical.

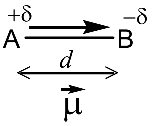


The electronic doublet in the middle
of the bond

on the other hand, if two bonded atoms are different, the more electronegative one attracts the doublet towards it.

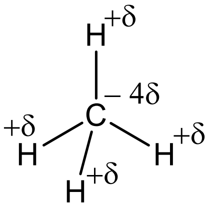


This electronic displacement causes a load (– δ) on B and (+ δ) on A with | δ | < | e |. So the link A – B is polarized. and dipole moment **μ = δ . d**



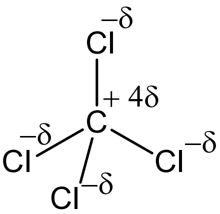
Exp 1 : CH_4

χ (C) > χ (H) ⇒ The 4 bond C–H are polarized



Exp 1 : CCl_4

χ (Cl) > χ (C) ⇒ The 4 bonds C–Cl are polarized



Remark:

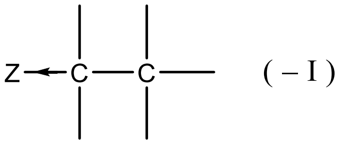
If | δ | = | e | ⇒ one ionic bond

IV.2 Inductive effect:

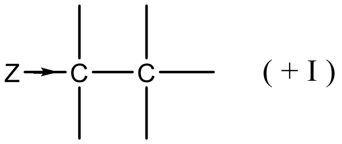
IV.2.1 Definition:

Inductive effects are atoms or groups of atoms that cause the displacement of σ electrons in a covalent bond. There are two types of inductive effect:

- The attractor inductive effect (-I): which attracts the electrons of the carbon skeleton towards it.



- The donor inductive effect (+I): which gives electrons to the carbon skeleton.



IV.2.2 Classification of inductive effects:

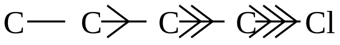
- Decreasing attractor inductive effect (-I)

Z= $NO_2 > SO_3H > F > Cl > Br > I > OH > OCH_3 > NH_2 > NHR > H$

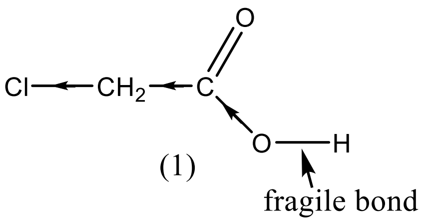
- Increasing donor inductive effect (+I)

Z= $H < -CH_3 < -C_2H_5 < -CH(CH_3)_2 < -C(CH_3)_3 < -C(C_2H_5)_3 < MgX < Na$

∗ The inductive effect weakens rapidly after transmission to two or three carbon atoms. It depends on the nature of the atom or group of atoms exerting on the carbon chain.

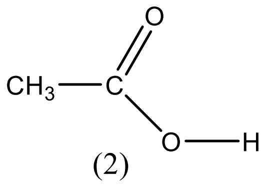


∗ The inductive effect decreases the bonding forces. For example:



(1)

2-chloroacetic acid



(2)

acétic acid acétique

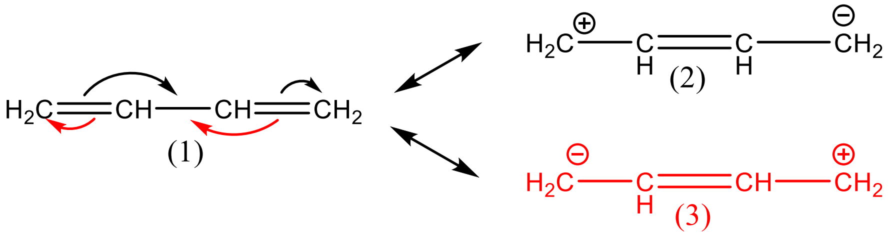
The O-H bond is more fragile in acid (1) than in acid (2) because of the inductive attractor effect of the chlorine atom (Cl).

So, the monochloroacetic aid is more acidic than the acetic acid.

IV.3 Mesomeria (resonance):

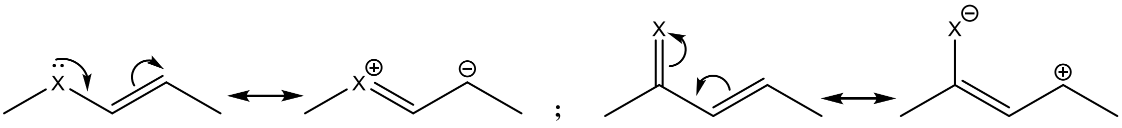
In some compounds, the real formula is difficult to represent because of the electron delocalization phenomenon. For example:

The molecule of buta-1,3-diene can be formulated by the representations:



The actual molecule of 1,3-butadiene is neither under formula (1), nor under formula (2) nor under formula (3), but a combination of the three. This combination is called ***resonance hybrid.*** Each of these formulas is called limit form, or mesomeric form or resonance form.

This delocalization phenomenon can also apply between the π electrons and free doublet electrons of an atom. For example:



X = O, N, S

Note:

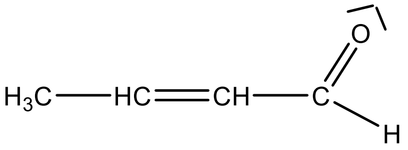
For a given compound, the greater the number of limit formulas, the greater the stability of that compound.

IV.3.1 Mesomeric Effect:

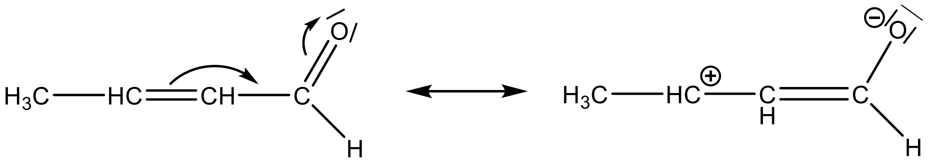
The mesomeric effect originates from the possibility of delocalization of π electrons or n electrons (free doublets).

Our aim is to distinguish attractor and donor groups by mesomeric effect.

Example 1: but-2-en-1-al

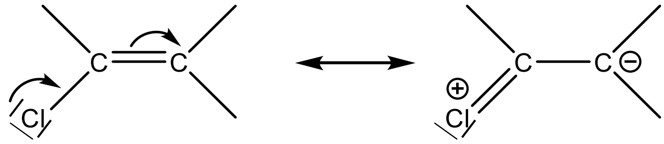


The presence of electronegative oxygen allows polarization of the ethylenic double bond.



The aldehyde group attached to the rest of the unsaturated carbon chain attracts the π electrons by mesomeric effect. It is said to exert an acceptor mesomeric effect (-M).

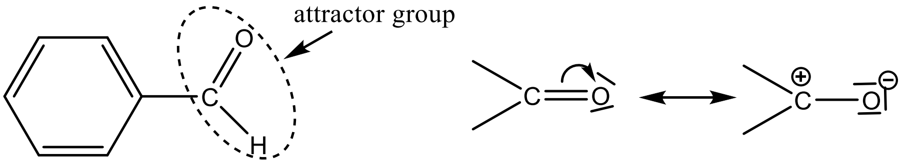
Similarly, a halogen atom attached to an ethylenic carbon can donate electrons (those of the free pairs) to the carbon skeleton.



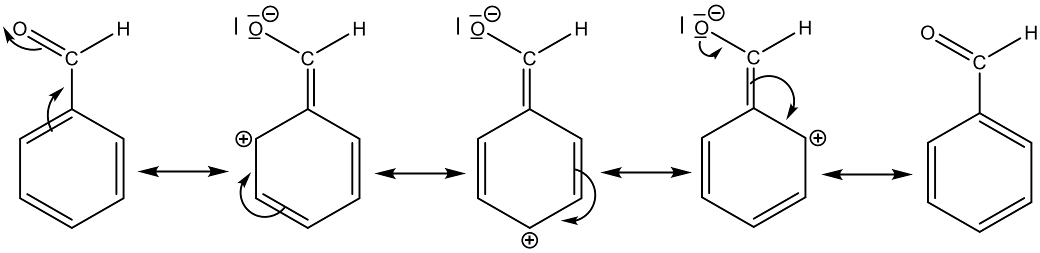
Chlorine plays the role of donor by mesomeric effect which is noted as the donor mesomeric effect (+M).

The mesomeric effect also occurs in benzene molecules.

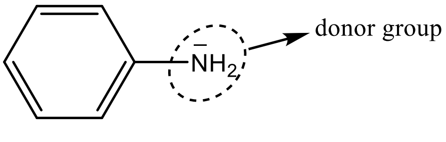
Example 1: benzaldehyde



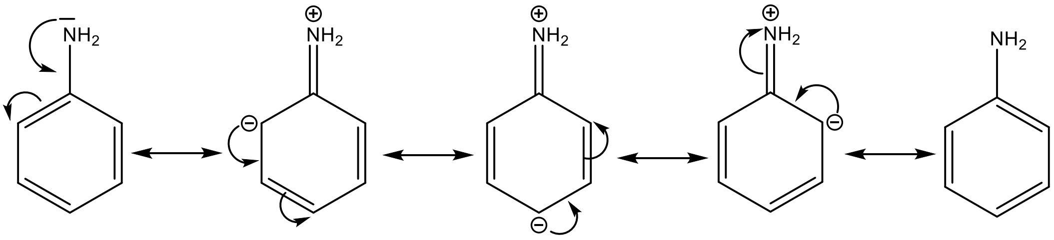
The limit formulas of benzaldehyde are:



Exemple 2 : aniline



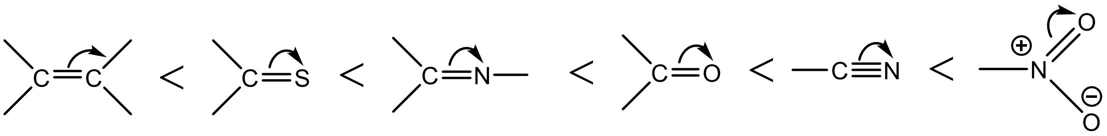
Limit formulas:



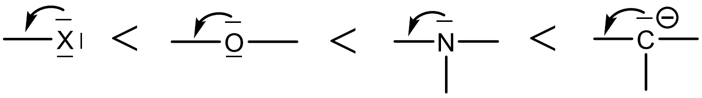
IV.3.2 Classification of mesomere effects:

As for the inductive effect, we will classify the substituents with an attractor mesomeric effect (-M) and a donor effect (+M).

- Attractor mesomeric effect (-M): Increasing

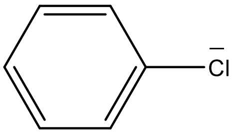


- Donor mesomeric effect (+M): Increasing



Note:

In some molecules the inductive and mesomeric effects can be competitive. For example, the molecule of monochlorobenzene.



- Chlorine is very electronegative, so chlorine attracts a σ doublet, so we have an attracting inductive effect (-I).

- But the chlorine doublet conjugates with the π doublets of the cycle, so chlorine is an electron donor, so we have a donor mesomeric effect (+M).

The high mobility of π electrons compared to σ => that the mesomeric effect (+M) prevails over the inductive effect (-I).

Generally speaking, the mesomeric effect is more powerful than the inductive effect with which it can compete.

Chapter V: Study of Reaction Mechanisms

V.1 Generalities:

Arbitrarily, the participants in the organic reaction are classified into three distinct categories:

$$\underset{\text{Substrate}}{\mathbf{A}} + \underset{\text{reagent}}{\mathbf{B}} \longrightarrow \underset{\text{reaction product}}{\mathbf{C}}$$

Substrate: it represents a complex organic compound that is the object of the attack of the reagent.

Reagent: it represents a simple organic compound or an inorganic compound, used to cause specific changes in the substrate.

Reaction product: we distinguish

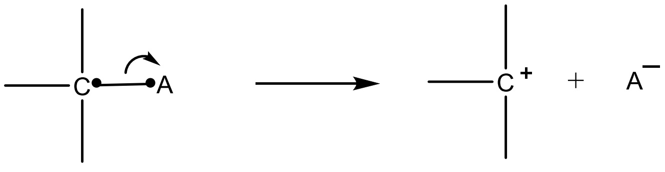
- reaction intermediate: which represents a very reactive chemical species and therefore of very short life and which is consumed during a later stage.
- the final product: which represents the final organic compound.

V.2 Reaction intermediate:

In most chemical reactions, the starting molecules are transformed into reaction intermediates, before giving the reaction products. Among the main reaction intermediate there are: carbocations, carbanions, carbon radicals.

V.2.1 Carbocations: are cations of the carbon atom, obtained by heterolytic breaking of a chemical bond.

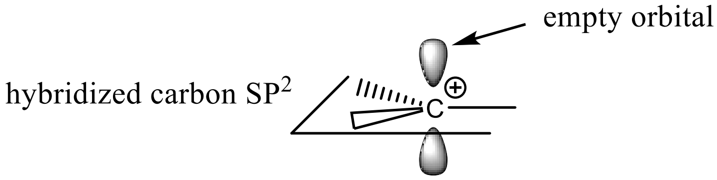
In a heterolytic break, the two electrons of the chemical bond are carried away by the more electronegative atom giving rise to two ions.

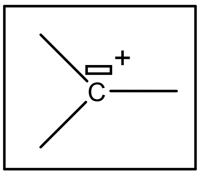


$\chi_{(A)} \rangle \chi_{(C)}$

Carbocation

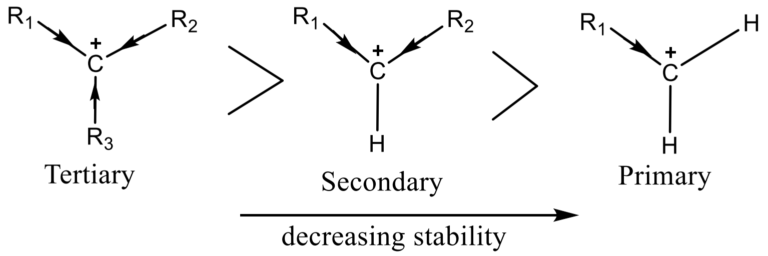
- The carbocation geometry is triangular plane, AX_3.





Carbocation structure

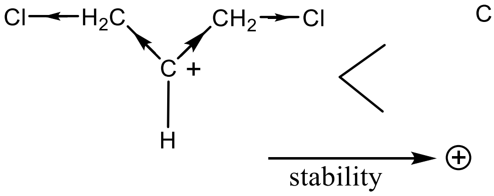
- The stability of a carbocation increases when its charge is distributed over a greater number of atoms. Therefore a tertiary carbocation is more stable than a secondary carbocation which is itself more stable than a primary carbocation by donor inductive effects.



R: donor alkyl radical

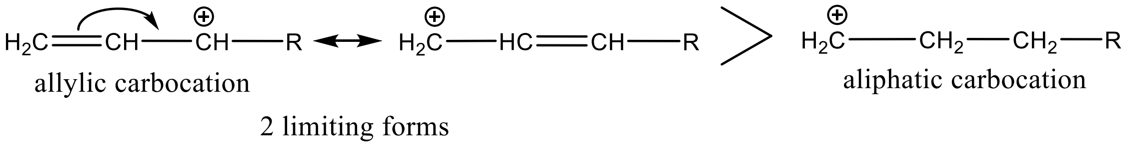
- Inductive attractor substituents destabilize the carbocation by increasing its positive charge.

Example :



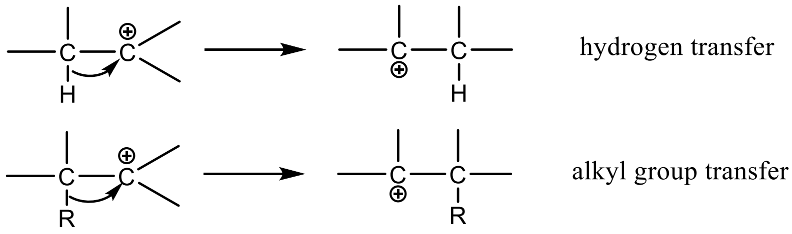
- The mesomeric effect can stabilize the carbocation.

Example: an allylic carbocation is much more stable than an aliphatic carbocation with the same carbon skeleton.

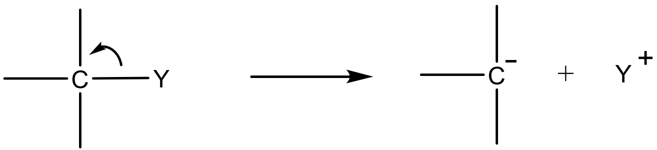


the more the number of limiting formulas increases the greater the stability of the compound increase

- It happens that carbocations evolve towards more stable carbocations by rearranging themselves:

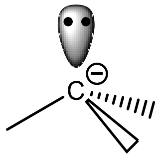


V.2.2 Carbanion: are anions of the carbon atom, obtained by heterolytic breaking of a chemical bond.



the carbon atom is more electronegative Carbanion

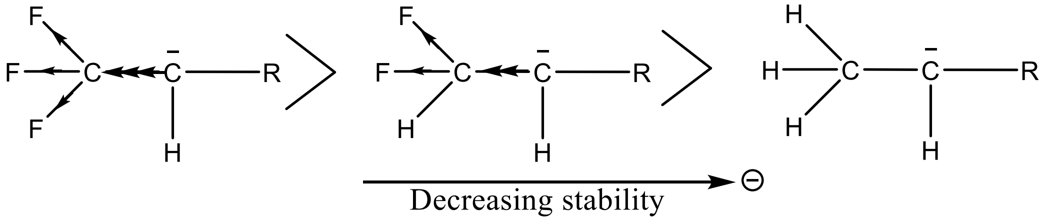
- The geometry of carbanion is pyramidal with a triangular base, AX_3E.



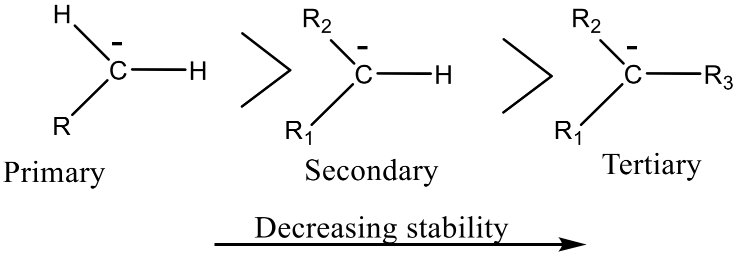
Carbon is hybridized SP^3

Carbanion structure

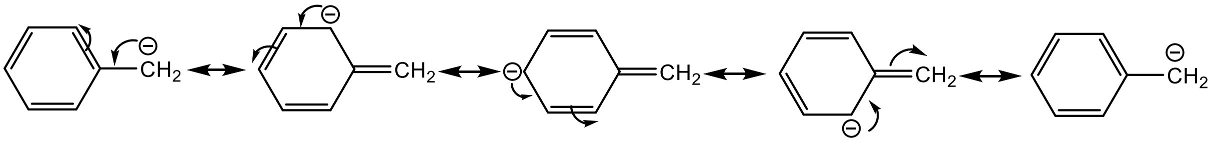
- Any substituent with inductive attractor effects decreases the charge of the carbanion and stabilizes it.



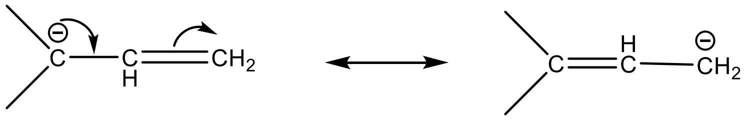
- On the other hand, any donor group destabilizes the carbanion by increasing its load.



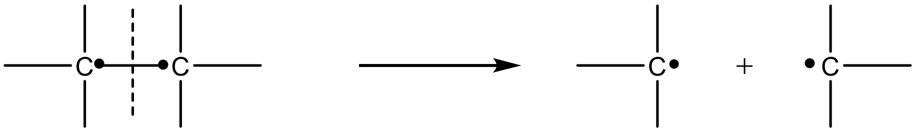
- As it can be stabilized by conjugation effect (mesomer).



similarly:



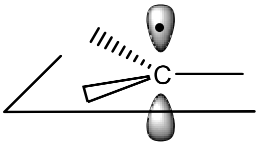
V.2.3 Carboradicals (or Carbon Radicals): Carbon radicals are the result of the symmetrical homolytic breaking of a chemical bond.



Carbon radical

Therefore, carboradicals are alkyl radicals, with the formula $RR_1R_2C^•$ and the central carbon atom carries a single electron.

- the geometry of the carbon radical can be triangular planar (SP^2) or pyramidal with a triangular base (SP^3) depending on the formation conditions.



Structure of carboradical (SP^2)

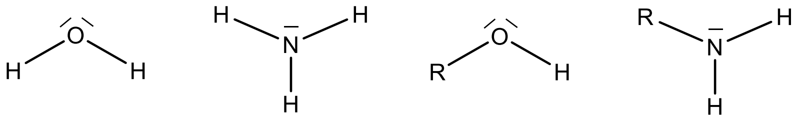
- the stability of carbon radicals varies similarly to that of cations.

V.3 Nucleophilic and electrophilic reagents:

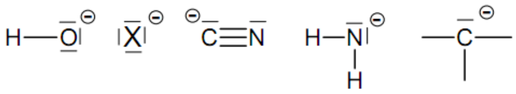
- A nucleophile (Nu) is an electron-rich chemical entity capable of donating a pair of electrons (free or bonding) to its reaction partner.

Nucleophiles can be:

Neutral molecules, which have at least one free doublet such as:



Anions such as:



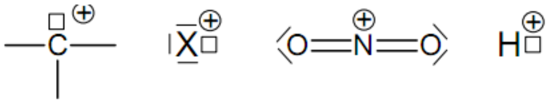
- An electrophile (E) is an electron-poor chemical entity capable of accepting a pair of electrons from its reaction partner.

Electrophiles can be:

- Lewis acid, molecules whose central atom has an electronic gap such as

□$AlCl_3$, □BF_3, □$MgCl_2$, □$ZnCl_2$ …

- Cations such as



V.4 Role of solvent in chemical reactions:

The solvent is a non-reactive liquid. On the one hand, it allow the dissolution of the different reactants and products formed. On the other hand, it can promote or inhibit certain reactions by solvating the reactants or products. There are two classes of solvents:

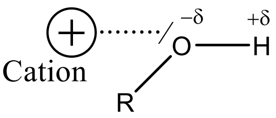
- Non-polar solvents:

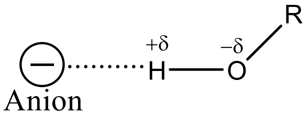
These solvents are characterized by a zero dipole moment. For example: Benzene (C_6H_6), toluene (C_6H_6— CH_3), carbon tetrachloride (CCl_4), and generally hydrocarbons such as: hexane, cyclohexane…

- Polar solvents: they are divided into two groups

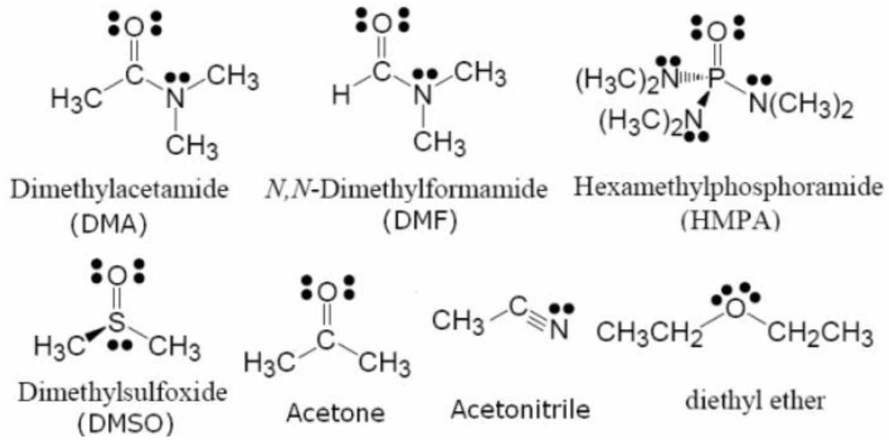
- Polar protic solvents: they have in particular a polar bond in their structure such as: O-H, H-N, H-S… wich results from a mobile hydrogen bonded to a heteroatom (O, N, S….). Protic solvent molecules can form hydrogen bonds.

Example of protic solvents: water H-O-H, alcohols (R-O-H), … these solvents solvate anions and cations





Polar aprotic solvents: they contain atoms with lone pairs of electrons but do not have mobile hydrogen. The molecules of aprotic solvents can not form hydrogen bonds. These solvents solvate cations.



V.5 Classification of organic reactions:

Chemical reactions can be classified into four groups

V.5.1 Substitution reaction:

$$R-X \quad + \quad Z \longrightarrow R-Z \quad + \quad X$$

Replacement of an atom or group of atoms by an atom or group of atoms.

Example:

$$H_3C—H + Cl—Cl \longrightarrow H_3C—Cl + HCl$$

V.5.2 Addition reaction:

$$A\overset{\pi}{=}B + X_2 \longrightarrow X\overset{\sigma}{—}A—B\overset{\sigma}{—}X$$

In general this type of reaction is carried out on unsaturated molecules. A π bond is attacked with the formation of two σ bonds.

Example :

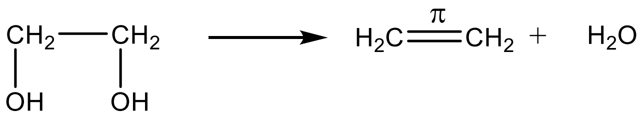
$$H_2C\overset{\pi}{=}CH_2 + Cl_2 \longrightarrow Cl\overset{\sigma}{—}CH_2—CH_2\overset{\sigma}{—}Cl$$

V.5.3 Elimination reaction

$$X—A—B—Y \longrightarrow A\overset{\pi}{=}B + XY$$

This is the reverse of an addition reaction. In the elimination reaction, two groups are removed from adjacent carbons and replaced by a π bond.

Example :

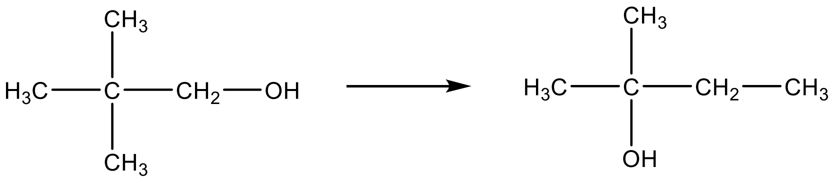


$$\underset{OH}{CH_2}—\underset{OH}{CH_2} \longrightarrow H_2C\overset{\pi}{=}CH_2 + H_2O$$

V.5.4 Rearrangement reaction (or transposition):

Is the migration of an atom or a group of atoms within the same molecule.

Example :

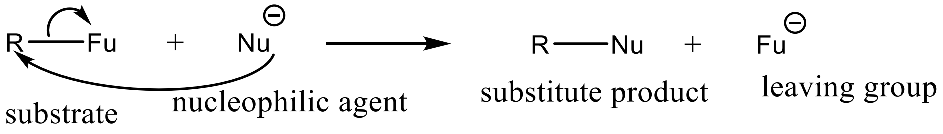


$$H_3C—\overset{CH_3}{\underset{CH_3}{C}}—CH_2—OH \longrightarrow H_3C—\overset{CH_3}{\underset{OH}{C}}—CH_2—CH_3$$

V.6 Substitution reaction

V.6.1 Nucleophilic substitution SN

In a SN reaction on saturated carbon, the nucleophilic agent Nu$^-$, replaces an atom/or group of atoms Fu, attached to the saturated carbon atom.



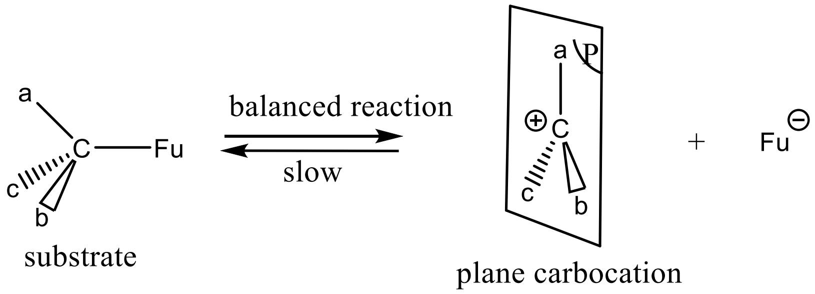
V.6.1.1 Reaction mechanism:

The kinetic and stereochemical study of nucleophilic substituents leads to the consideration of two mechanisms

a) SN_1 mechanism:

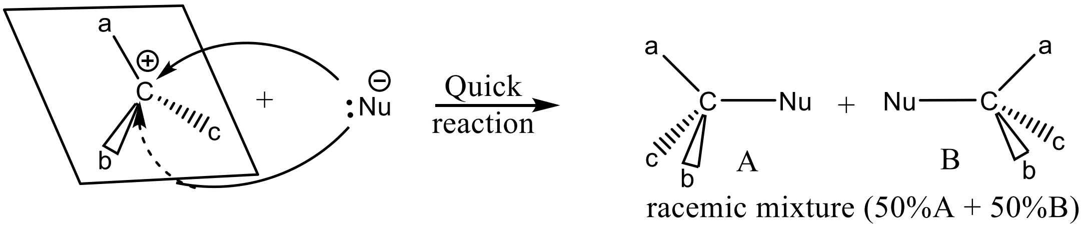
The reaction is divided into two stages:

- **1^{st} step :** formation of an intermediate carbocation by heterolytic cleavage of the C–Fu bond.



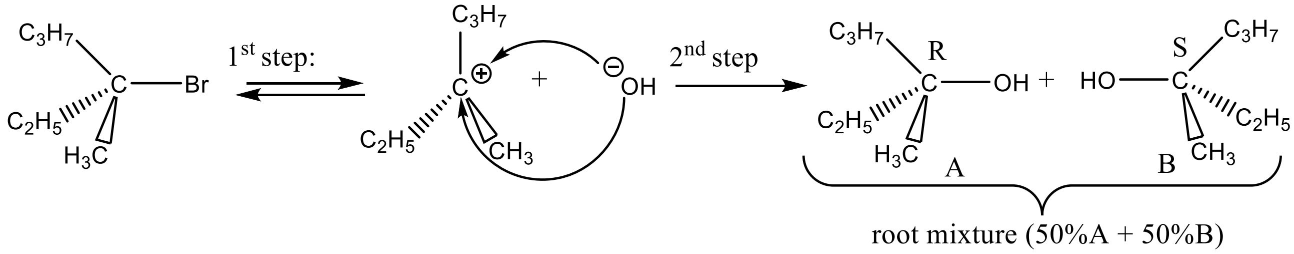
The speed of the reaction is given by the relation v = k [substrate]

- **2^{nd} step:** the attack of the nucleophile Nu^- on the carbocation

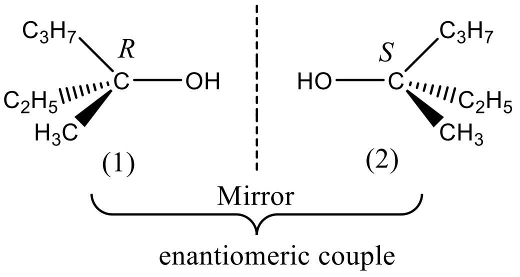


Example : reaction $C_3H_7–C(CH_3)Br–C_2H_5$ + OH^- ⟶ ?

SN_1mechanism :



The two molecules A and B are mirror images of each other. Therefore, they are enantiomers.

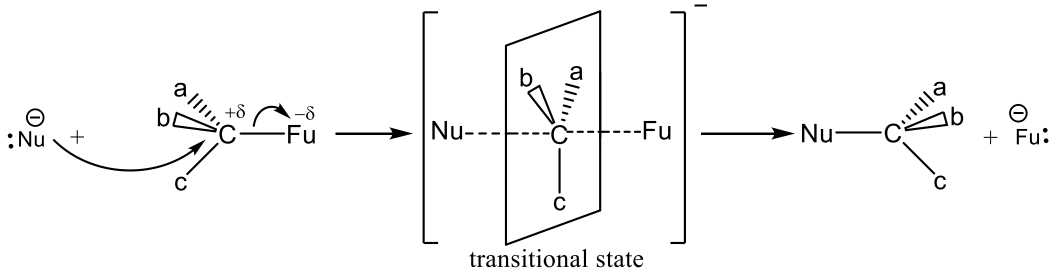


The SN1 reaction shows that:

- the carbocation is planar and the nucleophile can be attacked from either side of the plane.
- the product obtained is an inactive racemic mixture of 2 enantiomers.
- the reaction rate is of the form: v = k [substrate] (the [Nu^-] has no influence on its rate) and the kinetics is of order 1

b) SN_2 Mechanism:

The SN_2 reaction is carried out in a single step

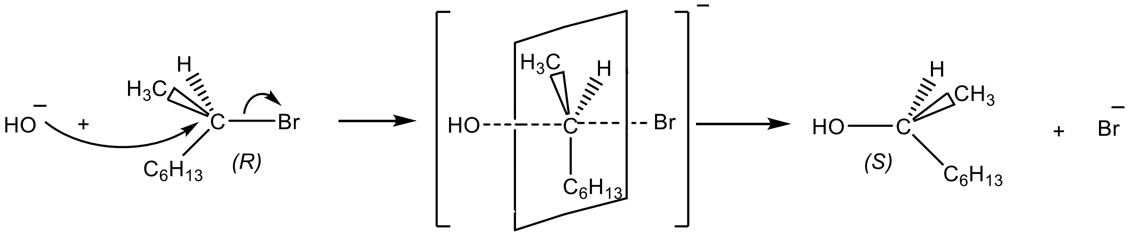


.

The attack by the nucleophile Nu– takes place on the side opposite to Fu.

The reaction rate is given by the equation v = k [substrate]x[Nu^-]

Example :



The SN_2 reaction shows that:

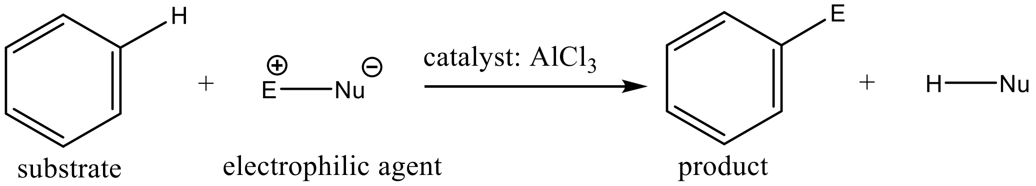
- the reaction gives a single final product
- the configuration of the asymmetric carbon is reversed
- the reaction rate is of the form: v=k[substrate][Nu^-] and the kinetics is of order 2.

V.6.1.2 Factors influencing an SN_1 and SN_2 reaction:

Mechanism	Stereochemistry of products	Kinetic	Substrate	Solvent	Reagent
SN_1	Two configurations 50%R + 50%S	v=k[substrate]	tertiary or secondary	protic	Weak nucleophile
SN_2	One configuration	v=k[substrate]x[reagent]	primary or secondary	Polar aprotic	Good nucleophile

V.6.2 Electrophilic Substitution (ES) :

This type of reaction mainly concerns aromatic compounds. We will study the case of benzene.



In an electrophilic reaction, the electrophilic agent E^+ replaces a hydrogen atom in the benzene cycle.

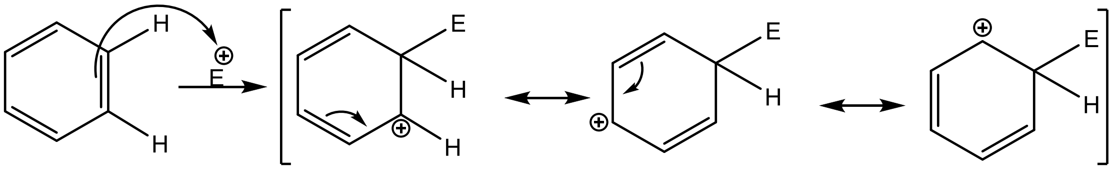
V.6.2.1 General mechanism:

We can distinguish 4 successive steps in an electrophilic substitution reaction.

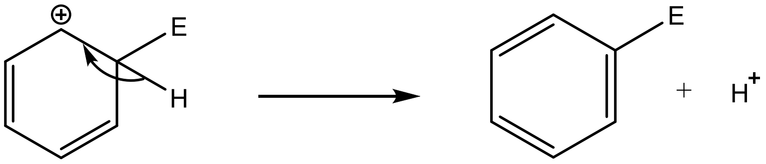
1) formation of the electrophilic reagent E+

$E{-}Nu$ + □$AlCl_3$ $\longrightarrow$ $[Nu{:}AlCl_3]^-$ + E^+

2) formation of a carbocation



3) obtaining a substitution product expulsion of a proton H+



product

4) regeneration of the catalyst

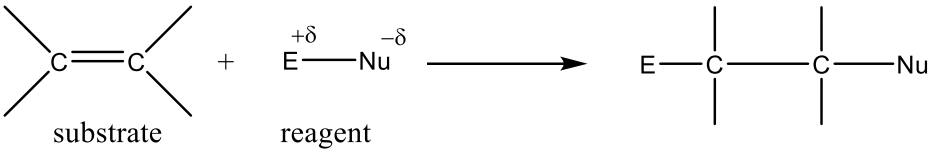
H^+ + $[Nu{:}AlCl_3]^-$ $\longrightarrow$ $H{-}Nu$ + $AlCl_3$

V.7 Addition reaction:

Addition reactions concern unsaturated compounds with multiple bonds, such as C=C; C≡C; C=O; C≡N …. (electron-rich centers) reacts as a nucleophile with an electrophilic chemical species (a cation or a molecule with an electron gap) causing the breaking of the π bond of the substrate.

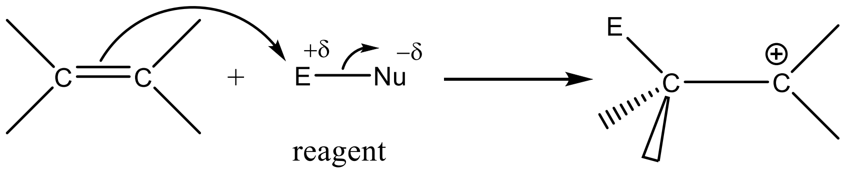
III.7.1 Electrophilic addition (AE):

The general scheme of addition reactions on an ethylenic bond C=C can be represented as follows:

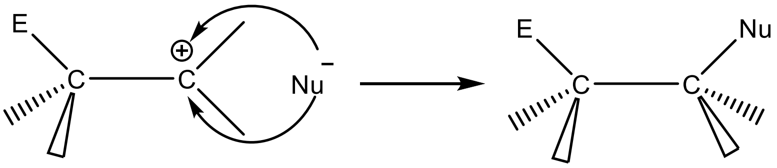


This addition reaction takes place in 2 steps:

1st slow step which corresponds to the nucleophilic attack of the alkene on the electrophilic site of the reagent E-Nu, leading to the formation of a carbocation



2nd step a fast step which corresponds to the attack of the nucleophile Nu⁻ on the carbocation.

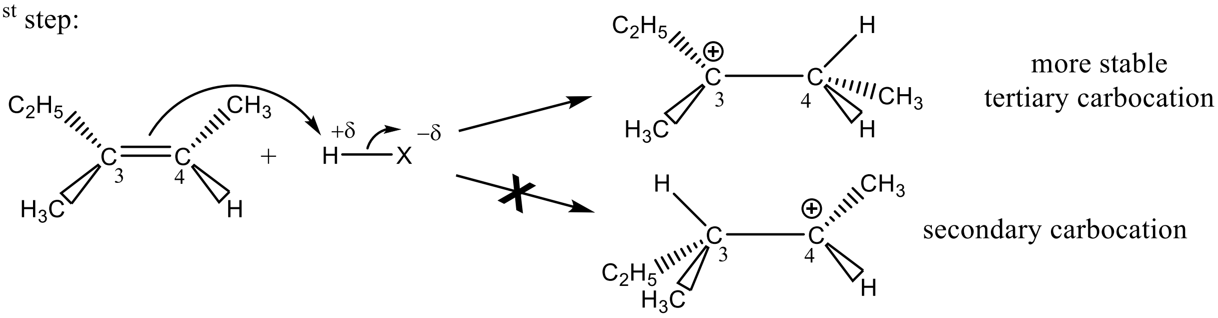


The reaction mechanism of electrophilic addition depends on the nature of the electrophile E^+

a) Addition of hydrogen halides: the electrophile E^+ is a proton H^+ (E-Nu= HX)

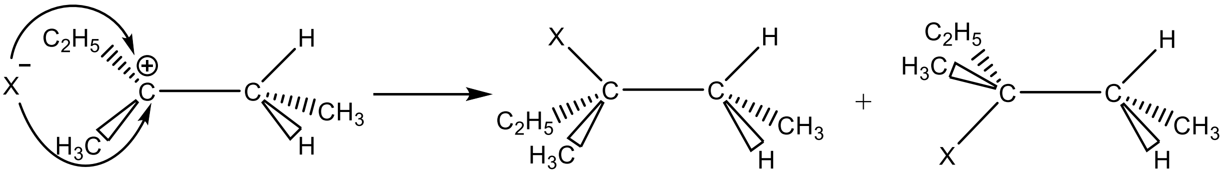
Addition mechanism:

1st step:

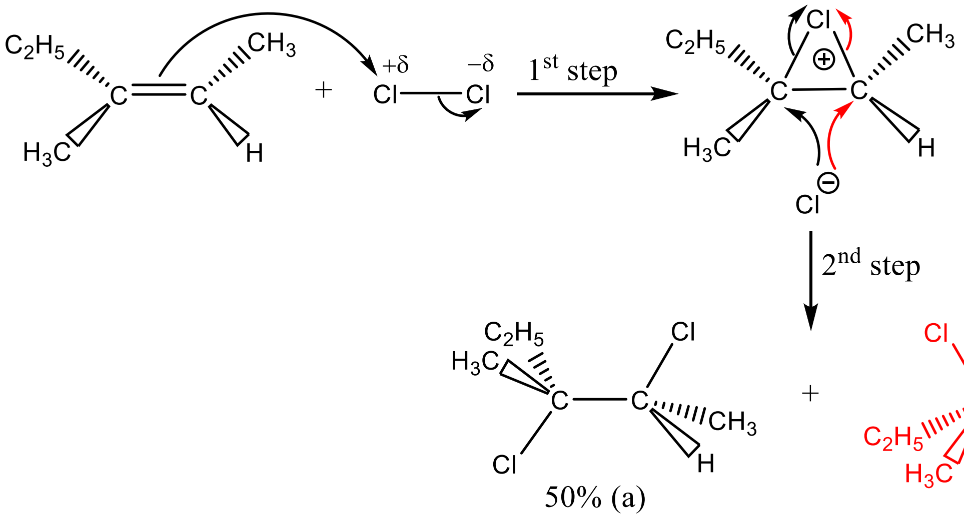


The H proton attaches to carbon 3 to give the most stable carboncation

2nd step:



b) Addition of dihalogens X_2: the electrophile E^+ is a halogen ion ($E^+ = Cl^+$, Br^+,….)

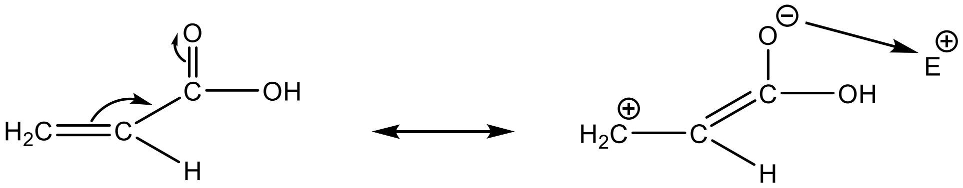


c) Addition of E^+ to a compound with mixed functions: the electrophile E^+ is any entity.

In all cases of electrophilic addition, E^+ binds to the carbon atom with the highest electron density, **Markovnikov's** rule.

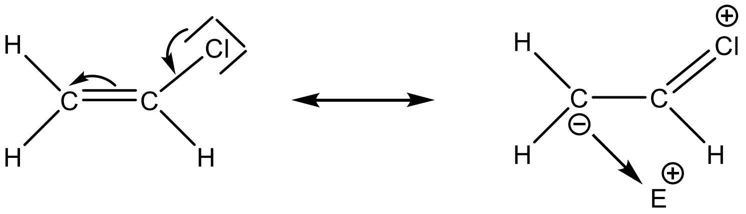
Examples:

- Addition of E^+ to the acid CH_2=CH−COOH:



mesomere effect (- M) de COOH

- Addition of E^+ to vinyl chloride CH_2=CH−Cl:

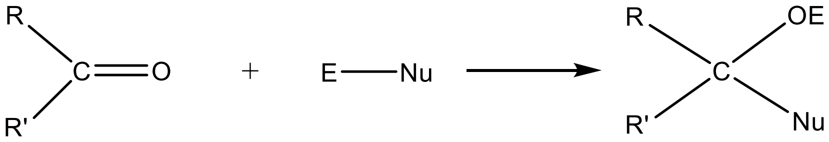


mesomere effect (+ M) de Cl

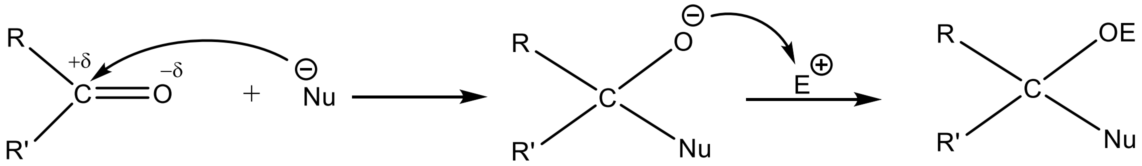
V.7.2 Nucleophilic addition (N_A):

Multiple bonded compounds, such as carbonyl compounds C=O, C=N and C≡N can undergo addition reactions.

Aldehydes and ketones can undergo nucleophilic additions, due to the strong polarization of the double bond which makes the carbon atom have a site of low electron density (electrophile site)

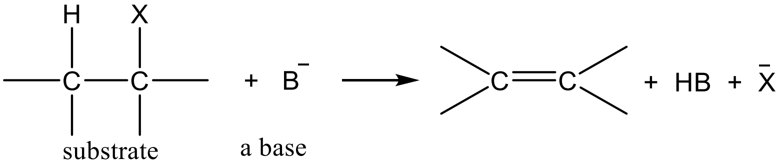


The mechanism of nucleophilic addition is as follows:



V.8 Elimination reaction:

An elimination on a saturated substrate leads to the formation of an alken, that is formation of the π-bond and elimination of two bonds.



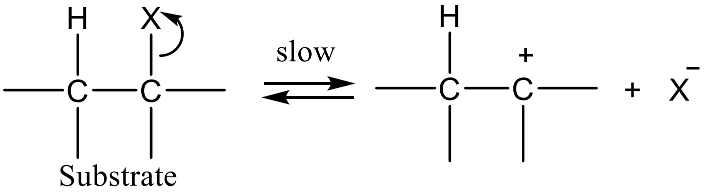
Elimination reactions are favored by an increase in temperature and the presence of a strong base such as: sodium hydroxide (Na^+, HO^-), potassium hydroxide (K^+, HO^-), alcoholate ions (Na^+, RO^-), amide ions (Na^+, NH^{2-}).

Two mechanisms can be used for this type of reaction:

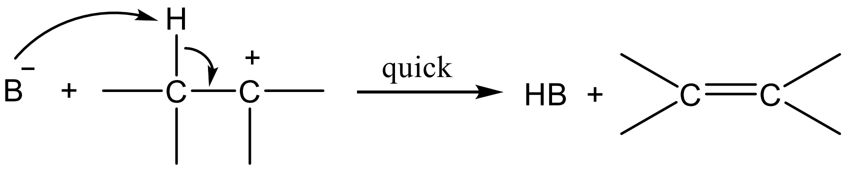
V.8.1 Mechanism E_1:

The mechanism is carried out in two stages:

1) slow formation of a carbocation under the action of an ionizing solvent

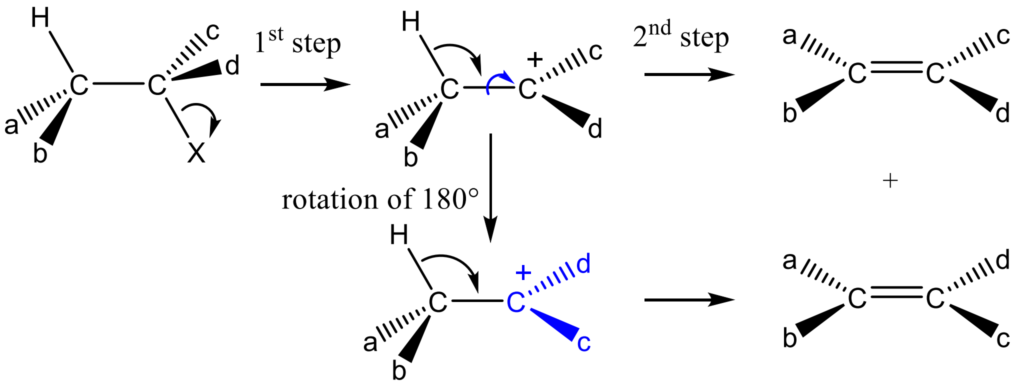


2- the attack of the carbocation by a base B^- which removes a proton H and formation of a double bond.

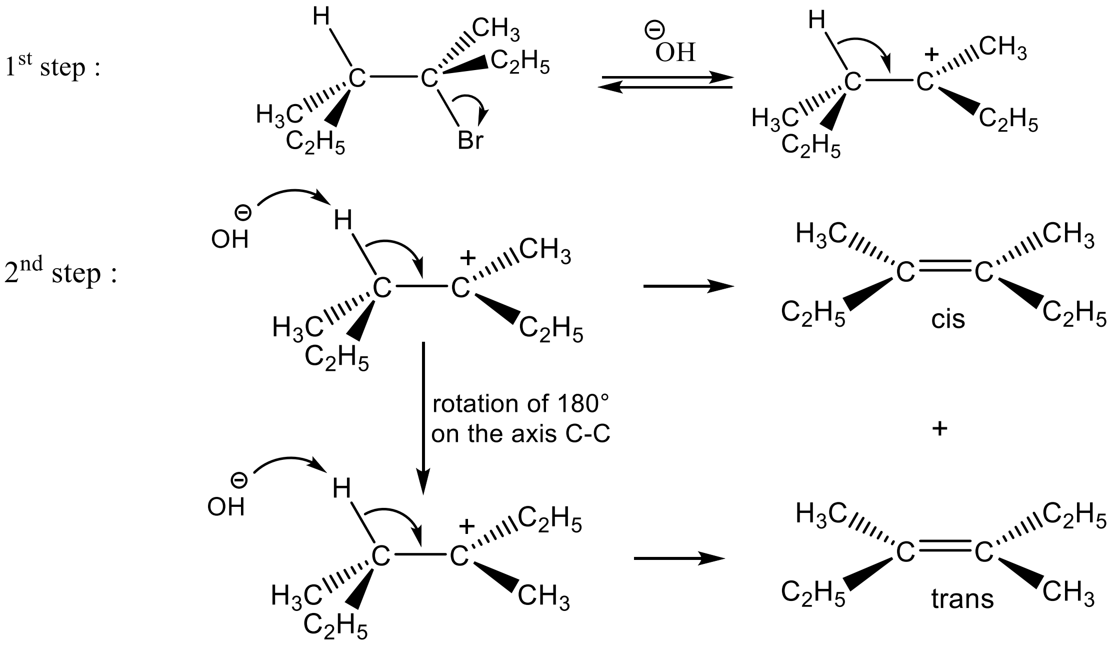


Kinetically, the elimination reaction E_1 is of order 1 and the speed v = k [substrate]

- ***Stereochemistry of the reaction:***



Example ; Reaction : 3-bromo-3,4-diméthylhexane + OH^- → ?

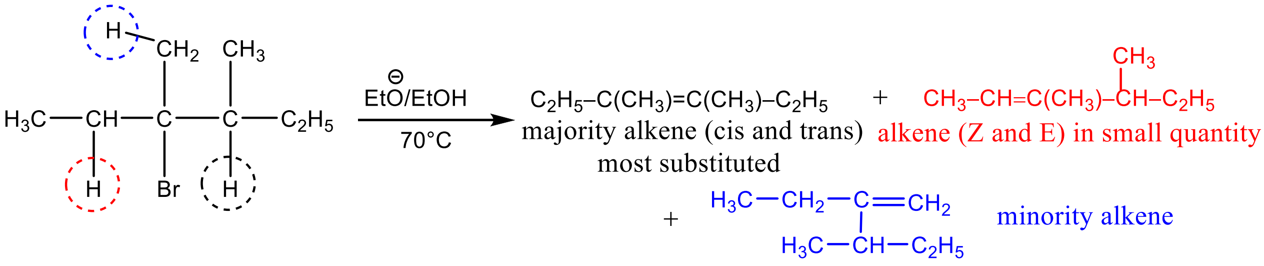


Free rotation of the C–C axis of carbocation leads to a mixture of cis and trans stereoisomers.

Note:

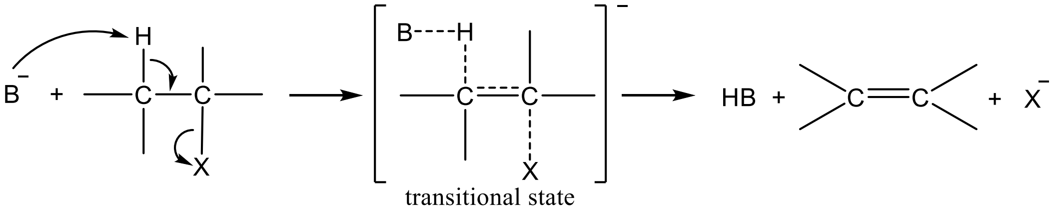
The elimination reaction E_1 can lead to a mixture of several alkenes, the most substituted is the majority, **Saytzeff** rule.

Example :



V.8.2 Mechanism E_2:

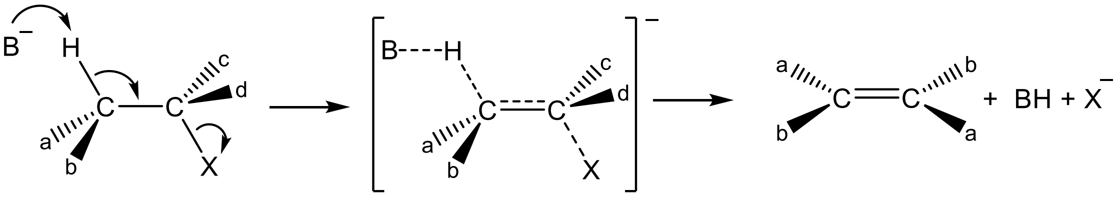
The elimination reaction E_2 is a reaction of order 2. The rate is of the form $v = k$ [sbstrate][B^-]. The mechanism is carried out in a single step:



transitional state

- Stereochemistry of the reaction:

The elimination occurs exclusively when H and X are in the same plane, in an antiparallel position. Obtaining a single alkene of configuration Z or E.



transitional state

V.8.3 Prediction of an E_1 and E_2 reaction:

In the presence of an elimination reaction, the E_1 or E_2 mechanism can be predicted.

Mechanism	Stereochemistry of products	Kinetic	substrate	reagent
E_1	Several alkenes	V=k[substrate]	Tertiary or secondary	Diluted weak base and bad nucleophile
E_2	One alkene	V=k[substrate] x[reagent]	Tertiary or secondary or primary	Strong concentrated base and bad nucleophile

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