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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

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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 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),
II.5. Ketones, carboxylic acids (preparation, reactivity).

II.1/ Saturated aliphatic hydrocarbons (linear, branched)

- Alkanes are saturated non-cyclic hydrocarbons, having the chemical formula C_nH_{2n+2}, ending **–ane**, with a symbol **RH**: Methane; Ethane

II.1.1. Physical properties of alkanes and cycloalkanes

- From methane to butane, alkanes occur in the gaseous state.
- Natural gas is essentially made up of methane. Oils contain a mixture of hydrocarbons (including alkanes ranging from CH4 to C40H82).
- From C5, we encounter liquids and from C17, solids.
- Liquid or solid alkanes have a fairly low density (around 0.7). They are insoluble in water; on the other hand, they are miscible with most organic liquids and are themselves solvents for many compounds organic.
- Boiling temperature increases with molecular weight. For branched alkanes, the boiling and melting temperatures are lower than that of normal alkane even number of carbon atoms.

|	Composé	Température d'ébullition (°C)
C_5H_{12}	Pentane	36
	Méthylbutane	25
	Diméthylpropane	9

- Cyclic alkanes generally have boiling and melting temperatures above those of linear alkanes with the same number of carbon atoms.

II.I.2. Reactivity of alkanes and cycloalkanes

- Generally speaking, alkanes are relatively unreactive, in other words stable. This is explained by the fact that the C-C and C-H bonds are quite strong:
- C-C = 82.6 kcal/mol
- C-H = 100 kcal/mol
- Alkanes can react in several reactions:

II.1.2.1. Combustion reactions (complete and partial)

- The combustion of alkanes is an exothermic reaction, it occurs by breaking the C-C bond (the skeleton of the molecule). These types of reactions are used as a source of energy calorific (fuels, heating, etc.)
- There are two types (Example with methane):
  ⇨ The complete which produces carbon dioxide and water:

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

$$C_nH_{2n+2} + (3n+1)/2\,O_2 \longrightarrow n\,CO_2 + (n+1)\,H_2O$$
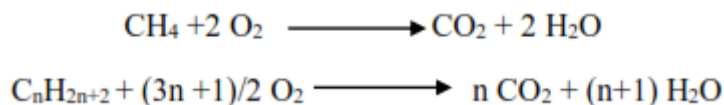
⇨ When there is not enough oxygen or there is too much methane, combustion is called incomplete. It may form carbon monoxide, carbon or both.
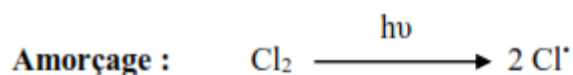
$$CH_4 + O_2 \longrightarrow C + 2\,H_2O$$

$$2\,CH_4 + 3\,O_2 \longrightarrow 2\,CO + 4\,H_2O$$
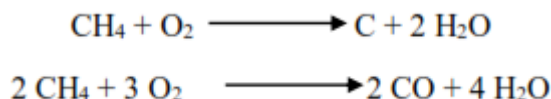
II.1.2.2. Halogenation reactions

- When the alkane is used in excess compared to the halogen, only monohalogenation is observed.
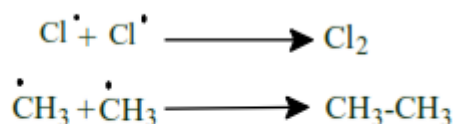
Example: Chlorination of methane

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

- Under heat and between 350 and 600°C, or in the presence of light ($\lambda < 490$ nm), we obtain a mixture of CH3Cl, CH2Cl2, CHCl3 and CCl4.
- The proportions of the various products depend on the initial Cl2/CH4 ratio.
- The mechanism of methane monochlorination as for all radical processes, includes three stages: initiation, propagation and termination.

Amorçage :

$$Cl_2 \xrightarrow{\ h\upsilon\ } 2\,Cl^{\bullet}$$

Propagation :

$$CH_4 + \overset{\bullet}{Cl} \longrightarrow \overset{\bullet}{C}H_3 + HCl$$

$$\overset{\bullet}{C}H_3 + Cl_2 \longrightarrow CH_3Cl + Cl^{\bullet}$$

Terminaison :

$$Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl_2$$

$$\overset{\bullet}{C}H_3 + \overset{\bullet}{C}H_3 \longrightarrow CH_3\text{-}CH_3$$

Bilan :

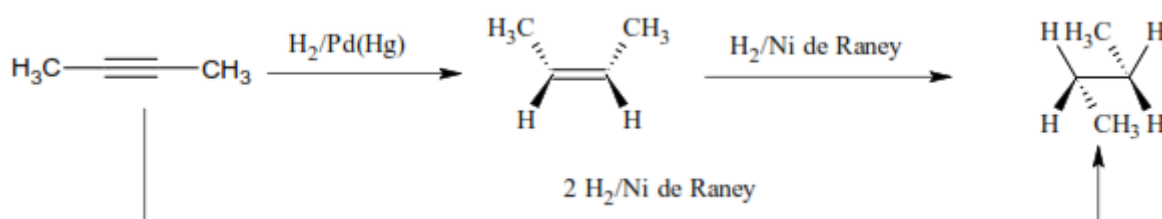$$CH_4 + Cl_2 \xrightarrow{\ h\upsilon\ } CH_3Cl + HCl$$

3
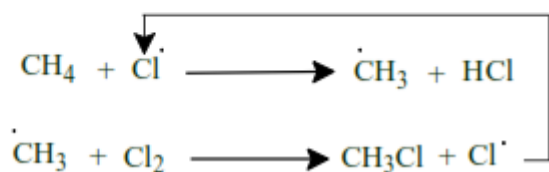
## II.2. Preparation of alkanes and cycloalkanes

II.2.1. Catalytic hydrogenation of alkenes and alkynes

-   It is the addition of hydrogen to an unsaturation (C=C, or C≡C). These reactions take place at low temperatures and in the presence of a catalyst (Pd, Pt, Raney Ni). The more the connection is congested, the slower the reaction.


II.2.2. Catalytic hydrogenation of aromatic compounds

-   The hydrogenation of benzene and its derivatives takes place in bulk and leads to cyclohexane. These reactions are generally slower and require high temperatures and pressures significant in hydrogen.
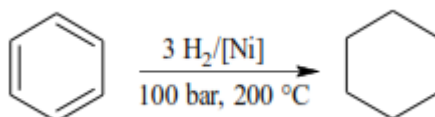
II.2.3. Dehalogenation (metallic coupling with Zn)

The reaction between a halogenated derivative and zinc leads to an organozincic compound. This last one is then treated with a proton donor such as hydrochloric acid.

$$CH_3Cl + Zn + HCl \longrightarrow CH_4 + ZnCl_2$$
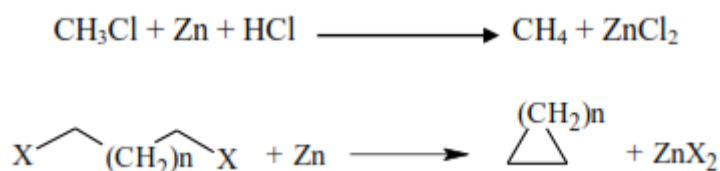
II.2.4. Wurtz reaction (metallic coupling with sodium)

The reaction allows the formation of an organosodium and the carbanion formed causes a nucleophilic substitution on the halogenated derivative

$$R-X + 2 Na \longrightarrow R^-,Na^+ + NaX$$

$$R^-,Na^+ + R-X \longrightarrow R-R + NaX$$
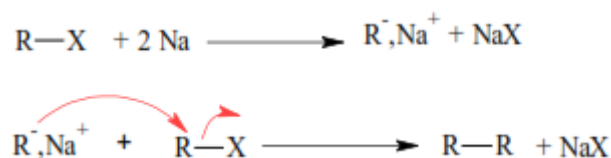
II.2.5. Reaction of a Grignard reagent with water

The reaction goes through the stage of formation of an organomagnesium (Grignard reagent) in anhydrous ether, then the latter transforms into alkane in the presence of water.
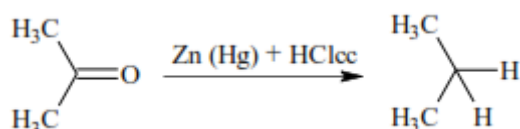
$$RX + Mg/\text{éther (anhydre)} \longrightarrow RMgX \text{ (organomagnésien)}$$
$$RMgX + H_2O \longrightarrow RH + MgXOH$$
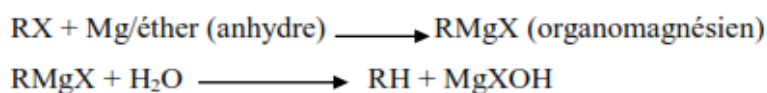
## II.2.6. Reduction of carbonyls

A) Clemmensen reduction (acidic medium)

Clemmensen reduction is a reduction reaction of the carbonyl function (ketone and aldehyde) aliphatic or aromatic in saturated hydrocarbons in the presence of Zinc amalgamated with Mercury in concentrated HCl.

B) Wolff-Kishner reduction (basic medium)

The Wolff-Kishner reduction is a reaction for the reduction of the carbonyl function to a saturated hydrocarbon. It is done in two stages: the condensation of the carbonyl with hydrazine, which gives hydrazone, which transforms into saturated hydrocarbon under the action a strong base (NaOH, KOH, etc.).
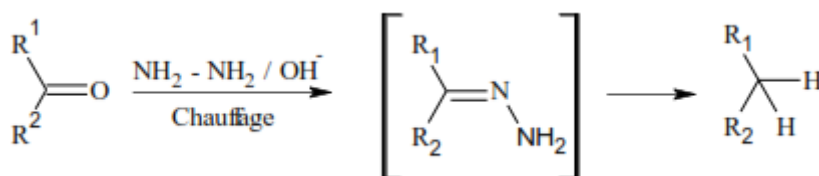
II.2. Alkenes (Preparation and reactivity)

Alkenes are non-cyclic unsaturated hydrocarbons with the formula CnH2n.

We call also ethylenic compounds any chemical species containing at least one C=C double bond.

For example cyclic hydrocarbons having a double bond (cyclenes) are ethylene compounds.

The main chain is the one with the greatest number of links. The name of the compound derives from that of the alkane by replacing the ending ane by ene. Propene; but-1-ène.

II.2.1. Physical properties of alkenes

The physical properties of alkenes are similar to those of alkanes:

- Boiling points are slightly lower than those of alkanes.

- They are insoluble in water, soluble in non-polar solvents such as: benzene, ether, chloroform; less dense than water.

- They are essentially nonpolar molecules interacting weakly with each other.

- Alkenes containing fewer than four carbon atoms are gaseous.

Boiling temperatures increase with molecular weight; branching decreases the boiling temperature.

| Composé	Téb	Composé	Téb
Butane	- 0,5°C	But-1-ène	- 6,5°C
Isobutane	- 11,7°C	Isobutène	- 7°C
But-2-ène (cis)	4°C	But-2-ène (trans)	1°C

II.2.2. Reactivity of alkenes

Alkenes are characterized by: addition and redox reactions following the presence of the π bond of the C=C double bond (weaker than a single C-C σ bond), and the reactions which involve the nucleophilic properties of alkenes resulting from the richness in polarizable electrons at the C=C double bond.

II.2.2.1. Addition of hydrogen halides (H-X):

a) Markovnikov type HX addition

This is an electrophilic addition reaction. The addition of HX to an alkene shows that the halogen atom (X = Cl, Br, I)) is generally found on the most substituted carbon atom and the hydrogen atom attaches to the carbon atom giving rise to the formation of the most stable carbocation: tertiary > secondary > primary (Markownikov rule).

The reaction between HBr dissolved in ethanoic acid and methylpropene at 20 °C gives mainly 2-bromo-2-methypropane (1) and only traces of 1-bromo-2methylpropane (2). It is regioselective.
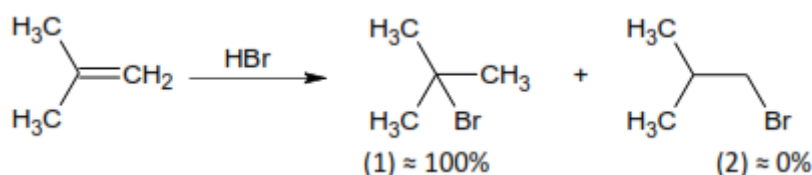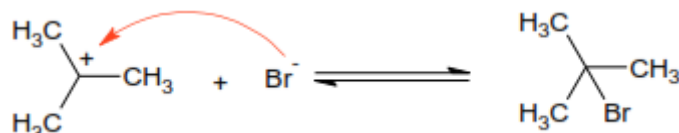

Mechanism:

First step: The alkene reacts with the proton to form the most stable carbocation.

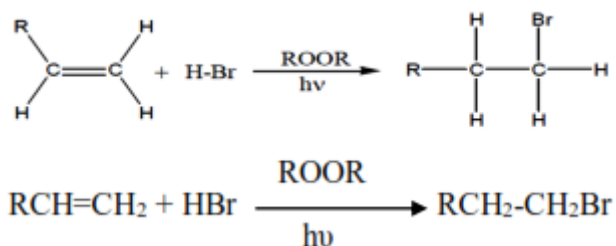

Carbocation tertiaire plus stable
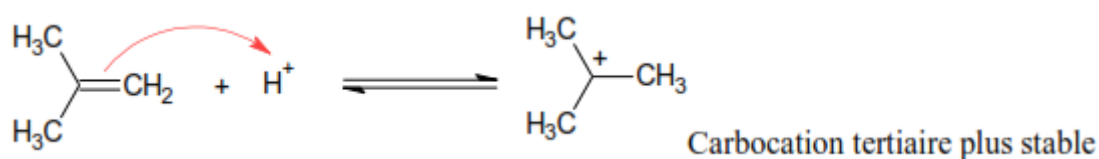
Second step: The nucleophilic halide anion attacks the carbocation formed during the first stage.
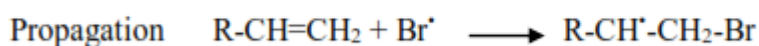

The reaction is therefore a strongly regioselective addition

b) Addition of anti-Markovnikov type HBr

The reaction of HBr with an alkene in the presence of peroxide, we obtain an addition of which the orientation is anti-Markownikow: it is a radical addition reaction on alkenes:
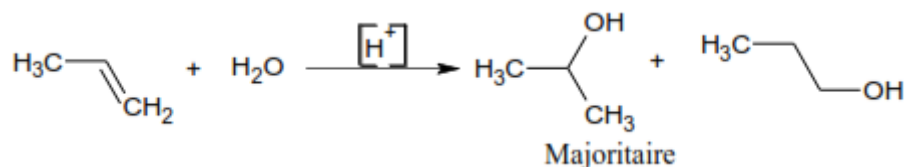
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$$RCH=CH_2 + HBr \xrightarrow[h\upsilon]{ROOR} RCH_2\text{-}CH_2Br$$

Mécanisme

Initiation $R\text{-}O\text{-}O\text{-}R \xrightarrow{h\upsilon} 2\ R\text{-}O^\bullet$

$R\text{-}O^\bullet + HBr \longrightarrow R\text{-}O\text{-}H + Br^\bullet$

Propagation $R\text{-}CH=CH_2 + Br^\bullet \longrightarrow R\text{-}CH^\bullet\text{-}CH_2\text{-}Br$

Formation du radical le plus stable

$R\text{-}CH^\bullet\text{-}CH_2\text{-}Br + HBr \longrightarrow R\text{-}CH_2\text{-}CH_2\text{-}Br + Br^\bullet$

II.2.2.2. Hydration in an acidic environment:

The addition of water to alkenes gives access to alcohols according to the Markovnikov rule.
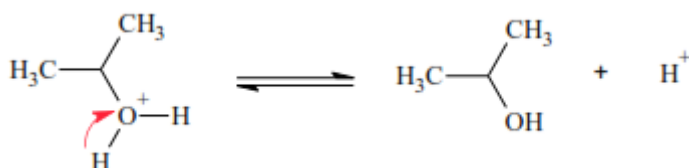

Majoritaire

⇨ Mechanism

First step: The alkene reacts with the catalyst proton added to the medium (addition of acid sulfuric for example) to form a carbocation.
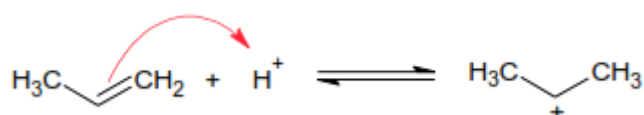
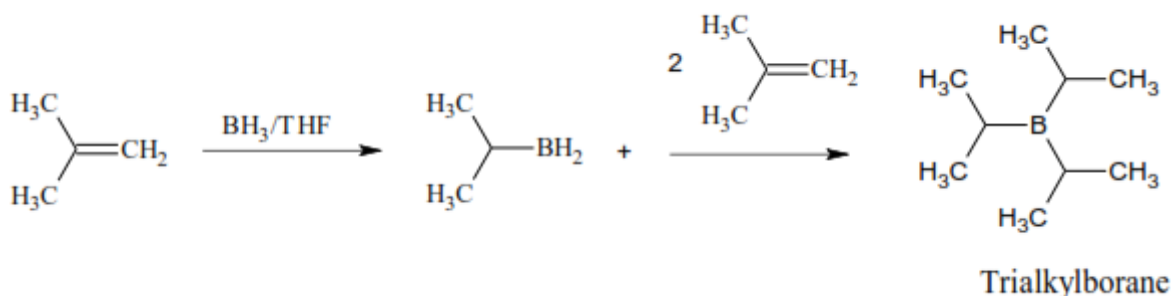**Second step:** Water, a nucleophile, attacks the carbocation formed during the first step.
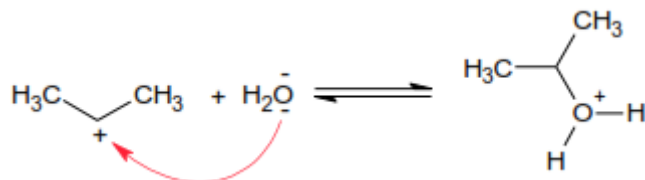
Third step: deprotonation and regeneration of the catalyst proton.

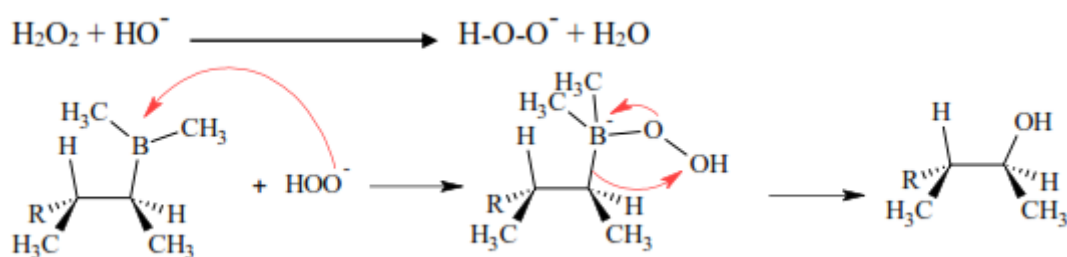## II.2.2.3. Hydration by hydroboration

The reaction leads to the replacement of the three hydrogen atoms of BH3 and we obtain a trialkylborane.

- Boron adds to the least hindered carbon (electronic and steric effects)

- Addition syn: H and B add on the same face of the alkene

 Oxidative hydrolysis by hydrogen peroxide in a basic medium.

$$H_2O_2 + HO^- \longrightarrow H\text{-}O\text{-}O^- + H_2O$$

Hydroboration followed by the action of hydrogen peroxide in a basic medium leads to an addition of H_2O to an anti-Markownikow type alkene.

II.2.2.4. Catalytic hydrogenation (or addition of hydrogen, H₂)

The hydrogenation of an alkene requires the use of a catalyst, most often metallic, among which we can cite Raney nickel (prepared by the action of sodium hydroxide on the alloy of Raney Ni-Al), platinum or its oxide (Adams catalyst), palladium and zinc oxide.
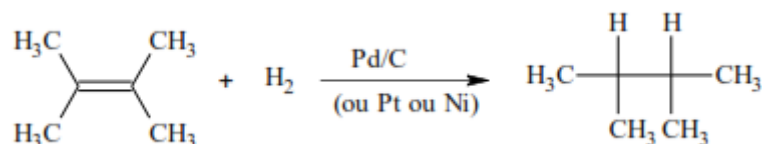
II.2.2.5. Halogenation (or addition of halogens, X2)

Alkenes react quickly with Br2 or Cl2 in nonpolar solvents (such as CCl4). The addition of the dihalogen is carried out in anti, that is to say that the two atoms of halogen enter on either side of the plane of the double bond (trans-addition).
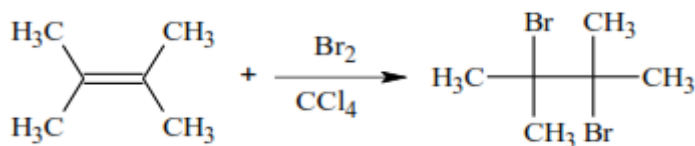
> **Note:** alkenes participate in several other reactions mentioned: Oxymercuration -demercuration, Mild oxidation with diluted potassium permanganate, Strong oxidation with KMnO4 or concentrated K2Cr2O7, Ozonolysis, epoxidation, Cycloadditions. Diels-Alder reaction etc.

II.2.3. Preparation of alkenes

II.2.3.1. Catalytic partial hydrogenation of alkynes

#### a) Controlled reduction of alkynes (formation of cis alkenes)

The hydrogenation of alkynes to alkenes uses the Lindlar catalyst (palladium deposited on calcium carbonate or barium sulfate). The addition leads to the cis alkene.
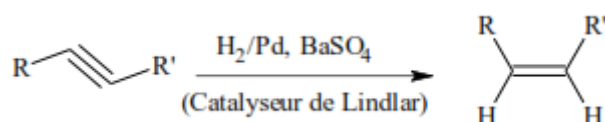
$BaSO_4$ or $CaCO_3$ is used to deactivate the catalyst; in the absence of BaSO4 and CaCO3, the reduction will be total and leads to an alkane.

b) Controlled reduction of alkynes (formation of trans alkenes)

In the presence of Na/NH3 or Li/NH3, the trans alkene is obtained.
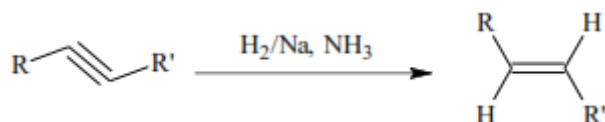
### II.2.3.2. Order 2 or Order 1 elimination reactions

Elimination reactions correspond to the intramolecular removal of two groups or and CaCO3 atoms A and B carried by one or two elements. A is most often a hydrogen atom and B an electrowithdrawing group (I). When the two groups (or atoms) are adjacent, it This is then a β-elimination (or 1,2 elimination); it leads to the formation of a double or triple bond.

If B is a halogen (Cl, Br or I) it is a dehalogenation reaction, it takes place in presence of a strong base (KOH or NaNH2).

If B is an (OH) it is a dehydration reaction in an acidic medium (H2SO4conc).

If B is a (NH2) it is a deamination reaction (Hofmann elimination).
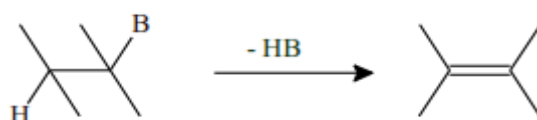
Mechanisms of elimination reactions: There are two types of mechanisms for elimination reactions (named E1 and E2) which have a lot of resemblance to the mechanisms of SN1 and SN2 substitution reactions respectively.

E1 elimination mechanism:

E1 type elimination reactions have a mechanism close to that of SN1. He takes place in two stages:

The first step is slow, and gives the speed of the total reaction. She permits the ionization of the C-X bond (X is an electron-withdrawing group) under the action of a polar solvent, with formation of a carbocation and the anion-. This step is identical to the first step of SN1.

The second step, very rapid, corresponds to the removal of a proton under the action of a basis to form a double bond. The elimination speed E1 is of order 1.
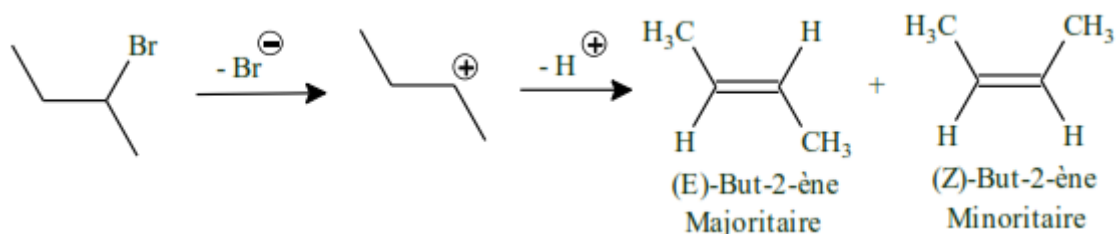
Première étape :

Deuxième étape :

Mélange (E + Z)
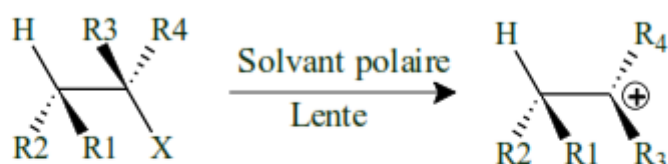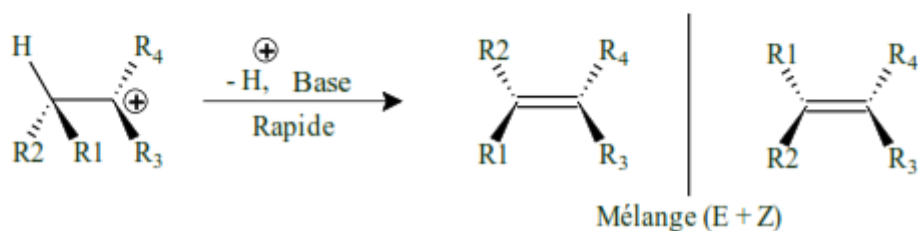
Elimination E1 gives a mixture of two alkenes (Z + E) in which the form (E) is in the majority because of its greater stability, therefore it is non-stereospecific.

Example: Elimination of HBr from 2-bromobutane.

(E)-But-2-ène
Majoritaire

(Z)-But-2-ène
Minoritaire

Due to the formation of a carbocation in the first step (SN1 or E1), the base can snatch a proton (E1) but in certain cases it can enter the reaction by as a nucleophile (SN1). Therefore, there is a competition between the SN1 mechanism and E1. The increase in temperature favors E1 elimination compared to SN1, like E2 compared to SN2.