



Content of the material:

Chapter 1: General

- I.1. Study of the carbon atom and these bonds.
- I.2. Functions and nomenclature of organic compounds: Ordinary, trivial, usual and systematic IUPAC nomenclature.

Chapter 2: Classification of organic functions

- II.1. Saturated aliphatic hydrocarbons (linear, branched),
- II.2. Alkenes (preparation, reactivity),
- II.3. Aromatic compounds (preparation, reactivity),
- II.4. Alcohols, thiols, aldehydes (preparation, reactivity), Ketones, carboxylic acids (preparation, reactivity).

Chapter 3: Notions of stereo-Isomeria

- III.1. Definition,
- III.2. Plane isomerism (definition),
- III.3. Functional isomerism,
- III.4. Positional isomerism,
- III.5. Tautomerism,
- III.6. Geometric isomerism,
- III.7. Stereochemistry: definition, representation of molecules in space,
- III.8. Configurational isomerism.

Chapter4: Electronic effects

- IV.1. Definition,
- IV.2. Chemical bond: pure covalent, polarized covalent and ionic.
- IV.3. Inductive effect: definition, Classification of inductive effects, Influence of the inductive effect on the acidity of a chemical compound, Influence of the inductive effect on the basicity of a chemical compound.
- IV.4. Mesomeric effect: definition, conjugated systems and electron delocalization. Classification of mesomeric effects, Influence of the mesomeric effect on the acidity of a chemical compound, Influence of the mesomeric effect on the basicity of an organic compound.

Chapter 5: The major reactions in organic chemistry

- V.1. Reagents and reaction intermediates;
- V.2. Classification of reactions: Addition; Substitution; Disposal; Rearrangement; Elementary rules: Markovnikov, Zaitsev;



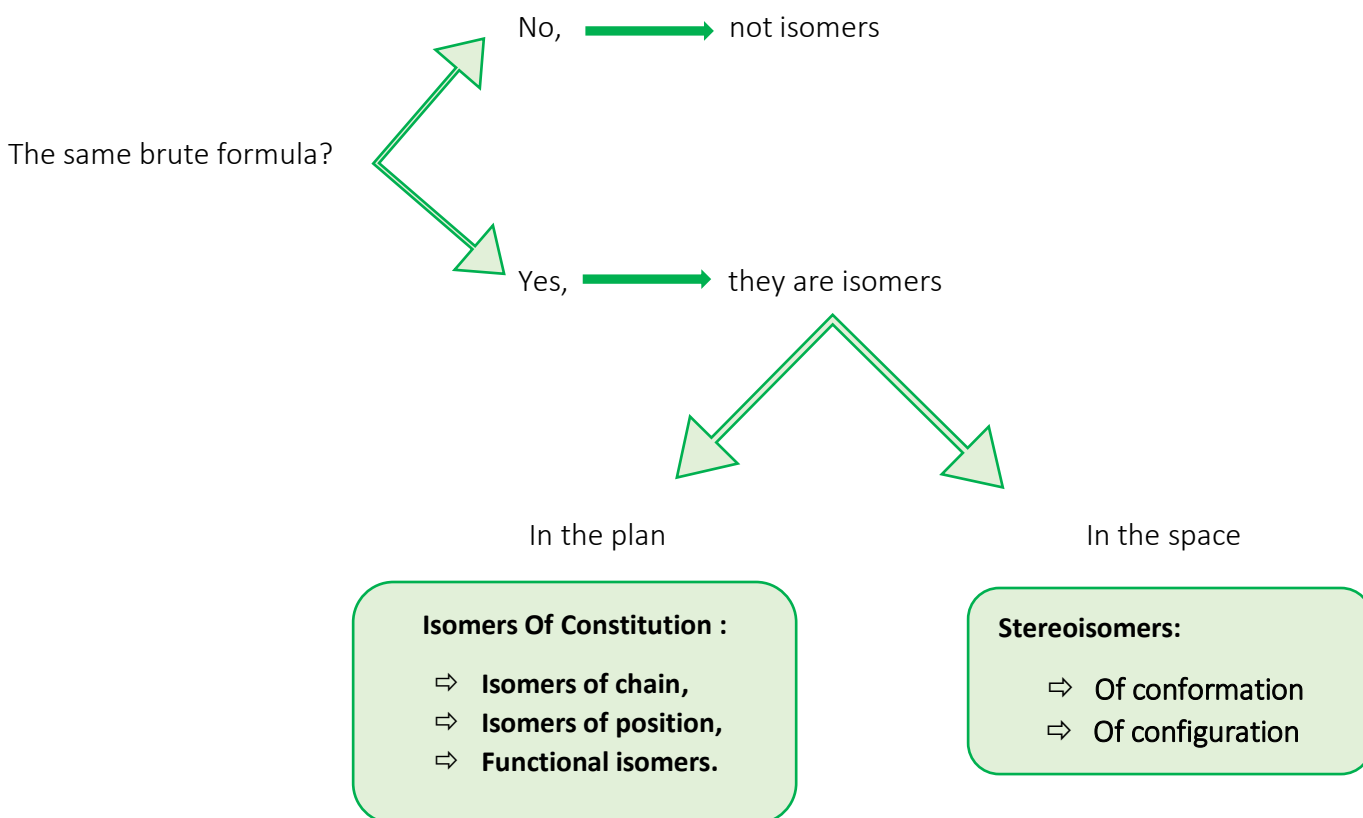
Chapter 3: Notions of stereo-Isomeria

- III.1. Definition,
- III.2. Plane isomerism,
- III.3. Functional isomerism,
- III.4. Positional isomerism,
- III.5. Tautomerism,
- III.6. Geometric isomerism,
- III.7. Stereochemistry: definition, representation of molecules in space,
- III.8. Configurational isomerism.

III.1/ Definition

Isomers are chemical species with the same chemical brute formula but which differ in the order or in the nature of the bonds or differ by the arrangement of atoms in space.

We can ask the following questions to know if the two molecules are isomers or no:





III.1. Isomers Of Constitution:

Also named “plane isomerism”.

The constitutional isomers are differentiated by the nature of the bonds which assemble the different atoms in the molecule. We distinguish for this type of isomerism: the isomers of chain (skeleton), position or function.

III.1.1. Chain isomerism:

They are isomers that differ by the carbon chain (they have identical functions and equal number).

example:

C_4H_{10} :		
$C_4H_{10}O$		

III.1.2. Positional isomerism:

The functions and the skeleton are identical, only the positions of the functions and unsaturations on the skeleton are different.

Example:

$C_4H_{10}O$		
C_4H_8		

III.1.3. Functional isomerism:

The functional isomers have the same carbon chain, but differ from each other by the nature of their function(s).

example:

C_4H_8O		
$C_4H_8O_2$		
C_4H_8		

⇒ Special case (tautomerism):



A special case of function isomerism is called "tautomerism". Two tautomers are two functional isomers in equilibrium with each other, which result from the transformation from one functional group to another by easy and rapid movement (migration) of one hydrogen atom between two atoms



III.2. Stereoisomers

Stereoisomers are isomers that differ from each other by the position of atoms groups in the space. In other word it is the study of the arrangements in space of atoms of a given structure.

There are conformational stereoisomers and configurational stereoisomers.

Note that plane representations do not specify the spatial distribution of atoms of a molecule, these for which before going further in the study of the different stereoisomerisms, it is therefore necessary to know the different modes of representation of molecules in space.

III.2.1. The different modes of representations

There are three types of representations:

a) Projective representation or "Cram" convention

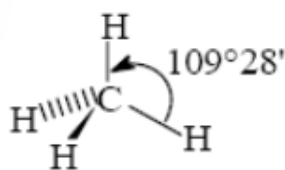
It is the most used representation in organic chemistry. Where, the connections are represented as follows:

- a band in the plane of the sheet
- a band in front of the plane
- a band behind the plane

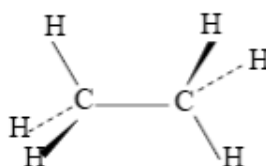
In aliphatic compounds, depending on the number of atoms in the main chain, we distinguish two cases:

- **A carbon atom:** Two bonds are in the projection plane, the others in a perpendicular plane.
- **Multiple carbon atoms:** The bonds that unite the two extreme carbons and one bond of each carbon are in the plane of the sheet (projection plane), the other connections in a perpendicular plane.

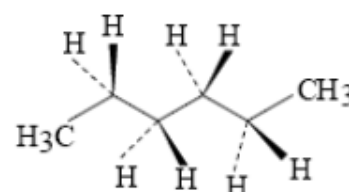
Example:



Methane



Ethane



Hexane

b) Newman's representation

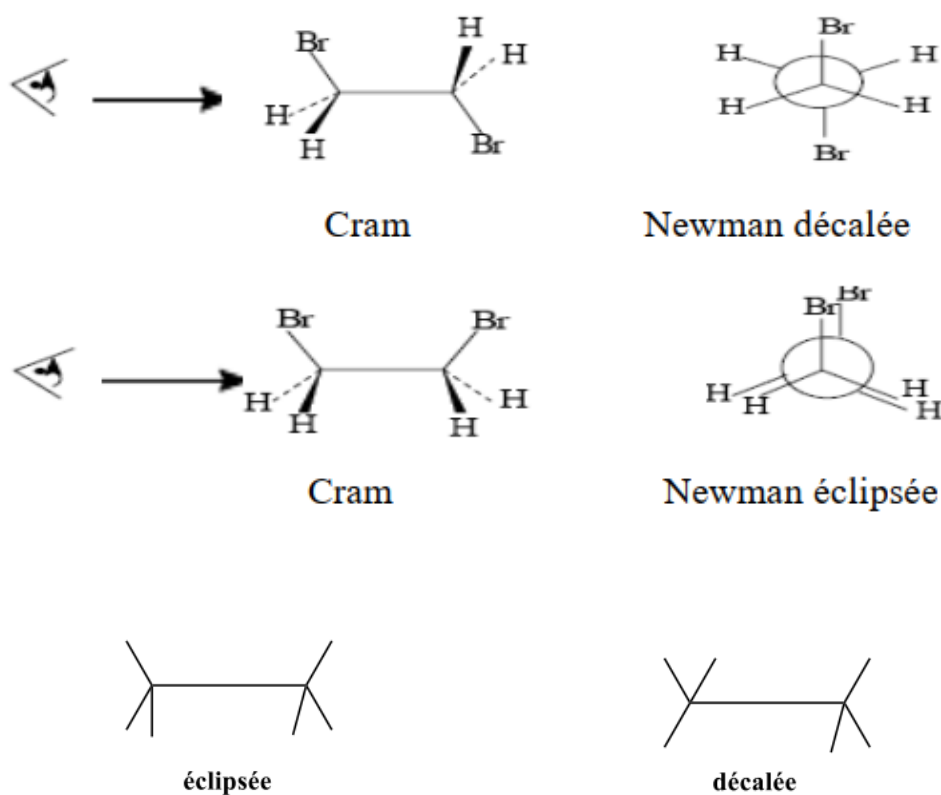


It consists of drawing what is seen by an observer when he arranges the molecule in front of it along the axis of the simple C-C bond. The bonds from the two atoms are projected onto a plane perpendicular to the axis of the bond studied:

- The bonds of the closest atom (to the observer) are represented by segments starting from the same point, forming angles of 120° .
- The second carbon (furthest from the observer), eclipsed by the first, is represented by a circle. The bonds of this atom are represented by segments stopping at the periphery of the circle.

Example: the representation of 1,2-dibromoethane

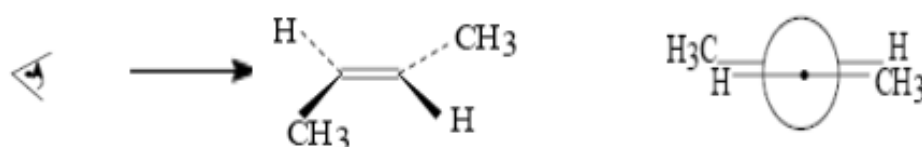
There are two representations: shifted and eclipsed



Remark 1: Generally speaking, the offset form is more stable than the eclipsed form.

Remark 2: The projection of C=C double bond is also possible. This system being planar (sp^2) the projections of the bonds of each ethylenic carbon form between them a 180° angle.

Example: but2ene

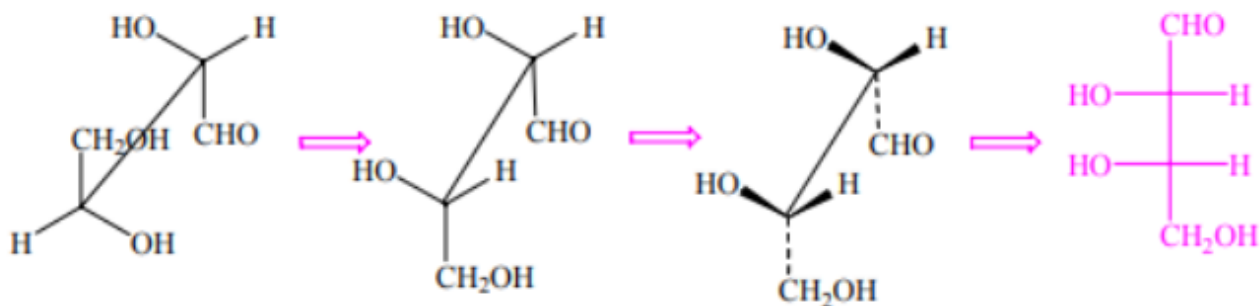
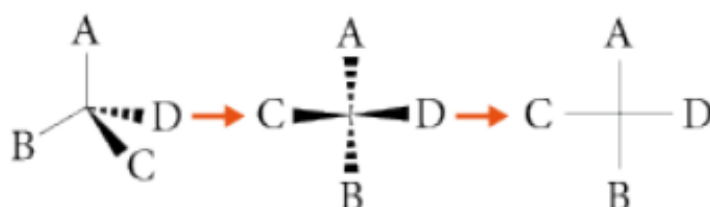


c) Fisher projection



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

- The vertical lines indicate the connections behind the plane of the figure.
- The Horizontal lines indicate the connections in front of the plane of the figure.
- The longest carbon chain is placed vertically and numbered top to bottom.



III.2.2. Conformational isomerism

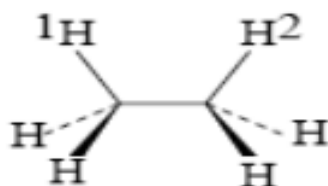
a) Definition

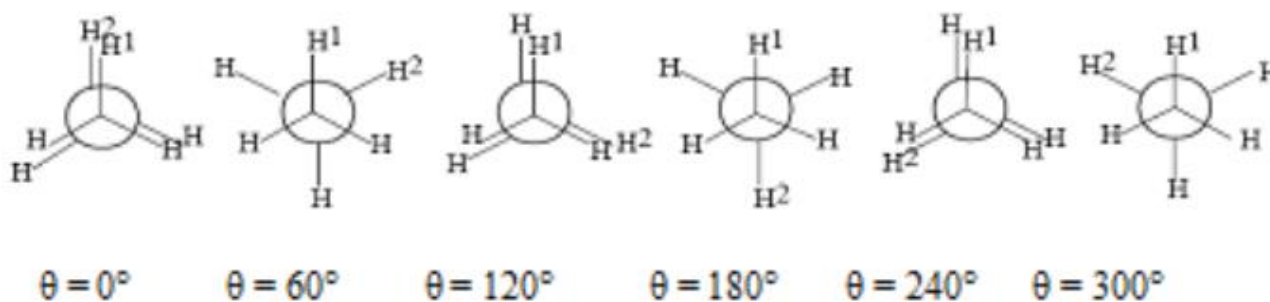
A conformation is a possible arrangement obtained by rotation around a simple bond σ . The different forms that the same molecule can take are called conformations.

The notion of conformation is due to chemical bonds which are relatively flexible, they can twist, lengthen, Angles can open or close and atoms can touch or interfere with each other.

b) Conformation of the ethane molecule ($\text{CH}_3\text{-CH}_3$)

By rotating through an angle θ one methyl group relative to the other, an infinity of conformations are possible.



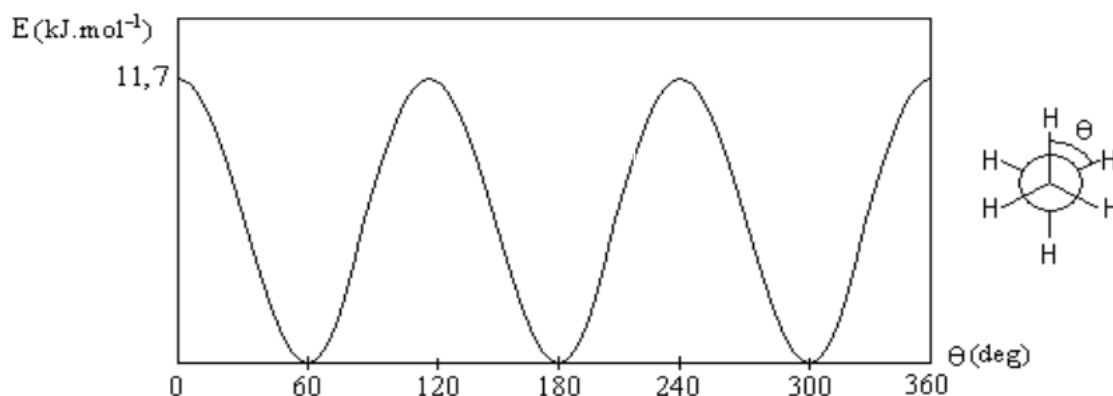


Eclipsed shapes: $\theta = 0^\circ$, $\theta = 120^\circ$ et $\theta = 240^\circ$

Left offset shapes: (or left shifted shapes): $\theta = 60^\circ$, $\theta = 300^\circ$

Anti-offset shapes: $\theta = 180^\circ$

The potential energy diagram of ethane versus the twist angle θ is:



According to this diagram:

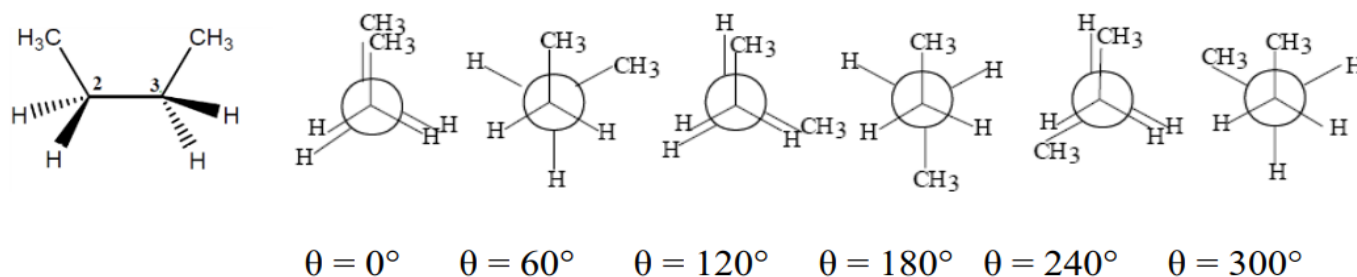
- The eclipsed conformation represents the highest energy state of ethane.
- And the shifted (anti) conformation is the most stable (because the atoms of hydrogens are the furthest from each other \equiv no steric hindrance).

Noticed:

The energy difference between the maximum value and the minimum energy value is called energy barrier. It represents the thermal agitation energy for molecules to pass from one conformation to another, following intermolecular shocks.

c) Conformation of the butane molecule ($\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_3$)

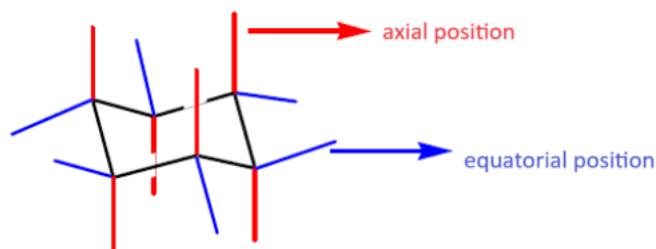
By observing the $\text{H}_3\text{C-CH}_2\text{-CH}_2\text{-CH}_3$ molecule along the Carbon2-Carbon3 axis, we obtain the following conformations:



Anti-shifted conformation. C1-C4 (one methyl at the top and the other at the bottom) for a torsion angle $\theta=180^\circ$ is the most stable.

d) Conformation of cyclic chains in the case of cyclohexane

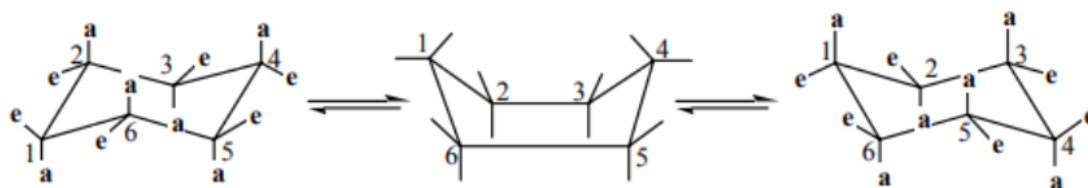
From three carbons, a chain can close on itself and form a cycle. We will study the conformations of cyclohexane.



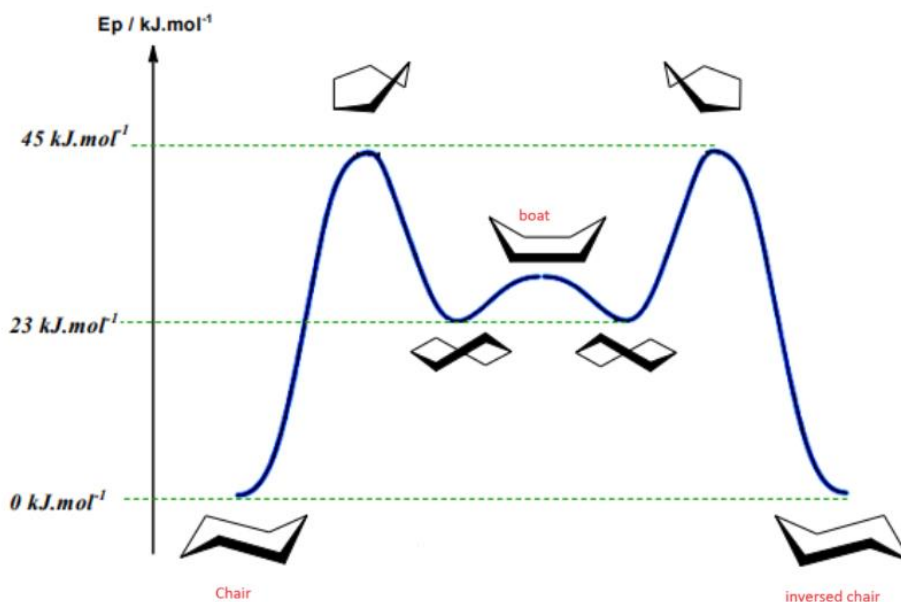
According to the perspective representation of cyclohexane, we see that the twelve C-H bonds are divided into two types:

- six axial connections, perpendicular to the average plane of the cycle (vertical on the drawing).
- six equatorial links, located approximately in the mean plane of the cycle.

Two conformations of cyclohexane are preferred, the conformations chair and boat:



The potential energy diagram of ethane versus the twist angle θ is:



III.2.3. Configurational isomerism

a) Definition

Configurational stereoisomers are molecules that have an identical developed formula (*the sequence of atoms is identical*). The difference being at the level of organization in space, of which it is necessary to break connections to pass from one to the other for these isomers.

Configurational stereoisomerism is linked to the presence of particular patterns in the molecule: *double bonds*, and the *asymmetric carbon*.

There are two types of configurational isomerism:

- Geometric isomerism;
- Optical isomerism.

Remark:

- A carbon is said to be asymmetric, chiral center, or stereocenter when its four substituents are different.
- A group of atoms consisting of a double bond with its substituents can give birth of geometric isomerism (E and Z).
- A large number of molecules (those with asymmetric carbons or those which have a double bond) have a given configuration. The determination of this configuration requires knowledge of the sequential rule of CAHN, INGOLD and PRELOG.

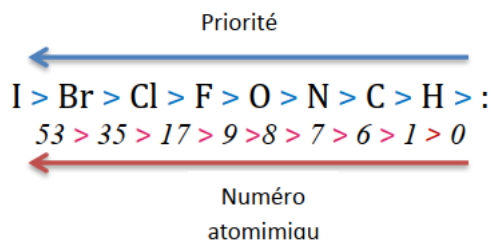
b) CAHN, INGOLD and PRELOG rule (C.I.P)

The rules for determining the order of priority of the four substituents of a tetrahedral carbon are based on the rules of Cahn, Ingold and Prelog known as C.I.P

Rule 1. Atoms directly bonded to the C concerned are classified by number atomic (Z) decreasing: by assigning number 1 to the heaviest and number 4 to the lighter.



Règle I : On classe les atomes directement reliés au C* étudié par numéro atomique décroissant :

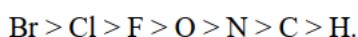


Rule 2. If the atoms directly attached to this carbon are the same, we must see the substituents of these atoms and apply rule 1 (The atoms must be compared row by row and stop at the 1st difference).

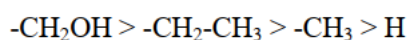
Rule 3. Double or triple bonds are broken down into 2 or 3 single bonds, by adding fictitious atoms (ghosts) in parentheses.

Rule 4. In the case of the presence of 2 isotopes, it is the heavier isotope (according to the mass number) which precedes.

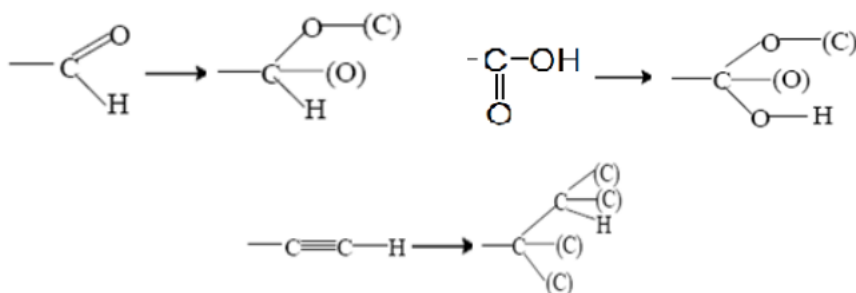
Exemple sur R1 :



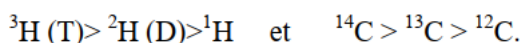
Exemple sur R2 :



Exemple sur R3 :



Exemple sur R4 :



C) Geometric isomerism

This type of isomerism is found in compounds that have a double bond (C=C, C=N, N=N, ..) or a cycle. The presence of these two unsaturations makes the molecule more rigid (the C=C double bond does not allow the free rotation).

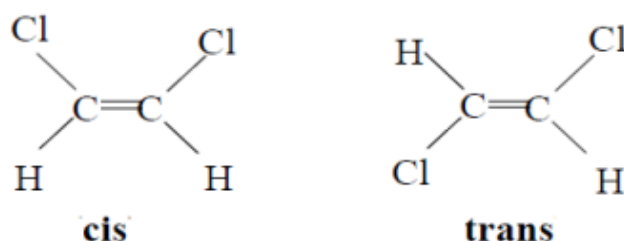


⇒ Case of alkenes

If the two ethylenic carbons each one have two different substituents, we can distinguish two different non-superimposable structures named as follows:

- Cis and Trans nomenclature: The four substituents are identical in pairs
 - ✓ If the 2 identical substituents are on the same side of a plane defined by the C=C bond; this is the "Cis" isomer.
 - ✓ If the 2 identical substituents are on either side of the plane defined by the C=C bond; This is the "Trans" isomer.

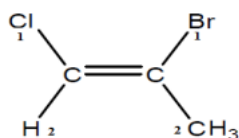
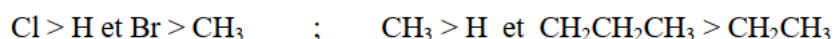
Example: The 1,2-dichloroethylene present two geometric isomers



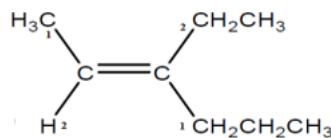
Z and E nomenclature: The two constituents of each sp^2 carbon are classified between them (1st and 2nd) according to the CIP rules.

- If the two priority substituents (ranked 1st) are on the same side by in relation to the double bond, the isomer is called Z (from the German 'Zusammen'= together)
- If the two priority substituents (ranked 1st) are not on the same side with respect to the double bond, the isomer is called E (from the German 'Entgegen' = opposite).

Example: according to CIP we have:



(Z) 2-bromo-1-chloropropene



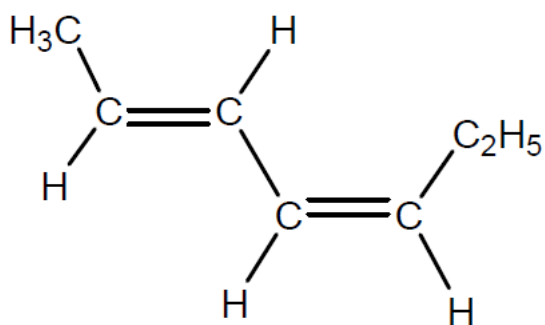
(E) 3-ethyle-2hexene

⇒ Case of alkenes with n double band

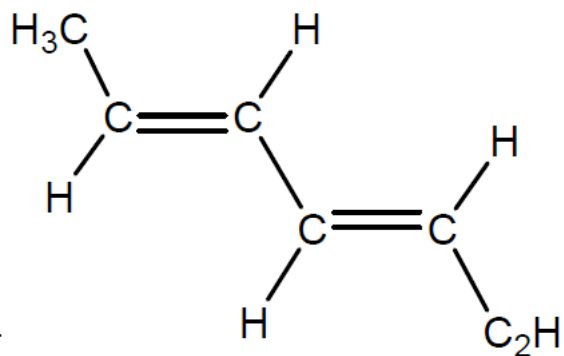
For a compound containing n double bonds, the maximum number of isomers geometric is 2^n .

Example: 2,4 heptadiene $\text{CH}_3\text{-CH=CH-CH=CH-CH}_2\text{-CH}_3$

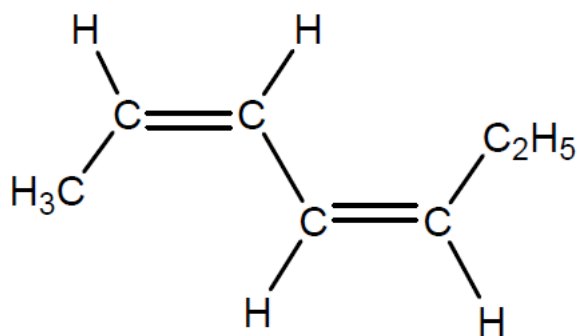
$n=2 \Rightarrow$ there are a maximum of 4 geometric isomers: (Z,Z) ; (Z,E) ; (E,Z) ; (E,E)



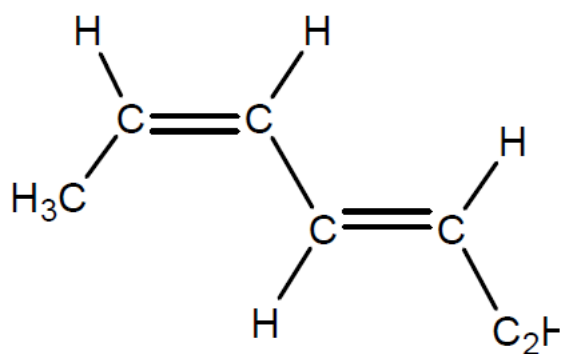
(2E,4Z) 2,4 heptadiene



(2E,4E) 2,4 heptadiene



(2Z,4Z) 2,4 heptadiene



(2Z,4E) 2,4 heptadiene