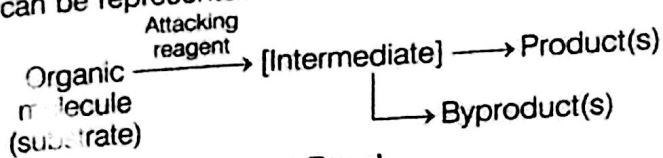
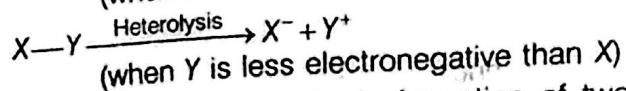
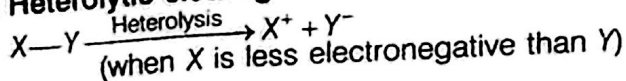


4. **Reaction Mechanism** A general organic reaction can be represented as



5. Fission of a Covalent Bond

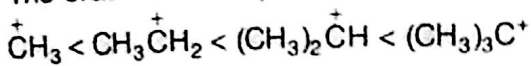
(i) Heterolytic cleavage or heterolysis



Heterolytic cleavage results in formation of two types of species. These are :

- (a) **Carbocation or carbonium ion** If the carbon has sextet of electrons and a positive charge, then the species is called carbocation (earlier called carbonium ion), e.g. CH_3^+ (methyl carbonium ion).

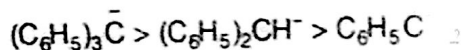
The order of stability of carbocations is



or methyl carbocation < 1° < 2° < 3°.

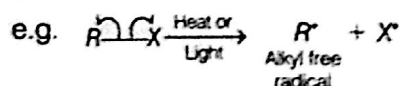
- (b) **Carbanion** If the carbon of the obtained species is negatively charged and have octet of electrons in its valence shell, then the species is called carbanion.

The order of stability of carbanions is as

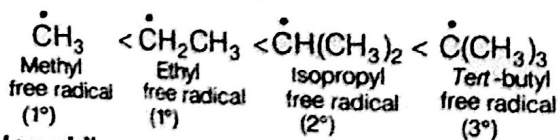


> allyl > CH_3^- (1° > 2° > 3° carbanions)

- (ii) **Homolytic cleavage or homolysis** This cleavage involves movement of only one electron, which is represented by half headed (fish hook) curved arrow



The neutral chemical species, thus formed are called the **free radicals**. Alkyl free radicals are also classified as primary, secondary or tertiary. Like carbocations, the order of stability of alkyl free radicals is



6. Nucleophiles and Electrophiles

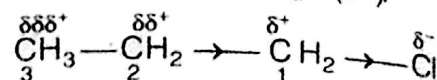
(i) Nucleophiles or nucleophilic reagents

An electron rich species having a lone pair of electrons is called a nucleophile (Nu^\ominus), i.e. nucleus loving species. e.g. Negatively charged species like H^- , Cl^- , Br^- , I^- , carbanions, OH^- , OR^- , SR^- , CN^- . Nucleophiles can also be seen in the form of neutral molecules.



- (ii) **Electrophiles or electrophilic reagents** An electrophile is defined as electron deficient species which attacks on electron rich areas. e.g. : Positively charged species like H^+ , Cl^+ , Br^+ , I^+ , NO_2^+ , SO_3^+ and carbocations. The electrophiles can also be seen in the form of neutral molecules, e.g. carbenes ($:\text{CR}_2$), nitrenes ($\ddot{\text{N}}\text{R}$), BF_3 , etc.

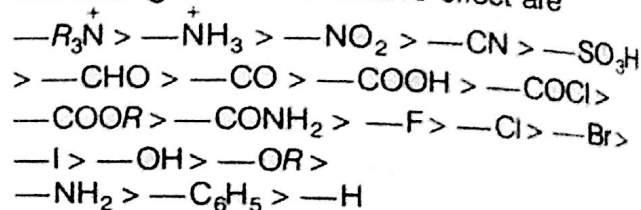
7. **Inductive Effect (I-effect)** In a polar covalent bond, the electrons are shifted to the more electronegative atom and hence, a polarity is developed in the bond. e.g. In a chain of carbon atoms having C—Cl bond, the C attached directly to the Cl-atom because of its less electronegativity acquires some positive charge (δ^+).



This induction of polarity due to presence of polar bond in an organic molecule called inductive effect.

Types of Inductive Effect

- (i) **Negative inductive effect** Atoms or groups having greater electron affinity than hydrogen are said to have **-I-effect** (electron attracting). Some of the -I-effect producing groups in decreasing order of inductive effect are

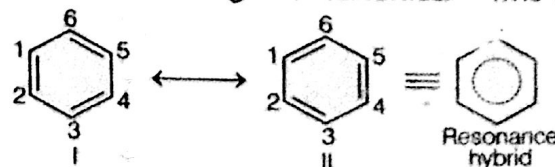


(-I power in decreasing order in respect of H)

- (ii) **Positive inductive effect** Atoms or groups having lower electron affinity than hydrogen are said to have **+I-effect** (electron withdrawing).

The order of +I-effect of some groups is as follows : 3° > 2° > 1° or CH_3 .

8. **Resonance Structure** Benzene is a resonance hybrid of following two canonical forms :



9. Resonance Effect (R-effect)

- (i) **Positive resonance effect (+R-effect)**

When the electrons move away from the atom or substituent group attached to the conjugated system, the effect is called positive resonance effect. In this effect, electron density increases at certain places. e.g. Groups like halogen, $-\text{OH}$, $-\text{OR}$, $-\text{OCOR}$, $-\text{NH}_2$, $-\text{NHR}$, $-\text{NR}_2$ show +R-effect.

(ii) **Negative resonance effect (-R-effect)**

When the electrons are transferred towards the atom or substituent group attached to the conjugated system, the effect is called negative resonance effect.

e.g. $-\text{COOH}$, $-\text{CHO}$, $\text{C}=\text{O}$, $-\text{CN}$ and $-\text{NO}_2$ show $-R$ -effect.

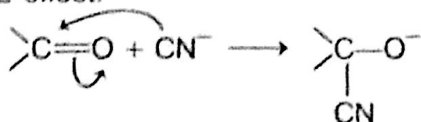
10. **Electromeric Effect (E-effect)** The polarity developed due to complete transfer of a shared pair of π -electrons to any of the atoms linked directly to the multiple bond in the presence of an attacking reagent is called the electromeric effect.

(i) **Positive electromeric effect (+E-effect)**

If the electrons of the π -bond are transferred to that atom of the double bond to which the reagent gets finally attached, then that effect is known as $+E$ -effect. e.g.

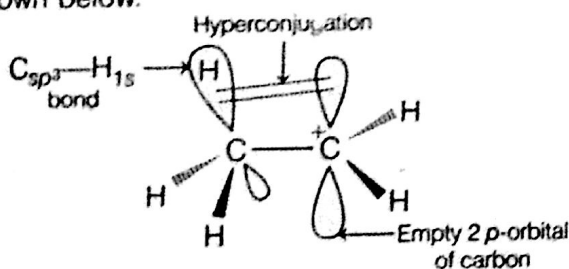


(ii) **Negative electromeric effect (-E-effect)** If the electrons of the double (π) bond are transferred to an atom of the double bond other than the one to which the reagent gets finally attached, then that effect is known as $-E$ -effect.

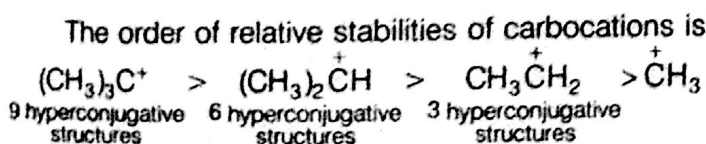


11. **Hyperconjugation** The stabilising interaction that involves delocalisation of σ -electrons of $\text{C}-\text{H}$ bond of an alkyl group linked directly to an atom of unsaturated system or to an atom having unshared p -orbital, is called hyperconjugation.

$\text{CH}_3\overset{+}{\text{C}}\text{H}_2$ has empty p -orbital, with which one of the $\text{C}-\text{H}$ bonds of the methyl group align in its plane and thus, the electrons of the $\text{C}-\text{H}$ bonds can be delocalised into the empty p -orbital as shown below.



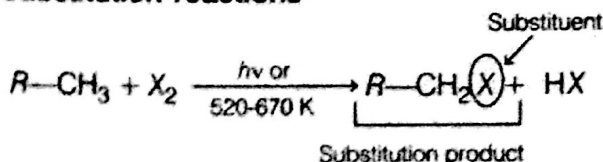
The order of relative stabilities of carbocations is



12. **Types of Organic Reactions and Mechanism**

The organic reactions can be categorised into following five categories:

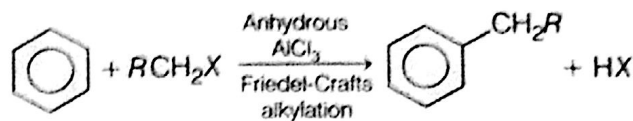
(i) **Substitution reactions**



These are further classified as follows :

(a) **Free-radical substitution** This reaction are brought by free radicals are called free radical substitutions. e.g. Halogenation of alkenes.

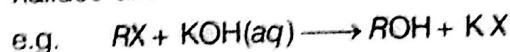
(b) **Electrophilic substitution reactions**



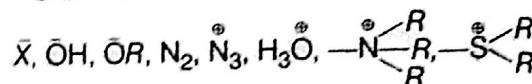
(c) **Nucleophilic substitution reactions**

These are usually written as S_N (S-substitution, N-nucleophile) and are of two types, i.e. unimolecular (shown as $\text{S}_\text{N}1$) and bimolecular (shown as $\text{S}_\text{N}2$).

These reactions are generally seen in alkyl halides and alcohols.



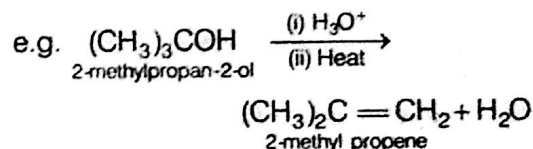
(ii) **Elimination reactions** An elimination reaction is one that involves the loss of two atoms or groups of atoms from the same or adjacent atoms of a substance leading to the formation of a multiple (double or triple) bond. Elimination reaction is given by those compounds which have a nucleophile as a leaving group, i.e.



Elimination reactions are of two types :

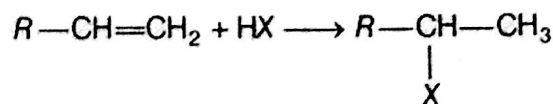
(a) α -elimination reactions

(b) β -elimination reactions



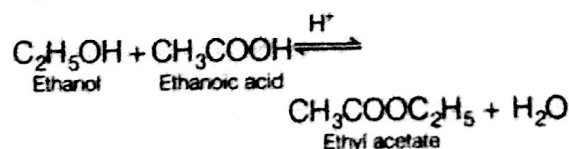
(iii) **Addition reactions** Reactions which involve combination between two reacting molecules to give a single molecule of the product are called addition reactions.

Such reactions are of typical compounds containing multiple bonds.



(iv) **Addition-elimination reactions**

These reactions involve addition of two molecules with elimination of smaller molecules like H_2O , e.g. esterification.



(v) **Rearrangement reactions** These reaction involve the migration of an atom or a group from one atom to another within the same molecule.

