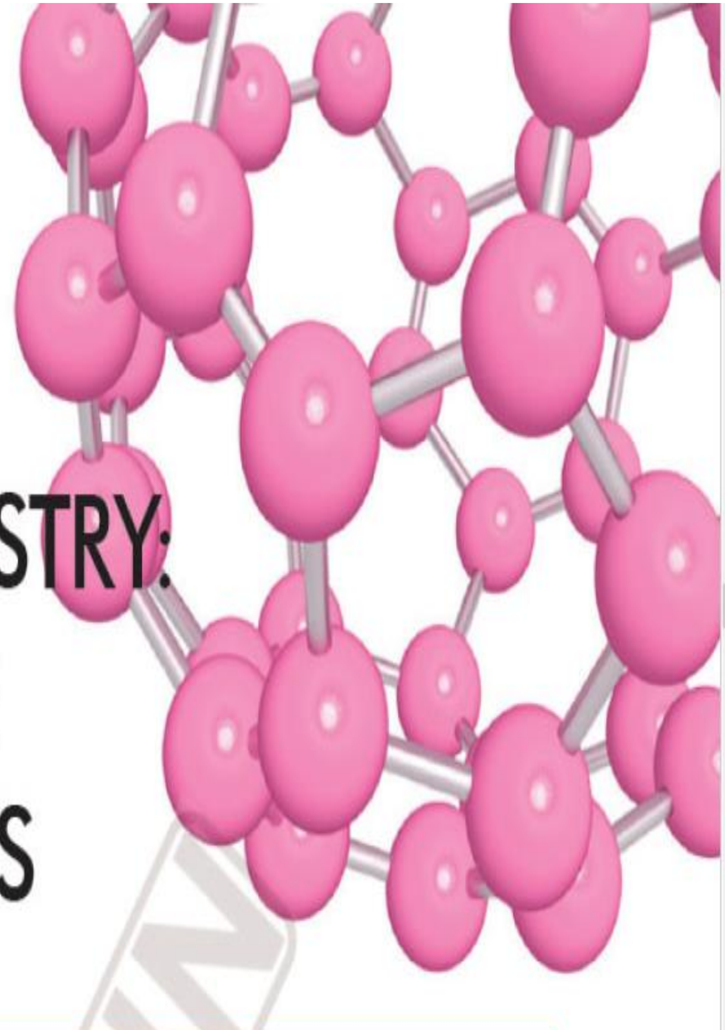
UNIT 12

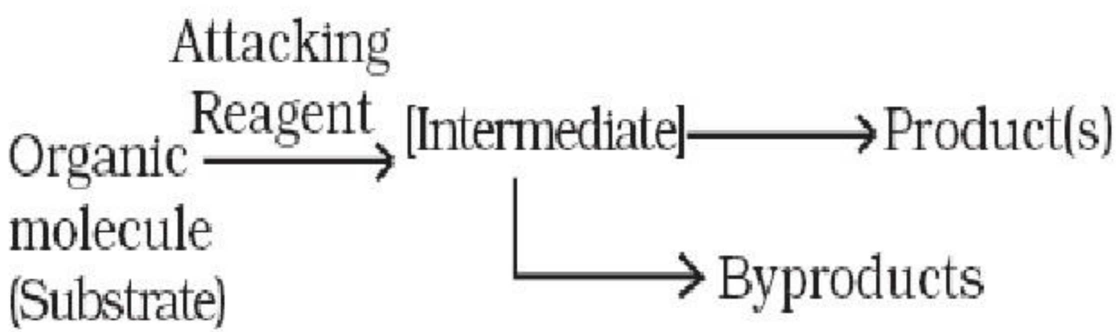
ORGANIC CHEMISTRY: BASIC PRINCIPLES AND TECHNIQUES



FUNDAMENTAL CONCEPTS IN ORGANIC REACTION MECHANISM

In an organic reaction, the organic molecule (also referred as a substrate) reacts with an appropriate attacking reagent and leads to the formation of one or more intermediate(s) and finally product(s)

The general reaction is depicted as follows :



✓ Substrate is that reactant which supplies carbon to the new bond and the other reactant is called reagent.

✓If both the reactants supply carbon to the new bond then choice is arbitrary and in that case the molecule on which attention is focused is called *substrate.*

Reaction mechanism: A sequential account of each step, describing details of electron movement, energetics during bond cleavage and bond formation, and the rates of transformation of reactants into products (kinetics) is referred to as reaction mechanism.

Fission of a Covalent Bond

Cleavages of covalent bonds

(Unsymmetrical fission)

(i) Heterolytic cleavage: In ***heterolytic cleavage***, the bond breaks in such a fashion that the shared pair of electrons remains with one of the fragments.

AB

$A - B \rightarrow \underline{\underline{\overset{\ominus}{A}}} + \underline{\underline{\overset{\oplus}{B}}}$

EN $\underline{\underline{A > B}}$

$A - B \rightarrow \overset{\oplus}{A} + \overset{\ominus}{B}$

$B > A$

$CH_3 - X \rightarrow -\overset{|}{\underset{|}{C}}^{\oplus} + \underline{\overset{\ominus}{X}}$

✓ one atom has a sextet electronic structure and a positive charge and the other, a valence octet with at least one lone pair and a negative charge.

$\overset{+}{C}H_3$ and Br^- as shown below.

$$H_3C - Br \longrightarrow H_3\overset{+}{C} + Br^-$$

- ✓ A species having a carbon atom possessing sextext of electrons and a positive charge is called a *carbocation (earlier called carbonium ion).*
- ✓ The observed order of carbocation stability is:

$$\overset{+}{C}H_3 < CH_3\overset{+}{C}H_2 < (CH_3)_2\overset{+}{C}H < (CH_3)_3\overset{+}{C}.$$

$$-\overset{\oplus}{C}-$$

- ✓ The organic reactions which proceed through heterolytic bond cleavage are called **ionic or heteropolar or just polar** reactions.

$$A-B \longrightarrow \overset{\oplus}{A} + \overset{\ominus}{B}$$

(a) $CH_3-SCH_3 \longrightarrow \overset{+}{C}H_3 + \overset{\ominus}{S}CH_3$

(b) $CH_3-CN \longrightarrow \overset{+}{C}H_3 + \overset{\ominus}{C}N$

(c) $CH_3-Cu \longrightarrow \overset{\ominus}{C}H_3 + Cu^+$

(Symmetrical fission)

(ii) Homolytic cleavage: In ***homolytic cleavage, one of the*** electrons of the shared pair in a covalent bond goes with each of the bonded atoms. Thus in homolytic cleavage, the movement of a single electron takes place instead of an electron pair.

$\dot{A} + \dot{B} \leftarrow A — B$

$H — H \rightarrow \dot{H} + \dot{H}$

✓ Such cleavage results in the formation of neutral species (atom or group) which contains an unpaired electron. These species are called *free radicals*.

✓ A homolytic cleavage can be shown as:

$CH_3 — X \xrightarrow[h\nu]{\Delta} \dot{C}H_3 + \dot{X}$

$$R—X \xrightarrow{\text{Heat or Light}} \underset{\text{Alkyl free radical}}{\dot{R}} + \dot{X}$$

✓ Organic reactions, which proceed by homolytic fission are called *free radical* or *homopolar* or *nonpolar reactions.*

Reagents

RMgX

R–Li

Lewis base

They are not electrophile

H_3O^+, NH_4^+, Na^+, Ca^{2+}

octet

Nucleophiles and Electrophiles

→ nucleus loving chemical species

$R-\ddot{O}-R$

Nucleophile (Nu) : A reagent that brings an electron pair i.e., nucleus seeking and the reaction is then called **nucleophilic.**

$R-\ddot{O}-H$

CN^-

–ve charged H^-, BH_4^-, AlH_4^-, X^-, $R-C\equiv C^-$, OH^-, OR^-, SH^-, NH_2^-, NO_2^-, $C_6H_5O^-$, $RCOO^-$

Neutral Nu^- — $H_2\ddot{O}:$, $\ddot{N}H_3$, $\ddot{N}H_3$

$R\ddot{N}H_2$, $R_2\ddot{N}H$, $R_3\ddot{N}$

Electrophile (E+): A reagent that takes away an electron pair i.e., electron seeking and the reaction is called **electrophilic.**

Lewis acid

Electron loving chemical species

✓ During a polar organic reaction, a nucleophile attacks an electrophilic centre of the substrate which is that specific atom or part of the electrophile that is electron deficient.

(+ve) $E^\oplus$ → H^+, Cl^+, Br^+, I^+, NO_2^+, NO^+, R^+ ---

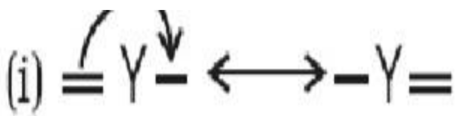
✓Similarly, the electrophiles attack at nucleophilic centre, which is the electron rich centre of the substrate.

neutral $E^\oplus$ $R^\cdot$, $:CR_2$, $\ddot{N}R$, SO_3, BF_3, $AlCl_3$, $FeCl_3$, $SnCl_4$

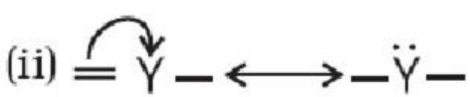
	Electrophiles	Nucleophiles
1.	These are deficient in electrons. $E^{\oplus} + :Nu^{\ominus}$	These are rich in electrons. $H_2\ddot{O}: + E^{\oplus}$
2.	These accept a pair of electrons from the substrate.	These donate a pair of electrons to the substrate. $R-\ddot{O}-H$
3.	These behave as Lewis acids. $e^{\ominus}n$ acceptor	These behave as Lewis bases. $e^{\ominus}n$ pair donar $R-\ddot{O}-R$
4.	These have at least one empty orbital due to which they accept electrons from the substrate molecule.	These have at least one lone pair of electrons which can be easily donated to the substrate molecule. $\ddot{N}H_3$, $R-\ddot{S}-R$
5.	BF_3, $AlCl_3$, SO_3 H^+, Cl^+ These are either neutral or positively charged chemical species. NO_2^+	These are neutral or negatively charged chemical species. CN^-, Br^-, I^-

Electron Movement in Organic Reactions

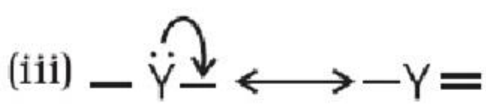
- ✓ The movement of electrons in organic reactions can be shown by curved-arrow notation.
- ✓ Presentation of shifting of electron pair is given below :



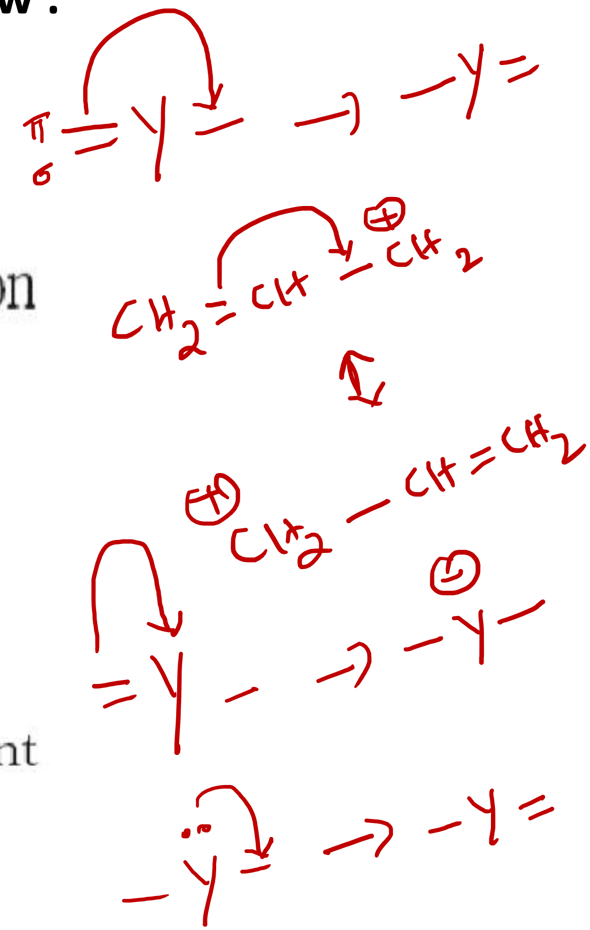
from π bond to adjacent bond position



from π bond to adjacent atom



from atom to adjacent bond position



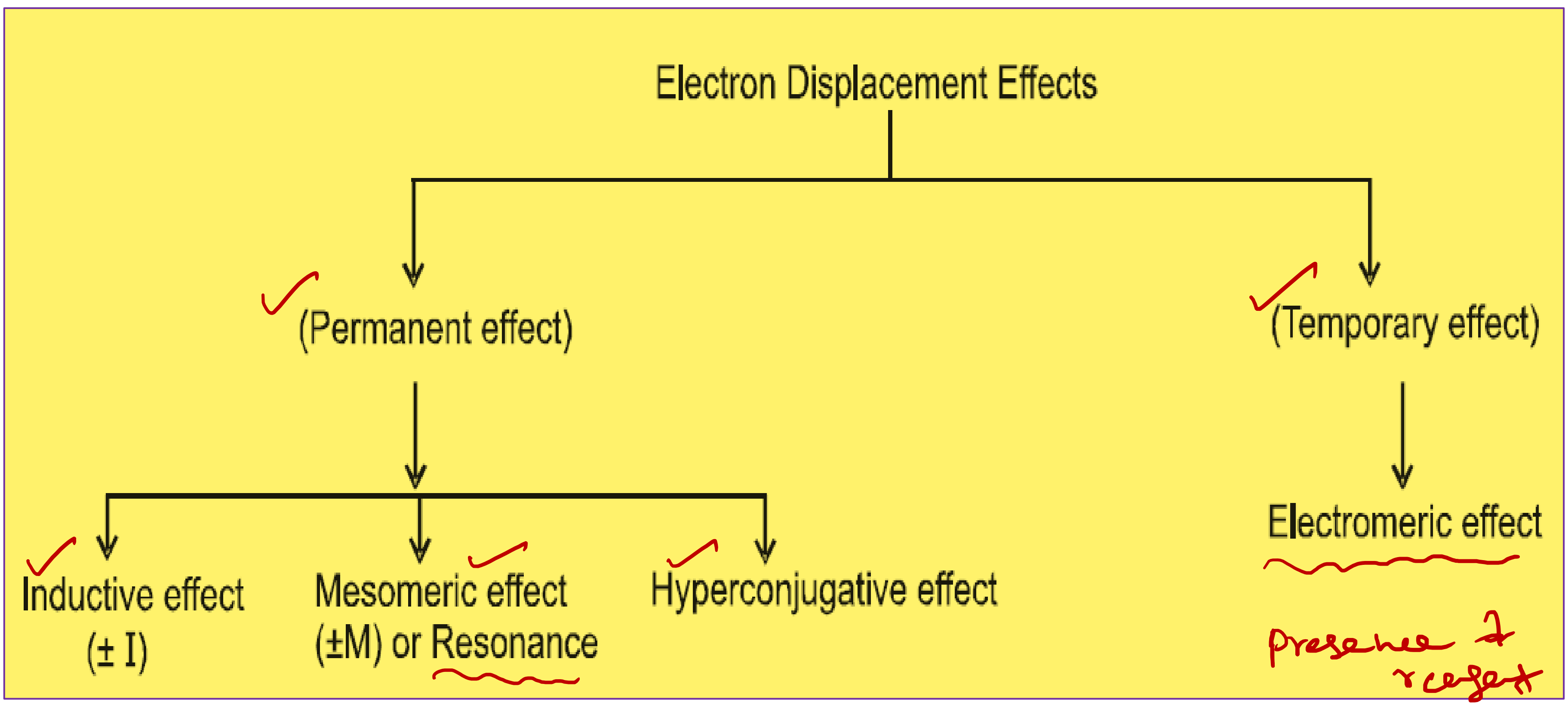
Electron Displacement Effects in Covalent Bonds

Electronic effect:

Introduction

- The effect which appears due to electronic distribution is called electronic effect.

Classification :



Inductive effect

- The normal C–C bond has no polarity as two atoms of same electronegativity (EN) value are connected to each other. Hence the bond is nonpolar.

$CH_3 - CH_2 - CH_2 - CH_2 - Cl \rightarrow$ more EN than C

- Consider a carbon chain in 1-Chloro butane, here due to more EN of Cl atom C–Cl bond pair is slightly displaced towards Cl atom hence creating partial negative (–) charge over Cl atom and partial positive (+) charge over C_1 atom.

- Now since C_1 is slightly positive, it will also cause shifting of $C_1 – C_2$ bond pair electrons towards itself causing C_2 to acquire small positive charge.
- Similarly C_3 acquires slightly positive charge creating an induction of charge in carbon chain. Such an effect is called inductive effect.

partially +ve

partially -ve

$$\underset{4}{C} - \underset{3}{\overset{\delta\delta\delta+}{C}} \rightarrow \underset{2}{\overset{\delta\delta+}{C}} \twoheadrightarrow \underset{1}{\overset{\delta+}{C}} \ggg \overset{\delta-}{Cl}$$

more

+I

-I

$CH_3 - CH_2 - Cl$

$\overset{\delta\delta+}{C} - \overset{\delta+}{C} - \overset{\delta-}{Cl}$

Thus inductive effect may be defined as a permanent displacement of σ bond pair electrons due to a dipole. (Polar bond)

Some important points are:

- ✓ It can also be defined as polarisation of one bond caused by polarisation of adjacent bond.

$C \rightarrow C \rightarrow Cl$

- ✓ It is also called transmission effect.
- ✓ It causes permanent polarisation in molecule, hence it is a permanent effect.
- ✓ The displacement of electrons takes place due to difference in electronegativity of the two atoms involved in the covalent bond.
- ✓ The electrons never leave their original atomic orbital.
- ✓ Its magnitude decreases with distance and it is almost negligible after 3rd carbon atom.

$\overset{\delta\delta\delta+}{C_4} - \overset{\delta\delta+}{C_3} - C_2 - \overset{\delta+}{C_1} - \overset{\delta-}{Cl}$

- ✓ The inductive effect is always operative through σ bond, does not involve π bond electron.

Types of inductive effects :

– I Effect : The group which withdraws electron cloud is known as – I group and its effect is called – I effect. Various groups are listed in their decreasing – I strength as follows.

$$-\overset{\oplus}{N}R_3 > -\overset{\oplus}{S}R_2 > -\overset{\oplus}{N}H_3 > -NO_2 > -SO_2R > -CN > -SO_2Ar > -COOH > -F > -Cl > -Br > -I > -OAr > -COOR > -OR > -COR > -SH > -SR > -OH > -C{\equiv}CR > Ar > -CH{=}CR_2$$

+ I effect : The group which release electron cloud is known as + I group and effect is + I effect.

$$-O^{\ominus} > -COO^{\ominus} > -C(CH_3)_3 > -CH(CH_3)_2 > -CH_2-CH_3 > -CH_3 > -D > -H$$