CHAPTER

1

General Organic Chemistry

1.1 Introduction:

Organic reactions involve the breaking and making of covalent bonds. The breaking and making of covalent bonds usually occurs in several descrete steps before transformation into product. The detailed sequential description of all steps of the transformation into products is called the mechanism of a reaction.

Complete information regarding all the steps is seldom obtained. However, a good deal of data can be gathered from the following

(a) study of kinetics of the reactions
(b) isolation of intermediate, if isolable.
(c) study of reactions in the presence of other similar substrate.
(d) study of the isotopically labelled atom in the reactants.
(e) trapping of free radicals
(f) crossover experiments
(g) stereochemical aspects etc.

Reaction mechanism containing following tools

$$\text{Reactant} \xrightarrow[\substack{\text{temperature/light} \\ \text{pressure}}]{\text{solvent}} \underset{\substack{OR \\ [\text{Transition state}]^{\neq}}}{[\text{Intermediate}]} \longrightarrow \text{Product}$$

(i) Reactant :

Reactants are classified into substrate and reagents

(A) substrates $\Rightarrow$ species at which reagent attack.

(B) Reagents $\Rightarrow$ attacking species (more reactive species)

Case-I: If reaction occurs between organic and inorganic species, organic species act as substrate and inorganic species act as reagent.

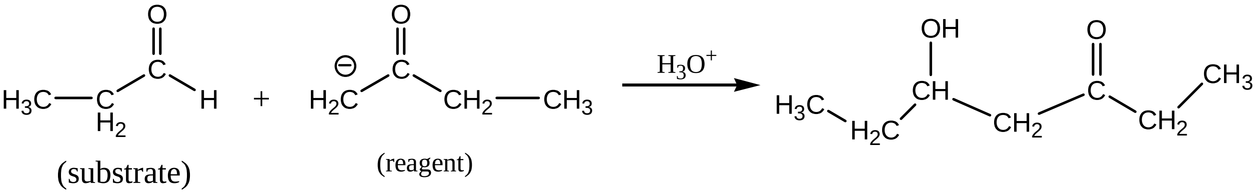
$$\underset{(\text{substrate})}{\text{Organic species}} + \underset{(\text{reagent})}{\text{Inorganic species}} \longrightarrow \text{Product}$$

Case-II: If reaction takes place between organic species then higher charge species act as reagent, other species act as substrate.

$$\underset{\substack{(\text{less charge}) \\ (\text{substrate})}}{\text{Organic species}} + \underset{\substack{(\text{excess charge}) \\ (\text{reagent})}}{\text{Organic species}} \longrightarrow \text{Product}$$

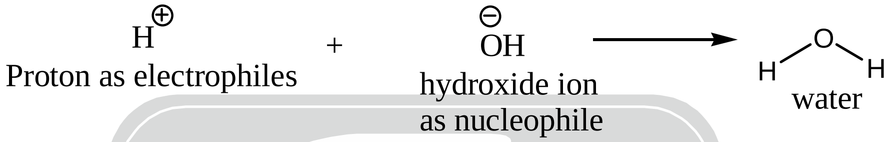
Example:

$$\underset{\text{substrate (organic)}}{H_3C-CH_2-CH_2-Br} + \underset{\text{reagent (inorganic)}}{KOH} \longrightarrow \underset{\text{product}}{H_3C-CH_2-CH_2-OH} + KBr$$



1.2. Electrophiles :

(Electron loving species) electrophiles are electron-deficient species and tend to attack the substrate at a site of high electron density. They may be neutral species as examplified by Lewis acid (such as BF_3, $AlCl_3$, $ZnCl_2$), carbene and carbocations.



Classification of electrophiles:

(a) Species having positive charge

Example : H^+, R^+, Cl^+, NO^+, NO_2^+, $C_6H_5-N_2^+$, $H_3C-\overset{+}{C}=O$ etc.

(b) Neutral species having vacant p-orbitals

Example : BF_3, BCl_3, BBr_3, carbene, etc.

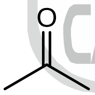
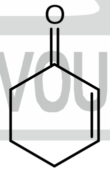
(c) Species having vacant d-orbital

Example : $FeCl_3$, $FeCl_2$ etc.

(d) Species having low lying σ-antibonding molecular orbital.

Example : Br_2, Cl_2, I_2 etc.

(e) π-bonding molecule:

Example : SO_3, CO_2,  , $R-C\equiv N$,  ,  etc.

(f) Element in their atomic state :

Example : O, S etc.

1.3. Nucleophiles:

(Nucleus-loving species) Nucleophiles are electron donar species. Nucleophilic reagents tend to attack the electron deficient species (electrophiles).

Classification of Nucleophiles:

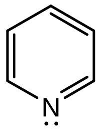
(a) Negative charge species:

$$OH^-, OR^-, SH^-, SR^-, R^-, Cl^-, Br^-, I^- \text{ etc}$$

(b) Organometallic reagent:

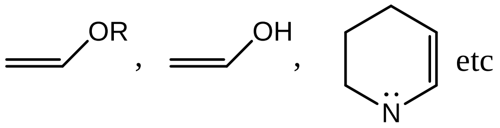
$$R^-MgX,\ R^-Li,\ R_2^-CuLi,\ R_2^-Cd,\ R_2^-Zn \text{ etc}$$

(c) Lone pair containing species:

$H_2\ddot{O}:$, $R-\underset{..}{\ddot{O}}-H$, $\ddot{N}H_3$, $H_2\ddot{S}:$,  etc

(d) π-bonded molecules:

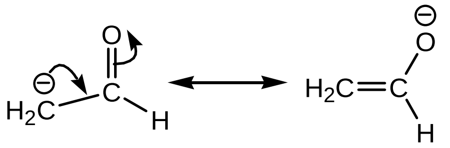
Alkene, Alkyne, Benzene,

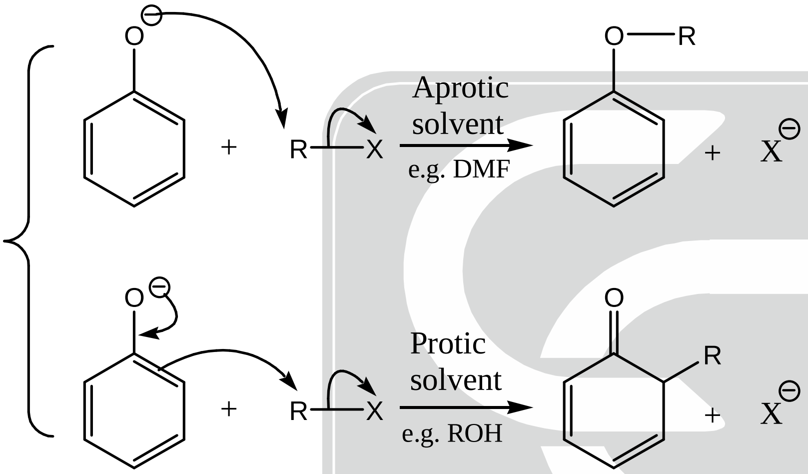


Note: Some species behave as the electrophiles as well as nucleophiles
Example : Br_2, Cl_2, I_2, etc.

Ambidentated nucleophile : Those nucleophile which posses more than one site for E^+ attack but at the same time only one side is used to form bond with electrophile. It is called ambidented nucleophile, such type of ambidentated nucleophile are regioselective.

Example :





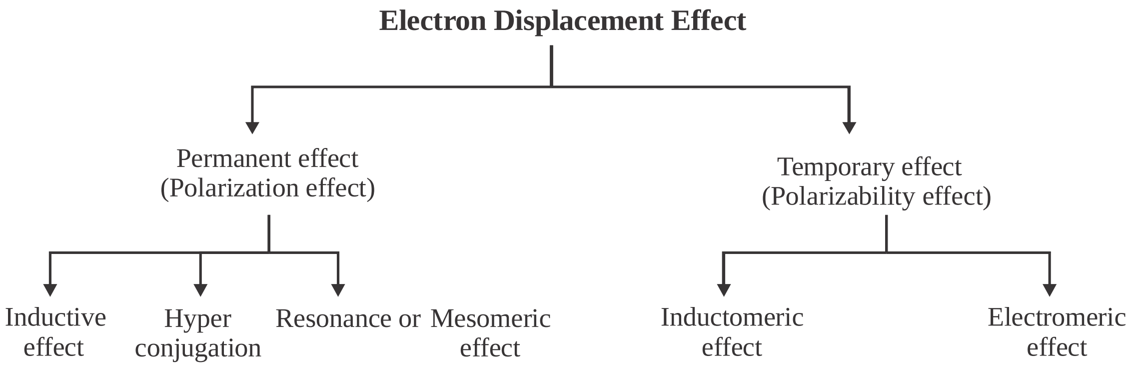
Note: $\xrightarrow[\text{Decreasing order of nucleophilicity}]{-,\ \bullet\bullet,\ =,\ \equiv}$

[Electronegativity $\propto$ % of S-character]

Note : Electron Displacement Effects:

Effect occuring due to displacement of electron in organic compound is called ***Electron Displacement Effect*** or electron delocalisation effect.

Electron displacement effect is of mainly two types.



Other Effect:

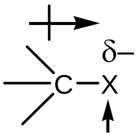
(a) Steric inhibition of resonance (b) Ortho effect.

1.4. Inductive effects:

In a covalent bond between two different atoms, the electrons in the $\sigma-\text{bond}$ are not shared equally. The electrons are attracted towards the most electronegative atom. An arrow drawn above the line representing the covalently bonded electrons shifts towards higher electronegative atom can show this. Electrons are pulled in the direction of the arrow.

When the atom (X) is more electronegative than carbon

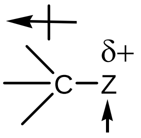
electrons attracted to X



negative inductive effect (–I effect)

When the atom (Z) is less electronegative than carbon

electrons attracted to carbon



positive inductive effect (+I effect)

–I groups

X=Br, Cl, NO_2, OH, OR, SH, SR, NH_2, NHR, NR_2, CN, CO_2H, CHO, COR

The more electronegative the atom(X), the stronger the –I effect

+I groups

Z=R(alkyl or aryl), metals (e.g. Li or Mg), anions (e.g. $\overset{\ominus}{O}$)

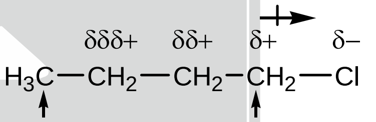
The more electropositive the atom (Z), the stronger the +I effect.

Pauling electronegativity scale

K = 0.8	I = 2.5
C = 2.5	Br = 2.8
N = 3.0	Cl = 3.0
O = 3.5	F = 4.0

Higher the value, more electronegative will be atom

The inductive effect of the atom rapidly diminishes as the chain length increases



$$H_3C-\overset{\delta\delta\delta+}{CH_2}-\overset{\delta\delta+}{CH_2}-\overset{\delta+}{CH_2}-\overset{\delta-}{Cl}$$

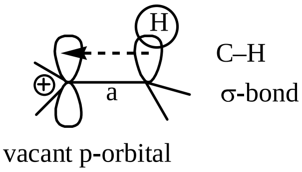
experiences a negligible –I effect

experiences a strong –I effect

The overall polarity of a molecule is determined by the individual bond polarities, formal charges and lone pair contributions, and this can be measured by the dipole moment (μ). Higher the dipole moment (measured in debyes (D)), more polar will be compound.

1.5. Hyperconjugation:

A $\sigma-\text{bond}$ can stabilise a neighbouring carbocation (or positively charged carbon) by donating electrons to the vacant p-orbital. The positive charge is delocalised or ‘spread out’, and this stabilising effect is known as *hyperconjugation* or “*no-bond resonance*”.



The electrons in the σ-bond spend time in the vacant p-orbital

Points to Remember :

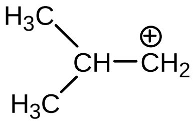
Number of α hydrogen $\propto$ number of hyperconjugating structure $\propto$ stability

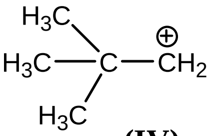
$$\propto \frac{1}{\text{Heat of hydrogenation}} \propto \text{Polarity} \propto \text{dipole moment} \propto \frac{1}{\text{bond length}\,(a)}$$

Problem : The correct order for the stability among following compound in solution phase is:

$CH_3\overset{\oplus}{C}H_2$ **(II)**

$CH_3CH_2\overset{\oplus}{C}H_2$ **(II)**

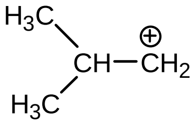
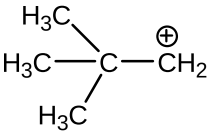

(III)


(IV)

(a) I > II > III > IV (b) **I > III > IV > II** **(c) IV > III > II > I** **(d) IV > III > I > II**

Soln. Number of α hydrogen $\propto$ stability.

Thus,

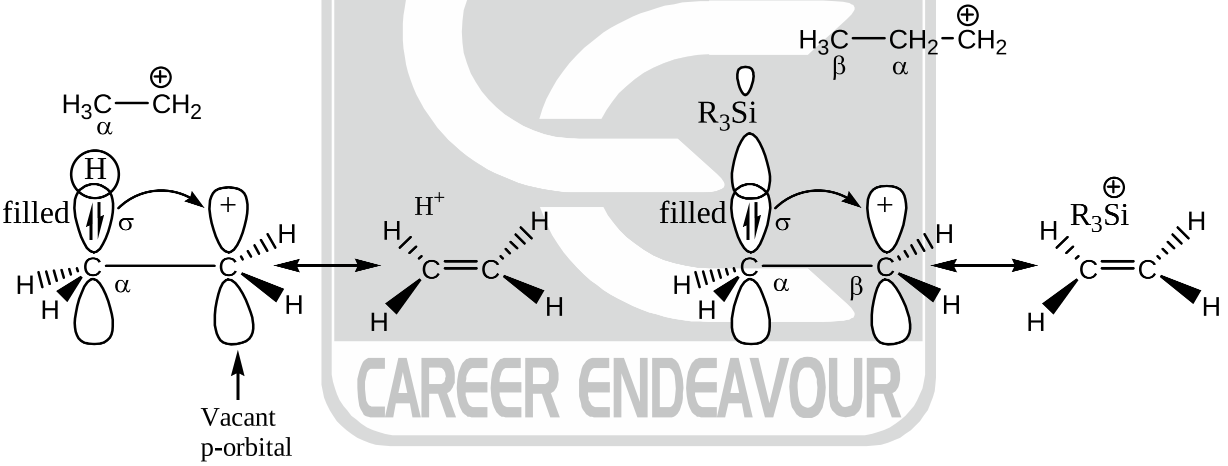
	(I)	**(II)**	**(III)**	**(IV)**
	$CH_3\overset{\oplus}{C}H_2$	$CH_3CH_2\overset{\oplus}{C}H_2$		
Number of α hydrogen	**3**	**2**	**1**	**0**

Stability, I > II > III > IV

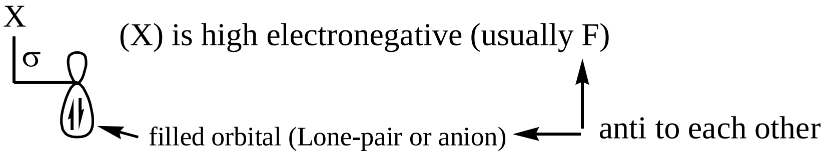
Hence, option (a) is correct.

Types of hyperconjugation:

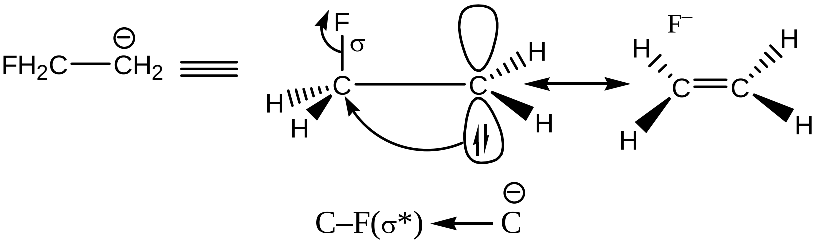
(i) Positive-Hyperconjugation (Separation of positive charge moiety)
Example: (For the stabilization of electron deficient species)



(ii) Negative-Hyperconjugation (separation of negative charge moiety)
(For the stabilization of electron rich species)



Example :



Note: CF_3 group attached to carbanion/aromatic ring shows negative-hyperconjugation.