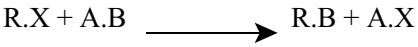
Organic Reaction Mechanisms

Organic reaction mechanisms are shorthand descriptions of how the starting compounds are made into the products. Molecules with the same functional groups usually react by similar mechanisms, and we can use mechanisms for known reactions to predict how other molecules will behave under similar conditions. Mechanisms are thus a connecting thread between similar reactions and allow us to rationalize the products of a known reaction and predict the reactivity of other organic molecules.

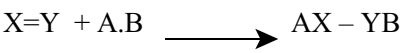
Classification of organic reactions

All organic reactions may be classified as one of the following four general types:

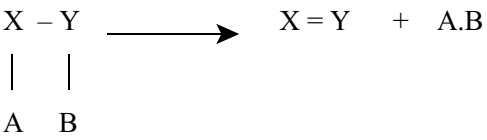
1. **Substitution** (or replacement) reactions involve exchanging on atom or group of atoms on the organic molecule for another:



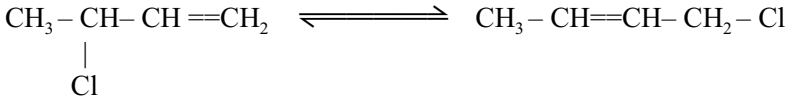
2. **Addition** reactions means just that one molecule adds onto another and nothing is lost:



3. **Elimination** reactions involve the loss of a relatively small molecule from the organic reactant:



4. **Rearrangement** reaction is where one molecule reacts to give a different molecule:

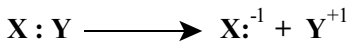


3-chlorobut-1-ene 1-chlorobut-2-ene

Types of Bond Fission

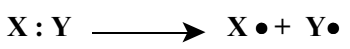
Organic reactions may also be classified according to the way in which covalent bonds are formed or broken during the reaction. A covalent (or electron-pair) bond between a carbon atom and an atom of an element X may be broken in two ways:

1) Unsymmetrically, so that one of the atoms retains both the bonding electrons:
   heterolytic fission



The resulting fragments are likely to be charged. If so, they are ions. Heterolytic fission of the bond may occur in one of two ways, the carbon atom retaining the two electrons to form a negatively charged **carbanion** or the carbon atom retaining the two electrons with the formation of a positively charged **carbocation.** Heterolytic reactions are sometimes known as ionic reactions, as they involve ionic species.

2) Symmetrically, so that each atom retains one of the bonding electrons:
   Homolytic fission



Homolytic reactions are also known as free radical reactions, as they involve the formation of free radicals, i.e. atoms or groups of atoms containing an unimpaired electron.
Energy must be supplied, either as heat or light, to break the bond. The free radicals formed possess this energy, and are very reactive. The steps in a free radical reaction are initiation, propagation and termination.

Classification of Reagents

In a covalent bond between A and B, if A is more electronegative than B, the distribution of bonding electrons can be represented as: $A^{\delta-} — B^{\delta+}$. The bond is thus said to be polar. The reagents which attack organic compounds seek out either the slightly positive ($\delta+$) end of the bond or the slightly negative ($\delta-$) end of the bond.

There are **three main types of reagents in organic chemistry**:

1. nucleophilic (or nucleus-seeking) reagents,

2. electrophilic (or electron-seeking) reagents;

3. homolytic reagents (free radical)

Nucleophilic reagents are substances containing non-bonded electron pairs which can be donated, i.e. they act as donors of electron pairs (i.e. Lewis bases) to electron-deficient atoms such as carbon ($\delta+$) to form a covalent bond.

They are 'electron rich'; they may be negatively charged ions such as OH^{-1}, CN^{-1}, Cl^{-1},
or they may be neutral molecules possessing non-bonded electron pairs such as NH_3, CH_3NH_2, CH_3CH_2OH, H_2O.

$$\mathbf{:NH_3} \qquad \mathbf{CH_3CH_2NH_2} \qquad \mathbf{:CN:^{-1}}$$

Electrophiles represent the other side of the coin. They are molecules or ions which are prepared to form a new covalent bond using a pair of electrons provided by another atom or molecule, often the organic reactant. This is to say that electrophiles are acceptor of electrons (i.e. Lewis acids) from electron-rich atoms.

Electrophiles may be uncharged molecules containing electron-deficient atoms, such as SO_3, BF_3, and $AlCl_3$ or molecules that are easily polarized such as Cl_2, Br_2, HBr.

$$\overset{\delta+1\quad\delta-1}{\mathbf{H - Br}} \qquad \overset{\delta+1\quad\delta-1}{\mathbf{Br - Br}}$$

Homolytic reagents are radicals that carry an unpaired electron which they use to form a covalent bond. Radicals are usually written with a dot to show these unpaired electrons. Examples of homolytic reagents are:

$$\mathbf{H\bullet,\ Cl\bullet,\ CH_3\bullet,\ C_6H_5}$$

Assignment

1. Explain the difference between:
a) homolytic fission and heterolytic fission, giving an example of each.
b) a substitution reaction and an addition reaction, giving an example of each.
c) an ion and a free radical, giving an example of each.
d) a carbocation and a carboanion,
e) a nucloeohilic reagent and an electrophilic reagent
f) Is a nucleophilic reagent more likely to attack a carbocation or a carboanion? Explain your answer.

2. a) What type of reaction is the following: addition, substitution, elimination or rearrangement?

$$C_2H_5Br + OH^{-1} \longrightarrow C_2H_5OH + Br^{-1}$$

b) What type of reagent is OH^{-1}: a nucleophile or an electrophile?
c) Name the organic compounds in the equation.