B.SC PART I PAPER ORGANIC

TOPIC:- Mechanism Of Organic Reaction

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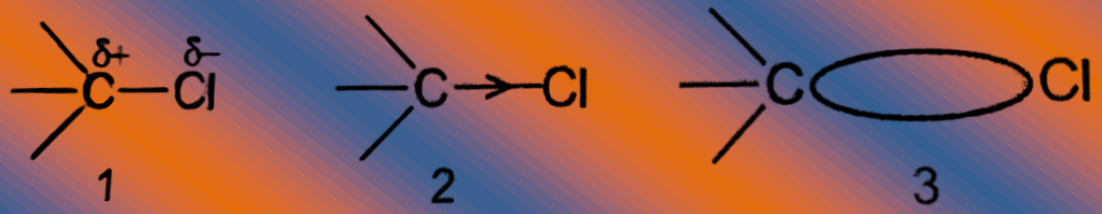
FACTORS WHICH INFLUENCE A REACTION

A reaction may occur or may not occur depending upon the density of electrons at the site of reaction in the substrate. The factors which influence the electron density in the substrate are:

(1) Inductive Effect
(2) Mesomeric Effect
(3) Electromeric Effect

Inductive Effect – It involve σ electrons. The σ electrons which form a covalent bond are seldom shared equally the two atoms. This is because different atoms have different electronegativity values, i.e., different powers of attracting the electrons in the bond. Consequently, electrons are displaced towards the more electronegative atom. This introduces a certain degree of polarity in the bond. The more electronegative atom acquire a small negative charge. The less electronegative atom acquire a small positive charge.



Consider the carbon-chlorine bond. As chlorine is more electronegative, it will become negatively charged with respect to the carbon atom.

Structure (1) indicates the relative charges on the two atoms. In (2), the arrow head placed in the middle of the bond indicates the direction in which the electrons are drawn. In (3), the more heavily shaded part show the region in which the electron density is greatest.

The inductive effect (I Effect) refers to the polarity produced in a molecule as a result of higher electronegativity of one atom compared to another.

The carbon-hydrogen bond is used as a standard. Zero effect is assumed in this case. Atom or groups which lose electrons toward a carbon atom are said to have a +I Effect. Such groups will be referred to in this book as electron-releasing. Those atoms or groups which draw electrons away from a carbon atom are said to have a –I Effect. Such groups will be referred to as electron-attracting.

Some common atom or groups which cause +I or –I Effects are shown below:

(a) -I Effect Groups (Electron-attracting):

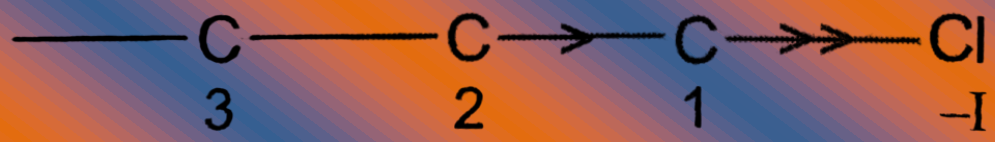
NO_2, F, Cl, Br, OH, C_6H_5-

(b) +I Effect Groups (Electron-releasing):

$(CH_3)_3C$-, $(CH_3)_2CH$-, CH_3CH_2-, CH_3-

Tertiary alkyl groups exert greater +I effect than secondary which in turn exert a greater effect than primary.

An inductive effect is not confined to the polarization of one bond. It is transmitted along a chain of carbon atoms, although it tends to be insignificant beyond the second carbon.



The inductive effect of C_1 upon C_2 is significantly less than the effect of the chlorine atom on C_1.

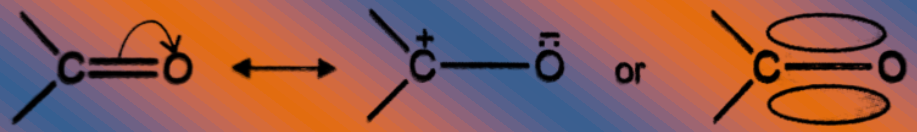
The inductive effect results in a permanent state of the molecule and can be observed practically in the form of dipole moments. The effect does not depend upon the presense of a regent.

Mesomeric Effect- It involves π electrons of double and triple bonds.

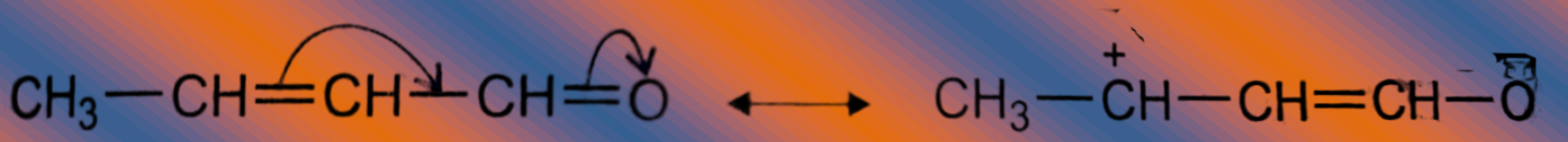
The mesomeric effect (M effect) refers to the polarity produced in a molecule as a result of interaction between two π bonds or a π bond and lone pair of electrons. The effect is transmitted along a chain in a similar way as are inductive effects.

The mesomeric effect is of great importance in conjugated compounds. (Conjugated compounds are those in which the carbon atoms are linked alternately by single and double bonds). In Such system, the π electrons get delocalized as a consequence of mesomeric effect, giving a number of resonance structure of the molecule.

Consider a carbonyl group (>C=O). The oxygen atom is more electronegative than the carbon atom. As a result, the π electrons of the carbon-oxygen double bond get displaced towards the oxygen atom. This gives the following resonance structures:



The mesomeric effect is represented by a curved arrow. The head of the arrow indicates movement of a pair of π electrons.If the carbonyl group is conjugated with a carbon-carbon double bond. The above polarization will be transmitted further via the π electrons.



The mesomeric effect like the inductive effect may be positive or negative. Atoms which lose electrons toward a carbon atom are said to have a **+M Effect**. Those atoms or groups which draw electrons away from a carbon atom are said to have a **–M Effect**.

Some common atoms or groups which cause +M or –M effects are listed below:

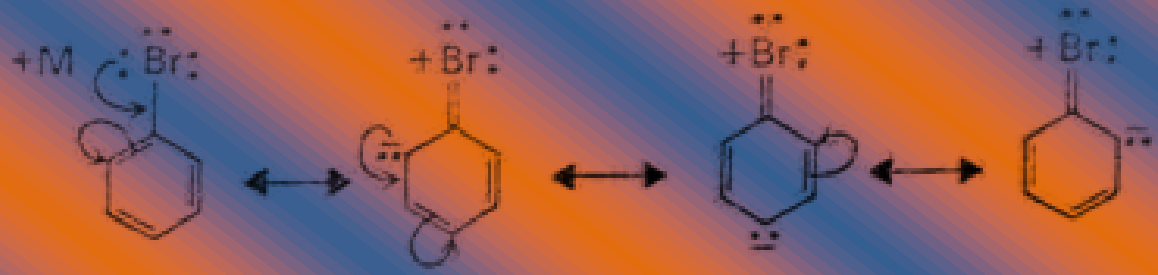
(a) +M Effect Groups:

Cl, Br, I, NH_2, OH, OCH_3

(b) –M Effect Groups:

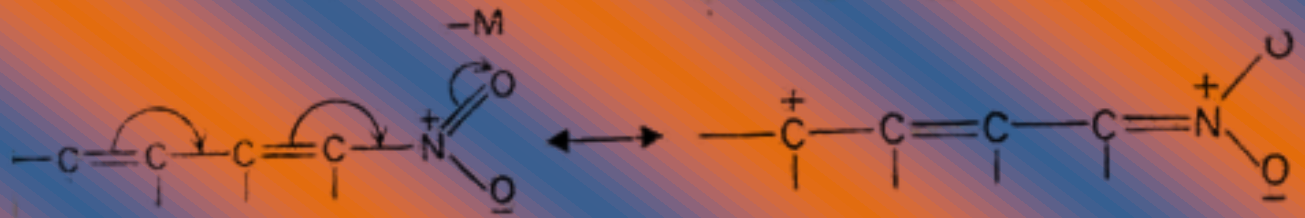
NO_2, CN, >C=O

The +M effect of the bromine atom is shown below:



BROMOBENZENE

The –M effect of the nitro group is shown below:



Electromeric Effect. Like the mesomeric effect, it also involves the π electrons.

The electromeric effect (E Effect) refers to the polarity produced in a multiple bonded compound as it a approached by a reagent.

When a double or a triple bond is exposed to an attack by an electrophile E^+ (a reagent), the two π electron which form the π bond are completely transferred to one atom or the other. The electromeric effect is represented as:

The curved arrow shows the displacement of the electron pair. The atom A has lost its share in the electron pair and B has gained this share. As result, A acquire a positive charge and B a negative charge. Notice that the arrow points away from the centre of the arrow points away from the centre of the bond and towards the atom that gains the electron pair.

HOMOLYTIC AND HETEROLYTIC FISSION

Every reaction of organic compounds involves the breaking (fission) of at least one bond and the making of another bond. To break a bond, in fact, we are breaking down a molecular orbital to give atomic orbitals. Therefore, energy has to be supplied to break a bond. Assuming that sufficient energy is available, a covalent bond (σ bond) can undergo fission in two ways:

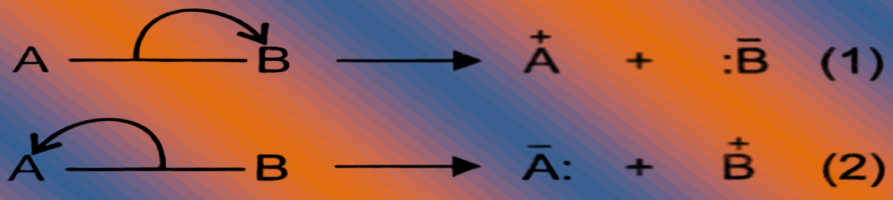
(1) By Homolytic Fission or Homolysis

(2) By Heterolytic Fission or Heterolysis

Homolytic Fission- In this process each of the atoms acquires one of the bonding electrons.

The product, A· and ·B, are called Free Radicals. They are electrically neutral and have one unpaired (odd) electron associated with them.

Heterolytic fission- In This process one of the atoms acquires both of the bonding electrons when the bond is broken.



Thank You