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Some Basic Principles of Organic Chemistry

For the better understanding of organic chemistry it is necessary to know some basic terms, processes and principles. Through these in particular the electron density distribution of a molecule can be visualised.

Such a visualisation proved very helpful in deciding the point of reagent attack during organic reactions. We all know organic reactions are slow reactions. Their slowness is due to the involvement of proper bond breakage and new bond fomations. So, here we begin with the first step of any organic reaction, i.e. lysis or breakage of bonds present within the molecule.

IN THIS CHAPTER ....

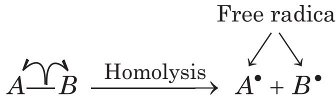
- Covalent Bond Fission
- Reagent or Attacking Species
- Reaction Intermediates
- Electronic Displacement in a Covalent Bond
- Conjugation, Mesomeric Effect and Resonance
- Hyperconjugation
- Organic Reactions and their Mechanisms

Covalent Bond Fission

Breakage or fission of any covalent bond can have following two possibilities.

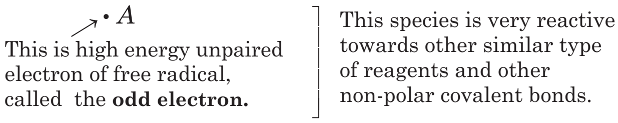
Homolysis or Symmetrical Fission

If a covalent bond breakes in such a way that each atom takes away one electron of shared pair, the fission is called **homolysis** or **homolytic fission**. e.g.



$$A{-}B \xrightarrow{\text{Homolysis}} \underbrace{A^{\bullet} + B^{\bullet}}_{\text{Free radicals}}$$

The neutral chemical species, thus formed is called **free radical** and is represented as



Favourable Factors for Homolysis

- The major factor which favours homolysis is zero or a small difference in electronegativity between the two atoms of a bond.
- Homolytic bond fission takes place in gaseous phase or in the presence of non-polar solvents (CCl_4, CS_2).
- Presence of peroxide, UV light, heat $(\geq 500°C)$, electricity also favour homolysis.

Heterolysis or Asymmetrical Fission

If a covalent bond breakes in such a way that both the electrons of shared pair are taken away by one of the bonded atoms, the bond fission is called **heterolytic fission**. e.g.

$$X\overset{\curvearrowright}{-}Y \xrightarrow{\text{Heterolysis}} X^+ + Y^-$$

(when X is less electronegative than Y)

$$X\overset{\curvearrowleft}{-}Y \xrightarrow{\text{Heterolysis}} X^- + Y^+$$

(when Y is less electronegative than X)

The cation formed here is called **carbocation** or **carbonium ion** as positive charge exist on carbon atom. Likewise the anion is called **carbanion**.

Favourable Factors for Heterolysis

- Heterolysis is seen in polar covalent bonds and is favoured by polar solvents.
- The energy required for the heterolytic bond fission is always greater than that for homolytic bond fission due to electrostatic force of attraction between ions.

Both the above type of bond fissions occur due to specialised attacking species called **reagents**.

Reagent or Attacking Species

It is considered as an agent which execute a reaction, i.e. *responsible for initiation, propagation and termination of a reaction.* It may be any organic or inorganic molecule or their part specialised for such a function, e.g. NaOH, Na in liquid NH_3, Na in liquid NH_3, RMgX etc.

Just like other organic molecules a reagent can also show homolysis and heterolysis resulting in the formation of free radicals and ions respectively.

The ions formed by heterolysis of a reagent are of uttermost importance and can be categorised are as follows

1. **Electrophiles** or **Electrophilic Reagents**

An electrophile is defined as **electron deficient species which attacks on electron rich areas.** In a reagent these are represented by E^+. Being electron deficient, the electrophiles behave as **Lewis acids**. e.g. H^+, Cl^+, Br^+, I^+, $NO_2^+, \overset{+}{N}O, \overset{\oplus}{S}O_3H$ and carbocations.

The electrophiles can also be seen in the form of **neutral molecules**, e.g. carbenes $(:CR_2)$, nitrenes $(\ddot{\dot{N}}R)$, $AlCl_3$, BF_3 etc. The neutral electrophiles can be categorised as,

- All neutral covalent compounds in which **central atom has incomplete octet**, e.g. $BeCl_2, BH_3, ZnCl_2, AlX_3, FeX_3, \dot{C}H_3, \ddot{C}X_2$ etc.
- All those compounds in which **central atom has incomplete or expanded octet** or **unfilled *d*-subshell**, e.g. $SnCl_4, SiCl_4, PCl_5, IF_7$, etc.
- All those compounds in which **central atom is bonded by two or more than two electronegative atoms**, e.g. $BX_3, AlX_3, FeX_3, PCl_3, PCl_5$, etc.

2. **Nucleophiles or Nucleophilic Reagents**

A **nucleophile** or nucleophilic reagent is infact an electron rich species that attacks on electron deficient areas. In a reagent these are represented by Nu^-.

Being electron rich, the nucleophiles behave as **Lewis bases,** e.g. H^-, Cl^-, Br^-, I^- carbanions, etc., alongwith $\bar{O}H$, $\bar{O}R, \bar{S}R$.

- Nucleophiles can also be seen in the form of neutral molecules.
- Neutral covalent compounds in which central atom, has at least one lone pair of electrons with complete octet and all atoms attached to central atom are not be electronegative, are considered as **neutral nucleophile**. e.g.

$$H_2\underset{\cdot\cdot}{\ddot{O}},\ \ddot{N}H_3,\ R\ddot{N}H_2,\ R\underset{\cdot\cdot}{\ddot{O}}H,\ R\underset{\cdot\cdot}{\ddot{S}}H,\ R\underset{\cdot\cdot}{\ddot{O}}H, \text{etc.}$$

- Organic compounds containing carbon-carbon multiple bonds behave as the nucleophile, e.g. alkene, alkyne, benzene, $CH_2{=}CH{-}CH{=}CH_2$, $CH_2{=}CH{-}C{\equiv}CH$, etc.

Nucleophilicity

The tendency of lone pair donation by molecule/ion/species is called its nucleophilicity. In technical terms, their electron donating atom is called **nucleophilic site.** Being tendency it is a comperable term and following rules are considered while comparing the nucleophilicities of different nucleophiles.

In case of same nucleophilic site, nucleophilicity parallels basicity, i.e. as the basicity of nucleophile increases, its strength also increases. e.g. The order of nucleophilicity is

$$RO^- > OH^- < ArO^- \quad (\text{Here, } R \neq CH_3)$$

Explanation

- This is because in all these, nucleophilic site is O. In RO^-, R group, being electron releasing, makes the O site more nucleophilic. OH^- is less nucleophilic because of the absence of any such group whereas ArO^- is least nucleophilic because of the presence of electron withdrawing Ar group. The conjugate acid of above bases have the following order of acidity.

$$ROH < H_2O < ArOH$$

- If atoms are different, nucleophilicity varies inversely with their electronegativity. e.g. The order of nucleophilicity of halide ion is

$$I^- > Br^- > Cl^- > F^-$$

(this order is solvent dependent)

Likewise, sulphur being less electronegative than oxygen, is more nucleophilic. Similar is true in case of P and N. The overall decreasing order of nucleophilicity of different nucleophile for S_N2 reaction in protic solvent is as follows

$$RS^- > ArS^- > I^- > CN^- > OH^- > N_3^- > Br^- > ArO^- > Cl^-$$

- A nucleophile carrying negative charge is more powerful electron donor as compared to its conjugate acid. e.g. OH^- is a strong nucleophile as compared to H_2O and NH_2^- is strong nucleophile than NH_3.

Example 1. *The decreasing order of nucleophilicity of the following is*

I. CH_3S^- II. CH_3O^- III. OH^- IV. EtO^-

(a) IV > III > II > I (b) I > II > III > IV
(c) IV > III > I > II (d) II > I > III > IV

Sol. (c) In II, III and IV nucleophilic site is same, i.e. O nucleophilicity follows the same order as basicity. The order of acidic character of conjugate acid of these base is

$$EtOH < H_2O < CH_3OH$$

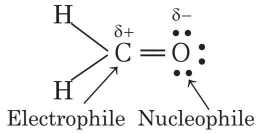
So, the order of basicity of their base is opposite, i.e.

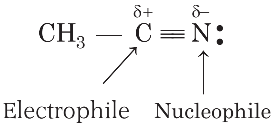
$$EtO^- > OH^- > CH_3O^-$$

Between I and II, CH_3S^- is more nucleophilic as S is less electronegative as compared to O. So the order of nucleophilicity is $\underset{IV}{EtO^-} > \underset{III}{OH^-} > \underset{I}{CH_3S^-} > \underset{II}{CH_3O^-}$.

Ambiphiles

Some molecules behave like both electrophiles and nucleophiles. These are called ambiphiles. Generally, organic compounds containing a multiple bond between carbon and a more electronegative atom can act as ambiphile. e.g.





Isocyanides although cannot behave in these ways as their structure is

$$—\overset{+}{N}\equiv\overset{-}{C}: \longleftrightarrow — N \rightleftarrows C \leftarrow \text{ (bivalent)}$$

It is attacked by Nu^- as well as E^+.

Reaction Intermediates

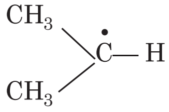
Most of the chemical reactions occur through certain chemical species formation. These species are generally short lived, highly reactive and are called **reactive intermediates**, e.g. free radicals, carbocations, carbanions, carbenes, nitrenes etc.

1. Free Radicals

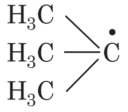
The free radicals and their odd electron we have already bee discussed earlier under homolytic fission. These free radicals can be classified as primary (1°), secondary (2°) and tertiary (3°) depending upon the nature of carbon carrying odd electron. e.g.

$CH_3\dot{C}H_2$

Primary or 1°

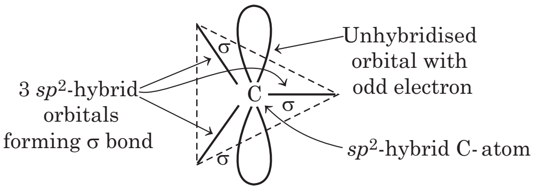


Secondary or 2°



Tertiary or 3°

These free radicals are sp^2-hybridised, i.e. **planar chemical species**. Their unhybridised orbital contains an odd electron as shown below,



Stability

- The stability of free radicals depends upon bond dissociation energies involved in homolytic cleavage. Generally, lower the bond dissociation energy, more stable is the free radical.
- The generalised order of the stability of free radicals is

$$(C_6H_5)_3\dot{C} > (C_6H_5)_2\dot{C}H > C_6H_5\dot{C}H_2$$
$$> CH_2 = CH—\dot{C}H_2 > 3° > 2° > 1° > CH_2 = \dot{C}H$$

- Carbonyl, cyano, nitro, methoxy and amino like groups have stabilising effect over free radials due to resonance.
- Reactions involving free radicals proceed with very fast rate, e.g. Wurtz and other substitution reactions of alkanes, anti-Markownikoff addition of HBr etc.
- Certain compounds like O_2, I_2, *p*-benzoquinone and diphenyl amine, retard the rate of these reactions.
- These are known as free radical inhibitors.
- The high reactivity of free radicals is due to their paramagnetic nature also.

Remember In substituted alkyl radicals, the *s*-character of odd electron containing orbitals has been found to increase, thus tendency to gain pyramidal shape increases in them gradually. i.e.

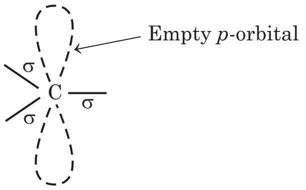
$$\underset{\text{(Planar)}}{\dot{C}H_3} < \dot{C}H_2F < \dot{C}HF < \underset{\text{(Pyramidal)}}{\dot{C}F_3}$$

2. Carbocation

A chemical species which bear a positive charge on carbon and carry 6 electrons in its valence shell is called carbocation.

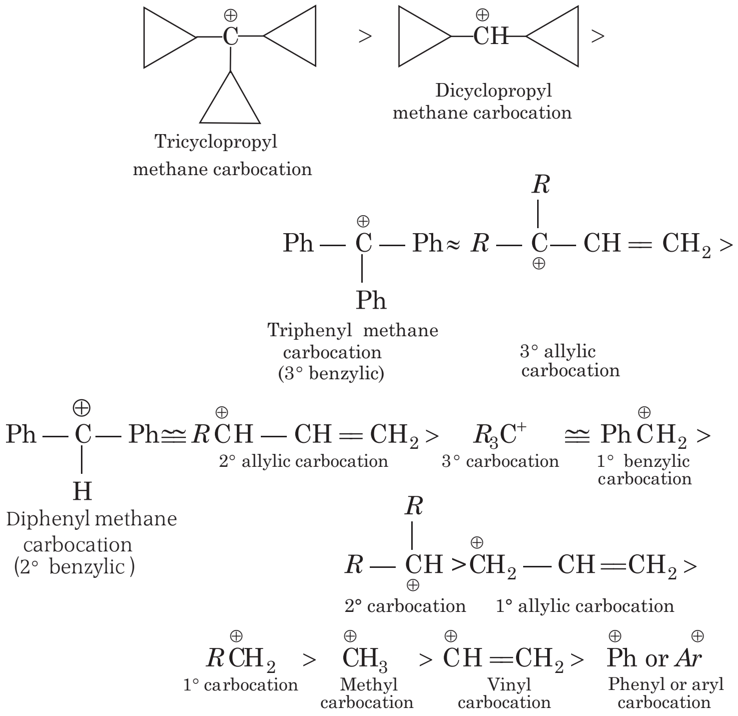
Just like free radicals these carbocations can also be categorised into primary (1°), secondary (2°) and tertiary (3°), depending upon the nature of carbon carrying positive charge.

Carbocations are also **planar chemical species**, i.e. sp^2-hybridised with an empty *p*-orbital as shown below



Stability

- The decreasing order of the stabilities of carbocation is



$$\overset{\oplus}{C}(\text{cyclopropyl})_3 > \overset{\oplus}{C}H(\text{cyclopropyl})_2 >$$

$$Ph-\overset{\oplus}{C}(Ph)-Ph \approx R-\overset{\oplus}{C}(R)-CH=CH_2 >$$

$$Ph-\overset{\oplus}{C}(H)-Ph \cong R\overset{\oplus}{C}H-CH=CH_2 > R_3C^+ \cong Ph\overset{\oplus}{C}H_2 >$$

$$R-\overset{\oplus}{C}H(R) > \overset{\oplus}{C}H_2-CH=CH_2 >$$

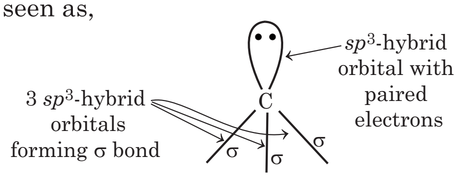
$$R\overset{\oplus}{C}H_2 > \overset{\oplus}{C}H_3 > \overset{\oplus}{C}H=CH_2 > \overset{\oplus}{Ph} \text{ or } \overset{\oplus}{Ar}$$

- The special stability of cyclopropyl methyl carbocations is a result of conjugation between the bent orbitals of cyclopropyl ring and the vacant *p*-orbital of the cationic carbon. This bonding type is more or less similar to banana bonding.
- Tropolium carbocation is about 10" times more stable than triphenyl methyl carbocation. All the electrophilic reactions usually proceed through carbocormation.

3. Carbanions

A chemical species bearing a negative charge on carbon atom and carrying 8 electrons in its valence shell is called **carbanion.** Just like free radicals and carbocations these can also be categorised into primary (1°), secondary (2°) and tertiary (3°).

The structure of simple carbanions is usually **pyramidal** with C-atom carrying the negative charge in sp^3-hybrid state and can be seen as,



The geometry of allyl and benzyl carbanions is almost planar and their hybridisation is sp^2.

Stability

- Anions in which negative charge is present on the carbon atom of aromatic system are called **aromatic carbanions**. These are most stable carbanions.
- The order of stability of carbanions is as follows Aromatic carbanion > benzyl carbanion > allyl carbanion > $CH{\equiv}C^-$ > $CH_2{=}\bar{C}H_2$ > alkyl carbanions (1° > 2° > 3°).

Remember Due to steric hindrance of three phenyl (Ph—) groups, and to acquire pyramidal geometry, lots of energy is required due to which Ph_3C^- is less stable than $Ph_2CH^{\ominus}$.

4. Carbenes

The neutral divalent carbon species in which two non-bonding electrons are present along with 2 bonding pairs are called carbenes.

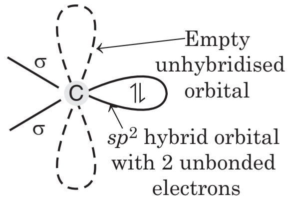
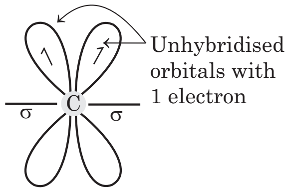
These are generally produced either by **photolysis** (photo = light; lysis = breaking) or by **pyrolysis**, i.e. breaking by temperature, e.g.

$$CH_2{=}C{=}O \xrightarrow[\text{or }\Delta]{h\nu} :CH_2 + :C{=}O$$

Carbenes are highly reactive chemical species with the tendency to gain electrons. As these have only 6 electrons in their valence shell, **thus their behaviour is equivalent to Lewis acids or electrophiles.** These are, infact, neutral electrophiles.

Simplest carbene, i.e. $\ddot{C}H_2$ is known as **methylene**. Hybridisation of the divalent carbon of carbene may be sp^2 or sp.

Carbenes are categorised to singlet and triplet carbenes. Their properties and structure are given below in the table.

Singlet	Triplet
With central C-atom ***sp*²-hybridised**. The unhybridised orbital contains no electron and a hybridised orbital contains two electrons as shown below  	With central C-atom ***sp*-hybridised**. The unhybridised orbitals here contain 1 electron each in them as shown below 
The singlet carbene has bent structure, i.e. $\begin{matrix}\sigma\\ \sigma\end{matrix}\rangle C\!:$	The triplet carbene has linear structure, i.e. $\overset{\sigma}{-}\ddot{C}\overset{\sigma}{-}$
Less stable	More stable

Stability

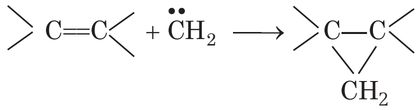
The decreasing order of stability of different types of singlet carbenes is as follows

$$\ddot{C}H_2 > \ddot{C}F_2 > \ddot{C}Cl_2 > \ddot{C}Br_2$$

Reactions Involving Carbenes as Intermediates

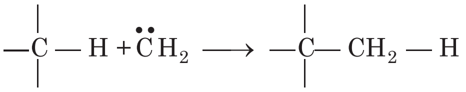
Carbenes are involved following reactions

- Addition with alkenes



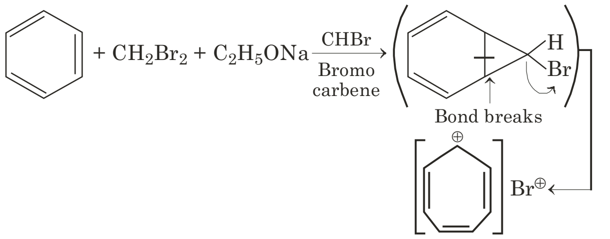
$$>C{=}C< + \ddot{C}H_2 \longrightarrow >C{-}C< \text{ (bridged by } CH_2)$$

- Insertion reaction between C—H bond.



$$-\overset{|}{\underset{|}{C}}-H + \ddot{C}H_2 \longrightarrow -\overset{|}{\underset{|}{C}}-CH_2-H$$

- Ring expansion reactions, e.g. halogenated carbene produced by CHX_3/base adds to (C═C) bond, followed by ring expansion. This gives product with one extra C atom ring.



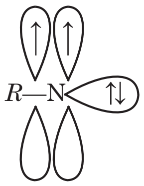
Tropylium bromide
(stabilised due to aromatic character)

5. Nitrenes or Imidogenes

Neutral monovalent nitrogen species in which nitrogen has two unshared pair of electrons with a monovalent atom or group attached is called **nitrenes**, i.e. $\overset{\sigma}{-}\ddot{N}:$.

These are produced by thermolysis of azides and are very reactive just like carbenes.

In general, nitrenes obey Hund's rule and are ground state triplet with two degenerate *sp*-orbitals containing a single electron each.



sp-triplet nitrene

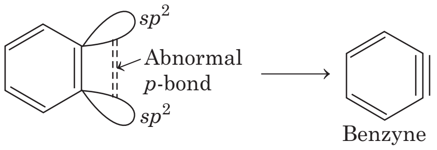
Arynes

A formal carbon-carbon triple bond containing aromatic molecule (in aromatic ring) is called aryne. The best known among these is **benzyne**.

In benzyne an additional bond is formed between two neighbouring C-atoms by side ways overlapping of two sp^2-orbitals.

The new bond orbital lies along with side of the ring and has little interaction with the π electron cloud lying above and below the ring.

This sideways overlapping is weak and thus, makes the benzyne more reactive.



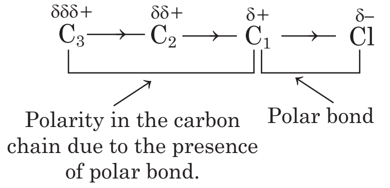
Electronic Displacement in a Covalent Bond

Presence of some atom or group in a molecule or presence of attacking reagent may lead to electronic displacement in a covalent bond. As a consequence of which, centres of different electron densities are generated. These centres are susceptible to attack by the reagents. The factors that create such centres of different electron densities are discussed below.

1. Inductive Effect

The inductive effect is defined as **polarity produced in a molecule due to the presence of a polar bond.**

e.g. In a chain of carbon atoms with a chlorine atom joined at one terminal as shown below. It is due to the higher electronegativity of chlorine atom, the electron distribution in carbon chain varies as,



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

Features

The inductive effect is

- a permanent effect
- operate through σ-bonds only
- decreases in magnitude as we move away from the cause of polarity (i.e. polar bond)
- generally considered in saturated compounds.

For practical purpose the inductive effect is ignored after the second C-atom. It must be born in mind that here, the electron pairs although permanently displaced but they do not leave their valence shells.

Positive and Negative Inductive Effects

- For measurement of relative inductive effects, atoms or groups having greater electron affinity than hydrogen are said to have **–*I*-effect.** These groups are considered as **electron attracting**.

- Similarly, atoms or groups having smaller electron affinity than hydrogen are said to have + *I* **effect**, These group are considered as **electron releasing** or **repelling**.
- These groups are responsible for producing a charge on C-chain, e.g. – *I*-group produces partial positive charge, i.e. decrease in electron density due to more electron attracting power.
- On the other hand, + *I*-groups produce partial negative charge, i.e. increase in electron density due to more repulsion or releasing power.
- Some of the – ***I*** effect producing groups in decreasing order of inductive effect with respect to H are given below

$$R_3\overset{+}{N} > \overset{+}{N}H_3 > NO_2 > CN > SO_3H > CHO > CO > COOH >$$
$$COCl > COOR > CONH_2 > F > Cl > Br >$$
$$I > OH > OR > NH_2 > C_6H_5 > H$$

- On the other hand alkyl groups, O and COO^- are +*I* effect producing groups. The + *I* effect of different alkyl groups is as under $—O^- > —COO^- >$ tertiary alkyl group > secondary alkyl group > primary alkyl group > $—CH_3$ > H.
- + *I* power of same type of alkyl groups varies directly with the number of C-atoms in the alkyl group.
- The terminology (+I and – I) is due to **Ingold,** while **Robinson** has suggested opposite signs. To avoid confusion, we shall use Ingold terminology throughout.

Applications of Inductive Effect

The applications of inductive effect include

(i) **In determining the stability of free radicals, carbocations and carbanions** following relationships are considered

- Stability of carbocation or free radical

$$\propto + \boldsymbol{I} \text{ power of the group}$$
$$\propto \frac{1}{-\boldsymbol{I} \text{ power of the group}}$$

Thus, the stability order for carbocations and free radicals is $1° < 2° < 3°$.

- Stability of carbanions $\propto - I$ power of the group

$$\propto \frac{1}{+I \text{ power of the group}}$$

and the stability order for carbanions is

$$3° < 2° < 1°.$$

(ii) **In determining the strength of acids and bases** following relationships are considered

- Strength of an acid $\propto K_a \propto \dfrac{1}{pK_a} \propto$ stability of acid anion

As stability of acid anion (or conjugate base)

$$\propto - \boldsymbol{I} \text{ power of group present}$$
$$\propto \frac{1}{+\boldsymbol{I} \text{ power of group present}}$$

Thus, strength of acid increases with the attachment of group showing **–*I*** effect and decreases with the attachment of group showing **+ *I*** effect.

Similarly strength of a base $\propto K_b \propto \dfrac{1}{pK_b} \propto + I$ power of group present in the base

$$\propto \frac{1}{-I \text{ power of group present in the base}}$$

However, this relation is not true for amines in their aqueous solutions as here the basicity is decided by combined or net result of **inductive effect**, **solvation effect** and **steric hindrance**.

The order of some of the amines are as follows

***R* of amine**	**Relative basic sterngth**
$CH_3—$	$2° > 1° > 3° > NH_3$
$C_2H_5—$	$R_2NH > R_3N > RNH_2 > NH_3$
$Me_2CH—$	$RNH_2 > NH_3 > R_2NH > R_3N$
$Me_3C—$	$NH_3 > RNH_2 > R_2NH > R_3N$

The above two relations can be summarised as

Acid/Base related function	**Group with +*I*-effect**	**Group with −*I*-effect**
Acidic strength of acid	Decreases with this group ↓	Increases with this group ↑
Basic strength of base	Increases with this group ↑	Decreases with this group ↓

(iii) **In determining the reactivities of carbonyl compounds towards nucleophilic reagent** following relationship is considered

Reactivity of carbonyl compound

$$\propto - \boldsymbol{I} \text{ power of the group}$$
$$\propto \frac{1}{+I \text{ power of the group}}$$

(iv) **Reactivity of alkyl halides is also determined** by considering *I*-effects.

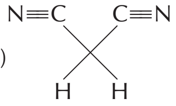
Reactivity of alkyl halide towards S_N1 reaction is

$$3° > 2° > 1°, \text{ i.e. } \propto + I$$
$$\propto \frac{1}{-\boldsymbol{I}}$$

Reactivity of alkyl halides towards S_N2 reactions follows reverse order of S_N1 reaction.

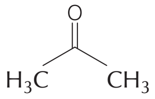
Example 2 *Which one of the following compounds possesses the most acidic hydrogen ?* ***(JEE Main 2020)***

(a)

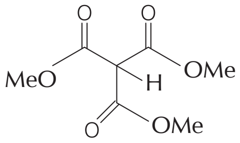


(b) $H_3C—C≡C—H$

(c)

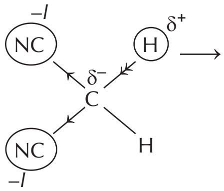


(d)



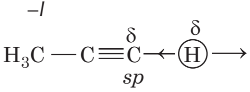
Sol. (*d*) Acidity of H-atom ∝ Attachment with more and stronger electron withdrawing groups.

(a)



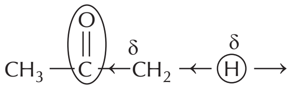
⟶ It experiences two –*I* effects, so can show acidity

(b)



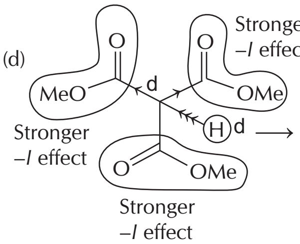
$H_3C—C≡\overset{\delta}{\underset{sp}{C}}\leftarrow\overset{\delta}{H}$ ⟶ It is also removable hydrogen

(c)

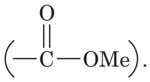


$CH_3—\overset{O}{\overset{||}{C}}\leftarrow\overset{\delta}{CH_2}\leftarrow\overset{\delta}{H}$ ⟶ It also shows acidity because of the –*I* effect

(d)



⟶ It is most acidic, because the carbon atom bearing this H-atom enjoys three stronger –*I* effects of ester groups



$\left(—\overset{O}{\overset{||}{C}}—OMe\right)$.

Compound (d) possess the most acidic hydrogen because of three stronger –*I*-effects.

2. Electromeric Effect

When a π-bond is exposed to a reagent, the two π electrons are completely transferred to any of the one atom forming such a bond, thus producing polarity.

Hence, the electromeric effect can be defined as "Polarity produced in a multiple bonded compound as a reagent approaches it".

Features

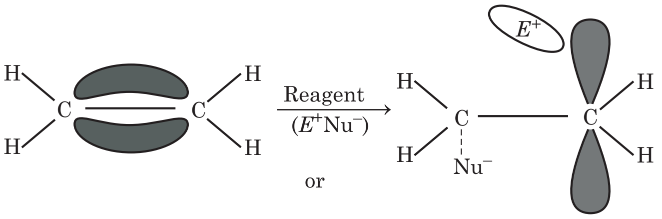
This effect is

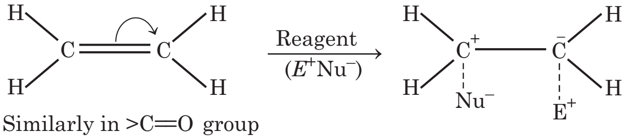
- temporary in nature
- operator through π-bond only
- generally, considered in unsaturated compounds.

It is a strong effect because of the involvement of weak π-electron clouds.

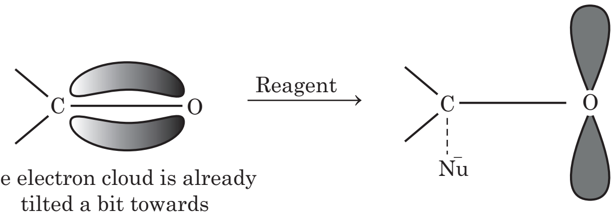
If π and σ-bond both are present in a compound, the reagent always attacks the π-electron cloud first because **π-electron cloud is much more exposed** than a σ electron cloud.

e.g. In ethylene molecule when electrophilic part of the a reagent attacks the π-bond, the symmetry of molecular orbital is disturbed as shown below.





Similarly in >C=O group



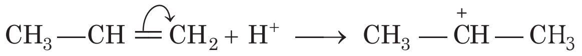
The electron cloud is already tilted a bit towards oxygen due to its high electronegativity

The electromeric effect is represented by means of a **curved arrow** beginning at original position of the electron pair and denoting where the pair has migrated.

Positive and Negative Electromeric Effect

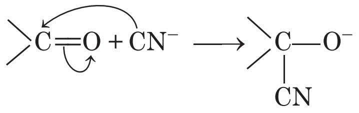
Just like inductive effect this effect may also be of +***E*** or – ***E* type**.

- If the electrons of the π-bond are transferred to that atom of the double bond to which the electrophile gets finally attached, it is known as +*E* effect.



$$CH_3—CH=CH_2 + H^+ \longrightarrow CH_3—\overset{+}{C}H—CH_3$$

- If the electrons of the double bond are transferred to the atom other than the one to which the electrophile gets finally attached, the effect is known as –*E* effect.



$$>C=O + CN^- \longrightarrow >C(CN)—O^-$$

Inductive vs Electromeric Effects

In cases where inductive and electromeric effect both occur together, these may be aiding or opposing each other. Here, it is note worthy that *when these two effects are working in opposite directions*, it is the electromeric effect that usually overcomes the inductive effect.

Conjugation, Mesomeric Effect and Resonance

These 3 concepts are deeply inter related although they have their own individual identity as well.

Their relationship in exact words can be described as,

"All the cases of mesomeric effect are explained on the basis of conjugation but all the cases of resonance does not involve mesomeric effect and conjugation." *Infact resonance in HCl cannot be explained via mesomeric effect or conjugation*. These both the phenomenon are limited to compounds containing π-bonds only.

Let us explore these phenomenon one by one.

1. Conjugation

The literary meaning of word conjugation is "To link" or "To join". The word is used to explain all such conditions where partial π-bond is present.

Conditions

A given atom or group is said to be in conjugation with an unsaturated system if it satisfies following two conditions

(i) It has either π**-bond** or **any charge** or **odd electron** or **lone pair** of electron. Above given entities are directly linked to one of the atoms of multiple bond through a single bond. e.g.

- $CH_2=CH-CH=CH_2$
  (conjugation between 2π-bonds)
- $CH_2=CH-\overset{\bullet}{C}H_2$
  (conjugation between π-bonds, and odd electron of carbon)
- $CH_2=CH-\overset{+}{C}H_2$
  (conjugation between a π-bond and a charge)
- $CH_2=CH-\ddot{N}H_2$
  (conjugation between a π-bond and a lone pair)

(ii) Atoms or groups in conjugation with π electron should be at alternate position and in the same plane and at the same angle with each other.

Types

Conjugation can be of following types

(i) π-π conjugation
(ii) π and charge conjugation
(iii) π and odd electron conjugation
(iv) π and lone pair conjugation
(v) Lone pair and charge or odd electron conjugation

Result

Conjugation results in delocalisation of electrons which is visible through following observations

- **Improper bond length**, i.e. bond length will not be as per expectations.
- The compound containing conjugated system will show **extra stability** with antiaromatic compounds as exception.
- As the compound will be extra stable that means its **heat of formation** will be greater than expected.

Important Points Regarding Conjugation

While looking for conjugation one must keep following points in mind

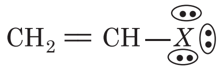
(i) If any conjugate position has more than one π-bond then only one π**-bond participates** in conjugation.

or in $CH_2=CH-C\equiv CH$

Here, only one π bond out of shown two participates in conjugation.

(ii) If any conjugate position has more than one lone pairs then only **one lone pair participates** in conjugation.

e.g.

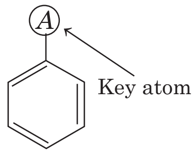


$CH_2=CH-X$

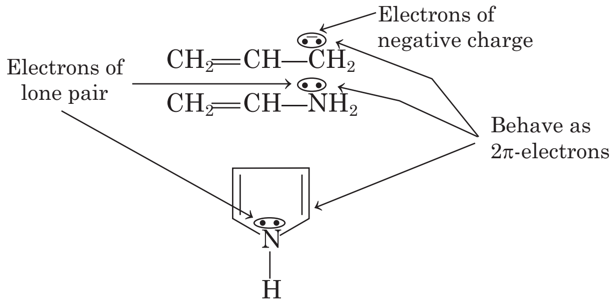
Here, out of 3 lone pairs of halogen only one participates in conjugation.

(iii) Key atom, i.e. atom other than hydrogen which is bonded with benzene ring, will be in conjugation with ring if it has one of the following

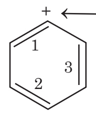
- A π-bond
- A charge
- A lone pair
- An odd electron



(iv) Electrons of negative charge or lone pair behaves as 2π-electrons if these are in conjugation with 2π-electrons.



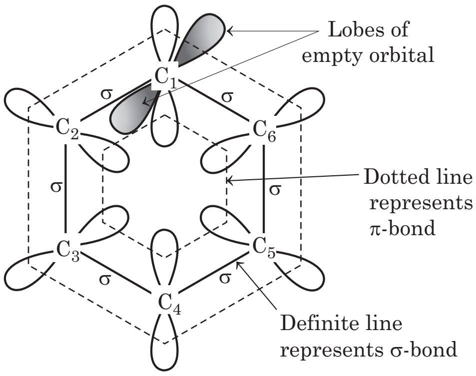
(v) Always remember alternate position and same plane with same angles are required for conjugation, e.g.



This charge does not conjugate with π-bond as both of them are not in the same plane although the charge seems as in alternate position with p-bond number 3.

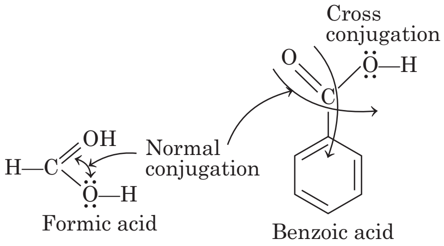
Here, alternate position does not work but **same plane with same angle works.**

The orbital picture of above structure in given below



- Actually, real conditions for conjugation are same plane with same angle while the alternate position is an assumption because these two conditions are normally fulfilled by this assumption.
- It is clear from the above figure that the orbitals of all the C-atoms with definite line are participating in conjugation because these are in the same plane.
- On the other hand, the orbital with positive charge, i.e. empty orbital of C_1 atom (here shown with grey colour) cannot participates in conjugation as it lies in different plane.

(vi) Although, phenyl group is $-I$ effect showing group, but still HCOOH (formic acid) is more acidic than benzoic acid (PhCOOH). This is because of cross conjugation present in benzoic acid which reduces the original conjugation in —COOH group, thus reduces acidic strength, i.e.



2. Mesomeric Effect or Mesomerism

The mesomeric effect is defind as "polarity produced in a molecule due to conjugation".

Features

- It is a permanent effect.
- Operates through π skeleton only.
- The effect is transmitted in a similar way as seen in inductive effect with the difference that the intensity of mesomeric effect remains same thruoghout the molecule unlike to inductive effect where intensity show a decrease as we move away from the cause of polarity.

Positive and Negative Mesomeric Effect

Just like inductive effect, mesomerism is also of following two types

- A group or atom is said to have −***M* effect** if it withdraws the electrons from conjugated system, −*M* power of groups in decreasing order is

$$NH_3 > NO_2 > CX_3 > CN > SO_3H > CHO > CO > COOH > COCl > COOR > CONH_2$$

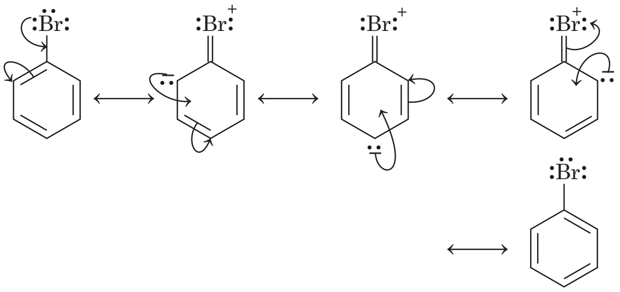
- A group or atom said to have +***M* effect** when direction of electron displacement is away from it, i.e. it donates the electrons into the conjugated system. +*M* power of groups in decreasing order is

$$O^- > NH_2 > OH > OR > NHAc$$

$$\underbrace{\text{Alkyl groups}}_{\text{In the order}} > \text{phenyl groups}$$

$$CH_3 > \text{pri} > \textit{sec} > \textit{tert}$$

The +*M* effect of Br is shown as,



Remember

- In the above example the curved arrows do not show the direction of movement of electrons rather these are helpful in drawing next structure from the previous one.
- The inductive and mesomers effects indicate the charge distribution in a molecule. Thus, they provide an effective way of determining the point of attack for an electrophile or a nucleophile on a molecule.

3. Resonance

Occassionally no reasonable single electronic picture can be drawn for a molecule which could satisfactorily account for its observed properties. In such a condition, we assume several structures of that compound each one of which contribute to some of its observed properties but none of these structures satisfactorily account for all of its observed properties.

Such several structures are called **canonical forms** or **resonating structures**. The actual structure of such a compound is said to be the hybrid of these structure and the phenomenon is called **resonance**.

Thus, this interesting hypothetical phenomenon have many canonical forms and a single resonance hybrid in its foundation.

The word "Resonance" for this situation should not pass an impression that the molecule resonates from one structure to the other and *vice-versa*. Likewise the electrons are jumping back and forth thus resulting to such a structure that cannot be described physically.

Remember, **here the difficultly lies in description and not in the molecule itself**. Hopefully following crude functional similarity will help us to understand the concept of resonance.

"The mule is a hybrid of the jackass and the mare". It has inherited characteristics from both the parents, e.g. it can carry load like an ass, and run faster like a mare.

However, when we look at the mule, we do not see a jackass at one glance and a mare at another, we see a mule always.

In the similar way, **a resonance hybrid does not oscillate between its canonical forms**. Its properties are fixed and are shown by the actual hybrid structure.

The problem is potentially we can not correlate these properties with a single structure. The process of resonance can be said to occur only in one condition and that is when we are unable to explain all the observed properties of a compound with a single Lewis structure.

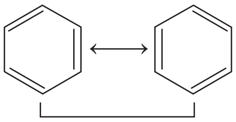
Key points

Always follow below given key points in resonance, i.e.

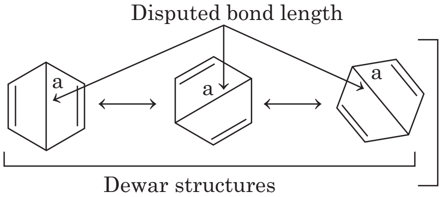
- The arrangement of atoms must be identical or almost same in every formula.
- The energy content of all the canonical forms must be nearly the same.
- Each canonical form must have the same number of unpaired electrons.
- The bond length in resonance hybrid is variable but it is fixed as compared to bond length in canonical forms.
- The resonance hybrid is always stable than any of its canonical forms. e.g.
  (i) CO_2 is said to have following canonical forms

$$\mathrm{O{=}C{=}O} \longleftrightarrow \mathrm{O^-{-}C{\equiv}O^+} \longleftrightarrow \mathrm{\overset{+}{O}{\equiv}C{-}O^-}$$

  (ii) Benzene may be represented by following structures



Kekule structures



Dewar structures

These structures were discarded as there one double bond (marked a in the figure) is lengthy than expected. Any π-bond between 2 carbon atoms cannot have such length.

In both the above examples, the actual structure of CO_2 or benzene is more stable than either of the structures described.

Resonance Energy

In a compound known to show resonance,
Heat of formation of resonance hybrid is abnormally high, w.r.t. its most stable structure. e.g. the observed heat of formation of CO_2(= 1590 kJ/mol) is greater than its calculated value (=1464 kJ/mol) The difference in heat of formation, i.e.

Heat of formation (observed) − Heat of formation (calculated)

is called the resonance energy, which is assumed to be the energy lost when a molecule acquires resonance hybrid formula.

Stability of a Canonical Form

Among the canonical forms the most stable canonical form can be judged by following rules

(i) Among all the canonical forms **the form without charges will be the most stable one.**

(ii) Among the **charged forms**

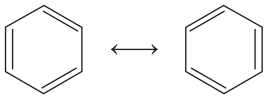
- The structure with minimum number of covalent bonds is most stable one.
- The structure with minimum charge separation comes second in number.
- The structure with **conventionally correct charges** comes at third place. Here, convention means the reason because of which charge arise.

Relation between Resonance and Bond Order

In compounds exhibiting resonance, bond order can be given by the formula

$$\text{Bond order} = \frac{\text{Total number of bonds between two atoms}}{\text{Total number of resonating structures}}$$

e.g. In benzene molecule with following canonical forms



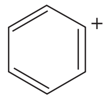
$$\text{Bond order} = \frac{2+1}{2} = 1.5$$

Real Facts Regarding Misconceptions of Resonance

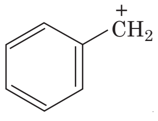
- The canonical forms have no real existence.
- There is no equilibrium between the canonical forms.
- The molecule does not exist for a certain fraction of time in one canonical form and for other fractions of time in other canonical forms.

Applications of Resonance and Mesomeric Effect

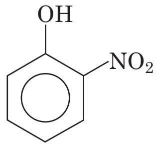
- These both the phenomenon are helpful in determining the stability of various species like benzyl carbocations, benzyl carbanions and free radicals. e.g.



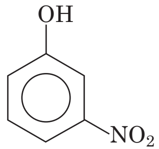
is less stable than



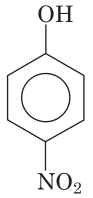
- The acidic and basic strengths of various compounds is estimated by the net result of mesomeric and inductive effects applicable over them, e.g. acidic strengths of *ortho*, *para* and *meta* nitrophenols is described as :



Phenoxide ion is stabilised by – *M* and – *I*-effect



Phenoxide ion is stabilised by – *I*-effect only



Phenoxide ion is stabilised by – *M* and – *I*-effect and symmetrisation effect

Hence, the order is
para-nitrophenol > *ortho*-nitrophenol > *meta*-nitrophenol > phenol.

Example 3. *Which of the following resonating structures of* 1-*methoxy*-1,3-butadiene is least stable ?

(a) $\overset{\ominus}{C}H_2—CH=CH—CH=\overset{\oplus}{O}—CH_3$

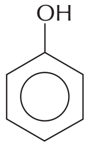
(b) $CH_2=CH_2—\overset{\ominus}{C}H—CH=\overset{\oplus}{O}—CH_3$

(c) $\overset{\ominus}{C}H_2—\overset{\oplus}{C}H—CH=CH—O—CH_3$

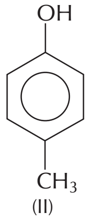
(d) $CH_2=CH—\overset{\ominus}{C}H—\overset{\oplus}{C}H—O—CH_3$

Sol. (c), In structures given in option (a) and (b), all the atoms have their complete octet. Moreover, these have more number of covalent bonds as compared to structure (c) and (d). In structure (d), the lone pair of electrons of adjacent oxygen atom compensates the electron deficiency of positively charged carbon whereas such neighbouring group support is not available in structure (c).
Hence, it is the least stable resonating structure.

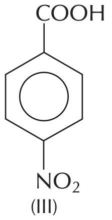
Example 4. *The acidic strength of the following compounds is in the order*



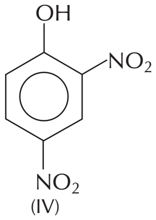
(I)



(II)



(III)



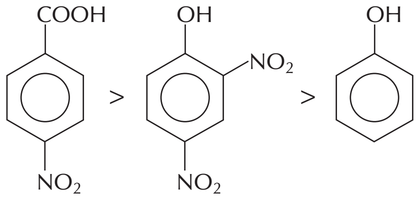
(IV)

(a) (II) > (I) > (III) > (IV)
(b) (III) > (IV) > (I) > (II)
(c) (I) > (IV) > (III) > (II)
(d) (IV) > (III) > (I) > (II)

Sol. (*b*) Presence of electron withdrawing group, i.e. the group showing –*I* effect, results in increased acidity while presence of electron releasing groups, i.e. the group showing + *I*-effect results in decreased acidity. —COOH, $—NO_2$, —OH all are electron withdrawing groups and the order of their –*I*-effect is

$$—NO_2 > —COOH > —OH$$

Thus, the order of acidity is

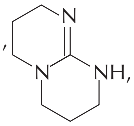


(III) (IV) (I)

However, is less acidic among the given compounds due to the presence of electron releasing $—CH_3$ group. Hence, the order of acidity is III > IV > I > II.

Example 5. *The increasing order of* pK_b *for the following compounds will be* ***(JEE Mains 2020)***

$NH_2—CH—NH,$
(*A*)

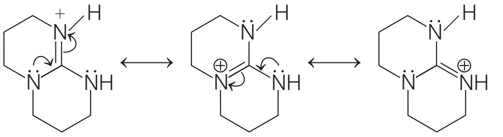


(*B*)

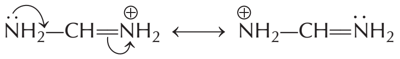
$CH_3—NH—CH_3$
(*C*)

(a) (*B*) < (*C*) < (*A*)
(b) (*C*) < (*A*) < (*B*)
(c) (*A*) < (*B*) < (*C*)
(d) (*B*) < (*A*) < (*C*)

Sol. (*d*) (*B*) is most basic because of high resonance stabilisation of its conjugate acid.



Among rest two compounds, $NH_2—CH=\ddot{N}H$ (*A*) has higher basicity than $CH_3—NH—CH_3$ (*C*) because conjugate acid of (*B*) is resonance stabilised but conjugate acid of (*C*) is not resonance stabilised at all.



$$\ddot{N}H_2—CH=\overset{\oplus}{N}H_2 \longleftrightarrow \overset{\oplus}{N}H_2—CH=\ddot{N}H_2$$

Hence, the correct order of basicity of the given compounds is, *B* > *A* > *C*. Stronger is the base, smaller will be its pK_b value. Thus, the increasing order of pK_b values is *B* < *A* < *C*.

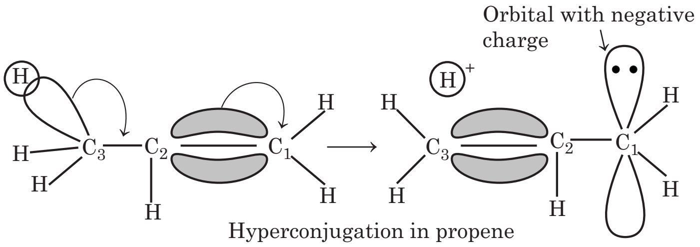
Hyperconjugation

It is shown by heat of hydrogenation data that alkenes are stabilised not only by conjugation but also by the presence of alkyl groups.

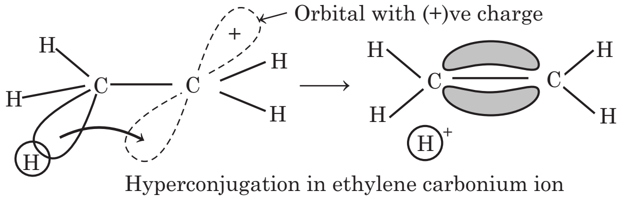
Greater the number of alkyl groups attached to the doubly bonded carbon atoms, the more stable is the alkene, e.g. propylene is more stable than ethylene.

Stabilisation by alkyl group has been due to delocalisation of electrons because of conjugation between a π-orbital and a σ-bond orbital of the alkyl group or C—H bond more precisely.

Such a conjugation is called **hyperconjugation** which results to actually **no bond resonance**. This phenomenon is also helpful in stabilising carbonium ions and free radicals, e.g.



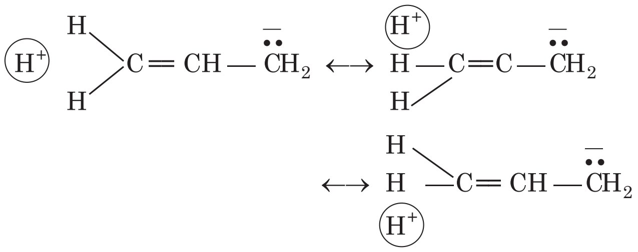
Hyperconjugation in propene



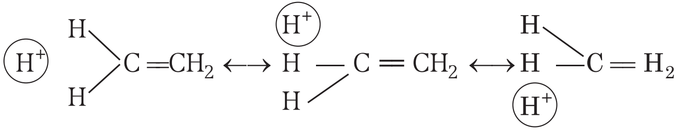
Hyperconjugation in ethylene carbonium ion

As in both the cases shown above a methyl group is present near to the π-bond as in propene or (+)ve charge as in ethyl carbonium ion.

All the three C—H bonds of it have equal probability of showing hyperconjugation. Thus, both of them have three hyperconjugative structures as shown below



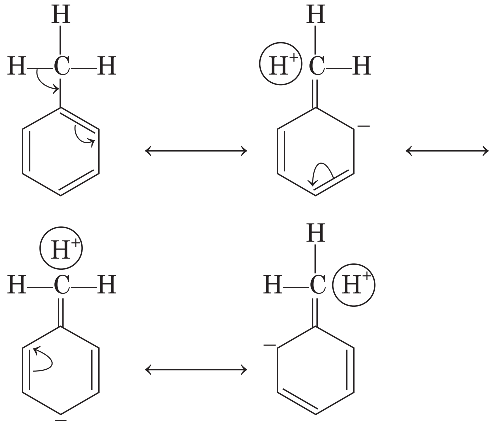
Hyperconjugative structures of propene



Hyperconjugative structures of ethyl carbonium ion

In both the above cases, it is seen clearly that C—H bond of alkyl group possess a partial ionic character due to resonance. In simpler words, C—H covalent bond is not visible in resonating structures that's why the process is also called **no bond resonance** or **Baker-Nathan effect**.

Hyperconjugation can also be seen in toluene as follows



Requirements for Hyperconjugation

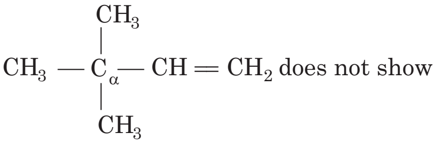
The structural requirements for hyperconjugation are as follows

- Compound should have at least one sp^2-hybrid carbon i.e. belongs to alkene, alkyl carbocation or alkyl free radical.
- α-carbon with respect to sp^2-hybrid carbon should have at least one hydrogen.
- More the number of H—C bonds attached to this carbon, more stable will be the alkene or carbocation or free radical.

Types of Hyperconjugation

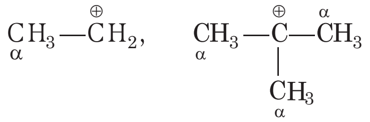
Hyperconjugation is of following three types

(i) (C — H), π-**conjugation** → This type of hyper conjugation seen in alkenes, e.g. $\underset{\alpha}{CH_3}-CH=CH_2$, show hyperconjugation.



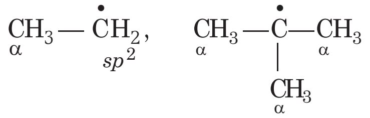
Remember $CH_3-\underset{CH_3}{\overset{CH_3}{C_{\alpha}}}-CH=CH_2$ does not show hyperconjugation as α carbon of it does not contain any directly linked H.

(ii) (C—H), **positive charge conjugation** → This type of conjugation occurs in alkyl carbocations.



$$\underset{\alpha}{CH_3}-\overset{\oplus}{C}H_2,\quad \underset{\alpha}{CH_3}-\underset{\underset{\alpha}{CH_3}}{\overset{\oplus}{C}}-\overset{\alpha}{CH_3}$$

(iii) (C — H), **odd electron conjugation** → This type of conjugation occurs in alkyl free radicals.



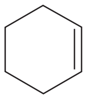
$$\underset{\alpha}{CH_3}-\underset{sp^2}{\dot{C}H_2},\quad \underset{\alpha}{CH_3}-\underset{\underset{\alpha}{CH_3}}{\dot{C}}-\underset{\alpha}{CH_3}$$

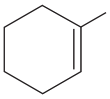
Applications of Hyperconjugation

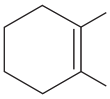
Important applications of hyperconjugation, are given below

(i) **The stability of alkene** can be determined on the basis of hyperconjugative structures. Always remember that more hyperconjugating structures an alkene possess, the more stable it is.

e.g. Out of


I

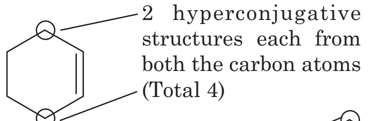

II


III

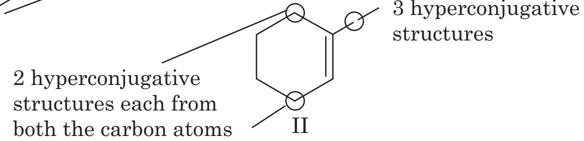
The stability order will be written as

$$\underset{\text{Most stable}}{\text{III}} > \text{II} > \underset{\text{Least stable}}{\text{I}}$$

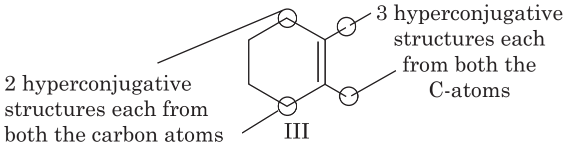
The reason being I has minimum number of hyperconjugative structures (i.e. 4) while 2nd have (7) and *III* rd have maximum number of hyperconjugative structures (i.e. 10) as shown below



I



Total 4 + 3 = 7 structures



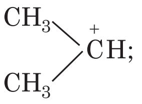
Total 6 + 4 = 10 structures

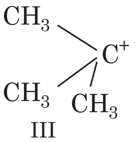
(ii) **Stability of alkyl free radicals and carbocations**

The stability of alkyl free radicals and carbocations can also be explained on the basis of hyperconjugation.

Just like alkenes, more the number of hyperconjugative structures seen in a free radical or carbonium ion more stable it is, e.g. ethyl carbonium ion has 3 hyperconjugative structures. When we compare the stability of following ions

$CH_3 — CH_2^+$;
I


$(CH_3)_2\overset{+}{C}H$;
II

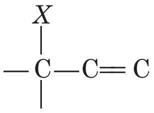

$(CH_3)_3C^+$
III

The I structure has 3 hyperconjugative structures, the II has 6 and the III has 9 hyperconjugative structures hence, the stability order of above three ions will be

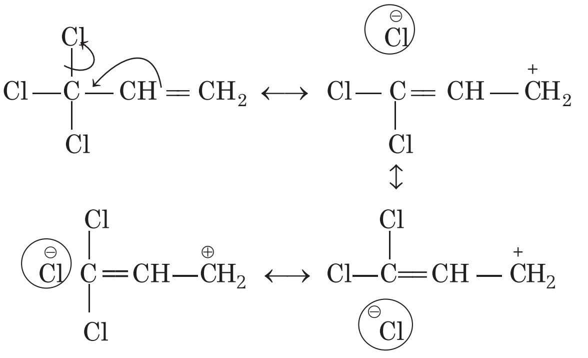
$$\underset{\text{Most stable}}{(CH_3)_3C^+} > (CH_3)_2CH^+ > \underset{\text{Least stable}}{CH_3CH_2^+}$$

Reverse Hyperconjugation

The phenomenon of hyperconjugation is also observed in the system given below.


$$—\overset{X}{\underset{|}{C}}—C{=}C \quad (\text{where, } X = \text{Halogen})$$

Here, C— X σ-bond is in conjugation with π-bond. So, in such systems, the effect operates in the reverse direction. Hence, the hyperconjugation in such system is known as **reverse hyperconjugation**.

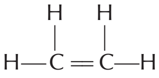


Example 6. *List the following in increasing order of stability.*

I. $CH_2 = CH_2$
II. $CH_3—CH=CH_2$
III. $CH_3CH=CHCH_3$
IV. $(CH_3)_2C=C(CH_3)_2$
V. $(CH_3)_2C=CHCH_3$

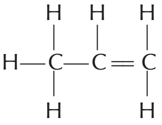
(a) I < II < III < V < IV
(b) II < III < V < IV < I
(c) III < II < IV < I < V
(d) IV < III < I < V < II

Sol. (a) I.


$$H—\overset{H}{C}=\overset{H}{C}—H$$

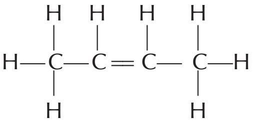
Total hyperconjugative structure = 0

II.


$$H—\overset{H}{\underset{H}{C}}—\overset{H}{C}=\overset{H}{\underset{H}{C}}$$

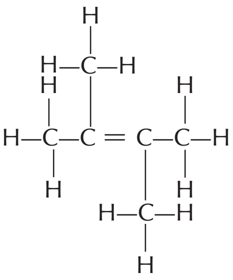
Total hyperconjugative structure = 3

III.

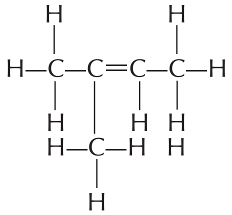

$$H—\overset{H}{\underset{H}{C}}—\overset{H}{C}=\overset{H}{C}—\overset{H}{\underset{H}{C}}—H$$

Total hyperconjugative structure = 6

IV.



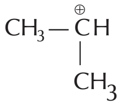
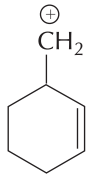
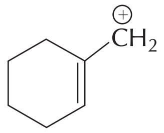
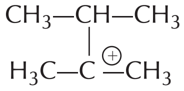
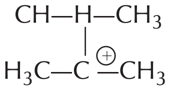
Total hyperconjugative structure = 12

V.


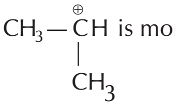
Total hyperconjugative structure = 9

So, the increasing order of stability is I < II < III < V < IV.

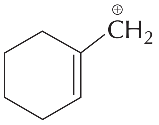
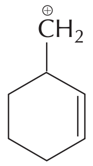
Example 7. *Find the incorrect match*

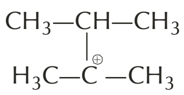
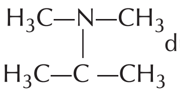
	More stable	Less stable
(a)	$C_6H_5\overset{\oplus}{C}H_2$	$CH_2=CH-\overset{\oplus}{C}H_2$
(b)	 $CH_3-\underset{\underset{CH_3}{\mid}}{\overset{\oplus}{C}H}$	$CH_3\overset{\oplus}{C}H_2$
(c)		
(d)	 $\underset{H_3C-\overset{\oplus}{C}-CH_3}{CH_3-\underset{\mid}{C}H-CH_3}$	 $\underset{H_3C-\overset{\oplus}{C}-CH_3}{CH-\underset{\mid}{H}-CH_3}$

Sol. (a) $C_6H_5\overset{\oplus}{C}H_2$ is more stable than $CH_2=CH-\overset{\oplus}{C}H_2$ due to resonance.



(b) $CH_3-\underset{\underset{CH_3}{\mid}}{\overset{\oplus}{C}H}$ is more stable than $CH_3\overset{\oplus}{C}H_2$ due to hyperconjugation.

(c)  is more stable then  due to hyper-conjugation.

(d)  is more stable than  due to hyperconjugation.

Organic Reactions and their Mechanisms

The organic reactions can be categorised into following five categories

1. Substitution reactions
2. Elimination reactions
3. Addition reactions
4. Addition-elimination reactions
5. Rearrangement reactions

1. Substitution Reactions

- A substitution reaction involves the direct replacement (displacement or substitution) of an atom or group of atoms by another atom or group of atoms without any change in the remaining part of the molecule.
- The product obtained as result of substitution is called the **substitution product** and the new atom or group of atoms which enters the molecule after substitution is called a **substituent**. e.g.

$$R-CH_3+X_2\xrightarrow[\text{520-670 K}]{h\nu\text{ or}}\underbrace{R-CH_2\overset{\text{Substituent}}{\boxed{X}}}_{\text{Substitution product}}+HX$$

Substitution reactions can further be classified into three categories on the basis of intermediate species which begins the reaction. These are

(i) Free Radical Substitution

Those substitutions which are reactant initiated and brought about by free radicals are called **free radical substitutions.**

The best example of this kind of reactions is **halogenation of alkanes** in the presence of sunlight or heat, i.e.

$$\underset{\text{Substrate-1}}{R-CH_3}+\underset{\substack{\text{Substrate-2}\\\text{or reagent}}}{X_2}\xrightarrow[\text{heat}]{\text{Sunlight}}\underset{\text{Product-1}}{RCH_2X}+\underset{\text{Product-2}}{HX}$$

Free radical reactions are chain reactions and their three step mechanism is given below

***Step* I Chain initiation step** It involves the formation of free radicals from the reagent, i.e.

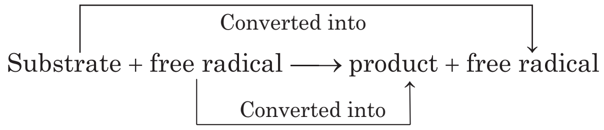
$$\text{Reagent or substrate}\xrightarrow[\substack{h\nu\text{ or free radical}\\\text{initiators}}]{\text{Heat or}}\text{two free radicals}$$

e.g. For the above halogenation reaction

$$X_2\xrightarrow[\text{free radical initiators}]{\text{Heat or }h\nu\text{ or}}X^\bullet+X^\bullet$$

This step can be recognised by the fact that free radicals are present on the product side, i.e. after the arrow.

***Step* II Chain propagation step** It Involves attack of radicals formed in step I on the substrate, i.e.



e.g. In the above reaction,

$$\underset{\text{Substrate-1}}{R-CH_3}+\underset{\text{Free radical}}{X^\bullet}\longrightarrow\underset{\text{Free radical-2}}{R\dot{C}H_2}+\underset{\text{Product-2}}{HX}$$

The free radical-2 obtained in this step continues the process as follows

$$\underset{\text{Free radical}}{R-\dot{C}H_2} + \underset{\substack{\text{Substrate-2}\\ \text{or reagent}}}{X_2} \longrightarrow \underset{\text{Product-1}}{R\,CH_2X} + \underset{\text{Free radical-1}}{X^\bullet}$$

Now, the free radical-1 formed in this step further attacks on substrate-1 and the reaction continues.

Thus, these both the steps continue repeating till one of the substrate is finished.

This step can be recognised by the presence of free radicals on both the sides of arrows.

***Step* III Chain termination step** This step comes into action only when one of the substrates is finished. Here, the free radicals which are present start combining randomly, resulting to various kinds of products in traces, i.e. For the above reaction

$$\dot{X} + \dot{X} \longrightarrow X_2$$

$$R-\dot{C}H_2 + R-\dot{C}H_2 \longrightarrow R-CH_2-CH_2-R$$

$$R-\dot{C}H_2 + \dot{X} \longrightarrow R-CH_2X$$

This step can be recognised by the presence of free radicals before the arrow only.

- Halogenation reactions are mainly given by those hydrocarbons which have at least one hydrogen on sp^3-hybrid carbon.
- The decreasing order of reactivity of halogens on the basis of their electronegativity is given below.

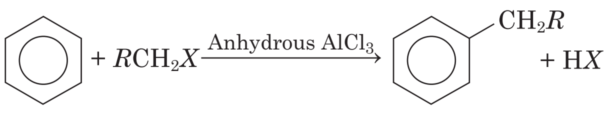
$$F_2 > Cl_2 > Br_2 > I_2$$

- The decreasing order of ease of abstraction of different kinds of hydrogens on the basis of hyperconjugation and + I-effect is as follows

$$3° \text{ hydrogen} > 2° \text{ hydrogen} > 1° \text{ hydrogen} > CH_3-H.$$

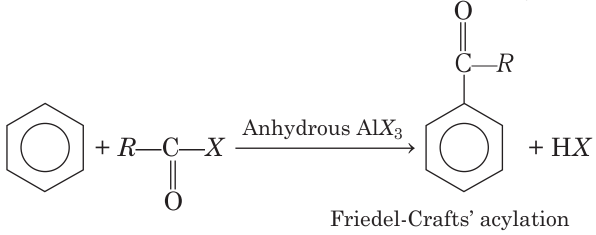
(ii) Electrophilic Substitution Reactions

The substitution reactions which are initiated by electrophiles, are called electrophilic substitution reactions. These reactions are characteristics of aromatic compounds, e.g.



Friedel-Crafts' alkylation

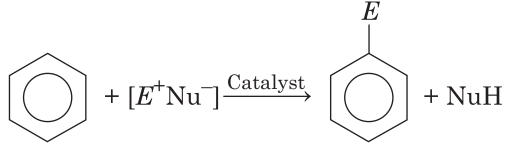
or



Friedel-Crafts' acylation

Mechanism

For the generalised reaction,



Any electrophilic substitution reaction involves following three steps

***Step* I Liberation of electrophile from the reagent**

$$[E^+Nu^-] + \text{catalyst} \longrightarrow \text{catalyst } Nu^-\text{complex} + E^+$$

This can be any Lewis acid, i.e. electron deficient compound

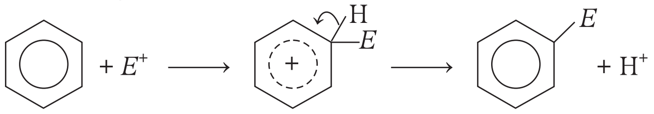
This reagent can be any compound which is broken heterolytically

Thus, for the above reaction

$$R-CH_2X + AlX_3 \longrightarrow \underset{\substack{Nu^-\text{ catalyst}\\ \text{complex}}}{AlX_4^-} + \underset{\text{Electrophile}}{RCH_2^+}$$

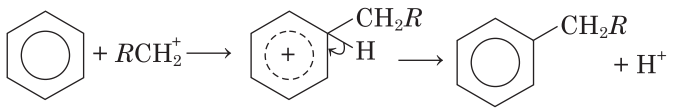
***Step* II Attack of electrophile on benzene ring**

The electrophile formed in step I then attacks on the benzene ring as follows



Transition state or σ-complex

Thus, in the above reaction,



***Step* III Liberation of catalyst from catalyst Nu⁻ complex** The H⁺ formed in step II attacks on catalyst Nu⁻ complex as

$$\text{Catalyst } Nu^- \text{ complex} + H^+ \longrightarrow H^+Nu^- + \text{catalyst}$$

Thus, in the above reaction

$$AlX_4^- + H^+ \longrightarrow HX + \underset{\text{Catalyst}}{AlX_3}$$

Any group because of which electron density is increased on the ring, i.e. electron donating group always favours electrophilic substitution. Electron withdrawing groups on the other hand produce opposite effect.

(iii) Nucleophilic Substitution Reactions

Those substitution reactions which are initiated by nucleophiles are called nucleophilic substitution reactions.

These are usually written as S_N (S-substitution, N = nucleophile) and are of two types, i.e. **unimolecular** (shown as S_N1) and **bimolecular** (shown as S_N2).

Mechanism

These reactions are generally seen in alkyl halides and alcohols, e.g.

$$RX + \mathrm{KOH}(aq) \longrightarrow R\mathrm{OH} + \mathrm{K}X$$

A. **Bimolecular Nucleophilic Substitution** (S_N2)

This mechanism is seen in primary alkyl halides and alcohols. The term bimolecular means, here, the rate of reaction depends upon the concentration of two molecule, just like for the reaction

$$A + B \longrightarrow C + D$$
$$\text{Rate} \propto [A][B]$$

In specific words, we can say that the rate of reaction depends upon the concentration of substrate as well as that of nucleophile and can be shown as

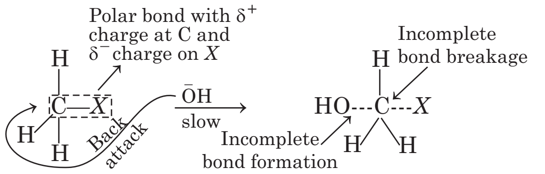
$$\text{Rate of reaction} \propto [\text{Substrate}]\ [\text{Nu}^-]$$

Now, for hydrolysis of any primary alkyl halide (say CH_3X) with aqueous KOH, i.e.

$$CH_3X + \mathrm{KOH}\,(aq) \longrightarrow CH_3OH + \mathrm{K}X$$

The reaction possess a multistep mechanism and proceeds as,

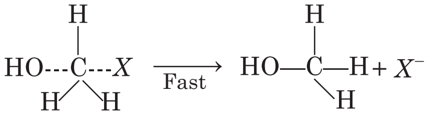
***Step* I** Attack of $\bar{\mathrm{O}}\mathrm{H}$ and formation of transition state



Here, C—X bond is polar thus negatively charged or electron dense nucleophile is attracted towards δ+ carbon atom and attacks over it from the back as shown.

A transition state is formed with incomplete C—OH bond formation and incomplete C—X bond breakage (both shown with dotted lines)

***Step* II**



Transition state

Product

Here, the C—X bond gets fully broken and HO—C bond is fully formed

- The alcohol formed here have **opposite configuration** to that of the parent alkyl halide or has been **inverted** as an umbrella turns inside out in a high wind. This change in configuration is called **Walden's inversion.**
- The step I of this reaction is slower step, i.e. formation of transition state is the rate determining step of this reaction. In this step involvement of both substrate and nucleophile (involvement can be judged by the presence of both in the transition state) suggests that

$$\text{Rate} \propto [\text{Alkyl halide}][\bar{\mathrm{O}}\mathrm{H}]$$

Hence, the reaction is considered as bimolecular. S_N2 **reactions are both stereospecific and stereoselective.**

Features

Some important facts and features related to this mechanism are

- The order of reactivity of alkyl halide towards S_N2 mechanism is

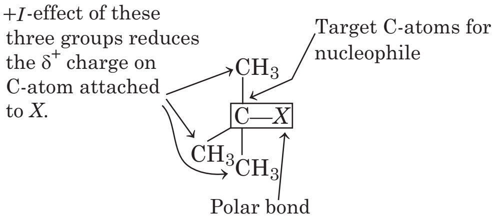
$$\mathrm{Me} > 1° > 2° > 3°.$$

- S_N2 reactions are catalysed by phase transfer catalysts, e.g. $R_4N^+X^-$ and by crown ethers.
- If Nu^- and reactant are uncharged, the rate increases with increase in solvent polarity.
- If either one or both $\mathrm{Nu}^\ominus$ and reactant are charged, the rate decreases with increase in solvent polarity.
- In polar aprotic solvent the rate increases (DMSO >DMF > acetone), since such solvents leave the most reactive nucleophile free.
- Rate of such reactions depends upon nucleophilicity. Greater is the nucleophilicity, faster is the rate of reaction.

B. **Unimolecular Nucleophilic Substitution**

This reaction is the characteristic of tertiary alkyl halides and alcohols. In these molecules S_N2 reaction is not possible due to steric hindrance (steric = structure).

Presence of three electron releasing alkyl groups along with an electron rich halide group or hydroxyl group hinders the reaction to occur through S_N2 pathway. This will be more clear if we examine the structure of a tertiary alkyl halide in the following manner.



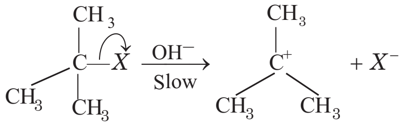
Reasons of S_N2 Failures

- Presence of $4e^-$rich group repel Nu^- to attack.
- Reduced positive charge on C-atom of (C—X) polar bond due to — CH_3 groups also does not favour S_N2 mechanism.
- Alkyl groups being large cover the C-atom from all sides.

  Thus, in such cases the structure hinders the process to occur in accordance with S_N2 pathway that's why the reaction proceeds through another alternate pathway, called S_N1 pathway or polar mechanism.

Different steps involved in this pathway are

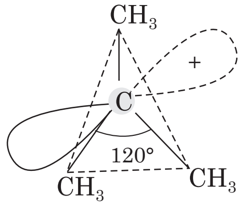
***Step* I** Breakage of C—X bond under the influence of nucleophile OH^-



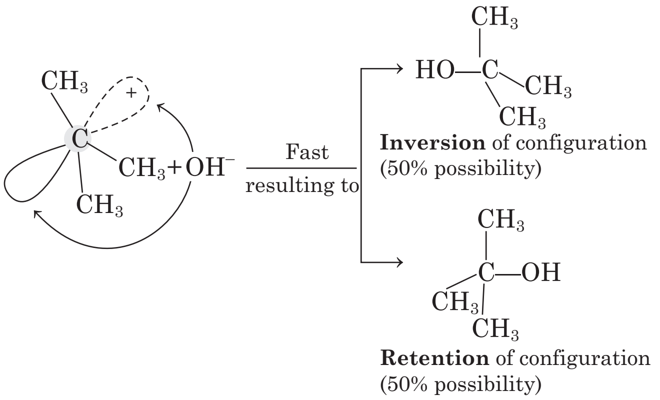
The C—X bond is broken due to the presence of nucleophile resulting to the formation of a tertiary carbonium ion and X^- instead of transition state formation. So, we can say that here ions are developed due to heterolysis in place of transition state.

During this step following changes take place

- The bond angle between three alkyl groups come to 120° from 109°·28′ as was visible in alkyl halide
- The empty orbital present in carbonium ion seems to present perpendicular to the plane of alkyl groups because the carbonium ion is sp^2-hybridised.



***Step* II** The OH^- attacks on empty orbital as,



- As the empty orbital is completely exposed and $\bar{O}H$ now can attack from both the sides so, the alcohol formed here can have two possibilities
  (i) 50% chances are there of retention in configuration.
  (ii) 50% chances are there of inversion in configuration.

The rate determining step, i.e. step I of this reaction involves one molecule only, i.e. alkyl halide, hence,

$$\text{Rate of reaction} \propto [\text{Alkyl halide}]$$

S_N1 reaction is non-stereospecific and non-stereoselective as the attack of nucleophile is not specific and the products are visible as mixture of enantiomers, i.e. racemic mixture.

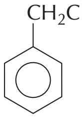
Features

Some important facts about this mechanism are

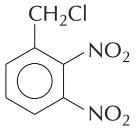
- The order of reactivity of halides towards S_N1 reactions is benzyl > allyl > 3° > 2° > 1° > Me.
- These reactions are catalysed by heavy metal ions, Lewis and Bronsted acids.
- The rate of such reactions increases in polar solvents,
- The rate of such reactions remain unaffected by the concentration of nucleophile.
- Secondary alcohols can proceed through either of these mechanisms.
- Rearrangement of the carbocation (formed in S_N1 reaction) leading to more stable carbocation is also observed in S_N1 reaction.
- High concentration of the nucleophile favours S_N2 reaction while low concentration favours S_N1 reaction.
- $(CH_3)_3CCH_2Br$ shows S_N2 reaction with $C_2H_5O^-$, but S_N1 reaction with C_2H_5OH.

Example 8. *The decreasing order of reactivity of the following compounds towards nucleophilic substitution* (S_N2) *is* ***(JEE Main 2020)***

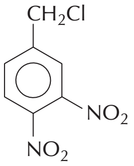
I.



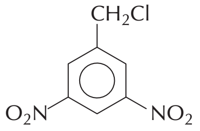
II.



III.



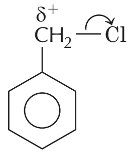
IV.



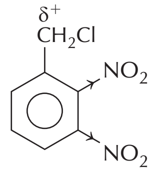
(a) (II) > (III) > (IV) > (I)
(b) (IV) > (II) > (III) > (I)
(c) (III) > (II) > (IV) > (I)
(d) (II) > (III) > (I) > (IV)

Sol. (*a*) Rate of S_N2 reaction $\propto \dfrac{1}{\text{Stability of carbocation}}$

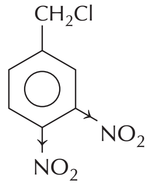
Stability of carbocation $\propto \dfrac{1}{-I\,/-M}$ (effective group)



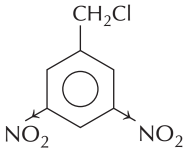
–*I*-effect
(I)



–*M*-effect
–*I*-effect
(II)
(Distance dominating)



–*M*-effect
–*I*-effect
(III)

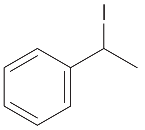


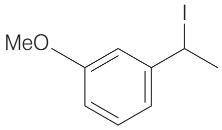
–*I*-effect
(IV)

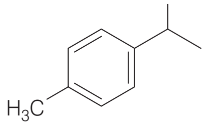
So, the decreasing order of reactivity of the given compounds toward S_N2 reaction is

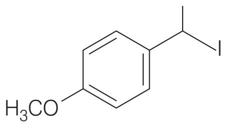
$$(II) > (III) > (IV) > (I)$$

Example 9. *Increasing rate of* S_N1 *reaction in the following compounds is*

(*A*)


(*B*)


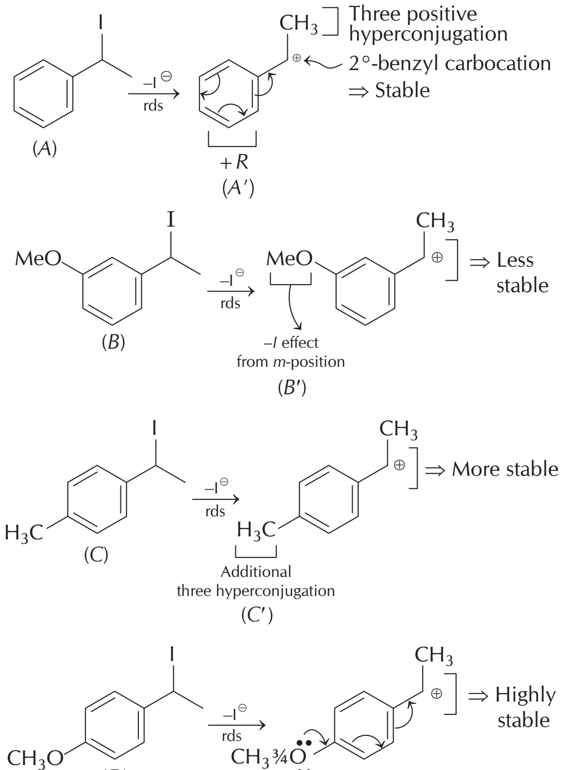
(*C*)


(*D*)


(a) (*A*) < (*B*) < (*C*) < (*D*)　(b) (*B*) < (*A*) < (*C*) < (*D*)
(c) (*A*) < (*B*) < (*D*) < (*C*)　(d) (*B*) < (*A*) < (*D*) < (*C*)

Sol. (*b*) More stable the carbocation intermediate, higher will be the rate of S_N1 reaction.

The reaction involving carbocation intermediate formation for the given compounds are as follows



Stability of intermediates will follow the order

$$\underset{(-I)}{B} < \underset{(-\text{HPC}=3)}{A} < \underset{(+\text{HPC}=6)}{C} < \underset{\begin{pmatrix}+\text{HPC}=3\\+R=1\end{pmatrix}}{D}$$

So, the rate of S_N1 reaction with the given compounds will be,

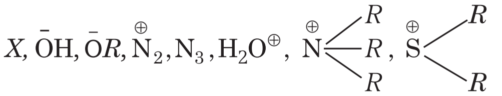
$$B < A < C < D$$

2. **Elimination Reactions**

An elimination reaction is one that involves the loss of two atoms or groups of atoms from the same or adjacent C-atoms leading to the formation of a multiple, i.e. double or triple bond.

Generalised Features

Elimination reactions are usually given by those compounds which have a weak base as leaving group, like



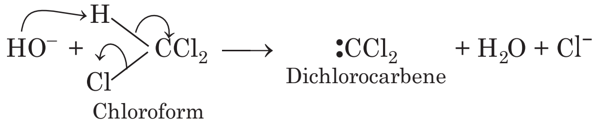
$$\bar{X}, \bar{O}H, \bar{O}R, \overset{\oplus}{N}_2, N_3, H_2O^{\oplus}, \overset{\oplus}{N}R_3, \overset{\oplus}{S}R_2$$

- These reactions are generally endothermic and take place on heating.
- In these reactions, there is loss of two σ bonds and gain of one π-bond, consequently, the product of such reactions is usually less stable than the reactant.
- Moreover, **these are very common in alcohols and alkyl halides.**

Types

Elimination reactions are of following two types

(i) **α-elimination Reactions or 1,1-elimination Reactions** In these reactions, the loss of two atoms or groups occur from the same atom of the substrate molecule, e.g. base-catalysed dehydrohalogenation of chloroform to form dichlorocarbene

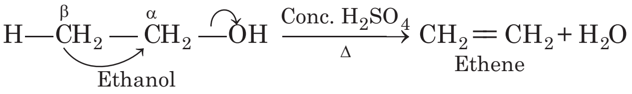


$$HO^- + \underset{\text{Chloroform}}{HCCl_2Cl} \longrightarrow \underset{\text{Dichlorocarbene}}{:CCl_2} + H_2O + Cl^-$$

Dichlorocarbene is the reaction intermediate involved in **carbylamine reaction** and **Reimer-Tiemann reaction**.

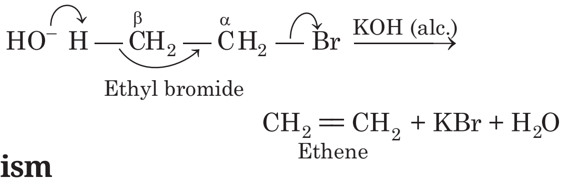
(ii) **β-elimination Reactions** In these reactions, the loss of two atoms or groups occurs from the adjacent atoms of the substrate molecule, e.g. acid-catalysed dehydration of alcohols and base-catalysed dehydrohalogenation of alkyl halides

Acid-catalysed dehydration of alcohols



$$\underset{\text{Ethanol}}{H-\overset{\beta}{C}H_2-\overset{\alpha}{C}H_2-OH} \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} \underset{\text{Ethene}}{CH_2=CH_2} + H_2O$$

Base-catalysed dehydrohalogenation of alkyl halides



$$HO^- \; \underset{\text{Ethyl bromide}}{H-\overset{\beta}{C}H_2-\overset{\alpha}{C}H_2-Br} \xrightarrow{\text{KOH (alc.)}} \underset{\text{Ethene}}{CH_2=CH_2} + KBr + H_2O$$

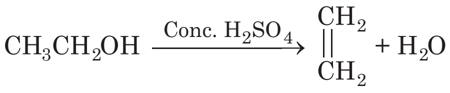
Mechanism

The β-elimination reactions proceed through two pathways just like nucleophilic substitution. These are infact **E1** and **E2** pathways, i.e. **unimolecular elimination** and **bimolecular eliminations** respectively.

A. **Bimolecular Elimination** (E2)

These reactions are **characteristic of primary alkyl halides and alcohols.** Just like S_N2 reaction pathway, here also a transition state is formed.

e.g. In the reaction,



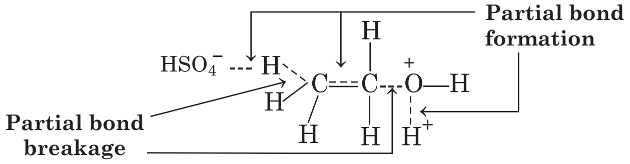
$$CH_3CH_2OH \xrightarrow{\text{Conc. } H_2SO_4} CH_2{=}CH_2 + H_2O$$

The suggested mechanism in as follows

***Step* I** H_2SO_4 gives H^+ and HSO_4^- as

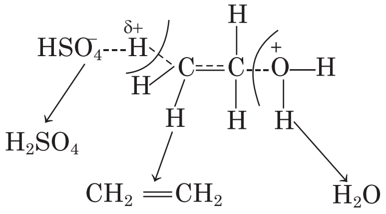
$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

***Step* II** H^+ attacks on the oxygen of —OH group while HSO_4^- attacks on the H-atom of adjacent C-atom to form the transition state.



This transition state formed can be explained with the help of hyperconjugation.

***Step* III** This transition stage shows lysis as follows



In the above reaction as the transition state involves the participation of both alcohol and H_2SO_4, thus

$$\text{Rate of reaction} \propto [\text{alcohol}]\,[H_2SO_4]$$

Another example of such a reaction is dehydrohalogenation of primary alkyl halides.

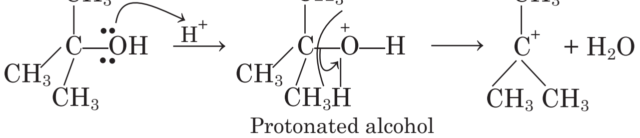
B. **Unimolecular Elimination** (E1)

This pathway is seen in tertiary alkyl halides and alcohols due to steric hindrance. The suggested mechanism for unimolecular elimination is as follows

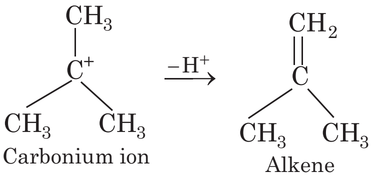
***Step* I** H_2SO_4 dissociates as

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

***Step* II** H^+ attacks on alcohol and a carbonium ion is generalised as



***Step* III** The carbonium ion generated in step II stabilises itself with hyperconjugation to form alkene as



This process is exactly as that of S_N1 pathway till the step II. The difference lies only in step III which involves substitution in S_N1 and elimination here in E1.

Substitution *vs* Elimination

A strong base favours elimination whereas a strong nucleophile favours substitution reactions. The proportion of elimination and substitution products depends upon the following factors

(i) **Nature of Substrate**

- The proportion of elimination increases with increase in the branching of carbon chain, i.e. 1° → 2° → 3° because the alkenes formed on elimination are stabilised by hyperconjugation.
- Secondly, the steric strain due to crowding is relieved on the formation of alkenes, whereas on substitution, the strain is reintroduced.
- Moreover, the substituted groups such as phenyl in the substrate favour elimination. These can stabilise the developing alkene. Thus, C_2H_5Br gives about 1% alkene while $PhCH_2CH_2Br$ gives about 99% Ph $CH{=}CH_2$ or styrene.

(ii) **Nature of Base**

- Strong base favours elimination over substitution the in particular if the case involves E2 over E1.
- In low base concentration and in polar solvents, S_N1 reaction is favoured over E1.
- High concentration of base in non-polar solvents favour E2 over S_N2. That's why alcoholic KOH favours eliminatio
- n and aqueous KOH favours substitution.
- Strong nucleophiles but weak bases promote substitution over elimination, whereas **strong bases but weak nucleophiles** promote elimination over substitution.
- A large quantity nucleophile favours elimination.

(iii) **Nature of Solvent**

- A more polar solvent increases the rate of S_N1 reactions and decreases S_N2 reactions. While a less polar solvent favours E2 over S_N2.
- The change of hydroxylic solvents to aprotic solvents increases the base strength because in the solvent layer around the base H-bonding become absent.

Thus, $Cl^{\ominus}$, $OH^{\ominus}$, $OR^{\ominus}$, etc., are very strong bases in DMF (dimethyl formamide) or DMSO (dimethyl sulphoxide).

- The use of aprotic solvents may sometimes change the pathway from E1 to E2,
- The nucleophilicity order increases with the decreasing basicity of elements. The nucleophilicity order of the halides is $I^{\ominus} > Br^{\ominus} > Cl^{\ominus} > F^{\ominus}$, but in aprotic solvents such as DMF or DMSO, the order is reversed, i.e. $F^{\ominus} > Cl^{\ominus} > Br^{\ominus} > I^{\ominus}$.

(iv) Effect of Temperature

In elimination, the strong (C—H) bond has to break, hence high activation energy is required for elimination. So, **high temperature favours elimination** rather than substitution.

To summarises, in general, elimination increases with

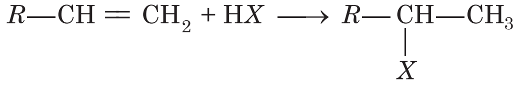
- strong base of high concentration,
- low polarity of solvent and
- high temperature.

On the other hand, substitution increases with

- the weak base of low concentration,
- high polarity of solvent, and
- low temperature.

3. 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 typical of compounds containing multiple bonds, e.g.



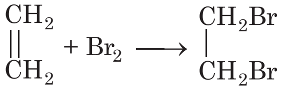
$$R\text{—CH}=\text{CH}_2 + \text{H}X \longrightarrow R\text{—}\underset{\displaystyle X}{\underset{|}{\text{CH}}}\text{—CH}_3$$

or $$R\text{—CH}=\text{CH}_2 + \text{H}_2 \xrightarrow{\text{Ni–250°C}} R\text{— CH}_2\text{CH}_3$$

Addition reactions can be further classified into following three categories on the basis of the intermediate species which begins the reaction.

(i) Electrophilic Addition Reactions

Here, the electrophilic part of reagents initiates the reaction, e.g.



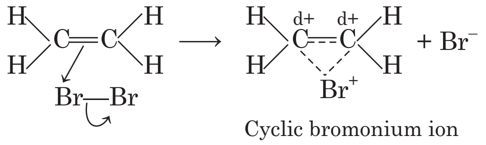
$$\begin{matrix}\text{CH}_2\\ \|\\ \text{CH}_2\end{matrix} + \text{Br}_2 \longrightarrow \begin{matrix}\text{CH}_2\text{Br}\\ |\\ \text{CH}_2\text{Br}\end{matrix}$$

These reactions are normally seen in those compounds where, π-electron cloud is evenly distributed, i.e. when π-bond is formed between two atoms of same or almost same electronegativity, like alkenes and alkynes etc.

Mechanism

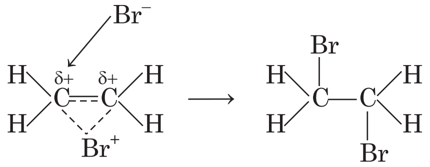
The reaction proceeds *via* the formation of a cyclic intermediate in following manner

***Step* I**

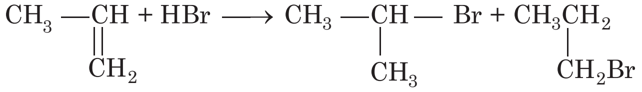


Cyclic bromonium ion

***Step* II** Br^- attacks on either of the δ + charge containing carbonium ions as,



The **Markownikoff's addition of HBr to propene** also involves electrophilic addition and its equation is shown below



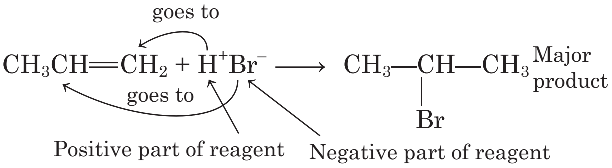
$$\text{CH}_3\text{—}\underset{\displaystyle \text{CH}_2}{\underset{\|}{\text{CH}}} + \text{HBr} \longrightarrow \text{CH}_3\text{—}\underset{\displaystyle \text{CH}_3}{\underset{|}{\text{CH}}}\text{— Br} + \text{CH}_3\underset{\displaystyle \text{CH}_2\text{Br}}{\underset{|}{\text{CH}_2}}$$

Major product

Minor product

Markownikoff Rule

This rule is useful in such conditions when an *asymmetrical reagent* is added to an *asymmetrical alkene*. It says that in such additions **positive part of addendum (reagent) goes to that C-atom which have more number of hydrogens** or negative part of addendum (reagent) goes to that C-atom which have lesser number of hydrogens. This can be analysed as



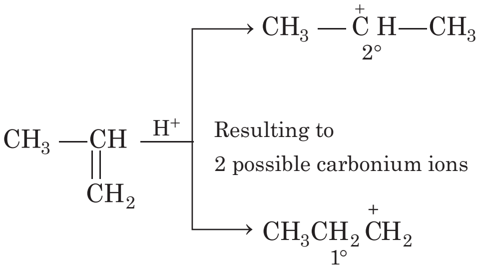
Mechanism

The mechanism involved in the above reaction involves following steps

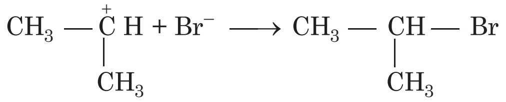
***Step* I** HBr gives a H^+ and a Br^- ion, i.e.

$$\text{H— Br} \longrightarrow \text{H}^+ + \text{Br}^-$$

***Step* II** The H^+ attacks the π bond of propene to form carbonium ion as,

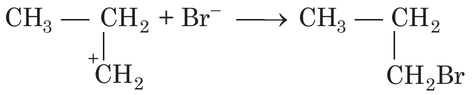


Out of these, the 2° carbonium ion is more stable, thus



$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{+}{C}}H+Br^-\longrightarrow CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-Br$$

Major product



$$CH_3-\underset{\underset{\displaystyle {}^{+}CH_2}{|}}{CH_2}+Br^-\longrightarrow CH_3-\underset{\underset{\displaystyle CH_2Br}{|}}{CH_2}$$

Minor product

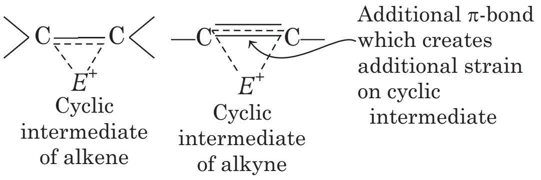
> **Stable Intermediates**
>
> Always remember stable intermediate give major product because of following two reasons
>
> (i) These decreases the activation energy of reaction, thus push, the reaction towards an alternate pathway with good yield of major product.
>
> (ii) Being stable these stay for a longer period with in the reaction, thus, provide more opportunities of attack on themselves.

Alkenes *vs* Alkynes in Electrophilic Addition

In these reactions, alkenes are more reactive than alkynes although unsaturation is more in alkynes.

Reason The reason for such a difference is more strained or less stable cyclic intermediate in the case of alkynes due to the presence of additional π-bond in it.

Both of these intermediates are shown below

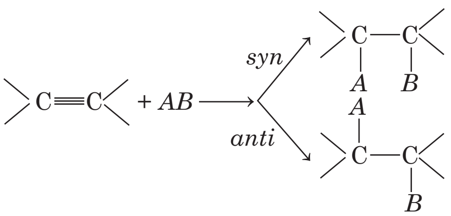


Syn and *Anti* addition

Technically, the electrophilic addition can be of following two types

(i) ***Syn* addition** When both the groups are added on the same side of π-bond.

(ii) ***Anti* addition** When both the groups are added on the opposite side of π-bond.

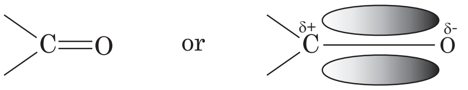


Following points give importance of *syn* and *anti*-addition.

- In *anti* addition like halogenation, *cis* alkene gives *d* and *l* products while *trans*-alkene gives *meso*-form.
- In *syn* addition like hydroxylation *cis* alkene gives *meso* product while *trans*-alkene gives *d* and *l*-products.

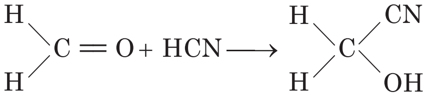
(ii) Nucleophilic Addition Reactions

In these reactions the nucleophilic part of reagent initiates the reaction. These additions are seen in those compounds **which have unevenly distributed electron cloud**, means have a π-bond between two atoms of different electronegativity, e.g. πe^- cloud in aldehydes and ketones, i.e.



π-electron cloud is inclined more towards oxygen atom.

The equation for nucleophilic addition of HCN to HCHO is given below



Cyanohydrin

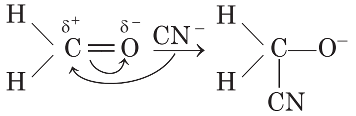
Mechanism

The reaction proceeds in the following manner

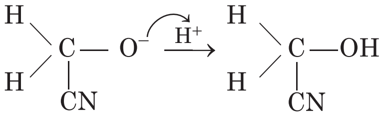
***Step* I** HCN gives H^+ and CN^- as

$$HCN \longrightarrow H^+CN^-$$

***Step* II** CN^- attacks on carbon atom of carbonyl group to form corresponding anion as



***Step* III** The proton attacks on anion to form the addition product as

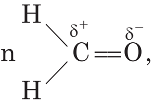


The reactivity of aldehydes and ketones towards **nucleophilic additions** follows the order

HCHO > other aldehydes > ketones

The reactivity in actual sense depends upon the magnitude of δ+ charge on the C-atom of $>C{=}O$ group,

i.e. in

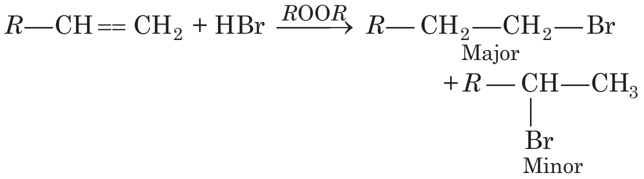


, C-atom bears maximum possible positive charge because in higher homologues, the magnitude of charge decreases due to the $+I$-effect of alkyl group attached in place of H.

The magnitude further decreases in ketones as there the second hydrogen atom of HCHO is also replaced by another alkyl group.

(iii) Free Radical Addition Reactions

The free radical addition reactions involve additions through free radicals. The most common example of this type of reaction is addition of HBr to any asymmetric alkene in the presence of peroxide, i.e.



$$R{-}CH{=}CH_2 + HBr \xrightarrow{ROOR} \underset{\text{Major}}{R{-}CH_2{-}CH_2{-}Br} + \underset{\text{Minor}}{R{-}\underset{\underset{Br}{|}}{CH}{-}CH_3}$$

This reaction commonly called **Kharasch effect** or **peroxide effect** or **anti-Markownikoff's** addition, as here addition occurs opposite to Markownikoff's rule.

Mechanism

The free radical addition pathway in above written reaction proceeds through following steps

***Step* I** Initiation step

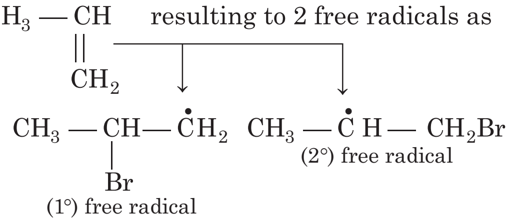
$$R{-}O{-}O{-}R \xrightarrow[\text{or free radical initiators}]{h\nu \text{ or high temperature}} 2RO^\bullet$$

***Step* II** Propagation steps

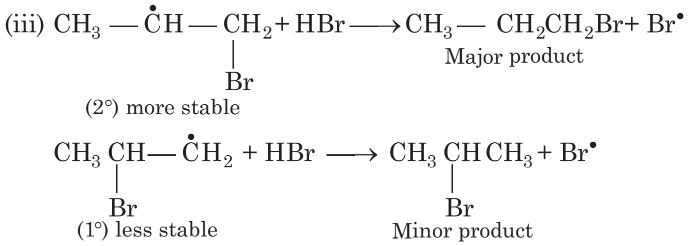
(i) Homolytic fission of HBr by $RO^\bullet$ free radical

$$RO^\bullet + HBr \longrightarrow ROH + Br^\bullet$$

(ii) $Br^\bullet + CH_3{-}CH$ resulting to 2 free radicals as



Out of these 2° free radical is more stable than 1° free radical.



(iii) $$\underset{(2°)\text{ more stable}}{CH_3{-}\dot{C}H{-}\underset{\underset{Br}{|}}{CH_2}} + HBr \longrightarrow \underset{\text{Major product}}{CH_3{-}CH_2CH_2Br} + Br^\bullet$$

$$\underset{(1°)\text{ less stable}}{CH_3\underset{\underset{Br}{|}}{CH}{-}\dot{C}H_2} + HBr \longrightarrow \underset{\text{Minor product}}{CH_3\underset{\underset{Br}{|}}{CH}CH_3} + Br^\bullet$$

Remember The reaction is true for HBr only among halogen acids. The reason is HF and HCl bonds are so strong that their homolytic breakage is not possible with $RO^\bullet$ while H—I bond breakes easily but iodine free radicals are very unstable and generally combine to form I_2 molecule thus reducing the possibility of completion of reaction in this manner.

4. Addition-Elimination Reactions

These reactions involve addition of two molecules with elimination of smaller molecules like H_2O. The best example of such a type of reaction is **esterification**, i.e.

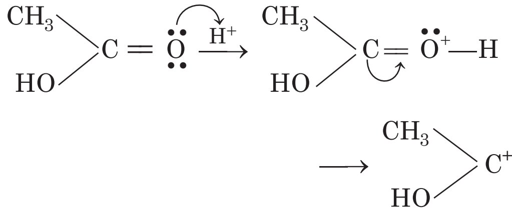
$$C_2H_5OH + CH_3COOH \overset{H^+}{\rightleftharpoons} CH_3COOC_2H_5 + H_2O$$

The reaction is said to proceed through **"nucleophilic addition-elimination"** and gives best result in the presence of mineral acids.

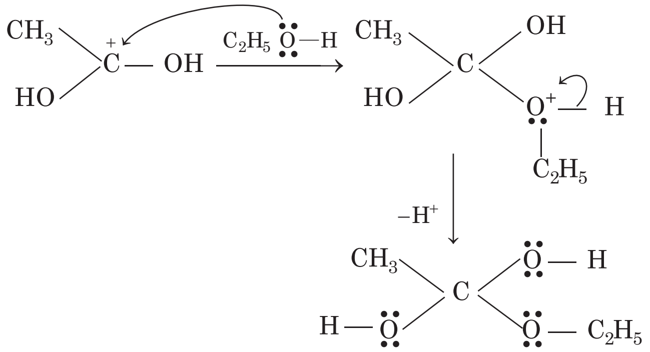
Mechanism

The nucleophilic addition-elimination pathway with acid catalysed condition for esterification proceed through following steps

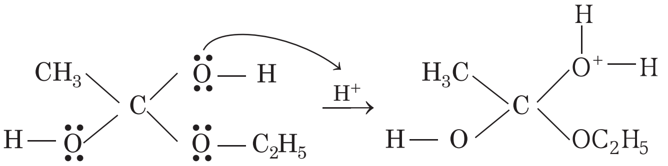
***Step* I** Initially, the H^+ of mineral acid attacks on O-atom of carbonyl part of —COOH group. Such an attack is said to create unit positive charge on C-atom of this group so that a proper site for nucleophilic attack is generated.



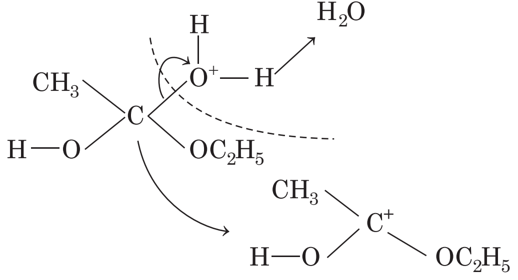
***Step* II** Now, the oxygen of alcohol donates its lone pair to positively charged C-atom of carbonium ion as



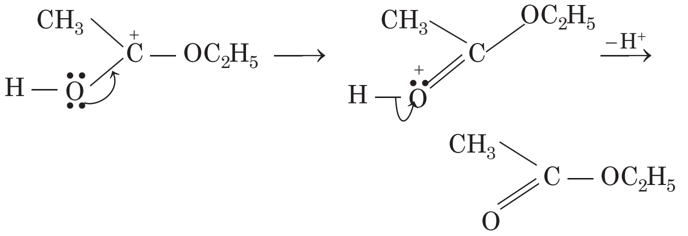
***Step* III** The H^+ liberated in step II attacks on the oxygen of —OH group, taking the lone pair from it, thus



This results in liberation of water molecule and formation of another carbonium ion as



This carbonium ion stabilises itself as



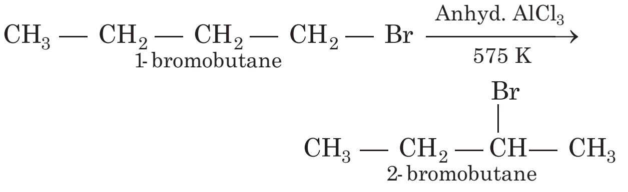
*In this process, the oxygen of alcohol remains intact and seen in ester itself. The process given above was fully worked out by **Fischer** in 1920, hence also called **Fischer Spierer** method commonly.*

Two H^+ are used in the process and two are eliminated thus showing that H^+ is working as a catalyst as during the reaction the concentration of catalyst remain unchanged. Other common examples of addition elimination reaction are addition of ammonia derivatives to aldehydes and ketones.

5. Rearrangement Reactions

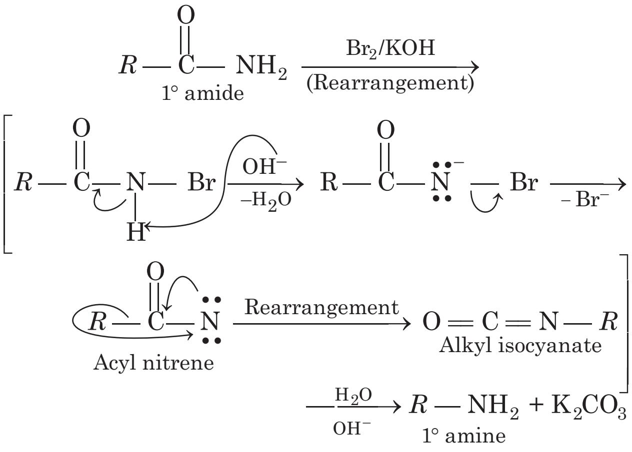
Reactions involving the migration of an atom or a group from one atom to another within the same molecule are called **rearrangement reactions,** e.g.

(i) 1-bromobutane rearranges to 2-bromobutane in the presence of anhydrous $AlCl_3$ at 575 K.



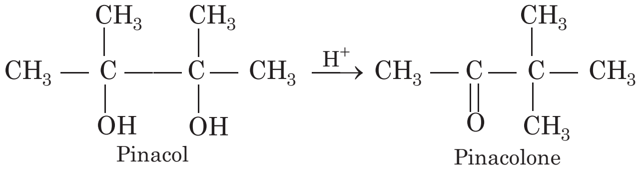
$$\underset{\text{1-bromobutane}}{CH_3-CH_2-CH_2-CH_2-Br} \xrightarrow[\text{575 K}]{\text{Anhyd. } AlCl_3} \underset{\text{2-bromobutane}}{CH_3-CH_2-\overset{\displaystyle Br}{\overset{|}{C}H}-CH_3}$$

(ii) **Hofmann bromamide degradation reaction** involving the conversion of 1° amides to 1° amines on treatment with Br_2 in the presence of KOH.



In this rearrangement reaction, the group R migrates from carbon to nitrogen to first give an **alkyl isocyanate** which upon hydrolysis gives a 1° amine with one carbon atom less than the original amide.

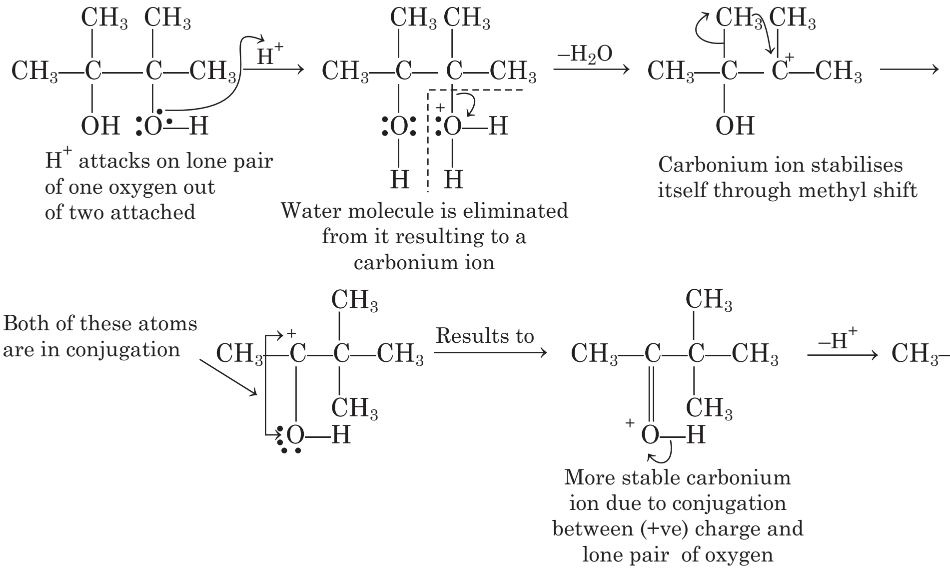
(iii) Another example of rearrangement reaction is a very common **pinacol-pinacolone** rearrangement which is shown below



$$\underset{\text{Pinacol}}{CH_3-\underset{OH}{\overset{CH_3}{C}}-\underset{OH}{\overset{CH_3}{C}}-CH_3} \xrightarrow{H^+} \underset{\text{Pinacolone}}{CH_3-\underset{O}{\overset{}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3}$$

Mechanism

The reaction proceeds as ,

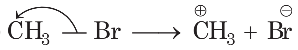


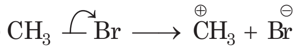
Practice Exercise

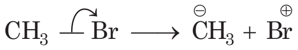
ROUND I Topically Divided Problems

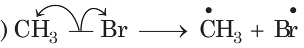
Covalent Bond Fission

1. Covalent bond can undergo fission in two different ways. The correct representation involving a heterolytic fission of $CH_3 — Br$ is ***(NCERT Exemplar)***

(a) 
$CH_3 — Br \longrightarrow \overset{\oplus}{C}H_3 + \overset{\ominus}{Br}$

(b) 
$CH_3 — Br \longrightarrow \overset{\oplus}{C}H_3 + \overset{\ominus}{Br}$

(c) 
$CH_3 — Br \longrightarrow \overset{\ominus}{C}H_3 + \overset{\oplus}{Br}$

(d) 
$CH_3 — Br \longrightarrow \overset{\bullet}{C}H_3 + \overset{\bullet}{Br}$

2. CH_3CH_2Cl undergoes homolytic fission to produce

(a) $CH_3\overset{\bullet}{C}H_2$ and $\overset{\bullet}{C}l$

(b) $CH_3\overset{+}{C}H_2$ and Cl^-

(c) $CH_3CH_2^+$ and $\overset{\bullet}{C}l$

(d) $CH_3\overset{\bullet}{C}H_2$ and Cl^-

3. In which of the following compound/s, the

(i) $CH_3—SCH_3$ (ii) $CH_3—CN$
(iii) $CH_3—Cu$

covalent bond shown by a dash undergoes heterolytic fission to form a carbanion?

(a) (i) and (iii)
(b) (ii) and (iii)
(c) (ii) only
(d) (iii) only

Attacking Reagent and Species

4. The correct statement regarding electrophile is

(a) electrophile is a negatively charged species and can form a bond by accepting a pair of electrons from another electrophile
(b) electrophiles are generally neutral species and can form a bond by accepting a pair of electrons from a nucleophile
(c) electrophile can be either neutral or positively charged species and can form a bond by accepting a pair of electrons from a nucleophile
(d) electrophile is a negatively charged species and can form a bond by accepting a pair of electrons from a nucleophile.

5. In which of the following compounds,

(i) $CH_3\overset{*}{C}H = O$ (ii) $CH_3\overset{*}{C}N$
(iii) $\overset{*}{C}H_3I$

starred carbon atom can act as electrophilic centre

(a) (i) and (ii)
(b) (i) and (iii)
(c) (ii) and (iii)
(d) All of these

6. Which of the following is an electrophile?

(a) Na^+ (b) Li^+ (c) H^+ (d) Ca^{2+}

7. Which of the following cannot act an electrophile?

(a) SO_3
(b) $:CH_2$
(c) $R—\ddot{N}:$
(d) $R—\ddot{N}H_2$

8. Which of the following species is a nucleophile?

(a) $\overset{+}{N}O_2$
(b) $:CX_2$
(c) $:\ddot{N}H_2^-$
(d) $—CH_3$

9. Which of the reagent(s) shown in bold in the following reactions will act as nucleophile(s)?

(i) $CH_3COOH + {}^-OH \longrightarrow CH_3COO^- + H_2O$
(ii) $CH_3COOCH_3 + —CN \longrightarrow (CH_3)_2C(CN)OH$
(iii) $C_6H_6 + CH_3CO^+ \longrightarrow C_6H_5COCH_3 + H^+$

(a) ${}^-OH$
(b) CH_3CO^+
(c) ${}^-OH$ and CH_3CO^+
(d) ${}^-OH$ and ${}^-CN$

10. Among the following, the strongest nucleophile is

(a) C_2H_5SH
(b) CH_3COO^-
(c) CH_3NH_2
(d) $NCCH_2^-$

11. Strongest nucleophile is

(a) RNH_2
(b) ROH
(c) $C_6H_5O^-$
(d) CH_3O^-

12. Which has the highest nucleophilicity?

(a) F^- (b) OH^- (c) CH_3^- (d) NH_2^-

13. For the following (i) I^- (ii) Cl^- (iii) Br^-
the increasing order of nucleophilicity would be

(a) $I^- < Br^- < Cl^-$
(b) $Cl^- < Br^- < I^-$
(c) $I^- < Cl^- < Br^-$
(d) $Br^- < Cl^- < I^-$

14. Which one of the following series contains electrophiles only

(a) H_2O, SO_3, H_3O^+ (b) $NH_3, H_2O, AlCl_3$

(c) $AlCl_3, SO_3, \overset{+}{N}O_2$ (d) H_2O, Cl^+, NH_3

15. Out of the following the one containing only nucleophiles is

(a) $AlCl_3, BF_3, NH_3$ (b) NH_3, CN^-, CH_3OH

(c) $AlCl_3, NH_2^-, H_2O$ (d) $RNH_2, :CX_2, H^-$

Reaction Intermediate

16. Which behaves both as a nucleophile as well as an electrophile?

(a) CH_3OH (b) CH_3NH_2

(c) CH_3CN (d) CH_3Cl

17. Heterolysis of $CH_3CH_2CH_3$ results in the formation of

(a) $\overset{\oplus}{C}H_3$ and $\bar{C}_2H_5$ (b) $\dot{C}H_3$ and $\dot{C}_2H_5$

(c) $\bar{C}H_3$ and $\overset{\oplus}{C}_2H_5$ (d) CH_3 and C_2H_5

18. The stability of a carbonium ion depends upon

(a) the bond angle of the attached group

(b) the substrate with which it reacts

(c) the inductive effect and hyper-conjugative effect of the attached group

(d) None of the above

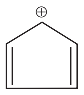
19. The most stable carbonium ion among the following is

(a) $C_6H_5CH_2\overset{+}{C}H_2$ (b) $CH_3\overset{+}{C}H_2$

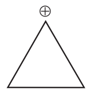
(c) $C_6H_5\overset{+}{C}HC_6H_5$ (d) $C_6H_5\overset{+}{C}H_2$

20. The most stable carbocation is

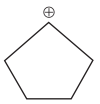
(a)



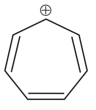
(b)



(c)



(d)



21. The stability of the free radicals; allyl, benzyl, 3°, 2°, 1°, vinyl and CH_3 is in the order

(a) benzyl > allyl > 3° > 2° > 1° > $\dot{C}H_3$ > vinyl

(b) allyl > 3° > benzyl > 2° > 1° > $\dot{C}H_3$

(c) vinyl > 3° > 2° > 1° > CH_3 > allyl > benzyl

(d) 3° > 2° > 1° > CH_3 > vinyl > allyl = benzyl

22. Correct order of stability is

(a) $HC\equiv\bar{C} > CH_2=\bar{C}H > CH_3-\bar{C}H_2$

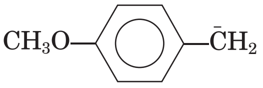
(b) $CH_3-\bar{C}H_2 > CH_2=\bar{C}H > CH\equiv\bar{C}$

(c) $CH_3-\bar{C}H_2 > CH\equiv CH \cong CH_2=\bar{C}H$

(d) All are equally stable

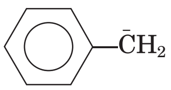
23. Consider the following carbanions

I.



II.

III.



Correct order of stability is

(a) I > II > III (b) III > II > I

(c) II > III > I (d) I > III > II

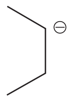
24. Which of the two : $O_2NCH_2CH_2O^-$ or $CH_3CH_2O^-$ is expected to be more stable? *(NCERT)*

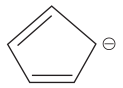
(a) $O_2NCH_2CH_2O^-$ (b) $CH_3CH_2O^-$

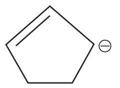
(c) Both are equally stable (d) Cannot say anything

25. The order of stability of the following carbanion is

$CH_3\overset{\ominus}{C}H_2$







I II III IV

(a) I > II > III > IV (b) I > III > II > IV

(c) IV > III > II > I (d) III > IV > I > II

26. State the hybridisation of carbon present in triplet carbene.

(a) sp^3 (b) sp^2

(c) sp (d) None of these

Inductive Effect and Application

27. Consider the following molecule, $\overset{3}{C}H_3\overset{2}{C}H_2\overset{1}{C}H_2Br$ Which of the carbon atom (numbered 1, 2 or 3) has least inductive effect?

(a) C_1 (b) C_2

(c) C_3

(d) same at all the three carbon atoms

28. Which of the following has minimum –I-effect?

(a) —NO_2 (b) —COOH (c) —F (d) —$\overset{+}{N}R_3$

29. Which of the following has minimum –I-effect of the substitutents?

(a) —NR_2 < —OR < —F (b) —NR_2 > —OR < —F

(c) —NR_2 < —OR > —F (d) —NR_2 > —OR > —F

30. Which of the following groups has the highest + I-effect?

(a) CH_3— (b) CH_3CH_2—

(c) $(CH_3)_2CH$— (d) $(CH_3)_3C$—

31. Which of the following correctly represents the + I-effect of the substitutents?

(a) $O^- > COO^- > {}^-CR_3$ (b) $COO^- > O^- > {}^-CR_3$

(c) $O^- < COO^- < {}^-CR_3$ (d) $COO^- < O^- < {}^-CR_3$

32. The arrangement of $(CH_3)_3C—$, $(CH_2)_2CH—$, $CH_3CH_2—$ when attached to benzene or an unsaturated group in increasing order of inductive effect is

(a) $(CH_3)_3C— < (CH_3)_2CH— < CH_3CH_2—$

(b) $CH_3CH_2— < (CH_3)_2CH— < (CH_3)_3C—$

(c) $(CH_3)_3CH— < (CH_3)_3C— < CH_3CH_2—$

(d) $(CH_3)_3C— < CH_3CH_2— < (CH_3)_2CH—$

33. Which of the following groups has the highest hyperconjugation effect but least $+I$-effect?

(a) $—CH_3$ (b) $—CH_2CH_3$

(c) $—CH(CH_3)_2$ (d) $—C(CH_3)_3$

34. The inductive effect

(a) implies the atom's ability to cause bond polarisation

(b) increases with increase of distance

(c) implies the transfer of lone pair of electrons from more electronegative atom to the lesser electronegative atom in a molecule

(d) implies the transfer of lone pair of electrons from lesser electronegative atom to the more electronegative atom in a molecule

35. Arrange the carbanions, $(CH_3)_3\bar{C}, \bar{C}Cl_3$, $(CH_3)_2\bar{C}H, C_6H_5\bar{C}H_2$ in order of their decreasing stability. ***(AIEEE 2009)***

(a) $C_6H_5\bar{C}H_2 > \bar{C}Cl_3 > (CH_3)_3\bar{C} > (CH_3)_2\bar{C}H$

(b) $(CH_3)_2\bar{C}H > \bar{C}Cl_3 > C_6H_5\bar{C}H_2 > (CH_3)_3\bar{C}$

(c) $\bar{C}Cl_3 > C_6H_5\bar{C}H_2 > (CH_3)_2\bar{C}H > (CH_3)_3\bar{C}$

(d) $(CH_3)_3\bar{C} > \bar{C}Cl_3 > C_6H_5\bar{C}H_2 > (CH_3)_2\bar{C}H$

Electromeric Effect and Application

36. Which of the following is not true about electromeric effect

(a) It results in appearance of partial charges on carbon atoms

(b) It is a temporary effect

(c) It operates on multiple bonds

(d) It requires attacking reagent

Conjugation, Resonance and Mesomeric Effect

37. The correct order of increasing basicity of the given conjugate bases ($R = CH_3$) is ***(AIEEE 2010)***

(a) $RCO\bar{O} < HC\equiv\bar{C} < \bar{R} < \bar{N}H_2$

(b) $\bar{R} < HC\equiv\bar{C} < RCO\bar{O} < \bar{N}H_2$

(c) $RCO\bar{O} < \bar{N}H_2 < HC\equiv\bar{C} < \bar{R}$

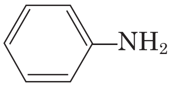
(d) $RCO\bar{O} < HC\equiv\bar{C} < \bar{N}H_2 < \bar{R}$

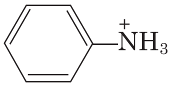
38. Resonance energy is more for

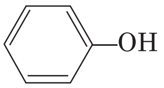
(a) benzene (b) cyclohexene

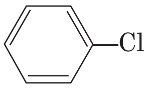
(c) cycloheptene (d) cyclohexa-1,2,3-triene

39. In which of the following molecules, the resonance effect is not present?

(a) 

(b) 

(c) 

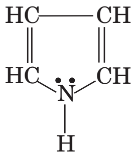
(d) 

40. Polarisation of electron in acrolein may be written as

(a) $\overset{-\delta}{C}H_2{=}CH{—}\overset{+\delta}{C}H{=}O$ (b) $\overset{+\delta}{C}H_2{=}CH{—}CH{=}\overset{+\delta}{O}$

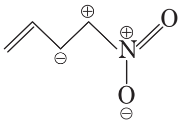
(c) $\overset{-\delta}{C}H_2{=}\overset{+\delta}{C}H{—}CH{=}O$ (d) $\overset{+\delta}{C}H_2{=}CH{—}CH{=}\overset{-\delta}{O}$

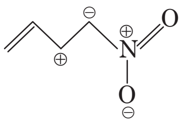
41. How many delocalised π-electrons are there in the compound

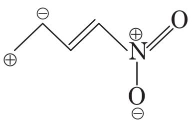


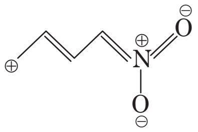
(a) 8 (b) 2 (c) 4 (d) 6

42. Among the following, the least stable resonance structure is

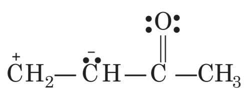
(a) 

(b) 

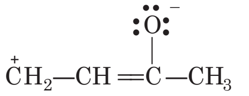
(c) 

(d) 

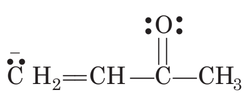
43. One of the stable resonating forms of methyl vinyl ketone is

(a) 

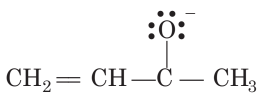
$\overset{+}{C}H_2—\overset{-}{\ddot{C}}H—\overset{\overset{\displaystyle :O:}{\|}}{C}—CH_3$

(b) 

$\overset{+}{C}H_2—CH{=}\overset{\overset{\displaystyle :\ddot{O}:^{-}}{|}}{C}—CH_3$

(c) 

$\overset{-}{\ddot{C}}H_2{=}CH—\overset{\overset{\displaystyle :O:}{\|}}{C}—CH_3$

(d) 

$CH_2{=}CH—\overset{\overset{\displaystyle :\ddot{O}:^{-}}{|}}{C}—CH_3$

44. Which among the following statements are true with respect to electronic displacement in a covalent bond?

(i) Inductive effect operates through π-bond.

(ii) Resonance effect operates through σ-bond.

(iii) In presence of electrophiles, alkenes show $+E$-effect.

(iv) In presence of nucleophiles, aldehydes/ketones show $-E$-effect.

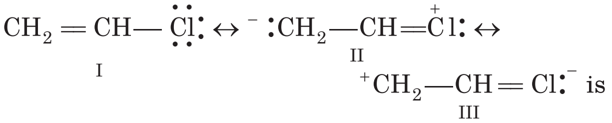
(v) Resonance effect operates through π-bond.

(a) (i), (ii), (v)
(b) (iii), (iv), (v)
(c) (ii), (iii), (iv)
(d) (i), (iii), (v)

45. Which amongst the following is the strongest acid? *(JEE Main 2019)*

(a) $CHBr_3$ (b) CHI_3 (c) $CHCl_3$ (d) $CH(CN)_3$

46. The decreasing order of stability of the following resonating structures



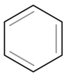
$$\underset{\text{I}}{CH_2=CH-\ddot{\underset{\cdot\cdot}{Cl}}\colon} \leftrightarrow \underset{\text{II}}{{}^{-}\colon CH_2-CH=\overset{+}{C}l\colon} \leftrightarrow \underset{\text{III}}{{}^{+}CH_2-CH=Cl\colon^{-}}$$ is

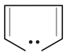
(a) II > III > I
(b) III > II > I
(c) I > III > II
(d) I > II > III

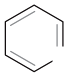
47. The dipole moment of vinyl chloride is lower than that of ethyl chloride. This is due to

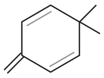
(a) resonance effect
(b) inductive effect
(c) electromeric effect
(d) hyperconjugation effect

48. Which of the following molecules is least resonance stabilised? *(JEE Main 2017)*









49. The correct order for acid strength of compounds $CH\equiv CH$, $CH_3-C\equiv CH$ and $CH_2=CH_2$ is as follows *(JEE Main 2019)*

(a) $CH_3-C\equiv CH > CH_2=CH_2 > HC\equiv CH$
(b) $CH_3-C\equiv CH > CH\equiv CH > CH_2=CH_2$
(c) $HC\equiv CH > CH_3-C\equiv CH > CH_2=CH_2$
(d) $CH\equiv CH > CH_2=CH_2 > CH_3-C\equiv CH$

Hyperconjugation and Its Application

50. Alkyl groups act as electron donors when attached to a π-system because of *(NCERT)*

(a) resonance
(b) mesomeric effect
(c) hyperconjugation
(d) Both (b) and (c)

51. Stability of which intermediate is not governed by hyperconjugation?

(a) Carbon cation
(b) Carbon anion
(c) Carbon free radical
(d) None of these

52. Alkyl groups in benzene are *o*, *p*-directing because of

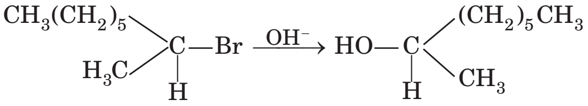
(a) inductive effect
(b) electromeric effect
(c) hyperconjugation effect
(d) All the three

53. The effect that make 2, 3-dimethyl-2-butene more stable than 2-butene is

(a) resonance
(b) hyperconjugation
(c) electromeric effect
(d) inductive effect

Substitution

54. The following reaction is described as



(a) S_E2 (b) S_N2 (c) S_N1 (d) S_N0

55. Which one is least reactive in a nucleophilic substitution reaction?

(a) CH_3CH_2Cl
(b) $CH_2=CHCH_2Cl$
(c) $CH_2=CHCl$
(d) $(CH_3)_3CCl$

56. *t*-butyl chloride reacts with OH^- by S_N1 mechanism and rate $\propto$ [*t*-butyl chloride]. One of the reasons for this is that

(a) stereochemical inversion takes place
(b) *t*-butyl carbocation is first formed which is more stable
(c) the product *t*-butyl alcohol is more stable
(d) the intermediate *t*-butyl carbocation is stabilized by solvation

57. Examine the following statements regarding S_N2 reaction

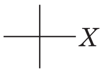
(1) The rate of reaction is independent of concentration of nucleophile
(2) The nucleophile attacks the carbon atom on the side of molecule opposite to the group being displaced
(3) The reaction proceeds with simultaneous bond formation and rupture

Which of the above written statements are correct?

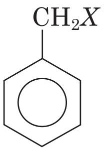
(a) 1, 2
(b) 1, 3
(c) 1, 2, 3
(d) 2, 3

58. Which of the following cannot show S_N1 reaction?

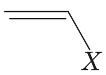
(a)



(b)

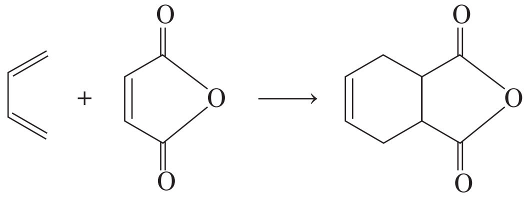


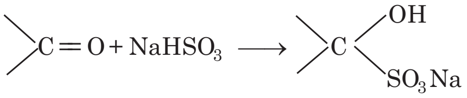
(c)



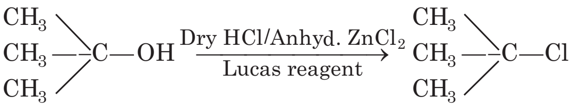
(d)

59. The substitution reaction among the following is

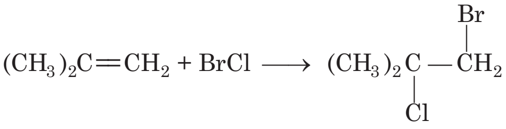
(a)


(b)


$\rangle C=O + NaHSO_3 \longrightarrow \rangle C(OH)(SO_3Na)$

(c)


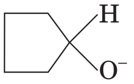
$(CH_3)_3C—OH \xrightarrow[\text{Lucas reagent}]{\text{Dry HCl/Anhyd. }ZnCl_2} (CH_3)_3C—Cl$

(d)


$(CH_3)_2C{=}CH_2 + BrCl \longrightarrow (CH_3)_2\underset{\displaystyle Cl}{C}—\overset{\displaystyle Br}{CH_2}$

60. List the following alkoxide nucleophile in decreasing order of their S_N2 reactivity

1. Me_3CO^-
2. MeO^-
3. $MeCH_2O^-$
4. Me_2CHO^-
5.



(a) 2 > 3 > 5 > 4 > 1 (b) 5 > 3 > 2 > 1 > 4
(c) 1 > 5 > 2 > 3 > 4 (d) 3 > 5 > 1 > 2 > 3

61. Consider the following reactions. Which of these does not involve attack of a nucleophile in first step? *(NCERT)*

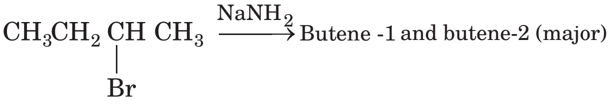
(a) $CH_3CH_2Br + HS^- \longrightarrow CH_3CH_2SH + Br^-$
(b) $(CH_3)_2C = CH_2 + HCl \longrightarrow (CH_3)_2CCl — CH_3$
(c) $CH_3CH_2Br + HO^- \longrightarrow CH_2 = CH_2 + H_2O + Br^-$
(d) $(CH_3)_2C — CH_2OH + HBr \rightarrow (CH_3)_2CBrCH_2CH_3 + H_2O$

Elimination

62. Which of the following is most reactive towards elimination reaction?

(a) $RCOO^-$ (b) CN^-
(c) NO_3^- (d) RO^-

63. The reaction,

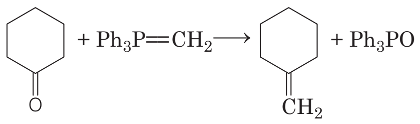


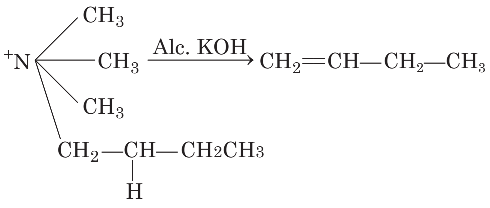
$CH_3CH_2\underset{\displaystyle Br}{CH}CH_3 \xrightarrow{NaNH_2}$ Butene -1 and butene-2 (major)

The correct statement(s) are
(a) 2-butene is Saytzeff product
(b) 1-butene is Hofmann(s) product
(c) the elimination reaction follows Saytzeff rule
(d) All of the above

64. Which of the following is elimination reaction?

(a) $CH_3CH_2Cl + \text{aq. } KOH \longrightarrow CH_3CH_2OH$

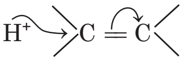
(b)


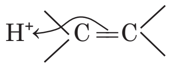
(c)


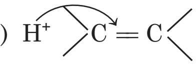
(d) None of the above

Addition Reaction

65. The addition of HCl to an alkene proceeds in two steps. The first step is the attack of H^+ ion to $\rangle C = C\langle$ portion which can be shown as *(NCERT Exemplar)*

(a)


(b)


(c)


(d) All of these

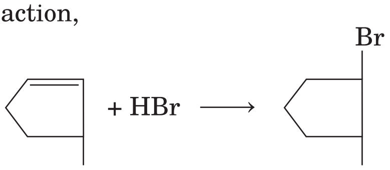
66. Electrophilic addition reactions proceed in two steps. The first step involves the addition of an electrophile. Name the type of intermediate formed in the first step of the following addition reaction.
$H_3C — HC{=}CH_2 + H^+ \longrightarrow ?$ *(NCERT Exemplar)*

(a) 2° carbanion (b) 1° carbocation
(c) 2° carbocation (d) 1° carbanion

67. Which one of the following explain, why does propene undergo electrophilic addition with HBr, but not with HCN ?

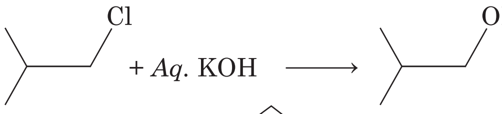
(a) Br^- is better nucleophile than CN^-
(b) HBr being better source of proton as it is stronger acid than HCN
(c) HCN attacks preferentially *via* lone pair of nitrogen
(d) The C—Br bond being stronger is formed easily as compared to C—CN bond

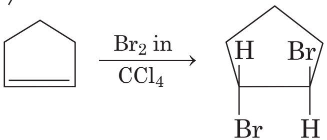
68. The reaction,

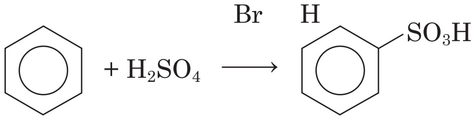


is an example of
(a) nucleophilic substitution (b) electrophilic addition
(c) elimination reaction (d) nucleophilic addition

69. The addition reaction among the following is

(a) 

(b) 

(c) 

(d) All of the above

70. Which of the following types of reaction occurs when a substituent has got a double bond with evenly distributed π-electron cloud ?

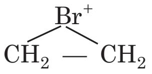
(a) Electrophilic addition

(b) Nucleophilic addition

(c) Any of the (a) and (b)

(d) None of the above

71. During addition of bromine on ethene, the first species formed is

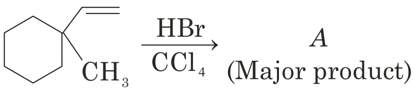
(a) 

$\overset{Br^+}{CH_2 — CH_2}$

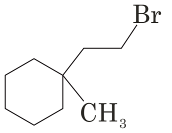
(b) $C_2H_4OH^+$

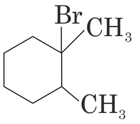
(c) $\overset{+}{C}H_2CH_2Br$

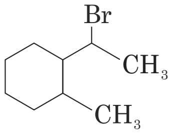
(d) $C_2H_5^+$

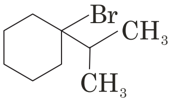
72. 

(JEE Main 2021)

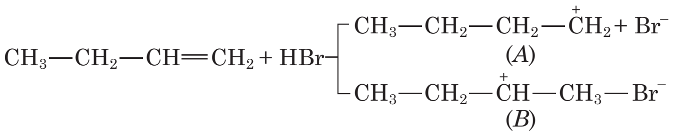
(a) 

(b) 

(c) 

(d) 

73. Choose the correct statement regarding the formation of carbocations *A* and *B* given



$$CH_3—CH_2—CH{=}CH_2 + HBr \begin{cases} CH_3—CH_2—CH_2—\overset{+}{C}H_2 + Br^- \\ \quad (A) \\ CH_3—CH_2—\overset{+}{C}H—CH_3 — Br^- \\ \quad (B) \end{cases}$$

(a) Carbocation *B* is more stable and formed relatively at faster rate

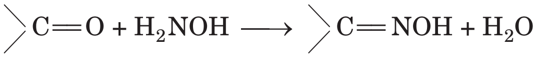
(b) Carbocation *A* is more stable and formed relatively at slow rate

(c) Carbocation *B* is more stable and formed relatively at slow rate

(d) Carbocation *A* is more stable and formed relatively at faster rate

Addition Elimination Reaction

74. Consider the following reaction,

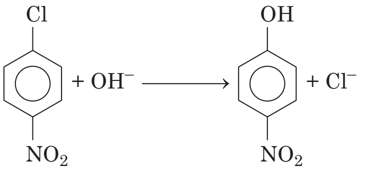


$$>C{=}O + H_2NOH \longrightarrow >C{=}NOH + H_2O$$

It is an example of

(a) substitution	(b) elimination
(c) addition	(d) addition elimination

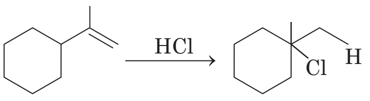
75. Consider the following reaction

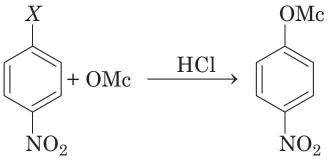


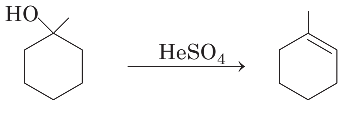
It is an example of

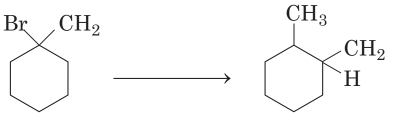
(a) addition-elimination	(b) nucleophilic substitution
(c) elimination	(d) addition

76. The addition elimination reaction among the following is,

(a) 

(b) 

(c) 

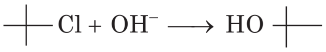
(d) 

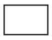
77. Acetaldehyde is the rearrangement product of

(a) methyl alcohol	(b) allyl alcohol
(c) vinyl alcohol	(d) All of these

78. Which one of the following reaction is possible?

(a) $CH_3CH_2CH_3 + OH^- \longrightarrow CH_3CH_2OH + CH_3^-$

(b) 

(c)  $+ OH^- \longrightarrow CH_3CH_2CH_2CH_2OH$

(d) None of the above

79. The reaction, $(CH_3)_3C—CH_2OH + HBr \longrightarrow (CH_3)_2CBrCH_2CH_3$ is classified as

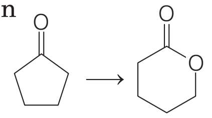
(a) nucleophilic substitution without rearrangement

(b) nucleophilic substitution with rearrangement

(c) electrophilc addition without rearrangement

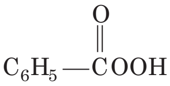
(d) electrophilic addition with rearrangement

80. The conversion



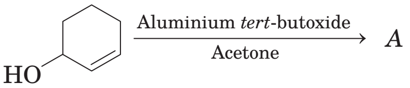
can be effected by using the reagent:

(a) H_2O, H_2SO_4 (b) O_2

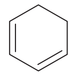
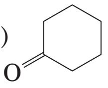
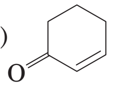
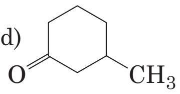
(c) 
$C_6H_5—\overset{\overset{O}{\|}}{C}OOH$

(d) CrO_3, H_2SO_4

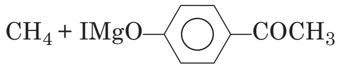
81.

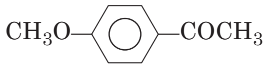


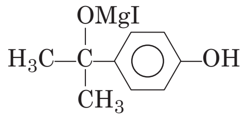
In the above reaction, A is

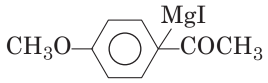
(a) 
(b) 
(c) 
(d) 

82. The reaction of 1 mole each of *p*-hydroxyacetophenone and methyl magnesium iodide will give

(a) 

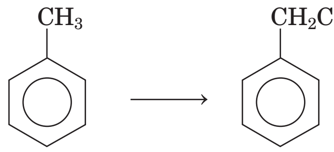
(b) 

(c) 

(d) 

ROUND II Mixed Bag

1.



The above reaction proceeds through

(a) free radical substitution

(b) nucleophilic substitution

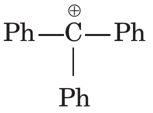
(c) electrophilic substitution

(d) None of the above

2. Which of the following species is paramagentic in nature?

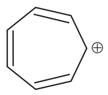
(a) Carbonium ion (b) Free radical

(c) Carbene (d) Nitrene

3. (1) 
$Ph—\overset{\oplus}{C}—Ph$ with Ph below the central C

(2) $Ph—\overset{\oplus}{C}H_2$

(3) $CH_2{=}CH—\overset{\oplus}{C}H_2$

(4) 

Correct order of stability is

(a) 1 > 4 > 2 > 3 (b) 1 > 2 > 3 > 4

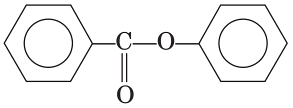
(c) 1 > 2 > 4 > 3 (d) 1 > 3 > 4 > 2

4. Formation of ethylene from acetylene is an example of

(a) elimination reaction (b) substitution reaction

(c) condensation reaction (d) addition reaction

5. In



electrophilic substitution occurs at

(a) *ortho*/*para* at first ring

(b) *meta* at first ring

(c) *ortho* /*para* at second ring

(d) *meta* at second ring

6. An S_N2 reaction at an asymmetric carbon of a compound always gives

(a) a mixture of diastereomers

(b) a single stereoisomer

(c) an enantiomer of the substrate

(d) a product with opposite optical rotation

7. Identify the most stable species in the following sets of ions. ***(NCERT Exemplar)***

(i) $\overset{\oplus}{C}H_3, \overset{\oplus}{C}H_2Br, \overset{\oplus}{C}HBr_2, \overset{\oplus}{C}Br_3$

(ii) $\overset{\ominus}{C}H_3, \overset{\ominus}{C}H_2Cl, \overset{\ominus}{C}HCl_2, \overset{\ominus}{C}Cl_3$

(a) $\overset{+}{C}Br_3, \overset{-}{C}Cl_3$ (b) $\overset{+}{C}H_3, \overset{-}{C}H_3$

(c) $\overset{+}{C}H_2Br, \overset{-}{C}H_3$ (d) $\overset{+}{C}H_3, \overset{-}{C}Cl_3$

8. SO_3 acts as an electrophile because ***(NCERT Exemplar)***

(a) S is an electron deficient element

(b) O is highly electronegative

(c) S is larger in size

(d) All of the above

9. Amino group is *ortho*/*para*- directing for aromatic electrophilic substitution. On nitration of aniline, a good amount of *m*-nitroaniline is obtained. This is due to

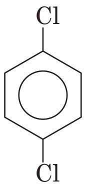
(a) the fact that in nitration mixture, *ortho, para*-activity of NH_2 group is completely lost

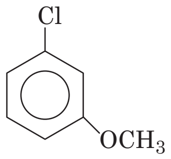
(b) $—NH_2$ becomes $—NH_3^+$, which is *m*-directing

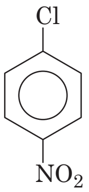
(c) $—NH_2$ becomes $—NH^+SO_4^-$; which is *m*-directing

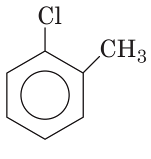
(d) $—NH_2$ becomes $—NH^-NO_2^+$, which is *m*-directing

10. Which of the following would react most readily with nucleophiles?

(a)


(b)


(c)


(d)


11. Which of the following statement is not characteristic of free radical chain reaction?

(a) It gives major products derived from most stable free radical

(b) It is usually sensitive to change in solvent polarity

(c) It proceeds in three main steps like initiation, propagation and termination

(d) It may be initiated by UV light

12. Arrange *p*-toluidine (I) N,N-dimethyl-*p*-toluidine (II) *p*-nitroaniline (III) and aniline (IV) in order of decreasing basicity

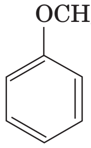
(a) I > IV > III > II

(b) I > II > III > IV

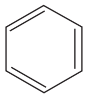
(c) II > I > IV > III

(d) III > I > II > IV

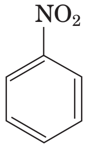
13. Among the following compounds (I—III) the correct order of reaction with electrophilic reagent is



I



II

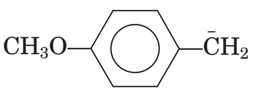


III

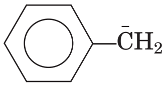
(a) II > III > I (b) III < I < II

(c) I > II > III (d) I = II > III

14. Consider the following carbanions

I.


II.

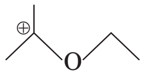

III.


Correct order of stability is

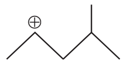
(a) I > II > III (b) III > II > I

(c) II > III > I (d) I > III > II

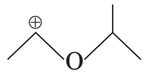
15. The correct stability order for the following species is



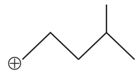
(I)



(II)



(III)

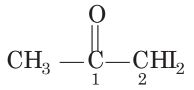


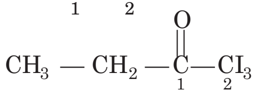
(IV)

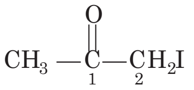
(a) (II) > (IV) > (I) > (III) (b) (I) > (II) > (III) > (IV)

(c) (II) > (I) > (IV) > (III) (d) (I) > (III) > (II) > (IV)

16. Which of the following compounds yields most stable carbanion after rupture of $(\underset{1}{C}-\underset{2}{C})$ bond?

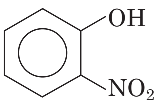
(a)

$CH_3-\underset{1}{\overset{\overset{O}{\|}}{C}}-\underset{2}{C}HI_2$

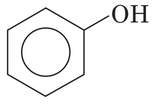
(b)

$CH_3-CH_2-\underset{1}{\overset{\overset{O}{\|}}{C}}-\underset{2}{C}I_3$

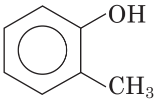
(c)

$CH_3-\underset{1}{\overset{\overset{O}{\|}}{C}}-\underset{2}{C}H_2I$

(d) None of these

17. Which one of the following compounds is most acidic?

(a) Cl—CH$_2$—CH$_2$—OH (b)


(c)


(d)


18. Which of the following is singlet carbene?

(a) $CH_3\ddot{C}HCH_3$ (b) $C_2H_5\ddot{C}-H$

(c) $CH_2=CH-\overset{\oplus}{C}H_2$ (d) $(CH_3)_3C^+$

19. Which of the following applies in the reaction

$CH_3CHBrCH_2CH_3 \xrightarrow{\text{Alc. KOH}} ?$

(I) $CH_3CH{=}CHCH_3$ (Major product)

(II) $CH_2{=}CHCH_2CH_3$ (Minor product)

(a) Hofmann's rule (b) Saytzeff's rule

(c) Kharasch effect (d) Markownikoff's rule

20. A solution of D-(+)-2-chloro-2-phenylethane in toluene racemises slowly in the presence of small amount of $SbCl_5$ due to the formation of

(a) carbanion (b) carbene

(c) free radical (d) carbocation

21. Which of the following statements is incorrect?

(a) The rate of reaction increases with increase in water concentration in the hydrolysis of tertiary butyl bromide in methanol and water

(b) The relative nucleophilicity in protic solvent is

$CN^- > I^- > \bar{O}H > Br^- > Cl^- > F^- > H_2O$

(c) In S_N2 reactions, the order of reactivity of alkyl halides is in the order

methyl > primary > secondary > tertiary

(d) S_N2 reaction involves carbonium ions

22. Which of the following statement(s) is (are) not true?

(a) Carbanions and carbonium ions, usually exist in ion pairs or else solvated

(b) Acidity increases and basicity decreases in going from left to right across a row of periodic table

$$CH_4 < NH_3 < H_2O < HF \text{ (acidity)}$$
$$CH_3^- > NH_2^- > OH^- > F^- \text{ (basicity)}$$

(c) RCOOH like RCOR reacts with H_2NOH to give an oxime

(d) Decreasing order of ionizing power of solvents is

$$CF_3COOH > HCOOH > H_2O > CH_3COOH > CH_3OH > C_2H_5OH > (CH_3)_2SO > CH_3CN$$

23. Match the terms mentioned in Column I with the terms in Column II and choose the correct answer using the codes given below ***(NCERT Exemplar)***

Column I	Column II
A. Carbocation	1. Cyclohexane and I- hexene
B. Nucleophile	2. Conjugation of electrons of C—H σ-bond with empty p-orbital present at adjacent positively charged carbon.
C. Hyperconjugation	3. sp^2 hybridised carbon with empty p-orbital
D. Isomers	4. Ethyne
E. sp-hybridisation	5. Species that can receive a pair of electrons
F. Electrophile	6. Species that can supply a pair of electrons

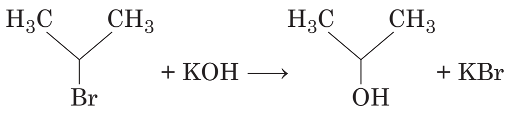
Codes

	A	B	C	D	E	F
(a)	1	2	3	4	5	6
(b)	3	6	2	1	4	5
(c)	2	3	6	5	4	1
(d)	6	3	2	1	4	5

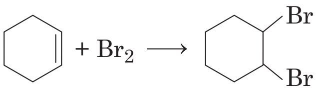
24. For the following reactions:

(A) $CH_3CH_2CH_2Br + KOH \longrightarrow CH_3CH{=}CH_2 + KBr + H_2O$

(B)



(C)



Which of the following statement is corect?

(a) (A) is elimination, (B) and (C) are substitution reactions

(b) (A) is substitution, (B) and (C) are addition reactions

(c) (A) and (B) are elimination reactions and (C) is an addition reaction

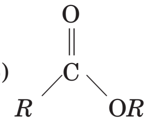
(d) (A) is elimination, (B) is substitution and (C) is addition reaction

Numeric Value Questions

25. Consider compounds/groups (a) to (h). If the number of electrophiles is x and that of nucleophiles in y then $x \times y$ is will be ....

(a) CH_3O

(b)

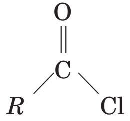


$R-\overset{\overset{O}{\|}}{C}-OR$

(c) $(CH_3)_2S$

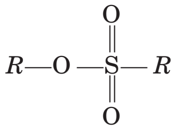
(d) CH_3CH_2

(e)



$R-\overset{\overset{O}{\|}}{C}-Cl$

(f)

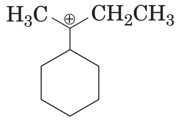


$R-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-R$

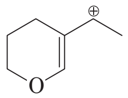
(g) $AlCl_3$

(h) CH_3-CN

26. The total number of contributing structure showing hyperconjugation (involving C—H bond) for the following carbocation is,

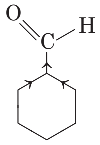


27. How many total resonance structure can be drawn for the following carbocation.

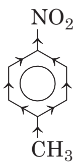


28. Identify total number of compounds which shows the correct direction of inductive effect.

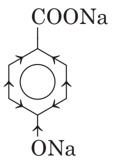
(I)



(II)

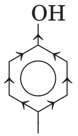


(III)



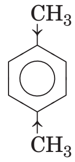
(IV) $CH_3-CH_2 \leftarrow K$

(V)

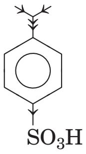


(VI) $CH_3—CH_2 \rightarrowtail Mg\,Br$

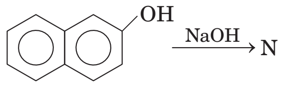
(VII)



(VIII)



29. The number of resonance structure for N is,



30. How many groups shows $-I$-effect ?

(I) $—CH_3$

(II) $N^+H_3^-$

(III) $—OH$

(IV) $O^{\ominus}$

(V) $—N(CH_3)_2$

(VI) $—SO_3H$

(VII) $—CHO$

(VIII) $—Cl$

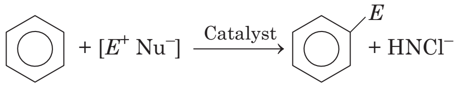
(IX) $—COO^{\ominus}$

(X) $—C_2H_5$

31. Total number of resonating structure in napthalene is x and total no. of resonating structure in anthracene is y. The $x + y$ will be ……… .

32. Consider the following reaction and compound given below that,

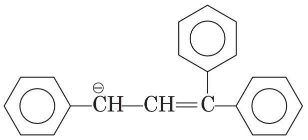
Reaction



Compound BF_3, $AlCl_3$, NH_3, $OH^{\ominus}$, $CH_3CO^{\oplus}$, $CH_3—S$, Al^{3+}, $SO_4^{2\ominus}$, Fe^{3+}, H_2O

How many compound behave as catalyst for the given reaction.

33. Total number of positions where negative charge can be delocalised (including the given position) by true resonance in the given compound is



Answers

Round I

1. (b)	**2.** (a)	**3.** (d)	**4.** (c)	**5.** (d)	**6.** (c)	**7.** (d)	**8.** (c)	**9.** (d)	**10.** (a)
11. (d)	**12.** (c)	**13.** (b)	**14.** (c)	**15.** (b)	**16.** (c)	**17.** (c)	**18.** (c)	**19.** (c)	**20.** (d)
21. (a)	**22.** (a)	**23.** (c)	**24.** (a)	**25.** (d)	**26.** (c)	**27.** (c)	**28.** (c)	**29.** (a)	**30.** (d)
31. (a)	**32.** (b)	**33.** (a)	**34.** (a)	**35.** (c)	**36.** (a)	**37.** (d)	**38.** (a)	**39.** (b)	**40.** (d)
41. (d)	**42.** (a)	**43.** (b)	**44.** (b)	**45.** (d)	**46.** (c)	**47.** (a)	**48.** (d)	**49.** (c)	**50.** (c)
51. (b)	**52.** (c)	**53.** (b)	**54.** (b)	**55.** (c)	**56.** (b)	**57.** (d)	**58.** (c)	**59.** (c)	**60.** (a)
61. (b)	**62.** (d)	**63.** (d)	**64.** (c)	**65.** (b)	**66.** (c)	**67.** (b)	**68.** (b)	**69.** (b)	**70.** (a)
71. (a)	**72.** (d)	**73.** (a)	**74.** (d)	**75.** (a)	**76.** (b)	**77.** (c)	**78.** (b)	**79.** (b)	**80.** (c)
81. (c)	**82.** (c)								

Round II

1. (a)	**2.** (b)	**3.** (a)	**4.** (d)	**5.** (c)	**6.** (b)	**7.** (d)	**8.** (b)	**9.** (b)	**10.** (c)
11. (b)	**12.** (c)	**13.** (c)	**14.** (c)	**15.** (d)	**16.** (b)	**17.** (b)	**18.** (b)	**19.** (b)	**20.** (d)
21. (d)	**22.** (c)	**23.** (b)	**24.** (d)	**25.** (20)	**26.** (6)	**27.** (3)	**28.** (6)	**29.** (9)	**30.** (6)
31. (7)	**32.** (5)	**33.** (11)							

Solutions

Round I

1. During the heterolytic fission of a covalent bond, species that loses its electron, acquires positive charge and other one with which the electron of previous species gone, acquires a negative charge. Thus,

$$CH_3 - Br \longrightarrow \overset{\oplus}{C}H_3 + \overset{\ominus}{Br}$$

2. $CH_3CH_2—Cl \xrightarrow[\text{fission}]{\text{Homolytic}} CH_3\dot{C}H_2 + \dot{C}l$

3. Although, both C and S have the same electronegativity but the cleavage of the C—S bond occurs towards S producing a carbonium ion because S being bigger in size than C can disperse the –ve charge more effectively.

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

(b) Similarly, C—CN bond breaks towards CN giving CH_3^+ carbonium ion because CN is more electronegative than CH_3

$$CH_3—CN \longrightarrow \overset{+}{C}H_3 + \overset{-}{C}N$$

Since Cu is more electropositive than S, CH_3—Cu bond breaks towards carbon producing CH_3 carbanion.

$$CH_3—Cu \longrightarrow CH_3^- + Cu^+$$

Thus, option (d) is correct.

5. The starred carbon atom in all the three compounds are electrophilic centres because they will have partial positive charge due to polarity of the covalent bond.

$$CH_3\underset{\delta+}{\overset{*}{C}H} = \underset{\delta-}{O} \quad CH_3\underset{\delta+}{\overset{*}{C}} \equiv \underset{\delta-}{N} \quad \underset{\delta+}{\overset{*}{C}H_3} — \underset{\delta-}{I}$$

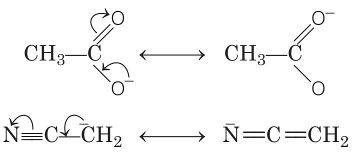
6. Na^+, Li^+ and Ca^{2+} have inert gas configuration, therefore, they have no tendency to accept electrons and hence cannot act as electrophiles. Only H^+ acts as an electrophile.

7. SO_3, $:CH_2$ and $R\ddot{N}:$ are all electron-deficient species/compounds and hence can act only as electrophile. In contrast, in $R—\ddot{N}H_2$, N has a lone pair of electrons and hence can act only as a nucleophile but not an electrophile.

8. $:\ddot{N}H_2^-$ has eight electrons in the valence shell. It has also tow lone pairs of electrons which it can easily donate and hence it acts as a nucleophile,: CX_2 also has a lone pair of electrons but it has only six electrons in the valence shell. Therefore, it acts as an electrophile.

9. Negatively charged (or electron-rich) species, i.e. ^-OH and ^-CN act as nucleophiles.

10. In CH_3COO^- and $NCCH_2^-$, the –ve charge is delocalized and hence these are weak nucleophiles.



Among C_2H_5SH and CH_3NH, S being less electronegative than N, has a stronger tendency to electrons and hence C_2H_5SH is a stronger nucleophile than CH_3NH_2.

11. RNH_2 and ROH being neutral electron-rich molecules, therefore, they should be weaker nucleophiles than $C_6H_5O^-$ and CH_3O^-. But in $C_6H_5O^-$, the electron density on the O atom decreases due to delocalisation on the benzene ring but in CH_3O^-, the electron density on the O-atom increases due in CH_3O^-, the electron density on the O atom increaes due to + *I*-effect of the CH_3 group. Thus, CH_3O^- is the strongest nucleophile.

12. Lower the electronegativity, higher is the tendency of the atom/group to donate its pair of electrons and hence higher is its nucleophilicity. Now among F (4.0), O (3.5), N (3.0) and C (2.5), C has the lowest electronegativity and hence CH_3^- has the highest nucleophilicity.

13. Electronegativity of Cl, Br and I decreases in the order: Cl (3.5) > Br (2.8) > I (2.5), therefore, nucleophilicity of their anions increases in the reverse order, i.e. $Cl^- < Br^- < I^-$.

14. $AlCl_3$, SO_3, NO_2^+ are all electrophiles.

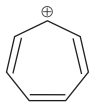
15. NH_3, CN^- and CH_3OH are all nucleophiles.

16. CH_3NH_2 and CH_3OH are nucleophiles, CH_3 — Cl is an electrophile. $CH_3 — \overset{\delta+}{C} \equiv \overset{\delta-}{N}:$ is a nucleophile due to the presence of a lone pair of electrons on N and is an electrophile as well due to the presence of a partial positive charge on C.

17. In heterolysis, the covalent bond is broken in such a way that one species (less electronegative) is deprived of its own electron, while the other species gain both the electrons.

$$CH_3CH_2CH_3 \longrightarrow \overset{\ominus}{C}H_3 + \overset{\oplus}{C}_2H_5$$

19. $C_6H_5\overset{+}{C}HC_6H_5$ is the most stable since the positive charge can be delocalise on both the phenyl rings.

20.  is the most carbocation as it has maximum conjugation in it (or resonating structures)

22. Stability of alkyl carbanion

$$\propto \frac{1}{\text{magnitude of negative charge}}$$

and magnitude of negative charge $\propto +I$ power of the group. Hence, acetylenic carbanion is more stable than vinylic carbanion which is more stable than alkyl carbanion.

23. The correct order of stability is II > III > I —NO_2 group shows –*M*-effect while CH_3O— group shows +*M*-effect (–*M* effect stabilises an anion).

24. Stability of a carbanion increases in the presence of electron withdrawing group but decreases in the presence of electron releasing group.

$O_2N—CH_2—CH_2O^-$ is expected to be more stable than $CH_3—CH_2O^-$ because —NO_2 group has – *I*-effect, this leads to the dispersal of negative charge. On the other hand, —CH_3 group has + *I*-effect, this leads to the intensification of the negative charge. Dispersal of the charge leads to the stability of ion while intensification of negative charge leads to the unstability of ion.

$$\underset{\text{More stable}}{O_2N \leftarrow CH_2 \leftarrow CH_2 \leftarrow O^-} \quad \underset{\text{Less stable}}{CH_3 \rightarrow CH_2 \rightarrow O^-}$$

25. The order of stability of carbanion is 1° > 2° > 3°. Moreover, III is resonance stabilised and IV also exists in two resonating forms. Thus, the order of stability is III > IV > I > II.

27. $\underset{3}{\overset{\delta\delta\delta+}{CH_3}} \rightarrow \underset{3}{\overset{\delta\delta+}{2}} \rightarrow \underset{1}{\overset{\delta+}{CH_2}} \rightarrow \overset{\delta-}{CH_2}$

Inductive effect decreases with distance, therefore, C_3 has least inductive effect.

28. –*I*-effect decreases in the order

$$—\overset{+}{N}R_3 > —NO_2 > —COOH > —F$$

Therefore, F has the minimum –*I*-effect.

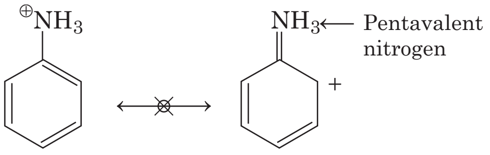
29. Greater the electronegativity, higher is the –*I*-effect, i.e. $—NR_2 < —OR < —F$.

30. Due to the electron-donating effect of three CH_3 groups, $(CH_3)C$— has the highest +*I*-effect.

31. The +*I*-effect of these substituents decreases in the order $O^- > COO^- > {}^-CR_3$.

36. Benzene is the most stable and we know that resonance energy is a direct measure of the stability of a molecule.

39. If positive charge is present on nitrogen then positive charge will not be in conjugation to the ring because in this case nitrogen will become pentavalent.



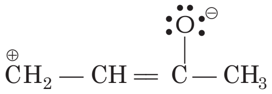
40. Due to –*R*-effect of —CHO group, oxygen carries –δ charge while the terminal carbon carries +δ, i.e.

$$\overset{+\delta}{CH_2}{=}CH—CH{=}\overset{-\delta}{O}$$

41. In the given compound four π-electrons of double bond and 1 lone pair on N atom leads to delocalisation of six electrons.

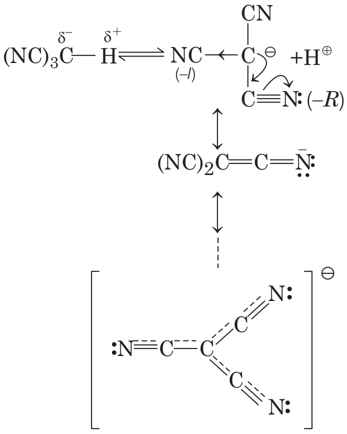
42. Two positive charges present at the adjacent place, elevates the energy, thus lowers the stability most.

43. The most stable one is that in which the positive and negative charges reside on the most electropositive and most electronegative atoms of the species respectively like



$$\overset{\oplus}{C}H_2—CH{=}\overset{\overset{\ominus}{:\ddot{O}:}}{\overset{|}{C}}—CH_3$$

45. We know, a stronger acid produces its stable or weaker conjugate base. Here, $CH(CN)_3$ produces the most stable conjugate base $(NC)_3C^-$. Stronger –*R* and –*I*-effects of the CN^- group, make the carbanion (conjugate base) very stable. The resonance hybrid structure of $[(NC)_3C]^-$ is as follows



Resonance hybrid structure of $[NC)_3C]^-$

46. Structure I is most stable since it does not carry any charge. Out of II and III, II is less stable since chlorine is an electronegative atom and is bearing a positive charge on it.

47. The dipole moment of CH_3CH_2Cl (vinyl chloride) is due to –*I*-effect of Cl.

$$\begin{gathered}\delta+ \longrightarrow \delta- \\ CH_3CH_2 \rightarrow Cl\end{gathered}$$

However, due to resonance effect, the lone pair electrons on Cl in vinyl chloride moves into the π-bond.

$$CH_2{=}CH—\ddot{\underset{\cdot\cdot}{Cl}}: \longleftrightarrow {:}\overset{-}{C}H_2—CH{=}\overset{+}{\underset{\cdot\cdot}{Cl}}:$$

As a result, partial – ve charge on Cl decreases and hence dipole moment of vinyl chloride is lower than that of ethyl chloride

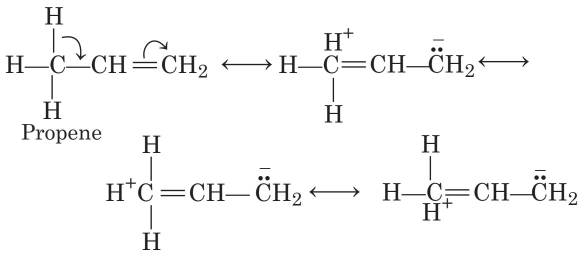
49. Ethene ($H_2C=CH_2$) is sp^2-hybridised and ethyne ($HC\equiv CH$) is sp-hybridised. In ethyne, the sp-hybridised carbon atom possesses maximum s-character and hence, maximum electronegativity.

Due to which, it attracts the shared electron pair of C—H bond to a greater extent and makes the removal of proton easier. Hence, alkyne is much more acidic than alkene.

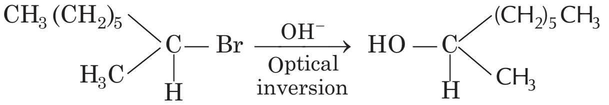
Presence of electron donating group in alkyne ($H_3C-C\equiv CH$) decreases the acidic strength of compound. Hence, the correct order of acidic strength is

$$HC\equiv CH > H_3C-C\equiv CH > CH_2=CH_2$$

50. Due to hyperconjugation, alkyl groups act as electron donors when attached to a π-system as shown below.

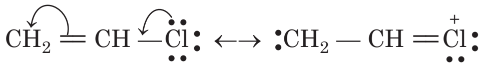


54.

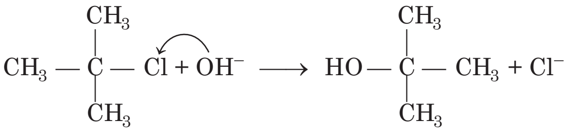


In this reaction, inversion takes place. Hence, it is an example of S_N2 reaction. In this mechanism the attack of OH^- ions take place from the back side while the Br^- ion leaves from the front side.

55. Vinyl chloride is least reactive for S_N reaction due to resonance stabilisation of C—Cl bond.



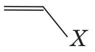
56.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Cl + OH^- \longrightarrow HO-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 + Cl^-$$

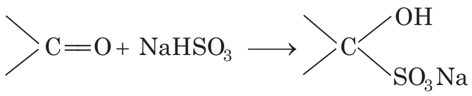
Rate ∝ [t-butyl chloride]

Tertiary butyl carbocation is first formed which is more stable.

58. Primary and secondary alkyl halides give S_N2 reaction. Substrates that give stable carbocation generally undergo S_N1 reaction. Vinyl carbocation is least stable so  does not give this reaction.

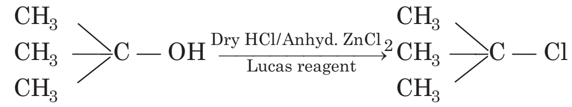
59. (a) It is Diels Alder's reaction (cyclo addition).

(b)



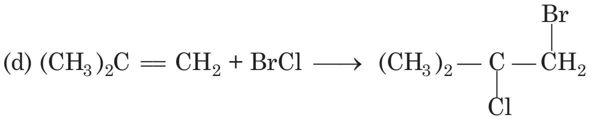
It is a nucleophilic addition reaction.

(c)



It is a nucleophilic substitution reaction.

(d)



$$(CH_3)_2C=CH_2 + BrCl \longrightarrow (CH_3)_2-\underset{Cl}{\overset{Br}{C}}-CH_2$$

It is an electrophilic addition reaction.

60. As the number of methyl group increases the reactivity of alkoxide nucleophiles decreases due to increase in sterio hinderance.

$$MeO^- > MeCH_2O^- > \ldots > Me_2CHO^- > Me_3CO^-$$

61. (a) Nucleophilic substitution reaction

(b) Electrophilic addition reaction, involve attack of electrophile

(c) β-elimination reaction

(d) Nucleophilic substitution reaction with rearrangement.

62. With the increasing basicity of the added base, the rates of the elimination reactions have been found to increase. Thus, RO^- is most reactive.

63. The elimination takes place according to Saytzeff rule. The most substituted alkene (butene-2) is called Saytzeff product whereas less substituted alkene (butene-1) is called Hofmann product.

64. $H_3C-HC=CH_2 + H^+ \longrightarrow H_3C-HC^+-CH_3$

2° carbocation
(more stable)

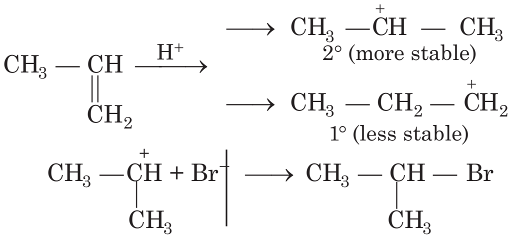
$\overset{+}{C}H_3CH_2CH_2^+$

1° carbocation
(less stable)

67. HBr is a better source of proton. It gives H^+ and Br^- ions.

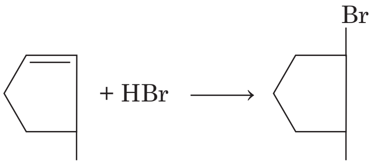
$$HBr \longrightarrow H^+ + Br^-$$

Thus, H^+ attacks the π-bond of propene to form carbonium ion as

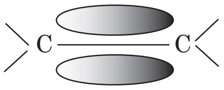


(major product)

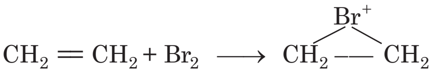
68. A hydrogen halide containing a highly polar H—X bond can easily lose $\overset{\oplus}{H}$ to the pi bond of an alkene. The result of the attack of $H^{\oplus}$ is an intermediate carbocation, which quickly undergoes reaction with the negative halide ion (X^-) to yield an alkyl halide.



70. Such a condition is seen in an electrophilic addition when π-bond is formed between similar atoms, i.e.



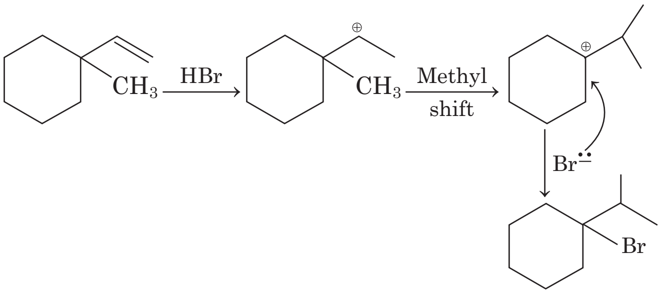
71. Addition of Br_2 on ethene follow electrophilic addition.



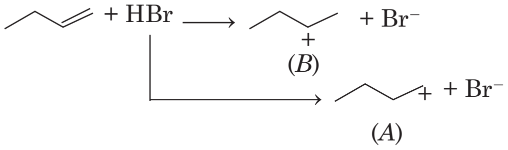
$$CH_2 = CH_2 + Br_2 \longrightarrow CH_2 \overset{Br^+}{\text{——}} CH_2$$

Intermediate is cyclic bromonium ion.

72.

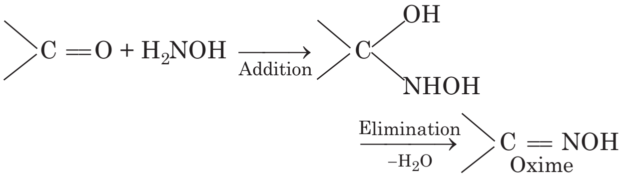


73.



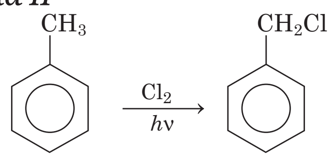
This is more stable due to secondary cation formation and formed with faster rate due to low activation energy.

74. The reaction occurs as



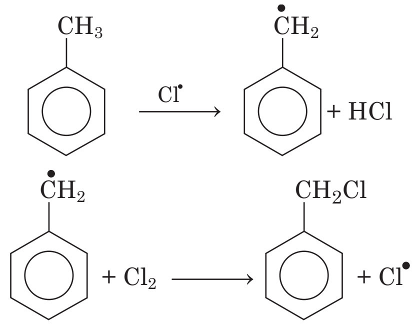
Round II

1.



This reaction proceeds through free radical substitution.

$$Cl_2 \xrightarrow{h\nu} 2Cl^\bullet$$

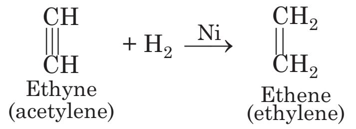


2.

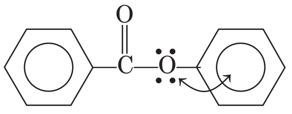
Species	Valence electrons	Magnetic behaviour
Carbonium ion	6	Diamagnetic
Free radical	7	Paramagnetic
Carbene	6	Diamagnetic
Nitrene	6	Diamagnetic

3. φ is phenyl group, and stability is based on the number of conjugative structures. Thus, the correct order is 1 > 4 > 2 > 3.

4. Formation of ethylene from acetylene is an example of addition reaction.



5. Second ring is in conjugation with lone pair of oxygen, thus electrophilic substitution occur at *o*/*p* position of second ring.



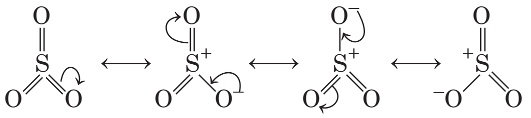
Conjugation

6. In S_N2 reactions, the nucleophile attaches itself from the direction opposite to that of the nucleophile already present in the second step, the previous nucleophile is removed and a single stereoisomer is obtained.

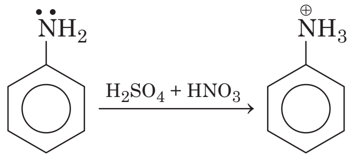
7. $\overset{\oplus}{CH_3}$ is the most stable species because the replacement of H by Br increases positive charge on carbon atom and destabilises the species.

$\overset{\ominus}{CCl_3}$ is the most stable species because on replacing H by Cl, negative charge on carbon is reduced and species is stabilised.

8. In SO_3, three highly electronegative oxygen atoms are attached to sulphur atom. It makes sulphur atom electron deficient. Further, due to resonance, sulphur acquires positive charge. Both these factors make SO_3 an electrophile.



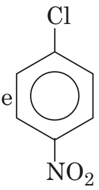
9. On direct nitration of aniline, lone pair of electrons present at nitrogen atom will accept proton from the nitrating mixture to give anilinium ion which is *meta*-directing.



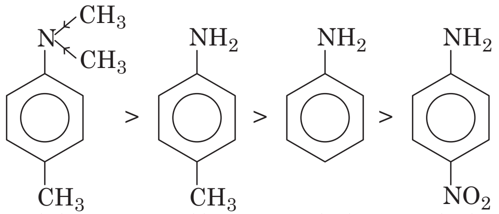
Anilinium ion

10. Nucleophile always attacks on electron deficient site.

Presence of electron withdrawing groups such as NO_2, CHO etc., decreases the electron density on benzene nucleus, hence such groups activate the ring towards nucleophilic attack. While presence of electron releasing groups such as *R* or O*R* increases the electron density, thus deactivates the nucleus towards nucleophilic attack.

NO_2 group activates the ring more than Cl towards nucleophilic attack, hence  reacts readily with nucleophile.

11. Free radical chain reaction is initiated by UV light. It proceeds in three main steps like initiation, propagation and termination. It gives major product derived from most stable free radical.

12. 

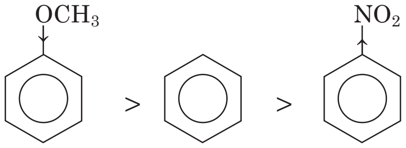
(II) (I) (IV) (III)

Order of basicity

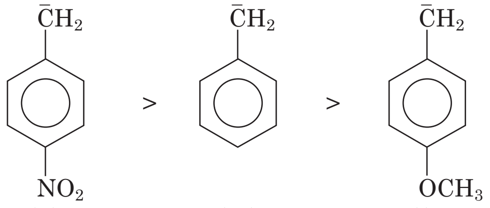
The reason for the above order of basicity is the presence of electron releasing —CH_3 group in II and I which facilitates the donation of lone pair by increasing electron density over N-atom.

13. Methoxy group is electron releasing group so it increases electron density at benzene nucleus while —NO_2 group is electron withdrawing group, so it decreases the electron density of benzene nucleus.

Thus, the order of reaction with electrophilic reagent is

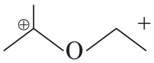


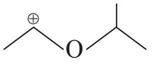
14. —NO_2 group shows –*M* effect while CH_3O— group shows + *M*-effect. (–*M*-effect stabilises the anion). Hence, the order of stability is

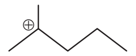


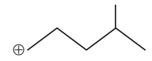
(II) (III) (I)

15. The correct order is I > III > II > IV.

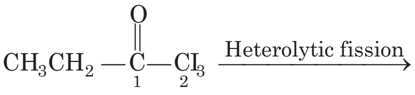

+ *M*-effect, hyperconjugation (6Hs) and +*I*-effect (2–Me groups)


+ *M*-effect, hyperconjugation (3Hs) and +*I*-effect (1–Me group)

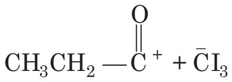

(2° carbocation)


Hyperconjugation (5Hs) and + *I*-effect

(1° carbocation) Hyperconjugation (2Hs) and + *I*-effect

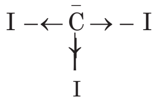
16. 

$$CH_3CH_2—\underset{1}{\overset{O}{\overset{\|}{C}}}—\underset{2}{C}I_3 \xrightarrow{\text{Heterolytic fission}}$$



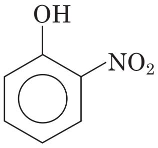
$$CH_3CH_2—\overset{O}{\overset{\|}{C}}{}^{+} + \bar{C}I_3$$

$\bar{C}I_3$ is the most stable carbanion because of –*I*-effect of I which disperses negative charge on $\bar{C}$ of



$$I - \leftarrow \bar{C} \rightarrow - I$$

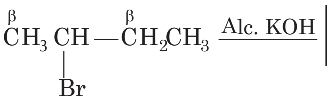
17. *ortho* nitrophenol is the most acidic because electron withdrawing group increases acidic character due to –*I*-effect of —NO_2 group.



o-nitrophenol

18. An organic reaction intermediate (neutral species) having divalent carbon atom with six valence electrons, out of which two are present in same orbital with opposite spin is called singlet carbene.

Thus, $C_2H_5\ddot{C}H$ is a singlet carbene.

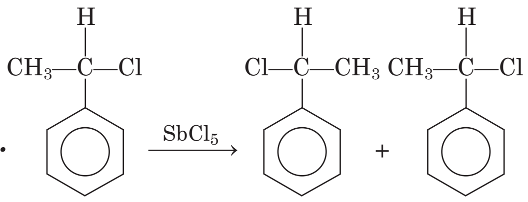
19. 

$\overset{\beta}{C}H_3\,\underset{|\,Br}{CH}-\overset{\beta}{C}H_2CH_3 \xrightarrow{\text{Alc. KOH}}$

$\longrightarrow \underset{\text{Major}}{CH_3CH=CH-CH_3}$

$\longrightarrow \underset{\text{Minor}}{CH_2=CH-CH_2CH_3}$

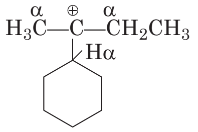
This reaction is governed by Saytzeff's rule. According to this rule, the elimination of β-hydrogen atom take place from the carbon having the lesser number of H-atoms or in other words a stable alkene is formed. (More substituted alkene is more stable.)

20. 

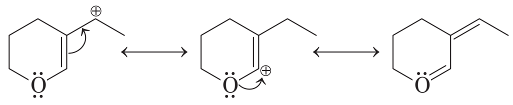
The solution of D-(+)-2-chloro-2-phenyl ethane in toluene racemises slowly in the presence of $SbCl_5$ due to the formation of carbocation.

21. S_N2 reaction does not involve ion formation, these infact involve formation of transition state.

25. There are four nucleophiles and five electrophiles so, the multiply of x and y will be 20.

26. 

Number of α-hydrogen = 6

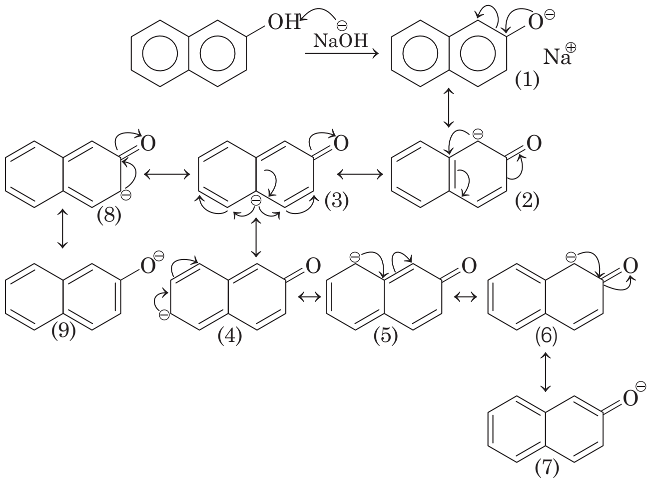
27. 

(1) (2) (3)

28. Total number of compound = 6.

Correct - I, II, III, IV, VII and VIII

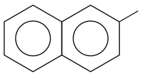
29. The number of resonance structure of N is 9.



30. Six groups shows – I-effect, i.e.

$\overset{\oplus}{N}H_3$, —OH, SO_3H, —CHO, —Cl and —COO$^{\ominus}$.

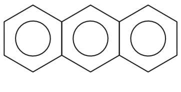
31. The number of resonating structures for polynuclear hydrocarbon containing n benzene ring fused together in a linear manner is $(n+1)$.



Napthalene

Resonating structure = $(n + 1)$
$= 2 + 1 \Rightarrow 3$

So, value of $x = 3$



Resonating structure = $n + 1$
$= 3 + 1$
$= 4$

So, value of $y = 4$

So, the sum of x and y will be 7.

32. Only Lewis acid are behave as catalyst so, here only five Lewis acids are present, i.e. BF_3, $AlCl_3$, CH_3CO^+, Al^{3+} and Fe^{3+}.

33. Count total number of positions which are in conjugation with negative charge and double bond.