Fundamental Concept of Organic Reaction Mechanism

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In an organic reaction, the organic compound called the substrate reacts with a suitable attacking species called the regent to form products. The formation of products may occur either directly from the reactants through a transition state or through the formation of one or more intermediates. In addition to the final products, sometime by products are also formed from the intermediates. The whole sequence of the events is sketched below:

Organic molecule $\rightarrow$ $^{\text{attacking reagent}}$ [intermediate] $\rightarrow$ products + by products.

During an organic reaction, a covalent bond between two carbon atoms or a carbon and some other atom is broken and a new bond is formed. Thus, 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 is called the reaction mechanism.

Electronic displacements in a covalent bond: Inductive effect: Whenever, an electron-withdrawing atom such as halogen i.e., -X (or a group such as nitro) is attached to the end of a carbon chain, the σ-electrons of the C-X bond are attracted by or displaced towards the more electronegative halogen atom. As a result the atom X acquires a small negative charge (δ^-) and C_1 acquires a small positive charge (i.e., δ^+) as shown:

$$C_4 \rightarrow C_3^{\delta\delta+} \rightarrow C_2^{\delta\delta+} \rightarrow C_1^{\delta+} \rightarrow X^{\delta-}$$
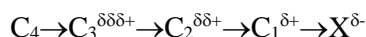
The small positive charge on C_1 in turn, attracts the σ- electrons of the C1 - C2 bond towards it. As a result C_2 acquires a small positive charge (i.e., $\delta\delta^+$), of course, smaller than that of C1. Similarly C_3 will acquire a small positive charge (i.e., $\delta\delta\delta^+$) that will still be smaller than that on C_2.   This type of displacement of σ- electron along a saturated carbon chain whenever an electron withdrawing or (electron donating) group is present at the end of the chain is called the inductive effect or the I – effect. This effect weakens steadily with increasing distance from the substituent (electron withdrawing or electron donating) group and actually dies down after three carbon atoms. There are two types of inductive effects i.e. – I- effect and + I-effect.

(i) If the substituent attached to the end of the carbon chain is electron-withdrawing, the effect is called – I- effect. For example,
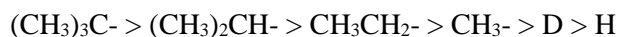
$$C_4 \rightarrow C_3^{\delta\delta+} \rightarrow C_2^{\delta\delta+} \rightarrow C_1^{\delta+} \rightarrow X^{\delta-} \quad (\text{ -I-effect})$$
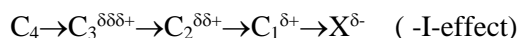
The – I-effect of some of the atoms and groups in the decreasing order is:

$$-NO_2 > -CN > -COOH > -F > -Cl > -Br > -I$$

(ii) If the substituent attached to the end of the carbon chain is electron donating, the effect is called + I-effect. For example

$$C^{\delta\delta\delta-} \leftarrow C^{\delta\delta-} \leftarrow C^{\delta-} \leftarrow CH_3 \quad (\text{+ I-effect})$$
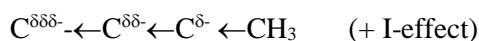
The + I -effect of some of the atoms or groups in the decreasing order is:

$$(CH_3)_3C- > (CH_3)_2CH- > CH_3CH_2- > CH_3- > D > H$$

Inductive effect is a permanent effect operating in the ground state of the organic molecules and hence is responsible for high melting point, boiling point and dipole moment of polar compounds.

Electromeric effect: It involves the complete transfer of electrons of a multiple bond (double or triple bond) to one of the bonded atoms (usually more electronegative) in presence of an attacking reagent. It is called E-effect.
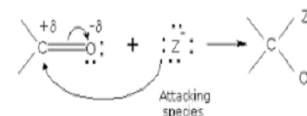
This effect is temporary and takes place only in the presence of a reagent. As soon as the reagent is removed, the molecule reverts back to its original position. Electromeric effect is of two types: +E- effect and – E-effect. If the electrons of the π-bond are transferred to that atom of the double bond to which the reagent gets finally attached, the effect is called + E-effect. For example, the addition of acids to alkenes.
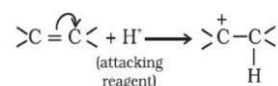
If on the other hand, the electrons of the double bond are transferred to an atom of the double bond other than the one to which the agent gets finally attached, the effect is called – E-effect. For example, the addition of cyanide ion to the carbonyl group
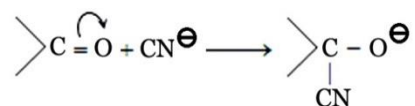
Electrophiles and nucleophiles:
(a) **Electrophiles** are electron loving chemical species. Their attraction for electrons is due to the presence of an electron deficient atom in them. Electrophiles may be either positively charged or electrically neutral chemical species,
   Positive electrophiles: H^+, H_3O^+, Cl^+, Br^+, I^+, N^+O_2, N^+O, R^+ (carbonation)
   Neutral electrophiles: $R^.$ (free radical), $:CR_2$ (carbenes), $:N^{..}R$ (nitrenes), SO_3, BF_3 $AlCl_3$, $FeCl_3$, $SnCl_4$, etc.
   Since both positively charged and neutral electrophiles are short by a pair of electrons (free radicals are however short by one electron), they have a strong tendency to attract electrons from other sources and hence behave as Lewis acid. Electrophiles always attack the substrate molecule at the site of highest electron density.
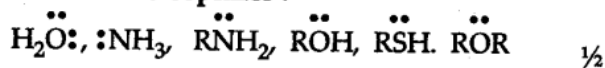(b) **Nucleophiles** are nucleus loving chemical species. Since the nucleus of any atom is positively charged therefore, nucleophiles must be electron rich chemical species containing at least one lone pair of electrons. They may be either negatively charged or neutral chemical species, examples:
   Negative nucleophiles: H^-,(hydride ion) Cl^-, Br^-, I^-, R^-(carbaion), OH^-, OR^- SR^- NH_2^-, CN^-, $RCOO^-$,etc.
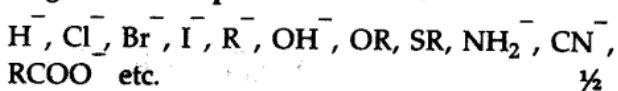   **Neutral nucleophiles:**

Since both negative charged and neutral nucleophiles contain at least one unshared pair of electrons, they behave a strong tendency to donate this pair of electrons to electron deficient species and hence behave as Lewis bases. Nucleophiles always attack the substrate molecule at the site of lowest electron density.

Neutral nucleophiles :

$\ddot{H_2O:}, :NH_3, R\ddot{N}H_2, R\ddot{O}H, R\ddot{S}H. R\ddot{O}R$ ½

Negative nucleophiles :

$\bar{H}, \bar{Cl}, \bar{Br}, \bar{I}, \bar{R}, \bar{OH}, \bar{OR}, \bar{SR}, \bar{NH_2}, \bar{CN},$
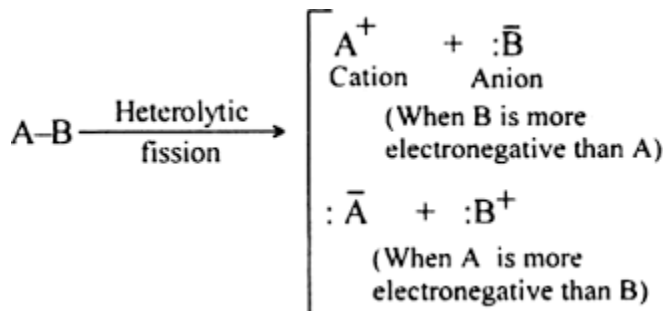$\bar{RCOO}$ etc. ½

Fission of a covalent bond:

(a) **Homolytic (symmetrical) fission:** If a covalent bond breaks in such a way that each atom takes away one electron of the share pair, it is called hemolytic or symmetrical fission. Homolytic fission is usually indicated by a fish arrow which denotes one electron displacement. For example, the neutral chemical species (such as A and B) which contain an odd or unpaired electron and which are produced by homolytic fission of covalent bonds are called free radicals. Homolytic fission usually occurs in non-

$$A \cdot \cdot B \xrightarrow{\text{Homolytic fission}} \dot{A} + \dot{B}$$
Free radicals

$$:\ddot{Cl} - :\ddot{Cl}: \xrightarrow[523 \text{ K}]{\text{u.v. light}} :\ddot{Cl} - \cdot\ddot{Cl}:$$
Free radicals

polar bonds and is favoured by high temperature, ultraviolet (UV) radiations and by the presence of radical initiators such as peroxides.
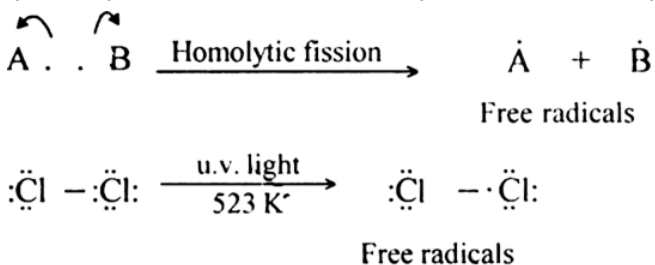
(b) **Heterolytic (unsymmetrical) fission:** When a covalent bond joining two atoms A and B breaks in such a way that both the electrons of the covalent bond (shared pair) are taken away by one of the bonded atoms, the mode of bond cleavage is called heterolytic fission. Heterolytic fission is usually indicated by a curve arrow which denotes a two electron displacement. Heterolytic fission results in the formation of charged species, cations and anions. It usually occurs in polar covalent bonds and is favoured by polar solvents.

$$A-B \xrightarrow[\text{fission}]{\text{Heterolytic}} \begin{cases} A^+ \quad + \quad :\bar{B} \\ \text{Cation} \quad\quad \text{Anion} \\ \text{(When B is more} \\ \text{electronegative than A)} \\ \\ :\bar{A} \quad + \quad :B^+ \\ \text{(When A is more} \\ \text{electronegative than B)} \end{cases}$$

Resonance or mesomerism: Sometimes it is not possible to assign a single electronic structure to a molecule which can explain all its properties. In such a case, it has been found that the molecule can be represented by two or more electronic structures, each one of which can explain most of the properties but none of them can explain all the properties of the molecule. Then the actual structure is intermediate or resonance hybrid of these structures. This phenomenon is called resonance. Resonance or Mesomerism describes the delocalized electrons within the certain molecules where one single Lewis structure does not express the bonds. An ion or molecule with these delocalized electrons can be represented by contributing several structures which are called resonance structures. The phenomenon of resonance can be explained with the help of carbon dioxide molecule. It has been represented by the structural formula: $O = C = O$.

Though this satisfies the conventional valency requirements, yet it cannot explain some experimental facts. The actual carbon oxygen bond in carbon dioxide has been found to be 115 pm whereas the normal carbon oxygen double bond is 122 pm and that for triple bond is 110 pm. This means that carbon oxygen bond in carbon dioxide is intermediate between a double and triple bond. To account for this, two other structures were proposed:
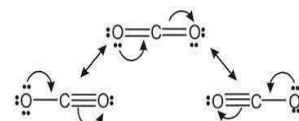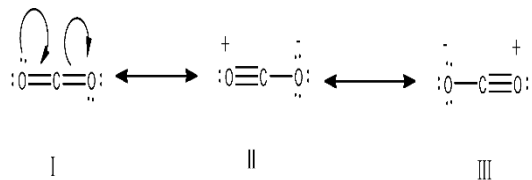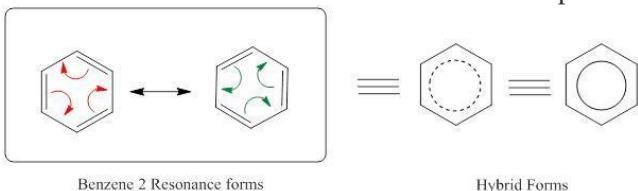
The actual molecule is said to be a resonance hybrid of the three structures.

Let us consider another example of benzene. It may be represented by a cyclic structure having alternate C-C single and C=C double bonds.
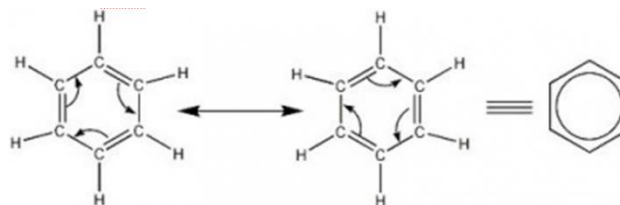
Therefore, we expect two different bond lengths of carbon -carbon bonds, one due to carbon - carbon single and other due to carbon =carbon double bonds. However, as determined experimentally, benzene has a uniform C-C bond distance of 139 pm. This value is intermediate between the carbon -carbon single (154 pm) and C=C double (134 pm) bonds. Thus, the structure of benzene cannot be represented by a single structure. The benzene molecule may be regarded as resonance hybrid of the following two structures.

Resonance energy: Resonance hybrid (or the actual molecule) is always more stable than any of its canonical structures. This stability is due to delocalization of electrons and is measured in terms of resonance energy or delocalization energy. It is defined as the difference in internal energy of the resonance hybrid and the most stable canonical structure. Further, more the number of equivalent resonance structures, greater is the delocalization of electrons, higher is the resonance energy and hence more stable is the compound. In case of benzene, this resonance energy has been determined to be 150.62 kilo joule/mole.

Rule for writing resonance structures: (a) The various resonance structures should differ only in the position of electrons and not in the position of atoms or nuclei. (b) All the resonance structures should have the same number of unpaired electrons. (c) In case of atoms of the second period in the periodic table, such resonance structures which violate octet rule should not be considered. For example, $CH_2=CH-N^+H_3$ (I) $\leftrightarrow$ X $^+CH_2 - CH=NH_3$ (II).   Structure (II) cannot be considered as a resonance structure since it violates the octet rule because nitrogen has 10 electrons in the valence shell. In other words, nitrogen cannot have more than 8 electrons because it does not have d- orbitals. (d) As far as possible, all the resonance structures should have nearly the same energy. The more the number of resonance structures more stable in the resonance hybrid. In general, the various resonance structures contribute to the resonance hybrid in proportion of their relative energies. The following points must be considered while deciding the relative energy of the various resonating structures.
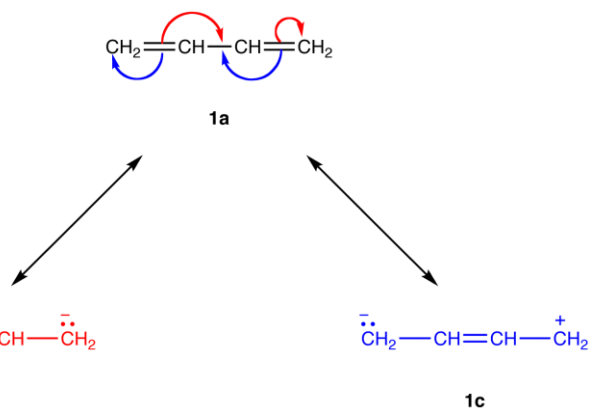
Relative contributions of resonance structures:

(i) Structures which are indistinguishable are of equal energy and hence contribute equally towards the resonance hybrid. for example, $^+CH_2 - CH= CH_2 \leftrightarrow CH_2=CH-^+CH_2$

Benzene contributing structures
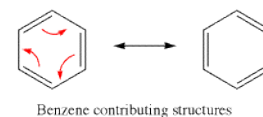
(ii) Structures with greater number of covalent bonds contribute more towards the resonance hybrid. For example, 1, 3 butadiene is a resonance hybrid of structures 1a, 1b and 1c.

Since formation of a bond is accompanied by release of energy, therefore, structure 1a with two π-bonds is more stable than structures Ib and Ic which contain one π-Bond each. Hence, structure 1a makes more contribution towards the resonance hybrid than structures (Ib and Ic).

$CH_2=CH-CH=CH_2$

1a

(iii) Structures which involve separation of positive and negative charges are of higher energy and hence contribute little towards the resonance hybrid. For example, contribution of structures 1b and 1c which involves separation of positive and negative charges is much less than the structure 1a.

$^+CH_2-CH=CH-\overset{..}{\overset{-}{C}}H_2$

1b

$^-\overset{..}{C}H_2-CH=CH-^+CH_2$

1c

(iv) Lesser the separation of positive and negative charges, more stable is the resonance structure. For example, out of the resonance structures for 1- methoxybuta-1,3-diene, which have the same number of covalent bonds, structure(III) is more stable than structure(II), since it involves less charge separation.
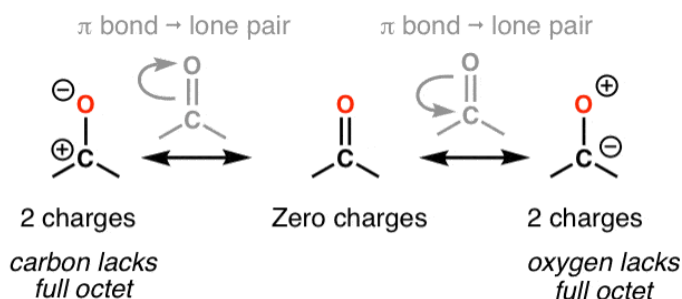
$CH_2=CH-CH= CH- OCH_3 \quad \leftrightarrow \quad :^-CH_2-CH=CH-CH=O^+-CH_3 \quad \leftrightarrow \quad CH_2=CH-^-CH -CH=O^+-CH_3$

1-methoxybuta-1,3-diene(I),   (II) less stable   (III) (more stable)

(v) When atoms of different electronegativities are involved, the structure with a negative charge on the more electronegative atom and positive charge on the less electronegative atom is of lower energy and hence contribute more towards resonance hybrid than the alternate structure in which the charges are reversed. For example, structure with positive charge on more electronegative oxygen atom and a negative charge on the less electronegative carbon atoms contributes less towards the resonance hybrid of a ketone as compared to the alternate structure with the charges reversed.

π bond → lone pair π bond → lone pair

2 charges   Zero charges   2 charges

carbon lacks full octet   *oxygen lacks full octet*

(vi) Structures having like charges on adjacent atoms are highly unstable and hence contribute little towards the resonance hybrid. For example, structure makes only negligible contribution towards the resonance hybrid of diketone.

(vii) Structures which help to delocalize the positive charge make important contribution towards the resonance hybrid regardless of the fact whether the positive charge is on less or more electronegative atom. For example structure (II) makes a significant contribution towards the resonance hybrid of carbocation (I) since it helps to disperse the positive charge. For example, $(CH_3)_2C^+$-OH $\leftrightarrow$ $(CH_3)_2C=O^+$-H

(I)   (II)
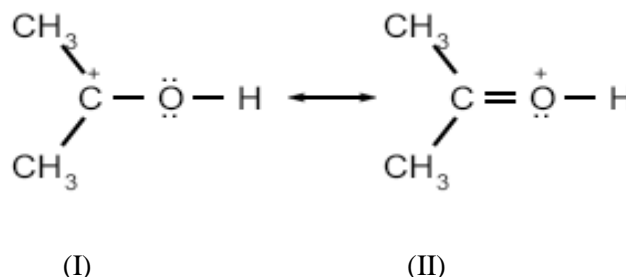
(viii) Resonance structures in which all the atoms have octet of electrons make larger contribution towards the resonance hybrid than those structures in which one or more of the atoms do not have octet of electrons. For example carbon atoms in structures bearing the positive charge have only a sextet of electrons and hence the contribution of these structures towards the resonance hybrid of their respective molecules is small.

Resonance effect or Mesomeric effect: In case of conjugated systems (having alternate Sigma and Pi bonds) the electrons can flow from one part of the system to the other due to resonance. "This flow of electrons from one part of the conjugated system to the other creating centres of low and high electron density due to the phenomenon of resonance is called resonance effect or mesomeric effect." It is of two types:

(i) Groups which donate electrons to the double bond or to a conjugated system are said to have + resonance effect (+R-effect). For example, -OH, -OR, -SH, -SR, -NH$_2$, -NHR, -NR$_2$, -Cl, -Br, -I
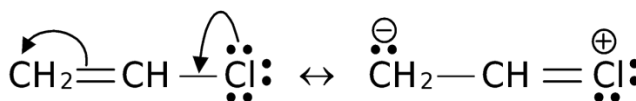
(ii) Groups which withdraw electrons from the double bond or from a conjugated system towards themselves due to resonance are said to have –R or –M –effect. For example; >C = O, -CHO, -COOR, -CN, -NO$_2$
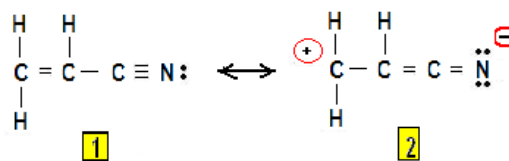
Resonance Structures

Hyperconjugation Effect: The inductive effect of the alkyl groups on a saturated carbon chain follow the order:

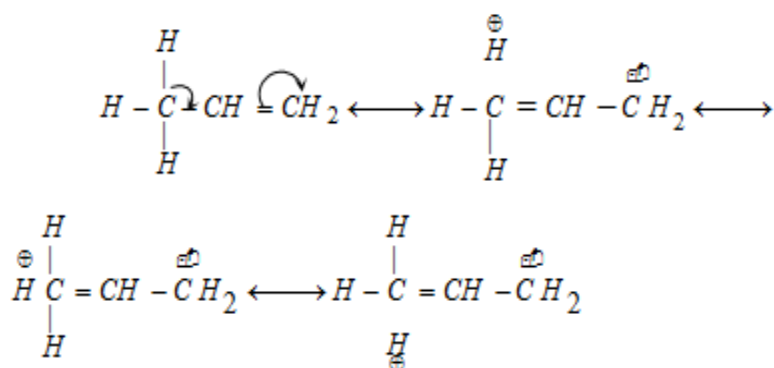$CH_3)_3C$- > $(CH_3)_2CH$- > CH_3CH_2-> CH_3-

However, when an alkyl group is attached to the unsaturated system such as a double bond or a benzene ring, the order of inductive effect is actually reversed. This effect is called hyperconjugation effect or Bakar -Nathan effect. In fact, hyperconjugation effect is an extension of the resonance effect. Whereas resonance effect involves the delocalization of π- electrons of two or more conjugated double bonds and or π electrons of double bond and non bonding, i.e., n- electrons of a heteroatom, hyperconjugation involves the delocalization of σ- electrons through overlapping of p- orbitals of a double bond with σ-orbital of the adjacent single bond (i.e., σ -π, conjugation).
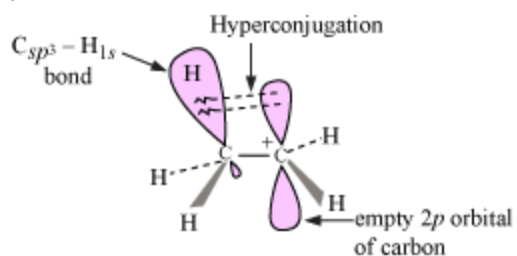
In terms of structures, hyperconjugation may be represented as shown in the figure.

Structures 1, 2 and 3 are called hyperconjugative structures. Since there is no bond between carbon and hydrogen atom in these structures, hyperconjugation is also called no bond resonance. It may be noted that although a free proton has been shown in the above structures, it is still bound quite firmly to the π- cloud and hence is not free to move. It is evident from the above structures that hyperconjugation occurs through the hydrogen atoms present on the carbon atom next to the double bond, i.e., α- hydrogen atoms. Naturally more the number of such α- hydrogen atoms, more the number of hyperconjugative structures and hence greater is the inductive effect. Clearly the number of hydrogen atoms is three(maximum) with methyl group, two with the ethyl group, one with the isopropyl group and none with the tertiary butyl group. Thus, the order of hyperconjugation effect decreases in the order: CH_3- > CH_3CH_2-   > $CH_3)_2CH$-   > $(CH_3)_3C$-

Signification of the hyperconjugation effect: Although hyperconjugation effect is a much weaker effect than resonance effect yet it is quite useful in explaining some of the physical and chemical properties of organic molecules. Some of these are:

(i) **Directive influence of alkyl groups**:
   The ortho, para- directing influence of CH_3- and other alkyl groups can be easily explained on the basis of hyperconjugation.


Hyperconjugation in toluene
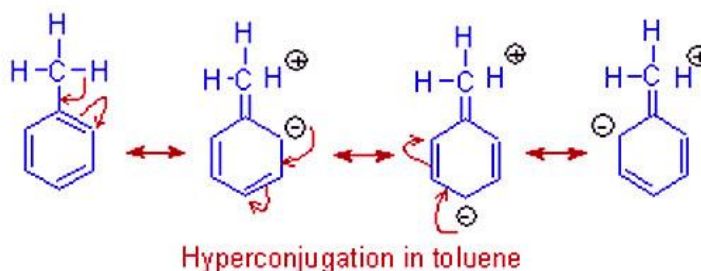
   As a result of hyperconjugation, the electron density at ortho and para positions w.r.t. the methyl group increases and hence the electrophilic substitution reaction in toluene (and other alkyl benzenes) will

occur at ortho and para positions with respect to methyl (or alkyl) group. Thus, alkyl groups are ortho, para directing.

(ii) **Shortening of carbon- carbon single bond adjacent to multiple bonds**,

Because of hyperconjugation C2 - C3 single bond in propene acquires some double bond character and hence is little shorter (1.49Å) than the normal carbon- carbon bond length(1.54Å) in propane. Similarly C1 - C2 bond in acetonitrile is shorter than the normal carbon -carbon single bond length (1.54 Å)

Acetonitrile

propyne
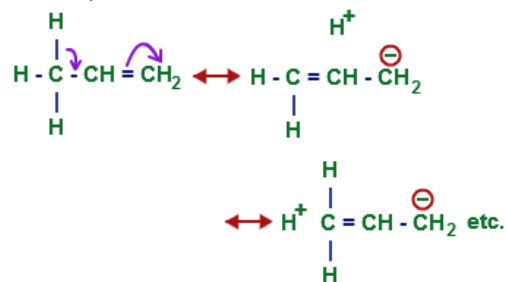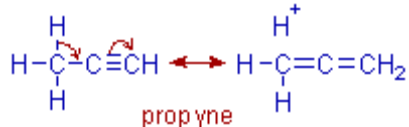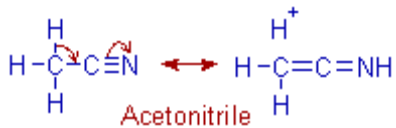
(iii) Relative stability of alkenes: Heats of hydrogenation (ΔH) show that greater the number of alkyl groups attached to the doubly bonded carbon atoms, greater is the stability (i.e., lower is the heat of hydrogenation) of alkene. Consider for example, the following alkenes: 2, 3 – dimethylbut-2-ene

Relative Stabilities of Alkenes

| I | II | III | IV | V | VI | VII |
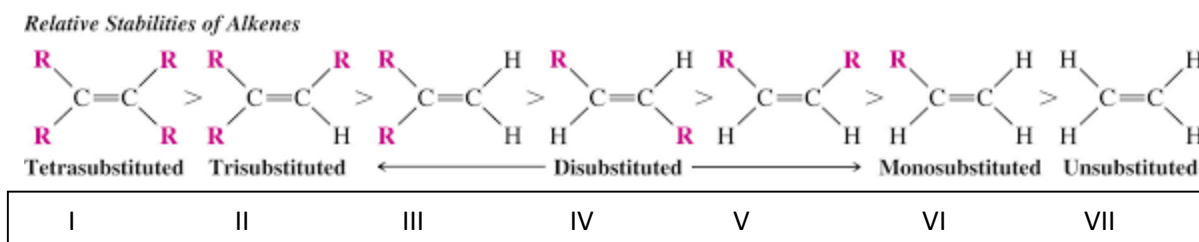
Alkenes I, II, III (or IV), V and VI have twelve, nine, six, three and none α- hydrogens respectively and hence equal number of hyperconjugation structures can be written for each one of them. Since greater the number of hyperconjugation structures, most stable is the alkene, therefore, the relative stability of these alkenes follows the sequence in above figure. Trans-but-2-ene is, however, more stable than cis-but-2-ene in which the two methyl groups are close together and hence their electronic clouds expel each other.

(iv) **Stability of carbocations and free radicals**: The relative stability of carbocations and free radicals follows the same sequence:

most stable ⟹ *least stable*

tertiary   secondary   primary   methyl

—00—