16. Cyanate ion, CNO^- has three important resonating structures :

$$\underset{\text{I}}{O=C=N^-} \longleftrightarrow \underset{\text{II}}{{}^-O-C\equiv N} \longleftrightarrow \underset{\text{III}}{{}^+O\equiv C-N^{2-}}$$

Which of the above structures contribute more to the resonance hybrid ?

(A) I **(B)** II **(C)** I and II equal **(D)** All equal

17. In which of the following, resonance will be possible ?

(A) $CH_2=CH-CH_2-CHO$ **(B)** $CH_2=CH-CHO$

(C) $CH_2=CH-COOH$ **(D)** $CH_2=CH-CH_2-CH=CH_2$

ORGANIC REACTIONS [BASICS] Section - 6

Organic compounds are covalent bonded. The carbon atom in these may be sp^3, sp^2 or sp hybridised. Hydrocarbons are almost non-polar, but their derivatives containing functional groups are polar covalent compounds. To understand and visualise the mechanisms of organic reactions, first we must go into details of various types of electrical effects that monitor the properties of various organic compounds. Then we have to understand various types of Substrates (main organic compound) ; Intermediates formed from these substrates; the various types of Reagents and the Medium (solvent) in which organic reactions occur.

All organic reactions can be classified into one of the following three categories for the purpose of understanding reaction mechanisms :

(i) Substitution Reactions **(ii)** Addition Reactions **(iii)** Elimination Reactions

Above three categories of reactions may involve : Rearrangement, Cyclisation (Ring opening & Ring closing) and stereo specific changes (involving optical and geometrical isomers), oxidation and reduction.

1. **Substrate :** It is the main organic compound acting as reactant and reacts with a reagent to give an new organic compound as main product. Substrates in general are of two types :

Nucleophilic : The organic compounds which have "electron rich centre or area" are referred to as nucleophilic in nature. They are acted upon by electron seeking reagents.

Alkenes, alkynes and benzene and its derivatives are some of such important substrates.

Electrophilic : The organic compounds which have "electron definicient centre or area" are referred to as Electrophilic in nature. They are acted upon by electron rich reagents usually most of organic derivatives containing functional groups act as electrophilic substrates. Organic Halides, Alcohols, Ethers, Aldehydes & Ketones and Carboxylic Acids & Derivatives are some of the important electrophilic substrates.

Electrophilic centre $\rightarrow \overset{\delta+}{C}-\overset{\delta-}{G}$

2. **Reagents :** Based on the attack by the type of attacking reagent, these are further categorised.

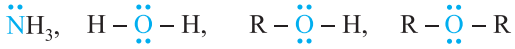
The main type of attacking reagents are :

(a) Nucleophile : Electron rich species, looking to attack a +vely charged centre (Electrophilic substrates).

These are classified as follows :

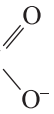
Charged : $H^-, OH^-, RO^-, CH_3^-, X^-, HS^-$ . . . .etc.

Neutral : Covalent compounds in which central atom has complete octet, has atleast one lone pair.



Ambident : Species having two nucleophilic centres, one is neutral (complete octet and has atleast one lone pair of electrons) and other is charged (negative charge). They basically have two nucleophilic sites / atoms.

(b) Electrophiles : Electron deficient species, looking to attack an electron rich site (Nucleophilic Substrate). These are classified as follows :

Charged : H^+, X^+, R^+,  . . . .etc. (X : Halogens except flourine)

Neutral : CO_2, $AlCl_3$, CS_2 . . . . .etc.

(c) Free radicals : Atom or group of atoms with their valencies unsatisfied, looking to attack a place so that they can satisfy their valencies. e.g., $Cl^\bullet$, $Br^\bullet$, $R^\bullet$ (alkyl).

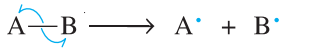
3. Reaction Mechanism :

It gives detailed aspect of as to "How actually an organic reaction proceeds". It depicts step-by-step visualisation of an organic reaction.

Organic reactions always involve breaking and reforming of covalent bonds. A covalent bond can break into two ways; In one of the ways, one of the fragments takes away the bonded electron pair *(Heterolytic cleavage)* and in other, each fragment takes away one of the electrons of bond *(Homolytic cleavage)*. Such fragments are known as Reaction intermediates such as : C^+ (carbocations), C^- (carbanions) and $C^\bullet$ (free radicals).

I. Homolytic Fission :

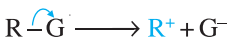
Such type of fission occurs in gas phase or in non-polar solvents (i.e., absence of polarising solvents) and is catalysed by free radical initiators. In such fission, free radicals are formed. Here the bond pair is equally shared after the fission.

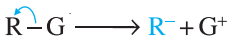


(free radicals)

II. Heterolytic fission :

Such type of fission occurs in polarising solvents (such as H_2O, alcohols and acids), catalysed by acids or bases, greatly influenced by polarity of solvents. Here, the ions are formed. In an organic compound such as R – G, two types of ions are formed.

(a)  (R^+ is known as carbocation)

(b)  (R^- is known as carbanion)

4. Electrical Effects :

For the detailed analysis of Reaction Mechanisms, we have to first understand "Electrical Effects" existing in the Organic Substrate and induced by External Reagents.

There are four kinds of Electrical Effects to be studied for the understanding of Reaction Mechanism.

I. Inductive Effect
II. Resonance (Mesomeric) Effect
III. Electromeric Effect
IV. Hyperconjugation Effect

I. Inductive Effect (Polar nature of covalent bonds) :

The displacement of an electron (shared) cloud along the carbon atom chain due to the presence of an electron withdrawing (*electron attracting*) or electron releasing (*electron repelling*) groups in the carbon chain is known as Inductive Effect (I-effect).

➤ It is a permanent effect which is transmitted along the carbon-carbon chain.

$$C \rightarrow C \rightarrow C \rightarrow G \qquad (G : \text{functional group})$$

But the effect is insignificant beyond the third carbon atom.

➤ Any atom or group which attracts electrons more strongly than hydrogen is said to exert a negative effect (–I effect) ; an atom or group which attracts electrons less strongly than hydrogen is said to exert a positive inductive effect (+I effect).

Group producing -I effect : (All functional groups)

$$-NO_2 > -CN \approx -SO_3H > -CHO > -COOH > -F > -Cl > -Br > -I > -OH > -OR > -NH_2$$
$$> HC \equiv C- > CH_2 = CH- > -C_6H_5 > -H$$

$$\longleftarrow \text{Increasing } -I \text{ effect} \longleftarrow$$

Note : **(i)** Alkynyl, vinyl and phenyl groups, because of *sp* and sp^2 hybrid carbon atom exert weak –I effect. Carbon atoms which are *sp* and sp^2 hybridised are electronegative in character due to dominance of '*s*' character over '*p*' character. [50% '*s*' character in '*sp*' and 33% '*s*' character in sp^2 hybrid carbon]

(ii) All such groups are called as Electron Withdrawing Groups (EWG).

Groups producing +I effect : (Only alkyl groups)

$$H- < D- < CH_3- < \underset{(1°)}{CH_3CH_2-} < \underset{(1°)}{CH_3CH_2CH_2-} < \underset{(2°)}{(CH_3)_2CH-} < \underset{(3°)}{(CH_3)_3C-}$$

$$\longrightarrow \text{Increasing } +I \text{ effect} \longrightarrow$$

Note : **(i)** All alkyl and cycloalkyl groups because of sp^3 hybrid carbon atom exert +I effect. An sp^3 hybrid carbon atom is an electron releasing (donating) due to dominance of '*p*' character over '*s*' character. [75% *p* character]

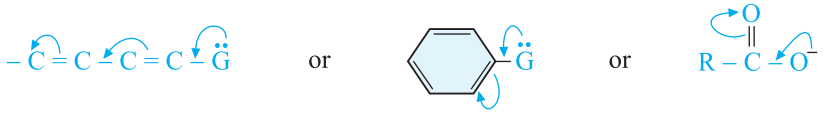
(ii) All these alkyl groups are called as Electron Releasing Groups (ERG) or Electron Donating Group (EDG).

II. Resonance (or Mesomeric) Effect :

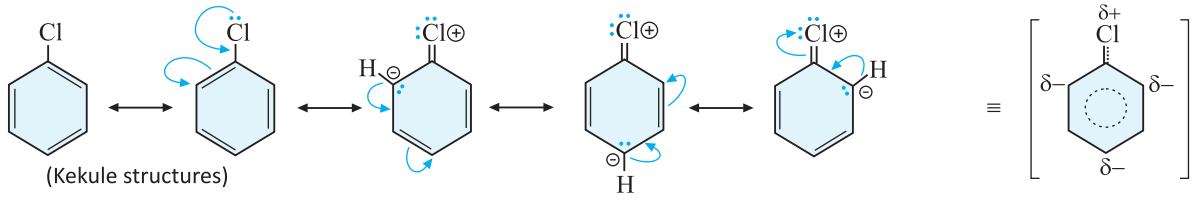
When a molecule or ion can be represented by two or more structures which have the same arrangement of atomic nuclei but differ in distribution of electrons, the phenomenon is called as Resonance. The various structures are called *contributing* or *resonating structures*. None of these structures truly represents all the properties of that molecule or ion. The actual structure is a *resonance hybrid* of several contributing structures.

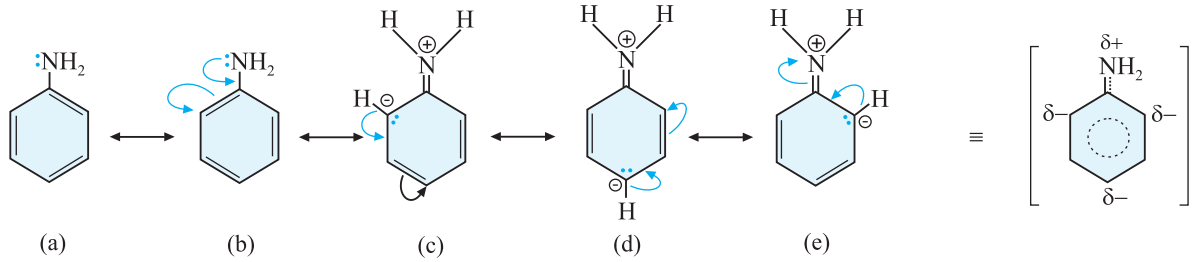
When multiple bonding is in conjugation with a functional group (G), then as per the electronic movement, we can visualise resonance in two ways illustrated below :

+M effect (+R-effect) : When the movement of electrons starts from a particular group (G) towards the carbon chain (C = C). It takes place when group (G) has a lone pair or an extra electron (in an anion).



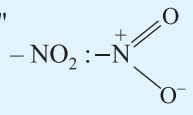
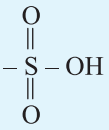
where G can be : $-NH_2, -OH, -Cl, -OR$ etc.

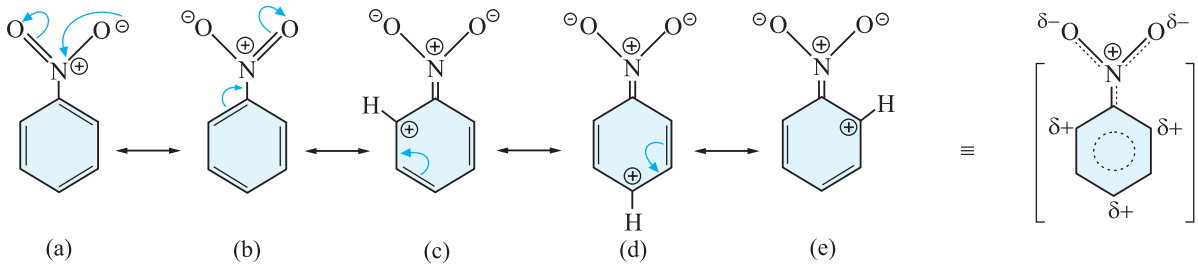




–M effect (–R-effect) : When the movement of electrons takes place towards a particular group (G) from carbon chain (C = C).

where G can be : $-NO_2, -C=O, -C\equiv N, -SO_3H$ etc.

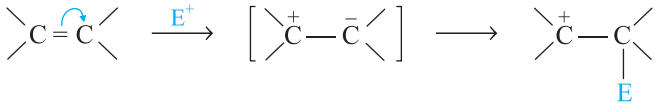
Note: In general, in the groups showing (–R/–M) effect, the "attached atom" of the group is unsaturated with a more electronegative atom e.g. $-NO_2$:  $-SO_3H$: 



III. Electromeric Effect :

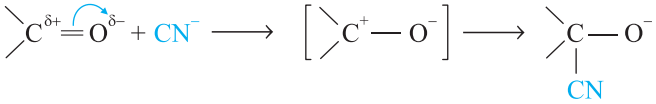
It is a temporary polarising effect and operates only in molecules having π - electrons (i.e., multiple bonded compounds) induced by the attacking reagents (nucleophiles & electrophiles) in a chemical reaction.

- In presence of electrophiles (E^+), π-electrons shifts to other carbon to make adjustment for the incoming electrophile to be added.



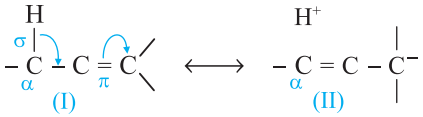
Observe that E^+ (electrophile) adds to the atom (group) where electrons are transferred. Such effect is known as +E effect i.e., when the transfer of electrons takes place towards the attacking reagent.

- In polar bonds, in presence of attacking reagents, a complete transfer of electron (one of π e^- pair) to more electronegative atom takes place, e.g., in $\overset{\delta+}{C}=\overset{\delta-}{O}$ in presence of nucleophiles like R^-, CN^-, HSO_3^-, π electrons shifts over to O.



Observe that CN^- (nucleophile) adds to the atom (group) from where electrons are transferred. Such effect is known as –E effect i.e., when the transfer of electrons takes place away from the attacking reagent.

IV. Hyperconjugation Effect :

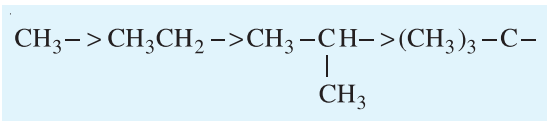


'Baker and Nathan' observed that alkyl groups (R) with at least one hydrogen (H) atom on the α-carbon, attached to an unsaturated carbon atom (i.e., having a – C = C – bond), or positive charge (as in carbocation, C^+) or odd electrons (as in free radicals, C°) are able to release electrons by a mechanism quite similar to that of 'electromeric effect' (*but it is a permanent effect*).

This type of electron released by alkyl group is called as hyperconjugation. It involves delocalisation of σ and π bond orbitals (σ – π conjugation). In structure (II), note that there is no definite bond between carbon and one hydrogen atom, hence it is also known as No bond resonance.

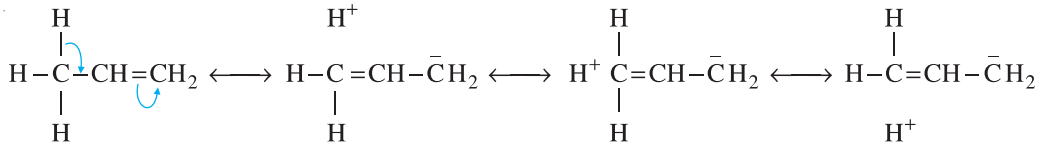
- Greater the number of C – H bond at α–carbon to the unsaturated system, greater will be the electron release and greater the hyperconjugation effect.

Hence electron release due to presence of three alpha (3α) – C – H bonds in methyl groups is greater than that by an ethyl group, in which there are only two alpha (2α) – C–H bonds. Similarly, the effect decreases in isopropyl group and further in tert-butyl group (no α–C–H bond).

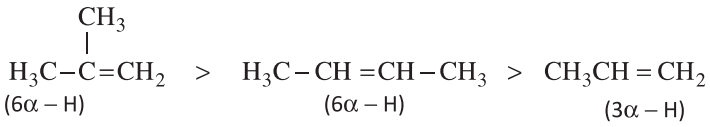


⟵ Increasing hyperconjugation effect ⟵ and ⟶ Increasing +I effect ⟶

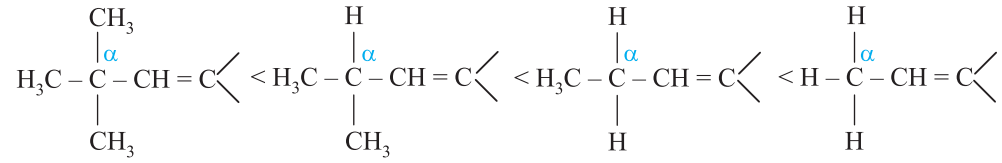
➤ **Stability of Alkenes :** Hyperconjugation explains the order of stability of alkenes. Propene is more stable than ethene because in propene, there are three H – C hyperconjugated bonds and hence σ–electrons of C – H bonds can delocalise over three different structures.



Hence greater the number of Methyl (each methyl group has 3 α-H) groups, attached to doubly bonded carbons, the more stable the alkene is



[more H - C bond on same carbon give greater effect]



(no H atom on α - C) (one H - atom) (two H – atoms) (three H – atoms)

Increasing hyperconjugation ⟶ and Increasing stability ⟶

➤ **Illustrating the Concept of Hyperconjugation :**

The hyperconjugative stabilities of tert-butyl cation and 2-butene, respectively, are due to :

(A) $\sigma \rightarrow p$ *(empty) and* $\sigma \rightarrow \pi^*$ *electron delocalisations*

(B) $\sigma \rightarrow \sigma^*$ *and* $\sigma \rightarrow \pi$ *electron delocalisations*

(C) $\sigma \rightarrow p$ *(filled) and* $\sigma \rightarrow \pi$ *electron delocalisations*

(D) *p (filled)* $\rightarrow \sigma^*$ *and* $\sigma \rightarrow \pi^*$ *electron delocalisations*

Note : π^* refers to π anti-bonding molecular orbitals.

Correct answer is (A)

Hyperconjugation is tert-butyl carbocation refers to delocalisation of σ-electrons of C – H bond over the empty p-orbitals of carbocation. In 2-butene, it refers to delocalisation of σ-electrons of C – H bond over the π* orbitals of C = C.

5 Reaction Int

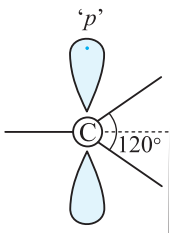
While unders Mechanism), we have to visualise the overall reaction in small steps. These s ntermediates, whose stability is the key to the acceptance of a particular rea here are three kinds of intermediates : Free Radicals, Carbocations and Carbanio

(a) Free Rad

An atom electron is called as Free Radical. These are formed via homolytic fission.

nd a halogen free radical is produced)

'C' of fr d hence the shape is planar, having an unhybrid ron (Paramagnetic in nature).

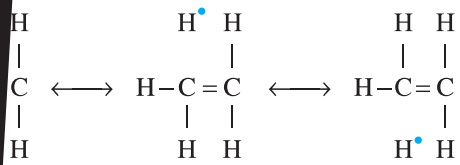


Tertiary an others. The stability of free radicals follows t

$$\underset{1^\circ}{CH_3CH_2^\bullet} > {}^\bullet CH_3$$

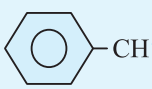
The stab via *hyperconjugation effect*. In methyl free radical, there is no hypercon ond.

Let us dr ures of ethyl radical.

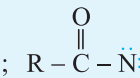


Similarly h a 1° alkyl radical (as number of alpha H-atoms are increasing, the hyp

Note : Another kind so formed. Carbenes are neutral, divalent and highly reactive intermediates.

: carbene),  (phenyl carbene)

Free radicals radicals generators such as : benzoyl peroxide, tert butyl peroxide.

There are als diates such as Nitrene ;  and Benzyne ;

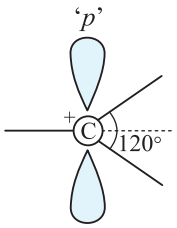
(b) Carbocations :

The organic compounds in which α-carbon is electrophilic due to function group attached to it, generally undergo heterolytic cleavage to form carbocations as follows :

$$C-G \longrightarrow C^+ + G^- \quad (C^+ \text{ is known as carbocation})$$

'C' of carbocation (alkyl) is sp^2 hybridised with one vacant unhybridised *p*-orbital. Hence the structure is planar.

Important carbocations include : Alkyl, allyl $(CH_2=\overset{+}{C}HCH_2)$ and benzyl $(C_6H_5\overset{+}{C}H_2)$.



The order of stability of carbocations is :

$$\underset{3°}{(CH_3)_3-C^+} > \underset{2°}{(CH_3)_2-C^+} > \underset{1°}{CH_3CH_2^+} > \underset{1°}{CH_3^+}$$

Stabilisation of carbocation is through +I effect and hyperconjugation effect.

- Electron releasing alkyl groups (R ⇢) disperse +ve charge over carbon.

e.g. $CH_3 \rightarrow \overset{\overset{CH_3}{\downarrow}}{\underset{+}{CH}}$ (2°) is more stable than $CH_3CH_2 \rightarrow \overset{+}{C}H_2$ (1°)

- More is the number of α–H attached to carbon atom having +ve charge, more is the number of hyperconjugative structures. Hence more stable is carbocation.

Observe that 3° butyl carbocation has 9α–H and hence more stable than 2° and 1° alkyl carbocations.

$$\begin{array}{l} CH_2-H \\ | \\ CH_3-C^+ \\ | \\ CH_3 \end{array} \longleftrightarrow \begin{array}{l} H_2C \quad H^+ \\ \| \\ H_3C-C \\ | \\ CH_3 \end{array} \quad [9 - \text{such structures}]$$

- Electron withdrawing (G ⇠ C^+) pulls electron density away from C^+ carbon and hence stability of carbocation decreases. G : CN^-, Cl^-, CHO, NO_2 etc. e.g. $\overset{+}{C}H_2-CH_2CHO$ is more stable than $CH_3\overset{+}{C}H-CHO$

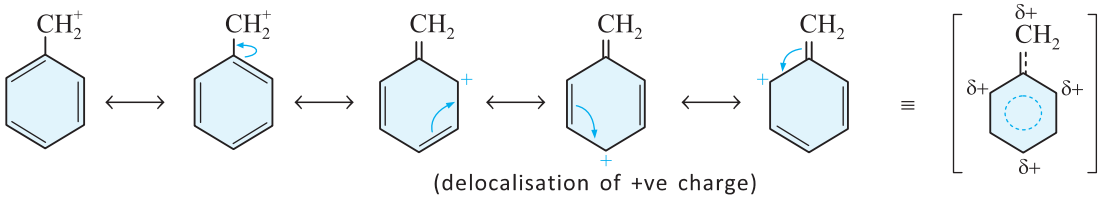
Stabilisation of carbocation is also takes place through resonance.

Allyl carbocation : $CH_2=CH-CH_2^+ \longleftrightarrow H_2C^+-CH=CH_2$

$$\left[H_2C \overset{\delta+}{\cdots} HC \overset{\delta+}{\cdots} CH_2 \right]$$

Resonance hybrid

Benzyl carbocation :



(delocalisation of +ve charge)

Note : More is the number of resonating structures dispersing the +ive charge over carbon, more is the carbocation stability e.g.

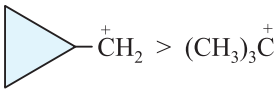
Stability order follows : $C_6H_5-\underset{\underset{C_6H_5}{|}}{\overset{+}{C}}-C_6H_5 > C_6H_5-\overset{+}{C}H-C_6H_5 > C_6H_5-\overset{+}{C}H_2$

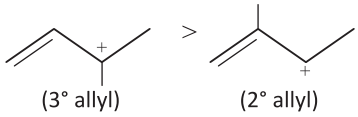
Order of stability of carbocation follows :

$$(CH_3)_3\overset{+}{C} > C_6H_5\overset{+}{C}H_2 \approx CH_3=CH-\overset{+}{C}H_2 \approx (CH_3)_2\overset{+}{C}H > CH_3\overset{+}{C}H_2 > \overset{+}{C}H_3$$

(3°) (1°) (1°) (2°) (1°)

[tert-butyl > 1° Benzyl ≈ 1° allyl > 3° alkyl > 2° alkyl > 1° alkyl > methyl]

Also Note :  ;



[A carbocation attached to a cyclopropyl group is exceptionally stable]

Properties of carbocations :

(i) $H_3C-H_2C^+ + Nu^- \longrightarrow CH_3CH_2Nu$ (combination with a nucleophile)

(ii) $H_3C-H_2C^+ \xrightarrow{\Delta} CH_2=CH_2 + H^+$ (elimination of proton at high temperature or in presence of strong bases)

➤ In order to achieve stability (before above two properties), carbocations go through rearrangement through shift of hydride ion (H^-) or methide ion (CH_3^-) from adjacent carbon atom. Hence these shifts are known as 1, 2 shifts.

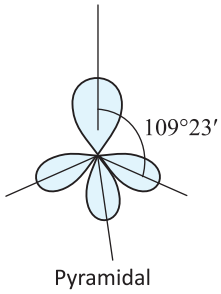
(a) $H_3C-H_2C-\overset{H}{\overset{|}{HC}}-H_2C^+ \xrightarrow{1,2\ H^- \text{ shift}} H_3C-H_2C-\overset{+}{C}H-CH_3$ (2° is more stable)

(b) $H_3C-\overset{H}{\overset{|}{\underset{H_3C}{\underset{|}{C}}}}-H_2C^+ \xrightarrow{1,2\ H^- \text{ shift}} H_3C-\underset{H_3C}{\underset{|}{C^+}}-CH_3$ (3° is more stable)

(c) $H_3C-\overset{CH_3}{\overset{|}{\underset{H_3C}{\underset{|}{C}}}}-\overset{+}{C}H_2 \xrightarrow{1,2\ CH_3^-} H_3C-\underset{H_3C}{\underset{|}{C^+}}-CH_2CH_3$ (3° is more stable)

(c) Carbanions : $\overset{\curvearrowleft}{C}-G \longrightarrow C^- + G^+$ (C^- is carbanion)

'C' of carbanions (alkyl) is sp^3 hybridised, hence structure is pyramidal with one of sp^3 hybrid-orbital containing a pair of elecrons.



e.g. $R\,MgBr \longrightarrow R^- + \overset{+}{M}gBr$

Stabilisation of carbanion (through –I effect).

➤ Electron-withdrawing group enhances stability whereas electron - releasing (R) group decreases stability.

$$CH_3^- > \underset{1°}{RH_2C^-} > \underset{2°}{R_2HC^-} > \underset{3°}{R_3C^-}$$

➤ The stability of carbanions increases with increase in 's' character (electron withdrawing).

$$\underset{\text{An alkynide ion 50\% 's' (sp)}}{R-C\equiv C^-} > \underset{\text{A vinylic ion 33\% 's' } (sp^2)}{RCH=CH^-} > \underset{\text{An alkyl ion 25\% 's' Character } (sp^3)}{R-H_2C^-}$$

Stabilisation of carbanion (through resonance).

- Allyl carbanion is resonance stabilised.

$$CH_2 = CH - \bar{C}H_2 \longleftrightarrow \bar{C}H_2 - CH = CH_2$$

$$\left[H_2C^{\delta-} \cdots\cdots CH \cdots\cdots H_2C^{\delta-} \right]$$

Resonance hybrid

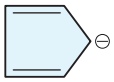
- Carbanions are negatively charge particles acting as nucleophiles. Other important carbanions are from carbonyl compounds, esters, nitro compounds.

$$\bar{C}H_2 - \underset{\|}{\overset{O}{C}} - R \longleftrightarrow CH_2 = \underset{|}{\overset{O^-}{C}} - R$$

$$\bar{C}H_2 - \underset{\|}{\overset{O}{C}} - OR \longleftrightarrow CH_2 = \underset{|}{\overset{O^-}{C}} - OR$$

These are resonance stabilised.

- Anions in which negative charge is present on the carbon of aromatic system is known as aromatic carbanions. These are most stable carbanions.



cyclopentadienyl carbanion

It obeys Hückel rule and is aromatic.

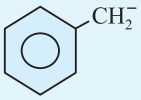
- Carbanions participate mainly in condensation reactions (to be studied later).

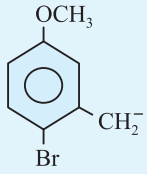
Note : **(i)** More is the number of resonating structure for a carbanion, more is its stability. e.g. consider the stability order :

$$C_6H_5 - \underset{\displaystyle C_6H_5}{\overset{\displaystyle |}{\bar{C}}} - C_6H_5 > C_6H_5 - \bar{C}H - C_6H_5 > C_6H_5 - \bar{C}H_2$$

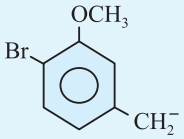
(ii) $\bar{C}Cl_3$ is more stable than $\bar{C}F_3$ even though – I effect is more pronounced in the latter and this is due to the formation of $p\pi - d\pi$ back bonding between the unhybridised p-orbital of carbanion and empty *d*–orbitals of Cl atom.

Illustration - 10 *Arrange the following in increasing order of stability on the basis of resonance* :

(A) (i) 

(ii) 

(iii)

(iv) 

(B) (i) $CH_2 = CH - CH = CH - \overset{\oplus}{C}H_2$

(ii) $CH_2 = CH - \overset{\oplus}{C}H - CH = CH_2$

(iii) $CH_2 = CH - \overset{\oplus}{C}H - \overset{\ominus}{C}H - \overset{\oplus}{C}H_2$

(iv) $\overset{\oplus}{C}H_2 - CH = CH - \overset{\ominus}{C}H - \overset{\oplus}{C}H_2$

SOLUTIONS :

(A) (i) < (iv) < (ii) < (iii)

In (iii) there is strong –M effect of $-NO_2$.

In (ii) and (iv) –I effect of Br and $-OCH_3$ are prominent.

In (i) delocalisation due to only phenyl ring is there.

5. Consider the following carbocations :

I. $C_6H_5\overset{+}{C}H_2$ II. $C_6H_5CH_2\overset{+}{C}H_2$ III. $C_6H_5\overset{+}{C}HCH_3$ IV. $C_6H_5\overset{+}{C}(CH_3)_2$

The correct sequence for the stability of these is :

(A) II < I < III < IV **(B)** II < III < I < IV **(C)** III < I < II < IV **(D)** IV < III < I < II

6. The order of decreasing stability of carbanions :

I. $(CH_3)_3C^-$ II. $(CH_3)_2CH^-$ III. $CH_3CH_2^-$ IV. $C_6H_5CH_2^-$

The correct choice is :

(A) I > II > III > IV **(B)** IV > III > II > I **(C)** IV > I > II > III **(D)** I > II > IV > III

7. The most stable free radical among the following is :

(A) $C_6H_5CH_2\overset{\bullet}{C}H_2$ **(B)** $C_6H_5\overset{\bullet}{C}HCH_3$ **(C)** $CH_3\overset{\bullet}{C}H_2$ **(D)** $CH_3\overset{\bullet}{C}HCH_3$

***8.** Which of the following is/are nucleophile(s) ?

(A) H_2O **(B)** NH_3 **(C)** $AlCl_3$ **(D)** $C_2H_5NH_2$

***9.** Which of the following can act as an electrophile?

(A) CN^- **(B)** OH^- **(C)** CH_3^+ **(D)** BF_3

10. Which of the following behaves both as a nucleophile and as an electrophilic substrate ?

(A) $CH_3C\equiv N$ **(B)** CH_3OH **(C)** $CH_2=CHCH_3$ **(D)** $C_6H_5CH_3$

11. Which organic species has only one type of hybridised carbon?

(A) $CH_2=C=CH_2$ **(B)** $CH_3-\overset{\oplus}{C}H-CH_3$

(C) $CH_3-C\equiv CH$ **(D)** $CH_2=CH-\overset{\oplus}{C}H_2$

12. Which free radical is the most stable ?

(A) $C_6H_5-\overset{\bullet}{C}H-CH_3$ **(B)** $CH_2=CH-\overset{\bullet}{C}H_2$

(C) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle \bullet}{\underset{|}{C}}}-CH_3$ **(D)** $\overset{\bullet}{C}H_3$

***13.** Which statement is(are) correct for inductive effect ?

(A) It is a permanent effect

(B) It is the property of single bond

(C) It cause permanent polarization in the molecule

(D) It is an electron delocalisation effect

***14.** Which statement is(are) correct for electromeric effect ?

(A) It is a temporary effect

(B) It is the property of π bond

(C) It takes place in presence of reagent, i.e., electrophile or nucleophile

(D) It can never occur in a free radical reaction

15. The kind of delocalization involving sigma bond in conjugation with pi electrons is called :

(A) Inductive effect **(B)** Hyper conjugation effect

(C) Electromeric effect **(D)** Mesomeric effect

16. $(CH_3)_4\overset{+}{N}$ is neither an electrophile, nor a nucleophile because it

(A) Does not have electron pair for donation as well as cannot attract electron pair

(B) Neither has electron pair available for donation nor can accommodate electron since all shell of N are fully occupied

(C) Can act as Lewis acid and base

(D) None of these

17. Arrangement of groups: $(CH_3)_3C-$, $(CH_3)_2CH$, CH_3CH_2- with respect to the hyper-conjugation effect, when attach to an unsaturated carbon atom, in increasing order is :

(A) $(CH_3)_3C- < (CH_3)_2CH- < CH_3CH_2-$ **(B)** $CH_3CH_2- < (CH_3)_2CH- < (CH_3)_3C-$

(C) $(CH_3)_2CH- < (CH_3)_3C- < CH_3CH_2-$ **(D)** $(CH_3)_3C- < CH_3CH_2- < (CH_3)_2CH-$

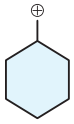
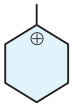
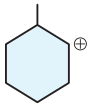
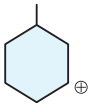
18. Which is more stable?

I. $CH_3-\overset{\oplus}{C}(CH_3)-CH_3$ (with CH_3 below C)

II. $CD_3-\overset{\oplus}{C}(CD_3)-CD_3$ (with CD_3 below C)

(A) I > II **(B)** II > I **(C)** I = II **(D)** Stability can't be predicted

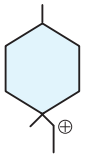
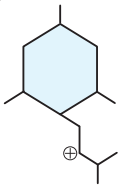
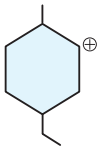
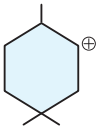
19. The stability order of the following carbocations is :

[I]  [II]  [III]  [IV] 

(A) I > II > III > IV **(B)** II > IV > III > I

(C) IV > III > II > I **(D)** II > III > I > IV

***20.** Which of the following will rearrange?

(A)  **(B)**  **(C)**  **(D)** 

21. Which one of the following has all the effects, namely inductive, mesomeric and hyperconjugative?

(A) CH_3Cl **(B)** $CH_3CH=CH_2$

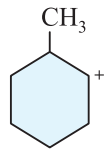
(C) $CH_3CH=CHCOCH_2Cl$ **(D)** $CH_2=CH\ CH=CH_2$

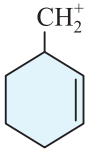
22. Stability of following alkenes in the increasing order is:

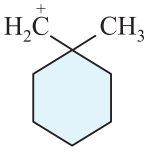
[I] $CH_3CH=CHCH_3$ [II] $CH_3-C(CH_3)=C(CH_3)-CH_3$ [III] $CH_3-C(CH_3)=CH_2$ [IV] $CH_3-C(CH_3)=CHCH_3$

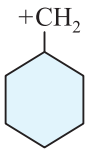
(A) I < III < IV < II **(B)** I < II < III < IV **(C)** IV < III < II < I **(D)** II < III < IV < I

23. Which of the following carbocations can undergo rearrangement via hydride shift?


[1]


[2]


[3]


[4]

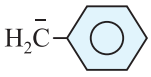
(A) 1 **(B)** 1 and 3 **(C)** 1, 4 **(D)** 1, 2, 4

24. Which of the following species is most stable?

(A) $p-O_2NC_6H_4-\overset{\oplus}{C}H_2$ **(B)** $C_6H_5\overset{\oplus}{C}H_2$

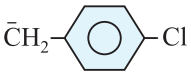
(C) $p-\ddot{\underset{\cdot\cdot}{Cl}}-C_6H_4-\overset{\oplus}{C}H_2$ **(D)** $p-H_3CO-C_6H_4-\overset{\oplus}{C}H_2$

25. Which one of the following is most stable ?


(A)

(B)

(C)


(D)

QUALITATIVE & QUANTITATIVE ANALYSIS OF ORGANIC COMPOUNDS — Section - 7

Qualitative Analysis :

Detection of functional groups is an important step in the analysis of organic compounds. It entirely depends on the correct determination of the constituent elements.

Elemental Detection :

The elements present in organic compounds are carbon and hydrogen. In addition to these, they may also contain oxygen, nitrogen, sulphur, halogens and phosphorus.

Detection of Carbon and Hydrogen :

Carbon and Hydrogen are detected by heating the compound with copper (II) oxide. Carbon present in the compound reacts with copper (II) oxide. Carbon present in the compound is oxidised to carbon dioxide (tested with lime-water, which develops turbidity) and hydrogen to water (tested with anhydrous copper sulphate, which turns blue).

$$C + 2CuO \xrightarrow{\Delta} 2Cu + CO_2$$

$$2H + CuO \xrightarrow{\Delta} Cu + H_2O$$

$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 \downarrow + H_2O$$

$$\underset{\text{White}}{5H_2O} + CuSO_4 \longrightarrow \underset{\text{Blue}}{CuSO_4 . 5H_2O}$$