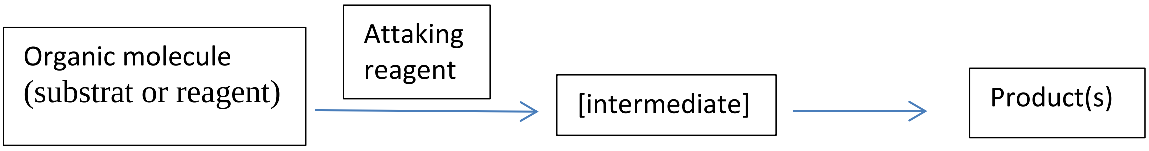
Organic reactions :

The general reaction is depicted as follows :



A *mechanism* is the actual process by which are action takes place:

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

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

The reaction in organic chemistry are three types :

1. Substitution Reactions

Y replaces X

Substitution Reaction

   a. *Nucleophilic substitution*
   b. *Electrophilic substitution*
   c. *Free-radical substitution*

2. Addition Reactions

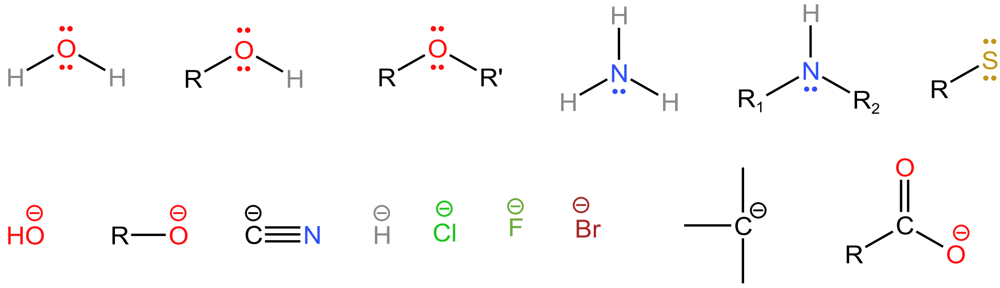
Addition Reaction

   a. *Nucleophilic addition*
   b. *Electrophilic addition*
   c. *Free-radical addition*

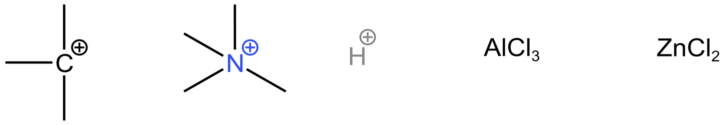
3. Elimination Reactions

I. 1 Nucleophilic and electrophilic reagents:

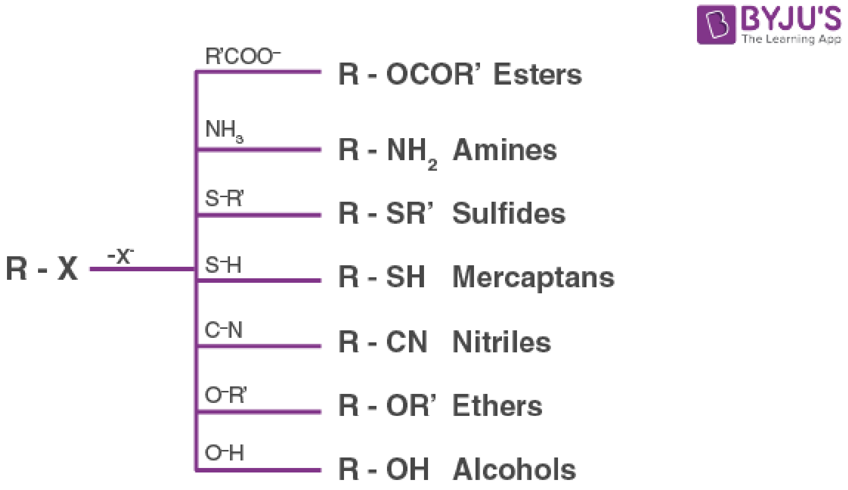
Nucleophiles: A reagent that brings an electron pair to the reactive site and the reaction is then called nucleophilic. A nucleophile has one or more n-doublets or is an anion.



Electrophile: Are electron-deficient species and tend to attack the substrate at a site of high electron density and the reaction is called *electrophilic*. An electrophile has an electron void. It is a cation or a neutral molecule.



II. Substitution reaction :

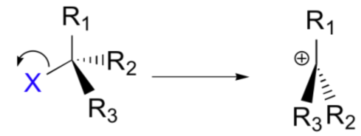


There are two mechanistic models for how a nucleophilic substitution reaction can proceed : **the S_N1 reaction and the S_N2 reaction**.

II.1. Dissociative nucleophilic substitution: the S_N1 reaction :

A second model for a nucleophilic substitution reaction is called the '**dissociative**', or '**S_N1**' mechanism: in this picture, the C-X bond breaks *first*, before the nucleophile approaches:

1st step: Slow step : formation of a carbocation: with trigonal planar geometry

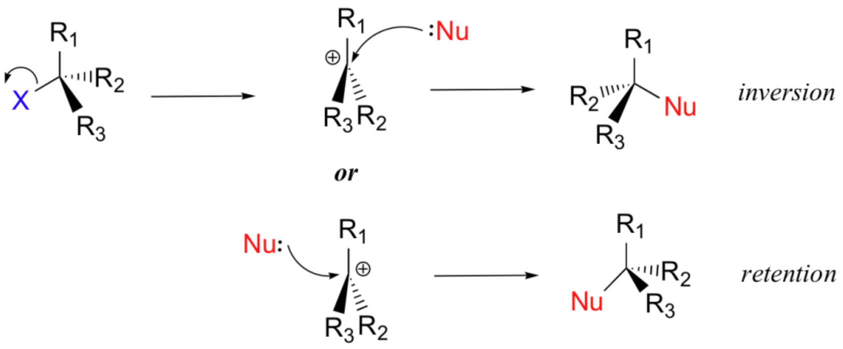


The SN1 mechanism is favored when the carbocation is stabilized by +I or +M.

Carbocations are most stable when there are more atoms to distribute

2nd step: Speed step

In the second step, the nucleophile attacks the empty, the carbocation, to form a new bond and return the carbon to tetrahedral geometry.

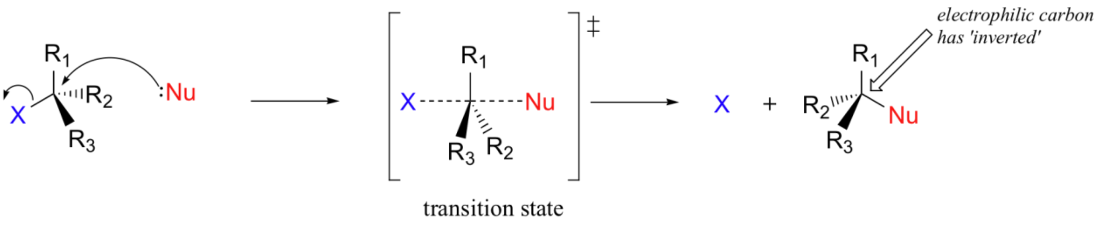


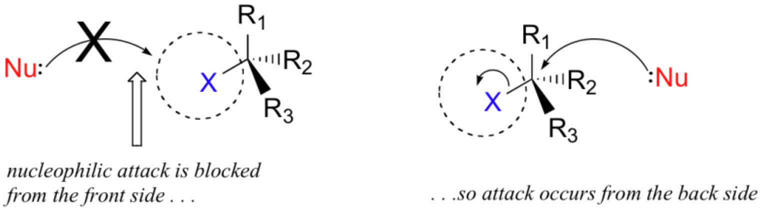
"racemic mixture

This means that about half the time the product has the same stereochemical configuration as the starting material (retention of configuration), and about half the time the stereochemistry has been inverted. In other words, *racemization* has occurred at the carbon center.

Associative Substitution reaction : the S_N2 reaction

The reaction takes place in a single step, and bond-forming and bond-breaking occur simultaneously.

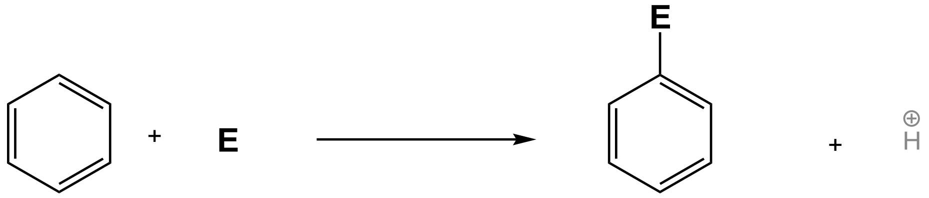




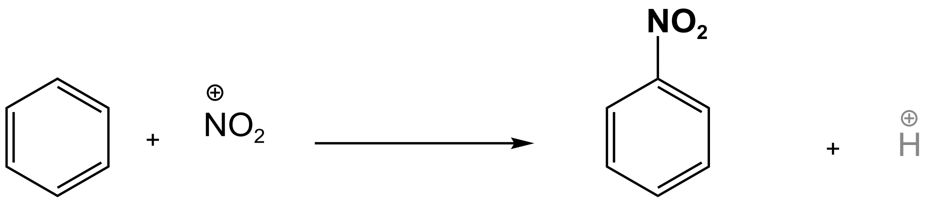
dorsal attack of the nucleophile leading to an inversion of configuration 2 molecules of reactant intervene in this mechanism in a single elementary act: bimolecular reaction SN2

I.3. Electrophilic substitution (ES) :

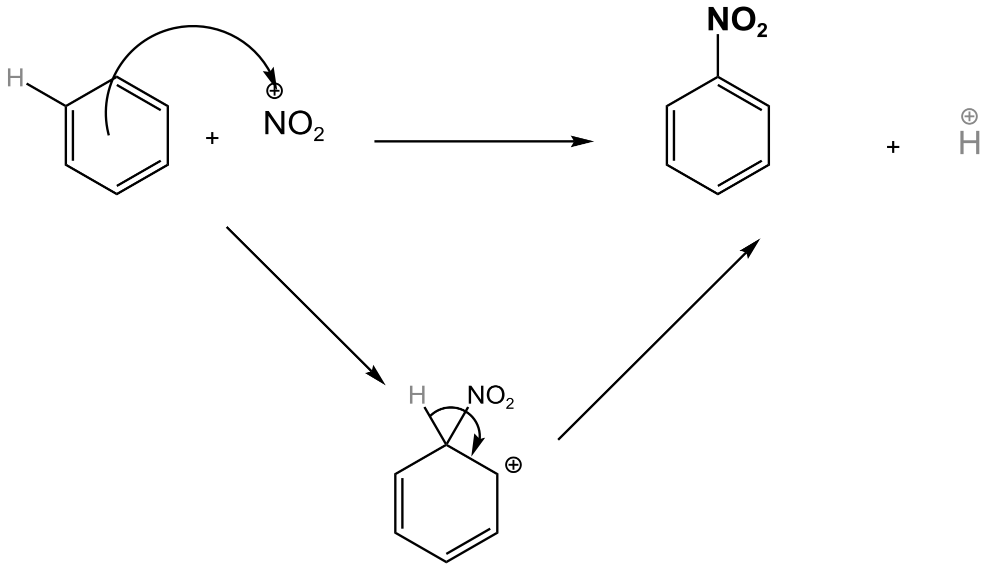
It occurs most often in the aromatic series:



Example :



Mechnism :



II.2. Addition reaction :

Addition reaction is a chemical process in which an atom or group of atoms is added to a molecule to form a larger one (the adduct).

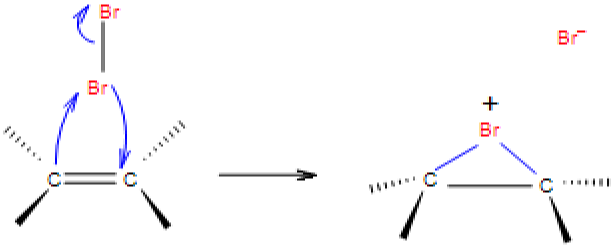
Addition reactions are limited to chemical compounds with multiple bonds, such as molecules with carbon–carbon double bonds, triple bonds, compounds with C-O double bond…….

II.2. Double bond addition reaction:

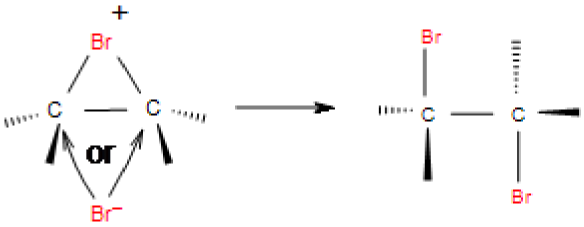
- Molecule of type X_2 (Cl_2, Br_2 , I_2)

Addition ofX_2on R_1-CR_2=CR_3-R_4. Here contains the electrophile X^+, which forms two enantiomeric bridged ions:

Step 1: In the first step of the addition the Br-Br bond polarizes, heterolytic cleavage occurs and Br with the positive charge forms a intermediate cycle with the double bond.

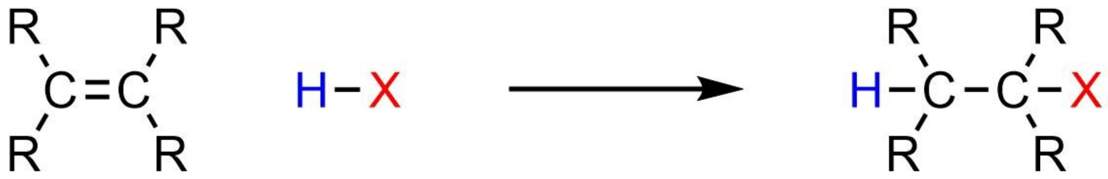


Step 2: In the second step, bromide anion attacks any carbon of the bridged bromonium ion from the back side of the cycle. Cycle opens up and two halogens are in the position **anti**.

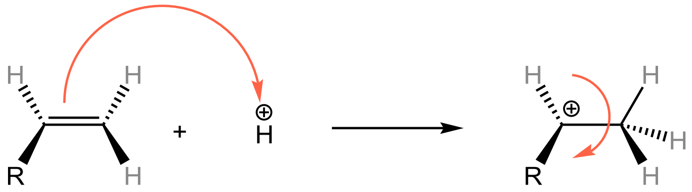


-Molecule of type HX:

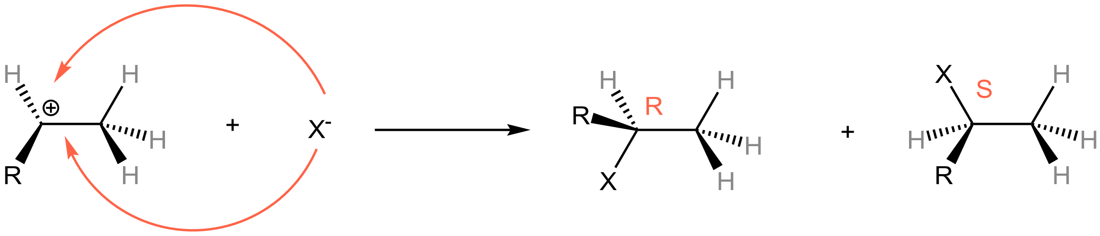
Addition of HX on R_1-CH=CH_2: it is an electrophilic addition, with application of the Markovnikov rule; the H+ electrophile binds to the doubly bonded carbon to give the most stable carbocation:



Step 1) Electrophilic Attack The 2 π electrons from the double bond attack the H (electrophile) in the HX makes one of the carbons become an electron deficient “carbocation intermediate (sp2 hybridized carbon) ”.

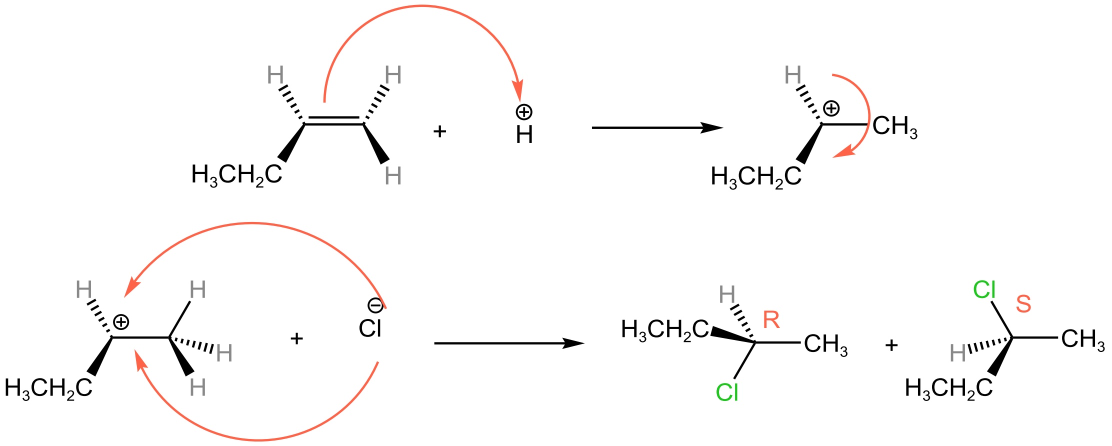


Step 2: Nucleophilic attack by halide anion : the definitive fixation of the nucleophile X^- can be done in 2 different ways generating a C* R or S. Because of the equiprobability, we obtain a racemic mixture either.



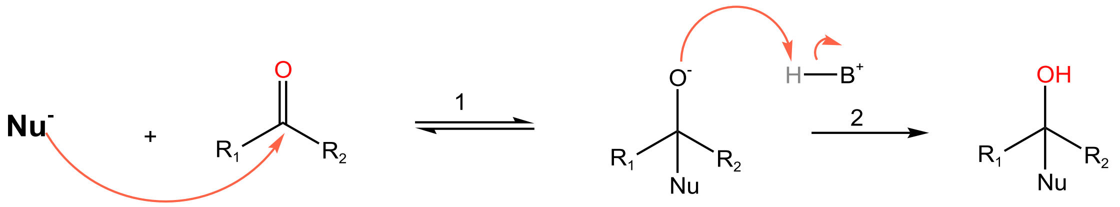
Example

Addition of HCl on C_2H_5-CH=CH_2



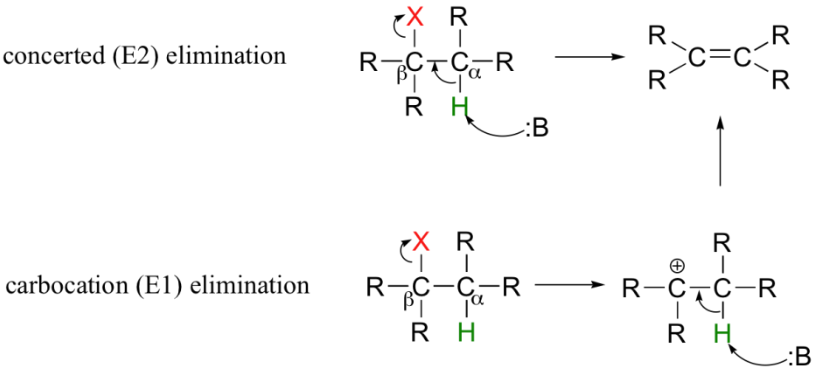
II.2. Nucleophile addition (NA): frequent on a carbonyl:

The reaction is initiated by the nucleophile X^-



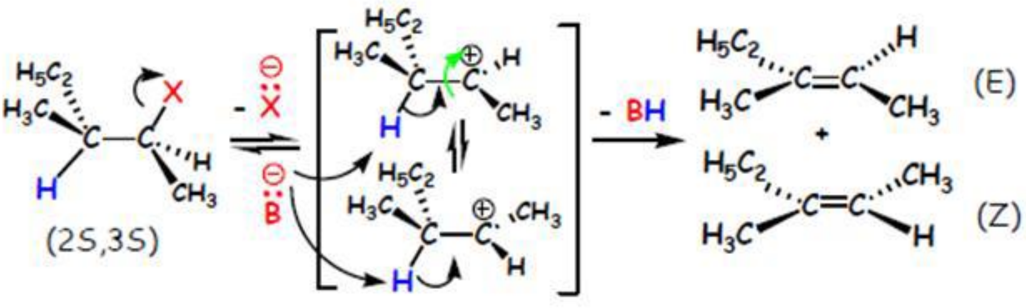
III. Elimination reaction:

It is the reverse of the electrophilic addition reaction. The elimination is always done between two atoms carried by two adjacent C. This type of elimination can be described by two model mechanisms: it can occur in a single concerted step (proton abstraction at C_α occurring at the same time as C_β-X bond cleavage), or in two steps (C_β-X bond cleavage occurring first to form a carbocation intermediate, which is then 'quenched' by proton abstraction at the alpha-carbon).



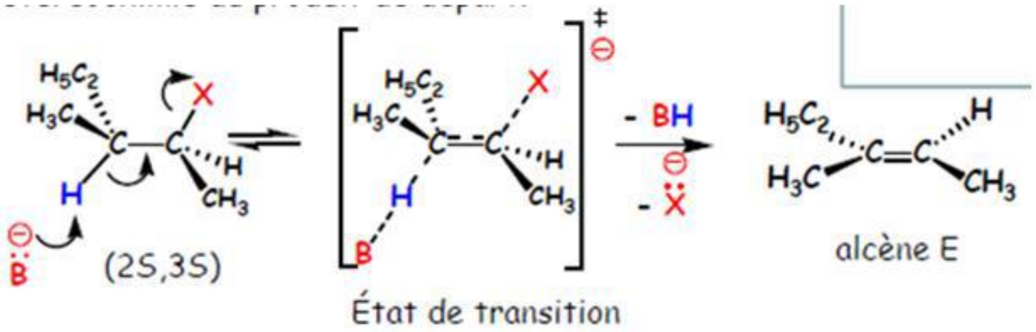
Note :*

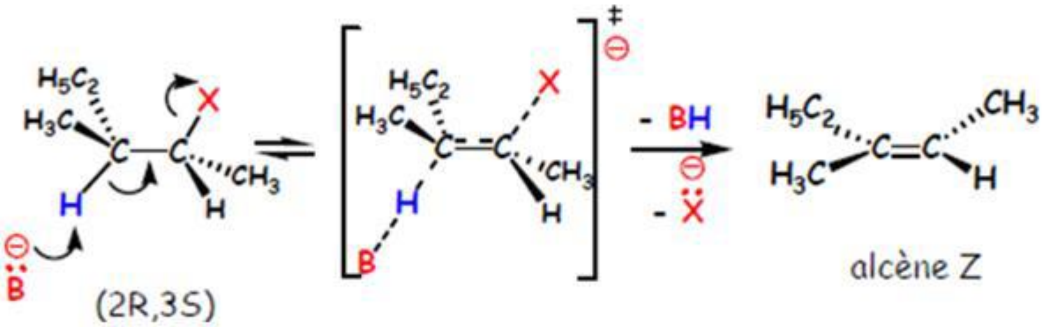
E_1 gives mixture of Z and E



Intermédiaire réactionnel: carbocation

E_2 gives one isomer Z or E


H$_5$C$_2$
H$_3$C
C
C
X
H
CH$_3$
H
B
(2S,3S)
‡
H$_5$C$_2$
H$_3$C
C
C
X
H
CH$_3$
H
B
État de transition
- BH
- X
H$_5$C$_2$
H$_3$C
C=C
H
CH$_3$
alcène E


H$_5$C$_2$
H$_3$C
C
C
X
CH$_3$
H
H
B
(2R,3S)
‡
H$_5$C$_2$
H$_3$C
C
C
X
CH$_3$
H
H
B
- BH
- X
H$_5$C$_2$
H$_3$C
C=C
CH$_3$
H
alcène Z