

15 Basic Principles of Organic Chemistry

QUICK LOOK

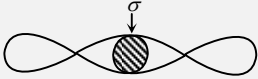
Most of organic reactions occur through the involvement of certain chemical species. These are generally short lived (10^6 seconds to a few seconds) and highly reactive and hence cannot be isolated. These short lived highly reactive chemical species. Through which the majority of the organic reactions occur are called reactive intermediates these intermediates are detected by spectroscopic methods or trapped chemically or their presence is confirmed by indirect evidence. On the other hand, synthetic intermediate are stable products which are prepared isolated and purified and subsequently used as starting materials in a synthetic sequence.

Carbon and Bonds in Organic Compounds

The atomic number of carbon is 6 and it has four electrons in its valence shell. In order to acquire stable inert gas configuration, it can share its electrons with the electrons of other atoms to form four covalent bonds, carbon has a covalency of four or is tetravalent. The angle between any two adjacent bonds is $109^\circ.28'$ (tetrahedral angle). This tetrahedral disposition of the four bonds of carbon laid the foundation of the present day fascinating field of 'Stereochemistry'.

Organic compounds normally contain only two types of C – C bonds *i.e.*, sigma (σ) and pi (π) bonds: The difference between sigma and pi bonds are as follows:

Table 15.1: Types of Bonds in Organic Compounds.

Sigma (σ) bond	Pi (π) bond
Sigma bond is formed by linear or co-axial overlapping of atomic orbitals as shown below. 	Pi bond is formed by lateral or parallel or sidewise overlapping of atomic orbitals as shown below. 
Sigma bond is formed by overlapping of two hybridized, one pure orbital and one hybrid or two pure orbitals.	It is always formed between two pure (<i>i.e.</i> unhybridized orbitals).
It exist independently.	It always exist along with a sigma bond <i>i.e.</i> it cannot exist independently.
It allows free rotation of two carbon atoms.	It restricts free rotation of the carbon atoms.
There is one electron pair cloud density.	There are two electron pair cloud densities, one above the other.

Sigma bond is stronger because of maximum overlapping of atomic orbitals, <i>e.g.</i> C–C bond dissociation energy 82kcal/mole.	Pi bond is comparatively weaker because of less overlapping of atomic orbitals. C=C bond dissociation energy 142kcal/mole and C $\equiv$ C is 198 kcal mole ⁻¹ .
Sigma bond has no effect on bromine water or alkaline KMnO ₄ (Baeyer's reagent).	It decolourises both reagent in case of alkene and alkyne.
There can be only one sigma bond between two atoms.	There can be more than one (generally two) pi-bond between two atoms.

Hybridisation of Carbon

(i) Concepts of Hybridisation of Carbon

The phenomenon of mixing of atomic orbitals of nearly same energy involving redistribution of energy to form orbitals of same energy is called hybridisation. The new orbitals of equal energy are called hybrid orbitals and their numbers are equal to the number of orbitals that take part in hybridisation. The number of 'p' orbitals that take part in hybridisation is called

hybridisation index (m) and for organic molecules: $\cos \alpha = -\frac{1}{m}$;

where, α is the bond angle between two hybrid orbitals

e.g. for sp hybridisation, $m=2$ hence $\cos \alpha = -1$ or $\alpha = 180^\circ$ for

sp^2 hybridisation, $m = 1$ hence $\cos \alpha = -\frac{1}{2}$ or $\alpha = 120^\circ$

The properties of hybrid orbitals are between those of parent orbitals. Hybridisation for organic molecules can be classified into three categories.

- **sp^3 hybridisation:** Involves mixing of one 2s and three 2p orbitals to produce four sp^3 hybrid orbitals. Each orbital is bilobed and has 25% s-orbital character. The bond angle between two sp^3 hybrid orbitals is 109.5° or $109^\circ 28'$. Single

bond means sigma bonds $\begin{array}{c} \sigma \\ | \\ -C- \\ \sigma \end{array} \leftarrow \begin{array}{c} \sigma \\ | \\ -C- \\ \sigma \end{array}$ sigma bond sp^3C

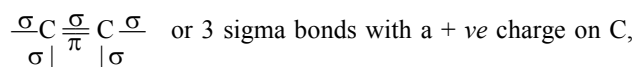
consists of 4 sigma bonds or 3 sigma bonds with –ve charge

on C $\begin{array}{c} | \\ -C- \\ | \end{array}$

- **sp^2 hybridisation:** Involves one 2s and any two 2p orbitals to form three sp^2 hybrid orbitals. Each orbital is bilobed and has 33% s-orbital character. The bond angle between two hybrid orbitals is 120° .

Double bond (==) consists of one sigma and one π bond

sp^2 C consists of 3 sigma and 1 π bonds, e.g.

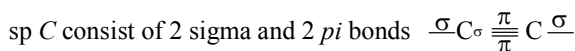


e.g. $\text{—}\overset{\cdot}{\underset{\cdot}{\text{C}}}\oplus$ or Carbon with one unshared electron pair



- **sp hybridisation:** Involves one 2s and one 2p orbital to form two sp hybrid orbitals. Each orbital is bilobed and has 50% s-orbital character. The bond angle between two hybrid orbitals is 180° .

Triple bond ($\equiv$) means one sigma and two pi bonds



or double bond with +ve charge $\text{—}\overset{\oplus}{\text{C}}=\text{C}\text{—}$ or A carbon

with two sigma bonds and two unpaired electrons $\text{—}\overset{\cdot}{\underset{\cdot}{\text{C}}}\text{—}$

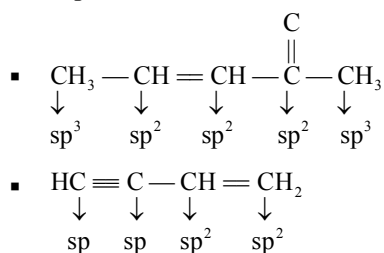
(ii) Determination of hybridisation at different carbon atoms—

It can be done by two methods.

First method: In this method hybridisation can be known by the number of π - bonds present on that particular atom.

Number of π - bond/s	0	1	2
Type of hybridisation	sp^3	sp^2	sp

Example:

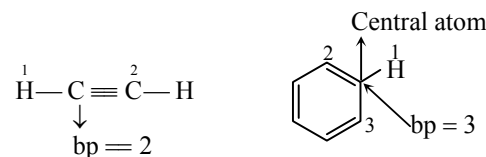
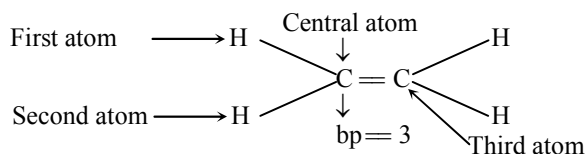


Note: This method cannot be used for those atoms of the molecule which have positive charge, negative charge or odd electron.

Second Method – Electron Pair Method

$ep = bp + lp$; where ep = electron pair present in hybrid orbitals, bp = bond pair present in hybrid orbitals

Number of bp = Number of atoms present on central atoms of the species



Number of lp's can be determined as follows:

(a) If carbon has π - bond/s or positive charge or odd electron, then lp on carbon will be zero.

(b) If carbon has negative charge, then lp will be equal to one.

Number of electron pairs (ep) tells us the type of hybridisation as follows:

ep	2	3	4	5	6
Type of hybridisation	sp	sp^2	sp^3	sp^3d	sp^2d^2

Example

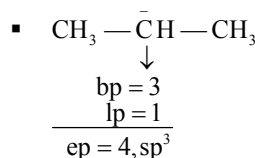
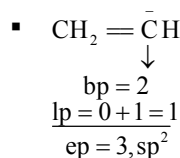
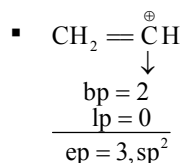
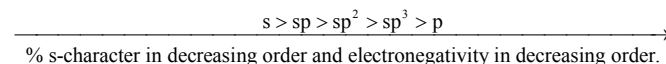


Table 15.2: Bond Angles and Geometry of the Molecule

Type of hybridisation	Number of orbitals used	Number of unused p-orbitals	Bond angle	Geometry	% s-character
sp	1s and 1p	Two	180°	Linear	50 or $\frac{1}{2}$
sp^2	1s and 2p	One	120°	Trigonal	33.33 or $\frac{1}{3}$
sp^3	1s and 3p	Nil	109.5°	Tetrahedral	25 or $\frac{1}{4}$

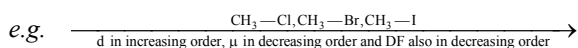
Electronegativity of different hybrid and unhybrid orbitals in decreasing order is as follows:



Intermolecular Forces

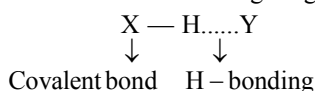
In an ionic compound, the structural units are ions. These ions are held together by very powerful electrostatic forces are known as inter-ionic forces. On the other hand, in non-ionic (covalent) compounds, the structural units are molecules. These molecules are held together by very weak forces are known as intermolecular forces, intermolecular non-bonding attractions or secondary forces. Secondary forces are of the following types:

- **Dipole-Dipole interactions:** These interactions exist between polar molecules which have permanent dipoles. The interactions of the permanent dipole in different molecules are called dipole-dipole interactions (DF). Magnitude of DF depends on the dipole moment (μ) of the bond of the compound and intermolecular distance (d), $DF \propto \mu \propto \frac{1}{d^4}$ (i.e. these forces are effective only over short distance)



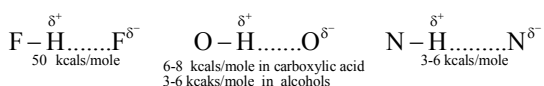
- **Vander Waal's forces:** These forces exist between non-polar molecules. The intermolecular electrostatic attractions between nuclei of one molecule and electrons of the other molecule are called Vander Waal's forces (VF). Magnitude of VF depends on the number of electrons (e^-) and protons (p) in the molecule as well as on the intermolecular distance (d), $VF \propto \text{number of } e^- \text{ and } p$
 $\propto 1/d^7$
 $\propto \text{MW}$
 $\propto \text{Surface area of the molecule and } \propto \text{Symmetry of the molecule (symmetry of molecule decreases intermolecular distance (d))}$

- **Hydrogen bonding:** Association of molecules through H-atom attached to more electronegative elements like F, O, N or S is called H-bonding. In general



(where, X = F, O, N and Y = O, N, F or S)

The strength of H-bond is as follows:



In general, strength of H-bond $\propto$ acidity of X-H $\propto$ basicity of Y.

It occurs in all three stages,

e.g. vapours of acetic acid, $\text{H}_2\text{O(l)}$ and ice (S).

H-bonding is of two types are intra-molecular H-bonding and intermolecular H-bonding.

Physical Properties of Organic Compounds

Melting point	Boiling point	Solubility
Temperature of which solid state of the substance converts into liquid state is known as m.pt. of the substance. Thus melting point $\propto$ strength of secondary forces present in the molecule.	Temperature of which liquid state of the substance converts into gaseous state is known as b.pt of the substance. Thus, boiling point $\propto$ strength of secondary forces present in the molecule	Solubility of the compound depends on the following factors: Non-polar compounds are soluble in non polar solvents.

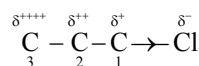
Electronic Displacements in Organic Molecules

The electronic displacement in organic molecules may be due to certain effects some of which are permanent (*e.g.* inductive and mesomeric effect) and others are temporary (*e.g.* electromeric and inductomeric effects). The permanent effects are called polarisation effect while the temporary effects disappear as soon as the attacking reagent is removed. Such effects are known as polarisability effects.

(i) Inductive Effect

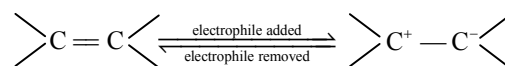
- The induction of polarity in an otherwise non-polar bond due to difference in electro-negativity is called inductive effect, *e.g.* $-\overset{\delta-}{\text{C}} \rightarrow \overset{\delta+}{\text{Cl}}$

- It is permanent effect represented by the symbol ‘ $\rightarrow$ ’
- It propagates through carbon chain, *e.g.*



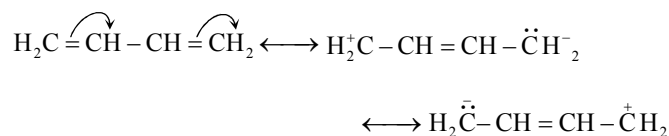
- Ingold, on the basis of electro-negativity of H atom, classified groups or atoms in two categories: – Inductive effect and + Inductive effect

(ii) Electromeric Effect: In presence of an attacking reagent, there is complete transfer of π -electrons from one atom to other to produce temporary polarity on atoms joined by multiple bonds, it is called Electromeric effect.

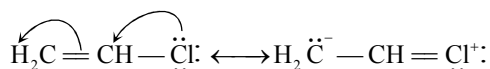


This effect is temporary and takes place only in the presence of a reagent. As soon as the reagent is removed, the molecule reverts back to its original position. Electromeric effect is of two types, *i.e.* +E effect and –E effect.

(iii) Resonance & Mesomeric Effect: There are many organic molecules which cannot be represented by a single Lewis structure. In turn, they are assigned more than one structure called canonical forms or contributing of resonating structures. The phenomenon exhibited by such compounds is called resonance. For example, 1, 3-butadiene has following resonance structure.

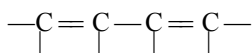


and canonical forms of vinyl chloride are



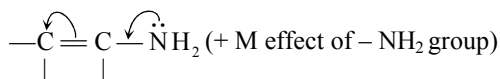
While drawing these canonical forms, the prime thing that has to be kept in mind is that the relative position of any of the atom should not change while we are allowed to change the relative positions of π -bonded electron pair or distribution of charge to other atoms. Also remember that it is not the case that some molecules have one canonical form and some have another form. All the molecules of the substance have the same structure. That structure is always the same all the time and is a weighted average of all the canonical forms. In real sense, these canonical forms have no expect in our imaginations. Now we are in a position to discuss about the conditions necessary for a compound to show resonance. The two essential conditions are:

(i) There must be conjugation in the molecule. Conjugation is defined as the presence of alternate double and single bonds in the compound like



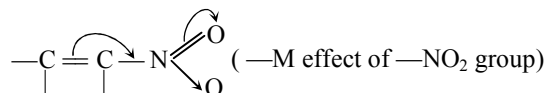
(ii) The part of the molecules having conjugation must be essentially planar or nearly planar. The first condition of conjugation is not only confined to the one mentioned above but some other systems are also categorized under conjugation. Types of Resonance (mesmeric) effect:

- If the atom or group of atoms is giving electrons through resonance, it is called +R or +M effect. For example,



Other groups that shows +M effect are —NHR, —NR₂ —OH, —OR, —NHCOR, —Cl, —Br, —I etc.

- If the atom or group of atoms is withdrawing electrons through resonance, it is called —R or —M effect. For example,



Resonance Energy: The difference in energy between the hybrid and the most stable canonical structure is called as resonance energy.

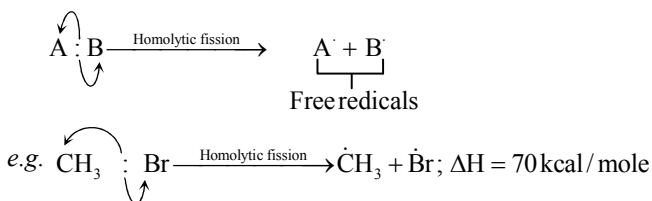
(iv) Hyperconjugation or no-bond Resonance or Baker-Nathan Effect: The delocalisation of sigma (σ) electrons is called hyperconjugation, *i.e.* hyperconjugation=sigma electrons + resonance. The hyperconjugation is of two types are sacrafacial and isovalent.

Cleavage of Covalent Bonds or Bond Fission

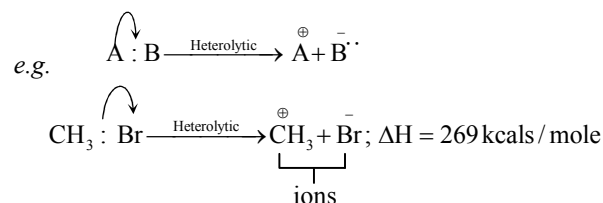
A covalent bond is formed by sharing of electron pair, A : B.

It can be broken by two ways:

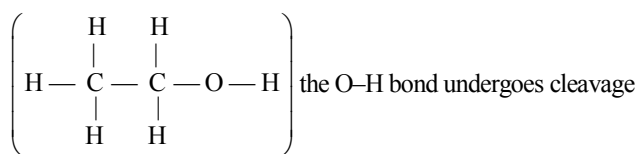
- Homolytic fission:** In this fission, the covalent bond is broken in such a way that each resulting species gets its own electron. Thus free radicals are formed



- Heterolytic fission:** In this fission, the covalent bond is broken in such a way that one species (less electronegative) is deprived off its own electron, while other species gains both electrons. Thus ions are formed



- The energy required for heterolytic fission is always **greater** due to electrostatic force of attraction between ions than for homolytic fission.
- As we go down a group of periodic table, the bond dissociation energy decreases, *e.g.* HF129kcal mole⁻¹, HCl101kcal mole⁻¹, kcal82kcal mole⁻¹, HI71kcal mole⁻¹,
- As electronegativity difference between two atoms increases, the cleavage of bond occurs readily, eg in ethyl alcohol

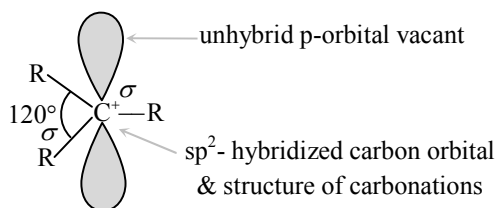


most readily

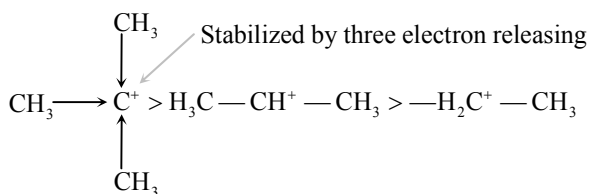
Carbocations (Earlier Called as Carbonium Ions)

Carbocations are the key intermediates in several reactions and particularly in nucleophilic substitution reactions and electrophilic addition reaction.

- **Structure:** Generally in the carbocations the positively charged carbon atom is bonded to three other atoms and has no nonbonding electrons. It is sp^2 hybridized with a planar structure and bond angles are of about 120° . There is a vacant unhybridised p orbital which (e.g. in the case of CH_3^+) lies perpendicular to the plane of C—H bonds.



- **Stability:** There is an increase in carbocation stability with additional alkyl substitution. Thus one finds that addition of HX to three typical olefins decreases in the order $(\text{CH}_3)_2\text{C}=\text{CH}_2 > \text{CH}_3-\text{CH}=\text{CH}_2 > \text{CH}_2=\text{CH}_2$. This is due to the relative stabilities of the carbocations formed in the rate determining step which in turn follows from the fact that the stability is increased by the electron releasing methyl group (+I), three such groups being more effective than two, and two more effective than one.



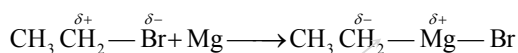
Stability of carbocations $3^\circ > 2^\circ > 1^\circ > \text{CH}_3^+$. Electron release: Disperses charge, stabilisation. The stability order of carbocation is explained by hyperconjugation. In vinyl cations ($\text{CH}_2=\text{CH}^+$), resonance stability lacks completely and therefore are very much less stable. Stability $\propto$ hyperconjugated structures $\propto$ number of α hydrogen.

Carbanions

Chemical species bearing a negative charge on carbon and

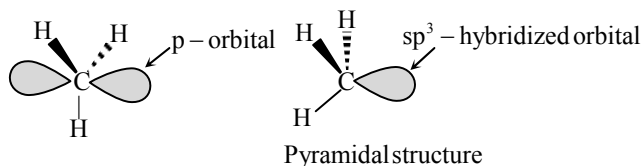
possessing eight electrons in its valence shell are called carbanions. These are produced by heterolytic cleavage of covalent bonds in which the shared pair of electrons remain with the carbon atom.

- **Structure:** A carbanion possesses an unshared pair of electron and thus represents a base. The best likely description is that the central carbon atom is sp^3 hybridized with the unshared pair occupying one apex of the tetrahedron. Carbanions would thus have pyramidal structures similar to those of amines. It is believed that carbanions undergo a rapid interconversion between two pyramidal forms.
- **Stability and generation:** The Grignard reagent is the best known member of a broad class of substances, called organometallic compounds where carbon is bonded to a metal lithium, potassium sodium, zinc, mercury, lead, thallium almost any metal known. Whatever the metal it is less electronegative than carbon and the carbon metal bond like the one in the Grignard reagent is highly polar. Although the organic group is not a full fledged carbanion an anion in which carbon carries negative charge, it however, has carbanion character organometallic compounds can serve as a source from which carbon is readily transferred with its electrons. On treatment with a metal, in RX the direction of the original dipole moment is reversed (reverse polarization)



$\text{R}-\text{C}\equiv\text{C}^-$ Considerable carbanion character
Also acetylide ion

- **Free radicals:** Free radicals are usually defected by electron spin resonance, which is also termed electron paramagnetic resonance. Simple alkyl radicals have a planar (trigonal) structure *i.e.*, these have sp^2 bonding with the odd electron in a p orbital. The pyramidal structure is another possibility when the bonding may be sp^3 and the odd electron is in an sp^3 orbital. The planar structure is in keeping with loss of activity when a free radical is generated at a chiral centre. Thus, a planar radical will be attacked at either face after its formation with equal probability to give enantiomers unlike carbocations, the free radicals can be generated at bridge. This shows that pyramidal geometry for radicals is also possible and that free radicals need to be planar



- (b) Soft electrophiles:** Large in size, valence e^- can be easily excited, e.g. I_2 , Fe^{+2} , Fe^{+3} , Cu^{+2} , and Cu^{+3} .

(ii) Nucleophile (Nucleus loving): Electron donors are nucleophile. A nucleophile may carry:

- **-ve charge:** H^- , Cl^- , C^- .

- **π electrons:** $\text{CH}_2 = \text{CH}_2$, $\text{HC} \equiv \text{CH}$, , $\text{R}-\text{C} \equiv \text{N}$.

Exception: CO_2 , SO_3 .

- **Lone pair of electrons:**

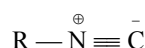
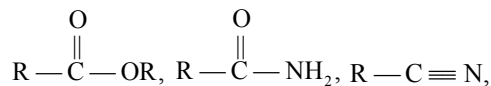
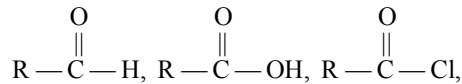
$\text{H}-\ddot{\text{O}}-\text{H}$, $\text{R}-\ddot{\text{O}}-\text{H}$, $\text{R}-\ddot{\text{N}}\text{H}_2$, NH_3 .

- The nucleophiles have been further classified in two categories

(a) Hard nucleophile: The electronegativity of donor atom is high but oxidation is difficult, *e.g.* H_2O .

(b) Soft nucleophile: The electronegativity of donor atom is low but oxidation is easy, *e.g.* RSH

- **Organic compounds which behave as electrophile as well as nucleophile:** Organic compounds in which carbon is bonded with electronegative atom (O, N, S) by multiple bond/bonds behaves as electrophile as well as nucleophile:



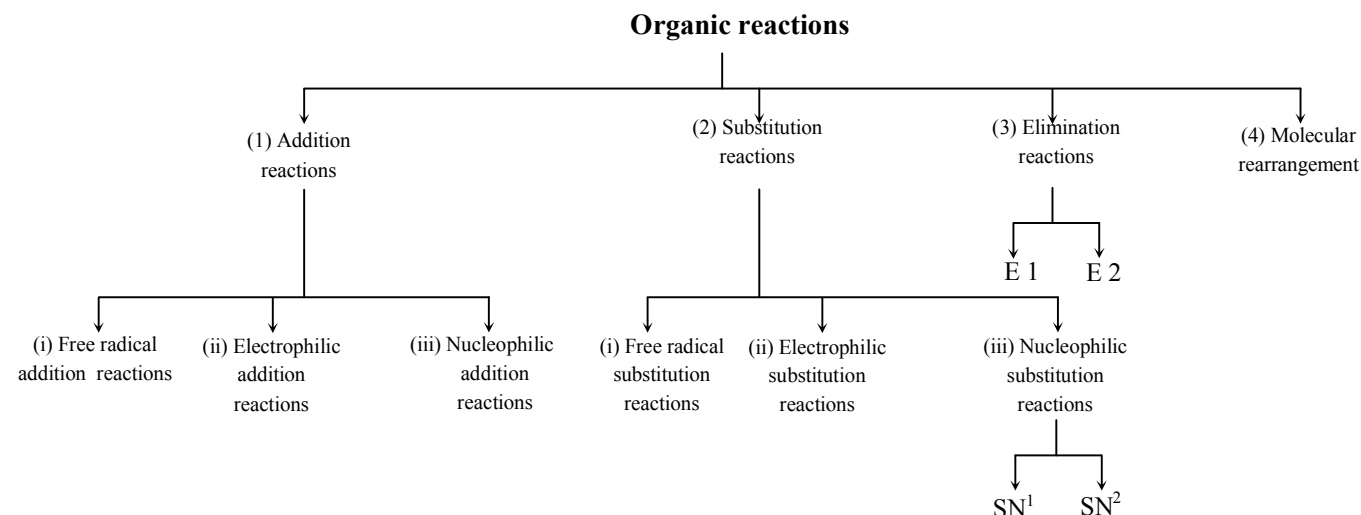
- **HAHB principle:** According to this principle a soft electrophile reacts with soft nucleophile and a hard electrophile reacts with hard nucleophile, *i.e.*,

Hard electrophile + Hard nucleophile $\rightarrow$ Product

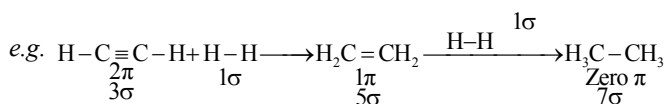
Soft electrophile + Soft nucleophile $\rightarrow$ Product

Type of Organic Reactions

The Classification of organic is as follows:

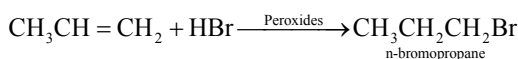


(1) Addition reactions: It may be defined as the organic reaction in which 1 π (pi) and 1 σ (sigma) bond is converted into 2 σ bonds, *i.e.* $1\pi + 1\sigma \longrightarrow 2\sigma$,

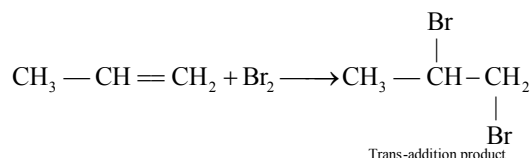


If this conversion is brought by a free radical, it is known as free radical addition reaction, if this conversion is brought by an electrophile, it is known as electrophilic addition reaction and if by a nucleophile, it is called nucleophilic addition reaction.

(i) Free radical addition reactions: These reactions are initiated by free radical, *e.g.* Halogenation of alkenes:

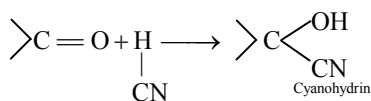


(ii) Electrophilic addition reactions: Carbonium ions are reaction intermediate, *e.g.* Addition of halogen to alkene,



(iii) Nucleophilic addition reaction: Such reactions involve anion as reaction intermediate, *e.g.*

Addition of HCN to carbonyl compounds (aldehyde and ketones)

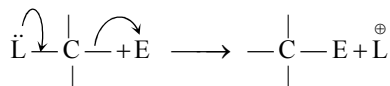


(2) Substitution Reactions: These reactions involve the replacement of an atom or group from the organic molecule with another similar part. During the reaction no change occurs in the carbon skeleton, i.e. no change in the saturation or unsaturation of the initial organic compound. They are of the following types:

(i) Free radical substitution reactions

- Chlorination of methane, $\text{CH}_4 + \text{Cl}_2 \xrightarrow{\text{UV light}} \text{CH}_3\text{Cl} + \text{HCl}$
Methyl chloride
- Arylation of aromatic compounds (Gomberg reaction)
 $\text{C}_6\text{H}_5-\text{H} + \text{C}_6\text{H}_5\text{N}_2\text{X} \xrightarrow{\text{Alkali}} \text{C}_6\text{H}_5-\text{C}_6\text{H}_5 + \text{N}_2 + \text{HX}$
Benzene diazonium halide Diphenyl
- Wurtz reaction, $2\text{C}_2\text{H}_5\text{Br} + 2\text{Na} \longrightarrow \text{C}_2\text{H}_5-\text{C}_2\text{H}_5 + 2\text{NaBr}$
Butane

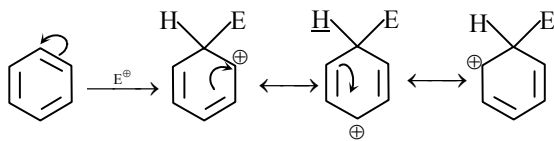
(ii) Electrophilic substitution reactions: Organic reactions in which a group or an atom is substituted by an electrophile along with transfer of an electron pair from leaving group to reaction center and reaction center to electrophile. In general, it may be represented as below:



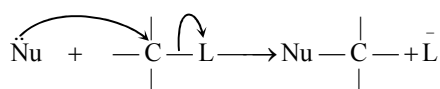
Where, E = Nucleophile, L = Leaving moiety

Mechanism

Benzene behaves as a nucleophile due to presence of π electrons, hence it undergoes electrophilic substitution reaction, i.e. one or more H atom(s) of benzene can be substituted by electrophile(s). The general mechanism is as follows:



(iii) Nucleophilic substitution reactions: Organic reactions in which a group or an atom is substituted by a nucleophile along with transfer of an electron pair from nucleophile to reaction center and from reaction center to the leaving group. In general, it may be represented as below:

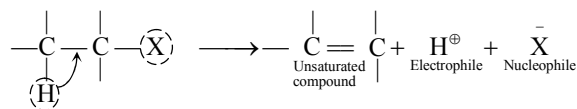


Where, Nu : Nucleophile, L : Leaving moiety

The changes take place in this reaction: Making of a new

covalent bond and breaking of old covalent bond. Therefore, these reactions on the basis of kinetics have been classified in two categories are bimolecular nucleophilic substitution reaction (SN^2) and unimolecular nucleophilic substitution reaction (SN^1)

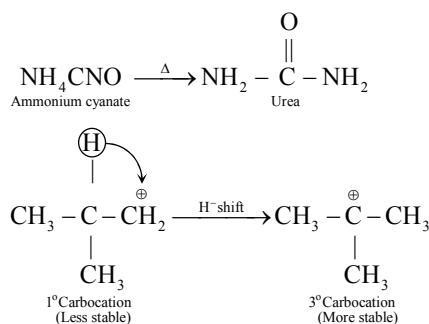
(3) Elimination Reactions: Organic reactions in which two groups or atoms are removed simultaneously, one in the form of a nucleophile and other in the form of an electrophile resulting in the formation of unsaturated compound, are known as elimination reactions, e.g.



If the two groups or atoms are removed from same carbon atom, it is known as α -elimination reaction. If these are removed from alternate carbon atoms, it is known as γ -elimination and it results a cyclic product. If these are removed from adjacent carbon atoms, it is known as β -elimination reaction. On the basis of kinetic studies, the β -elimination reactions have been classified in two categories:

- Unimolecular elimination (E_1):** Kinetic studies reveal that the rate of reaction depends upon the concentration of substrate only.
- Bimolecular elimination reaction (E_2):** The rate of reaction depends upon the concentration of both species hence bimolecular.

(4) Molecular Rearrangement Reactions: They involve the atomic rearrangement within the molecule or ion to give another species with different characteristics.



Rearrangement of Carbocations

Carbocations are prone to rearrangements. During these rearrangements, less stable (1° or 2°) carbocations are converted into more stable (2° or 3°) carbocations either by 1, 2-hydride shift or by 1, 2-methyl shift.

MULTIPLE CHOICE QUESTIONS

Hybridisation of Carbon

- A straight chain hydrocarbon has the molecular formula C_8H_{10} . The hybridisation for the carbon atoms from one end of the chain to the other are respectively sp^3 , sp^2 , sp^2 , sp^3 , sp^2 , sp^2 , sp and sp . The structural formula of the hydrocarbon would be:
 - $CH_3 - C \equiv C - CH_2 - CH = CH - CH = CH_2$
 - $CH_3 - CH_2 - CH = CH - CH_2 - C \equiv C - CH = CH_2$
 - $CH_3 - CH = CH - CH_2 - C \equiv C - CH = CH_2$
 - $CH_3 - CH = CH - CH_2 - CH = CH - C \equiv CH$
- The bond between carbon atom (1) and carbon atom (2) in compound $N \equiv C - CH = CH_2$ involves the hybridised carbon as:
 - sp^2 and sp^2
 - sp^3 and sp
 - sp and sp^2
 - sp and sp
- Number of π electrons present in naphthalene is:
 - 4
 - 6
 - 10
 - 14
- In benzene the total number of σ bonds is:
 - 3
 - 6
 - 9
 - 12
- The number of sp^3 hybridized carbon atoms in cyclohexene are:
 - 2
 - 3
 - 4
 - 6
- The number of π bonds in 3-hexyne-1-ene is:
 - 1
 - 2
 - 3
 - 4
- Example of sp^2 hybridization is:
 - CH_3^+
 - CH_3
 - $C_2H_5^+$
 - C_2H_5
- Carbon atoms in the compound $(CN)_4C_2$ are:
 - sp hybridized
 - sp^2 hybridized
 - sp and sp^2 hybridized
 - sp , sp^2 and sp^3 hybridized

Electronic Displacements in Organic Molecules

- Orbital interaction between the sigma bonds of a substituent group and a neighbouring π orbital is known as
 - Hyperconjugation
 - Inductive effect
 - Steric effect
 - Dipole-dipole interactions
- Which of the following is the most stable compound?
 - $Ph_3\overset{+}{C}$
 - $Ph_2\overset{+}{C}H$
 - $Ph_3\overset{+}{C}H_2$
 - $Ph\overset{+}{C}H_2$
- Reactivity towards nucleophilic addition reaction of (I) $HCHO$, (II) CH_3CHO , (III) CH_3COCH_3 is:
 - $II > III > I$
 - $III > II > I$
 - $I > II > III$
 - $I > II < III$
- Which of the following resonating structures of 1-methoxy-1,3-butadiene is least stable?
 - $\bar{C}H_2 - CH = CH - CH = \overset{\oplus}{O} - CH_3$
 - $CH_2 = CH_2 - \bar{C}H - CH = \overset{\oplus}{O} - CH_3$
 - $\bar{C}H_2 - \bar{C}H - CH = CH - O - CH_3$
 - $CH_2 = CH - \bar{C}H - \bar{C}H - O - CH_3$
- Which amongst the following is the most stable carbocation?
 - $CH_3 - \overset{+}{C} \begin{array}{c} | \\ CH_3 \end{array}$
 - $CH_3 - \overset{+}{C} \begin{array}{c} CH_3 \\ | \\ CH_3 \end{array}$
 - $\overset{+}{C}H_3$
 - $CH_3\overset{+}{C}H_3$
- Which is the decreasing order of stability?
 - $CH_3 - \overset{+}{C}H - CH_3$
 - $CH_3 - \overset{+}{C}H - O - CH_3$
 - $CH_3 - \overset{+}{C}H - CO - CH_3$
 - (i) < (ii) < (iii)
 - (i) > (ii) > (iii)
 - (iii) < (ii) < (i)
 - (ii) > (iii) > (i)
- The order of decreasing stability of the carbanions:
 - $(CH_3)_3\bar{C}$
 - $(CH_3)_2\bar{C}H$
 - $CH_3\bar{C}H_2$
 - $C_6H_5\bar{C}H_2$
 - $1 > 2 > 3 > 4$
 - $4 > 3 > 2 > 1$
 - $4 > 1 > 2 > 3$
 - $1 > 2 > 4 > 3$

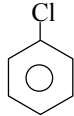
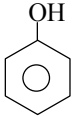
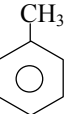
Types of Organic Reactions

16. Which of the following can't be used in Friedal Craft's reactions?
 - a. FeCl_3
 - b. FeBr_2
 - c. AlCl_3
 - d. NaCl
17. Dehydrohalogenation of an alkyl halide is a/an:
 - a. Nucleophilic substitution reaction
 - b. Elimination reaction
 - c. Both nucleophilic substitution and elimination reaction
 - d. Rearrangement
18. Formation of ethylene from acetylene is an example of:
 - a. Elimination reaction
 - b. Substitution reaction
 - c. Addition reaction
 - d. Condensation reaction
19. Conversion of CH_4 to CH_3Cl is an example of which of the following reaction:
 - a. Electrophilic substitution
 - b. Free radical addition
 - c. Nucleophilic substitution
 - d. Free radical substitution
20. Which is an electrophile?
 - a. BCl_3
 - b. CH_3OH
 - c. NH_3
 - d. AlCl_4^-
21. The following compound will undergo electrophilic substitution more readily than benzene:
 - a. Nitrobenzene
 - b. Benzoic acid
 - c. Benzaldehyde
 - d. Phenol

Bonding and Hybridisation in Organic Compounds

- 22.** Which of the following hybridisation has highest percentage of *s*-character?
- a.** sp^3 **b.** sp^2
c. sp **d.** None of these
- 23.** The compound in which carbon uses only its sp^3 hybrid orbitals for bond formation is?
- a.** $HCOOH$ **b.** $(NH_3)_2CO$
c. $(CH_3)_3COH$ **d.** $(CH_3)_3CHO$
- 24.** The bond between carbon atom (1) and carbon atom (2) in compound $N \equiv C - CH = CH_2$ involves the hybridised carbon as:
- a.** sp^2 and sp^2 **b.** sp^3 and sp
c. sp and sp^2 **d.** sp and sp

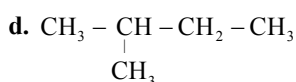
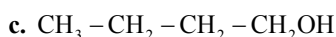
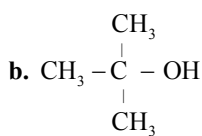
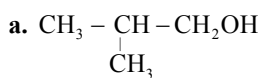
25. Number of π -electrons in cyclobutadienyl anion (C_4H_4)⁻² is:
a. 2
b. 4
c. 6
d. 8
26. Homolytic fission of C—C bond in ethane gives an intermediate in which carbon is:
a. sp^3 hybridised
b. sp^2 hybridised
c. sp hybridised
d. sp^2d hybridised
27. In which of the compounds given below is there more than one kind of hybridisation (sp , sp^2 , sp^3) for carbon:
(i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
(ii) $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3$
(iii) $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$
(iv) $\text{H} - \text{C} \equiv \text{C} - \text{H}$
a. (ii) and (iv)
b. (i) and (iv)
c. (ii) and (iii)
d. (ii)
28. The number of sp^3 hybridized carbon atoms in cyclohexene are:
a. 2
b. 3
c. 4
d. 6
29. Acetylene molecules contain:
a. 5σ bond
b. 4σ bond and 1π bond
c. 3σ and 2π
d. 3σ and 3π
30. In compound X, all the bond angles are exactly $109^\circ 28'$ X is:
a. Chloroform
b. Carbon tetrachloride
c. Chloromethane
d. Iodoform
31. Allyl cyanide contain σ - and π -bonds:
a. 9σ , 3π
b. 9σ , 9π
c. 3σ , 4π
d. 5σ , 7π
32. Strongest acid is:
a. $\text{HC} \equiv \text{CH}$
b. C_2H_6
c. C_6H_6
d. CH_3OH
33. Which is most acidic of the following?
a. Methane
b. Acetylene
c. 1-butene
d. Neo-pentane
34. The C—H bond distance is longest in:
a. C_2H_2
b. C_2H_4
c. C_2H_6
d. C_6H_6

35. The shape of ethylene molecule is:
a. Square planar **b.** Furan
c. Trigonal planar **d.** Tetrahedral
36. The hybridization involved in the six carbon atoms of benzene is:
a. $3sp^3$, $3sp^2$ **b.** $3sp^3$, $3sp$
c. All $6sp$ **d.** All $6sp^2$
37. Which is an acidic hydrocarbon?
a. $CH_3CH_2CH_2CH_3$ **b.** $CH_3C \equiv CCH_3$
c. $CH_3C \equiv CH$ **d.** $CH_2 = CH - CH = CH_2$
38. Example of sp^2 hybridization is:
a. CH_3^+ **b.** CH_3
c. $C_2H_5^+$ **d.** C_2H_5
39. The numbers of sigma (σ) bonds in 1-butene is:
a. 8 **b.** 10
c. 11 **d.** 12
40. In alkene (ethene) number of sp^2 hybrid carbon atoms are:
a. 1 **b.** 2
c. 3 **d.** 0
41. Number of π electrons present in naphthalene is:
a. 4 **b.** 6
c. 10 **d.** 14
42. Which of the following statements is false for isopentane?
a. It has three CH_3 groups
b. It has one CH_2 group
c. It has one CH group
d. It has a carbon which is not bonded to hydrogen
43. The number of σ and π bonds present in pent-4-ene, 1-yne is:
a. 10, 3 **b.** 3, 10
c. 4, 9 **d.** 9, 4
46. Benzene is unreactive because:
a. It has double bonds
b. It has carbon-carbon single bond
c. Carbon are sp^2 hybridised
d. π electrons are delocalised
47. Which of the following will be most easily attacked by an electrophile?
- a.** 
- b.** 
- c.** 
- d.** 
48. Which of the following resonating structures of 1-methoxy-1, 3-butadiene is least stable
- a.** $\bar{C}H_2 - CH = CH - CH = \overset{\oplus}{O} - CH_3$
- b.** $CH_2 = CH_2 - \bar{C}H - CH = \overset{\oplus}{O} - CH_3$
- c.** $\bar{C}H_2 - \overset{\oplus}{C}H - CH = CH - O - CH_3$
- d.** $CH_2 = CH - \bar{C}H - \overset{\oplus}{C}H - O - CH_3$
49. An aromatic compounds among other things should have a π -electron cloud containing electrons where n can't be:
a. 1/2 **b.** 3
c. 2 **d.** 1
50. Which of the following is an electrophile?
a. H_2O **b.** SO_3
c. NH_3 **d.** ROR
51. Which is the most stable carbocation?
a. iso-propyl
b. Triphenylmethyl cation

Dipole Moment, Resonance and Reaction Intermediates

44. Dipole moment is shown by:
- 1, 4-dichloro benzene
 - Cis-1, 2-dichloro ethane
 - Trans-1, 2-dichloro, 2-pentene
 - Trans-1, 2-dichloro ether
45. All bonds in benzene are equal due to:
- Tautomerism
 - Inductive effect
 - Resonance
 - Isomerism
46. π -propyl cation
47. C-C bond length in benzene is:
- 1.39 Å
 - 1.54 Å
 - 1.34 Å
 - Different in different bonds
48. Among the given cations, the most stable carbonium ion is:
- sec*-butyl
 - ter*-butyl
 - n*-butyl
 - None of these

54. The compound, which gives the most stable carbonium on dehydrogenation?



55. The reagent in Friedel Craft's reaction is?

a. Pyridine

b. RCOCl

c. RCOOH

d. HCl

56. 'C-C' bond length in benzene lies between single and double bond. The reason is:

a. Resonance

b. Isomerism

c. Metamerism

d. Inductive effect

57. Resonance structure of molecule does not have:

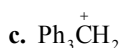
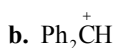
a. Identical arrangement of atoms

b. Nearly the same energy content

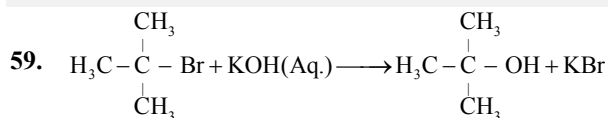
c. The same number of paired electrons

d. Identical bonding

58. Which of the following is the most stable compound?



Organic Reactions and their Mechanism



above reaction is:

a. SN^1

b. SN^2

c. E_1

d. Both (a) and (b)

60. Which of the following can't be used in Friedel Craft's reactions?

a. FeCl_3

b. FeBr_2

c. AlCl_3

d. NaCl

61. Conversion of CH_4 to CH_3Cl is an example of which of the following reaction?

a. Electrophilic substitution

b. Free radical addition

c. Nucleophilic substitution

d. Free radical substitution

62. Which is an electrophile?

a. BCl_3

b. CH_3OH

c. NH_3

d. AlCl_4^-

63. The following compound will undergo electrophilic substitution more readily than benzene.

a. Nitrobenzene

b. Benzoic acid

c. Benzaldehyde

d. Phenol

64. Strongest nucleophile is:

a. RNH_2

b. ROH

c. $\text{C}_6\text{H}_5\text{O}^-$

d. CH_3O^-

65. Which one of the following is least reactive in a nucleophilic substitution reaction?

a. $\text{CH}_3\text{CH}_2\text{Cl}$

b. $\text{CH}_2 = \text{CHCH}_2\text{Cl}$

c. $(\text{CH}_3)_3\text{C} - \text{Cl}$

d. $\text{CH}_2 = \text{CHCl}$

66. Bromination of alkanes involves:

a. Carbanions

b. Carbocations

c. Carbenes

d. Free radicals

67. Which of the following cannot undergo nucleophilic substitution under ordinary conditions?

a. Chlorobenzene

b. *tert*-butylchloride

c. Isopropyl chloride

d. None of these

68. Which of the following alkyl groups has the maximum + I effect?

a. $\text{CH}_3 -$

b. $(\text{CH}_3)_2\text{CH} -$

c. $(\text{CH}_3)_3\text{C} -$

d. $\text{CH}_3\text{CH}_2 -$

69. Formation of ethylene from acetylene is an example of:

a. Elimination reaction

b. Substitution reaction

c. Addition reaction

d. Condensation reaction

70. To which of the following four types does this reaction belong $\text{B}^- + \text{R} - \text{A} \rightarrow \text{B} - \text{R} + \text{A}^-$?

a. Unimolecular electrophilic substitution

b. Bimolecular electrophilic substitution

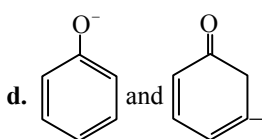
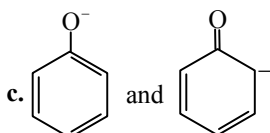
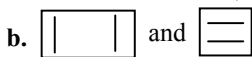
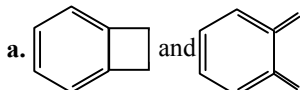
c. Unimolecular nucleophilic substitution

d. Bimolecular nucleophilic substitution

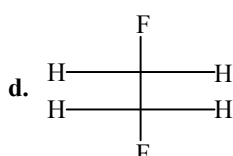
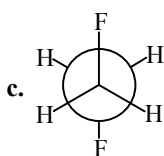
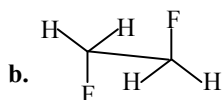
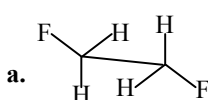
NCERT EXEMPLAR PROBLEMS

More than One Answer

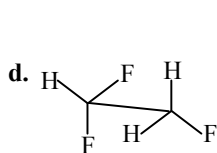
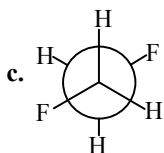
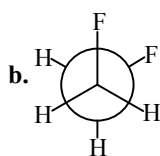
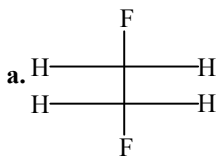
71. Which of the following pairs of structures represent resonance forms?



72. Which of the following conformations have zero dipole moment?



73. Which of the following conformations have non-zero dipole moment?

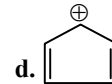
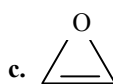
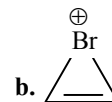
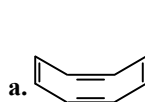


74. Among the following statements regarding antibonding molecular orbitals, which is/are correct?

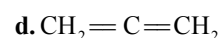
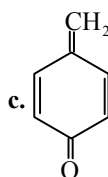
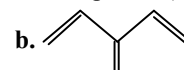
- They (ABMO) have higher energy than atomic orbital
- Electron charge density is maximum between the nuclei involved
- They (ABMO) are formed out phase overlap subtraction
- Atomic orbitals which are in the plane as shown below can form AMBO



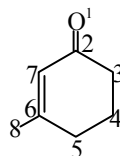
75. Identify the anti-aromatic system(s) among the following:



76. Which among these is/are planar compound (s):



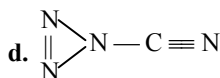
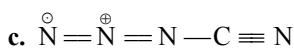
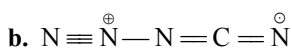
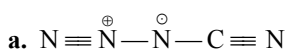
77. The correct statement regarding the molecule:



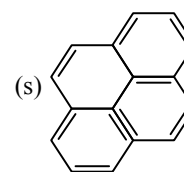
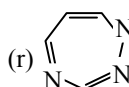
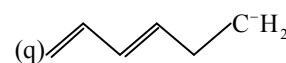
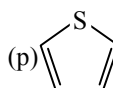
is (if the atoms are numbered from 1-8).

- The atoms 1,2,3,4,5,6,7 and 8 all lie in the same plane
- The atoms 1,2,6,7 and sp^2 hybridized
- The atoms 1,2,3,5,6,7 and 8 all lie in the same plane
- The 3,4,5 and 8 are sp^3 hybridized

78. N_3CN is a neutral molecule, i.e. the sum of the formal charges must be equal to zero. Then the acceptable structure(s) is/are:



79. The correct statement regarding the molecules given below is:



- a. 'p' is aromatic. The sulfur is sp^2 -hybridized. One of the lone pairs of electrons is in sp^2 and the other lone pair is in a p-orbital parallel to the p-orbital of the carbons
- b. 'q' is planar $6\pi e^-$ system aromatic
- c. If 'r' is planar, the system is anti-aromatic
- d. 's' is aromatic even though it does not obey Huckel's rule

Assertion and Reason

Note: Read the Assertion (A) and Reason (R) carefully to mark the correct option out of the options given below:

- If both assertion and reason are true and the reason is the correct explanation of the assertion.
- If both assertion and reason are true but reason is not the correct explanation of the assertion.
- If assertion is true but reason is false.
- If the assertion and reason both are false.
- If assertion is false but reason is true.

80. Assertion: Cis-1, 3-dihydroxy cyclohexane exists in boat conformation.

Reason: In the chair form, there will not be hydrogen bonding between the two hydroxyl groups.

81. Assertion: Benzyl bromide when kept in acetone water it produces benzyl alcohol.

Reason: The reaction follows SN^2 mechanism.

82. Assertion: Carbon possesses property of catenation.

Reason: Carbon atoms form double as well as triple bonds during catenation.

83. Assertion: Saturated hydrocarbons are chemically less reactive.

Reason: All isomeric paraffins have same parent name.

84. Assertion: A mixture of glucose and m-dinitrobenzene can be separated by shaking it with ether.

Reason: Glucose is soluble in water.

85. Assertion: Tertiary carbonium ions are generally formed more easily than primary carbonium ions.

Reason: Hyperconjugative as well as inductive effect due to additional alkyl groups stabilize tertiary carbonium ions.

86. Assertion: Heterolytic fission involves the breaking of a covalent bond in such a way that both the electrons of the shared pair are carried away by one of the atoms.

Reason: Heterolytic fission occurs readily in polar covalent bonds.

87. Assertion: The order of reactivity of carbonium ions is $2^\circ > 3^\circ > 1^\circ$.

Reason: Carbon atom in carbonium ions is in sp^3 state of hybridisation.

88. Assertion:Free radicals are short lived and highly reactive.

Reason: Free radicals are highly unstable.

89. Assertion: Each carbon in ethylene molecule is sp^2 hybridised.

Reason: The H—C—H bond angle in ethylene molecule is 120° .

Comprehension Based

Paragraph –I

Organic molecules show chemical reaction on account of hemolytic bond fission or heterolytic bond fission in addition to inductive effect, electromeric effect, resonance and hyper-conjugation. The usual reactions shown by organic molecules are substitution (S_N1) and (S_N2) addition (syn and anti) and elimination (E_1 and E_2) reactions along with rearrangement reactions. In addition to these, various oxidation and reduction reactions are also given. The species which attacks a +ve centre is called nucleophile and the species capable of attacking -ve centres are called electrophile.

90. Which is not formed during hemolytic or heterolytic fission of covalent bond?

- a. Free radical
b. Carbocation
c. Carbanion
d. Bridged carbocation

91. The electromeric effect in a molecule occurs only if it has at least one:

- a.** σ -bond **b.** lone pair
c. π -bond **d.** three centred bond

92. The most stable carbocation among the following is:

- a. C_6H_5^+
- b. $\begin{array}{c} \text{C}_6\text{H}_5\text{CH}^+\text{CH}_2 \\ | \\ \text{CH}_3 \end{array}$
- c. $\text{C}_6\text{H}_5 - \overset{+}{\text{C}}(\text{CH}_3)_2$
- d. $\text{C}_6\text{H}_5\text{CH}_2$

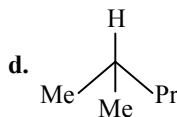
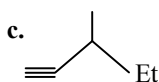
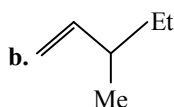
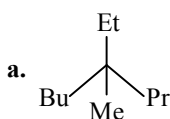
93. During nitration of an organic compound, HNO_3 acts as:

- a. acid** **b. base**
c. neutral **d. salt**

94. Dextro 2-bromobutane on treatment with NaOH (aq) will not give:

- a. racemic mixture of 2-butanol if S_N1 is obeyed
b. laevo form of 2-butanol if S_N2 is obeyed
c. dextro form of 2-butanol if S_N2 is obeyed
d. 100% inversion if S_N2 is obeyed

95. Which does not represent the simplest chiral alkane, alkene or alkyne?



96. Which of the following is neither a nucleophile or electrophile?



Match the Column

97. Match Column II with Column I:

Column I	Column II
(A) The alkene $\text{CH}_3 - \text{C} = \text{CH} - \text{CH}_3$ is more stable than its isomer $\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH}_2$	1. $p_\pi - d_\pi$ bonding effect
(B) The carbocation $\text{CH}_3 - \text{O} - \text{C}^+ \text{H}_2$ is less stable than its another canonical form $\text{CH}_3 - \text{O}^+ = \text{CH}_2$	2. Hyper conjugation
(C) The carbanion is more stable than: CF_3^- .	3. Fulfillment of octet
(D) Phenol is more acidic than alcohol	4. Resonance effect

a. A→2, B→3, C→1, D→4

b. A→2, B→4, C→3, D→1

c. A→1, B→3, C→2, D→4

d. A→4, B→1, C→3, D→2

98. Match the reaction in Column I with appropriate options in Column II:

Column I	Column II
(A)	1. Racemic mixture

(B)	2. Addition reaction
(C)	3. Substitution reaction
(D)	4. Coupling reaction
	5. Carbonation intermediate

a. A→3,4, B→5, C→1-2, D→3

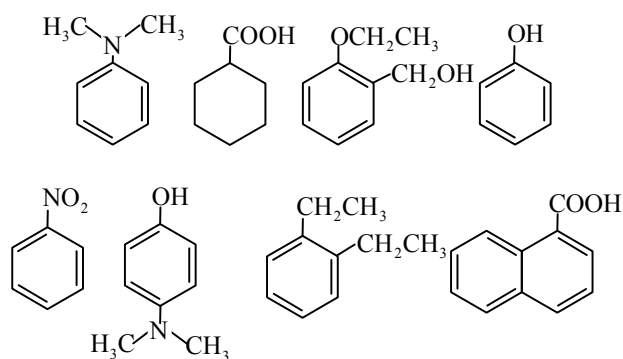
b. A→2, B→4, C→3, D→1

c. A→1, B→3, C→2, D→4

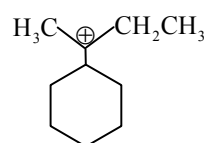
d. A→4, B→1, C→3, D→2

Integer

99. Amongst the following, the total number of compounds soluble in aqueous NaOH is:



100. The total number of contributing structures showing hyperconjugation (involving C—H bonds) for the following carbocation is:

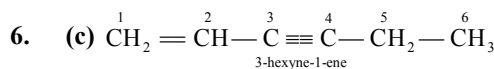
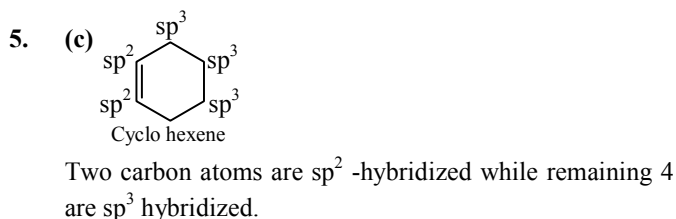
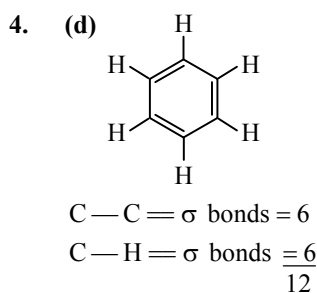
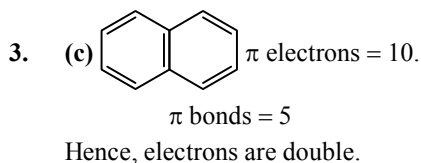
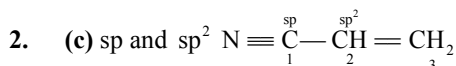
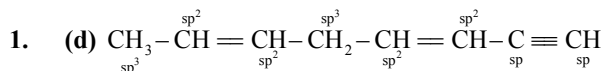


ANSWER

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
d	c	c	d	c	c	a,c	c	a	a
11.	12.	13.	14.	15.	16.	17.	18.	19.	20.
c	c	b	b	b	d	b	c	d	a
21.	22.	23.	24.	25.	26.	27.	28.	29.	30.
d	c	c	c	d	b	d	c	c	b
31.	32.	33.	34.	35.	36.	37.	38.	39.	40.
a	d	b	c	c	d	c	a,c	c	b
41.	42.	43.	44.	45.	46.	47.	48.	49.	50.
c	d	a	b	c	d	b	c	a	b
51.	52.	53.	54.	55.	56.	57.	58.	59.	60.
b	a	b	b	b	a	d	a	a	d
61.	62.	63.	64.	65.	66.	67.	68.	69.	70.
d	a	d	d	d	d	d	c	c	d
71.	72.	73.	74.	75.	76.	77.	78.	79.	80.
c,d	a,b,c	a,b,d	a,c,d	b,c,d	b,c	b,c,d	all	a,c,d	d
81.	82.	83.	84.	85.	86.	87.	88.	89.	90.
a	b	b	b	a	b	d	b	b	d
91.	92.	93.	94.	95.	96.	97.	98.	99.	100.
c	c	b	c	a	a	a	a	4	6

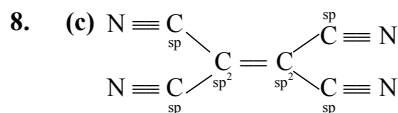
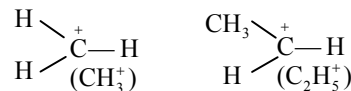
SOLUTION

Multiple Choice Questions



Three π bonds.

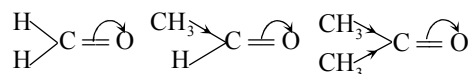
7. (a,c) Carbonium ions are sp^2 hybridized species.



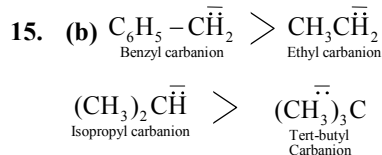
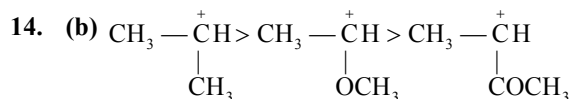
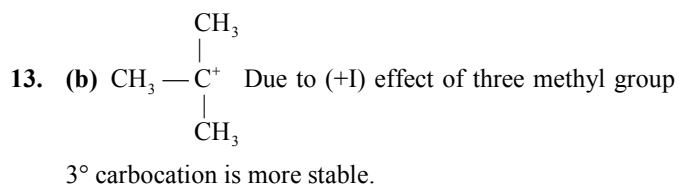
9. (a) It is hyperconjugation process.

10. (a) Triphenyl methyl cation has three benzene resonating ring so it is most stable compound.

11. (c) Carbonyl carbon becomes more reactive toward nucleophilic addition by increasing the +I effect of alkyl group so the reactivity order is as

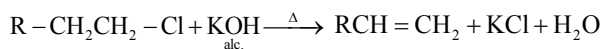


12. (c) The octet of all atoms are complete in structures (a) and (b). In structure (d) electron deficiency of positively charged carbon is duly compensated by lone pair electrons of adjacent oxygen atom while such neighbour group support is not available in structure (c).



16. (d) All cations are expected to act as Lewis acid since they are electron deficient in nature. However cation such as Na^+ , K^+ etc. (Inert gas configuration) have a very little tendency to accept electrons. Therefore they do not act as Lewis acids in Friedel-Craft's reaction.

17. (b) Dehydrohalogenation of an alkyl halide on presence of alcoholic potash is an example of elimination reaction.



18. (c) $CH \equiv CH + H_2 \longrightarrow CH_2 = CH_2$

That is called addition reaction.

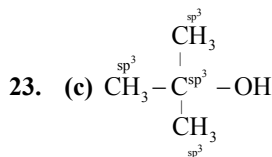
19. (d) When methane gas is treated with chlorine in the presence of sunlight, one hydrogen of methane replaced by the chlorine atom and forms methyl chloride. The mechanism involved in this reaction is free radical mechanism. So it is an example of free radical substitution reaction.

20. (a) Electron deficient species (in complete octet) acts as an electrophile *i.e.* BCl_3 .

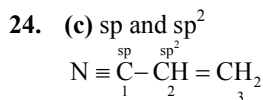
21. (d) Phenol will undergo electrophilic substitution more readily than benzene.

22. (c) Type s -character

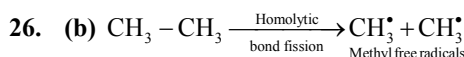
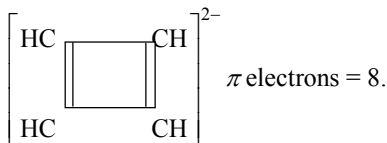
sp^3	25%
sp^2	33.33%
sp	50%



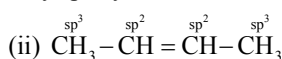
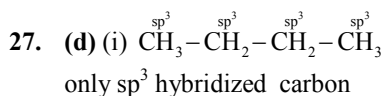
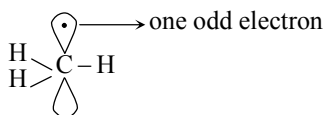
All the carbon atoms are sp^3 hybridized.



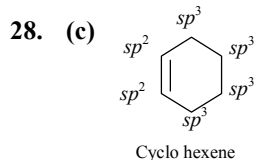
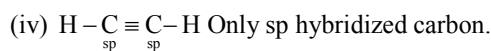
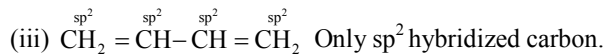
25. (d) Cyclobutadienyl anion (C_4H_4)²⁻



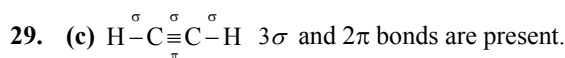
free radical is formed which is sp^2 -hybridized.



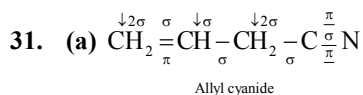
Both sp^2 and sp^3 hybridized carbon.



Two carbon atoms are sp^2 -hybridized while remaining 4 are sp^3 hybridized.



30. (b) In CCl_4 all bond angles are same *i.e.* of $109^\circ 28'$ the carbon is sp^3 hybridised.



Total 9 σ bond and 3 π bond.

32. (d) Because hydrogen is attached with high electro-negative element.

33. (b) The s -character of C-H bond of acetylene is higher in comparison to C-H bond of ethene and ethane. The electrons of the C-H bond in acetylene are strongly held by carbon nuclei. This facilitates the removal of hydrogen as proton.

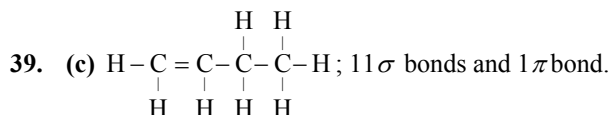
34. (c) Single bond has longest distance of bonds so C_2H_6 ethane is correct answer.

35. (c) In ethylene molecule carbons are sp^2 hybridised so its structure is trigonal planar.

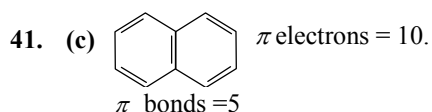
36. (d) In benzene all 6 carbons are sp^2 hybridised.

37. (c) Propyne has one acidic hydrogen.

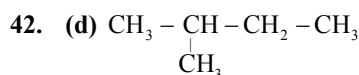
38. (a, c) Carbonium ions an sp^2 hybridized species.



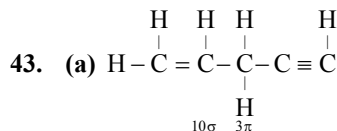
40. (b) $CH_2 = CH_2$ both the carbon atoms are sp^2 hybridised.



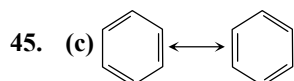
Hence electrons are double.



It has 3 CH_3 groups, one CH_2 group and one CH group.



44. (b) Due to presence of two chlorine atom on the same side of carbon atom produces dipole moment in molecule.



All the bonds (C–C) are equal in benzene. The C–C bond length is $1.39\text{\AA}$ which is in between C–C bond ($1.54\text{\AA}$) and C = C ($1.34\text{\AA}$).

46. (d) Benzene is unreactive instead of having 3π bonds because of resonance π -electrons are delocalized.

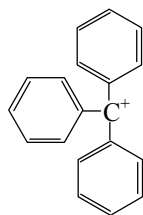
47. (b) Due to mesomeric effect (+) of –OH group the electron density on benzene ring increase. So the electrophile easily attacked on these electron rich center.

48. (c) The octet of all atoms are complete in structures (a) and (b). In structure (d) electron deficiency of positively charged carbon is duly compensated by lone pair electrons of adjacent oxygen atom while such neighbour group support is not available in structure (c).

49. (a) According to Huckel rule, all aromatic compounds must have $(4n+2)\pi$ electrons where n is an integer, *i.e.*, $n = 0, 1, 2, 3, \dots$ and possesses unusual stability due to the complete delocalisation of π -electrons.

50. (b) $\text{H} - \ddot{\text{O}} - \text{H}$, $:\text{NH}_3$, $\text{R} - \ddot{\text{O}} - \text{R}$ - nucleophiles SO_3 has electron deficient centre (a reagent which can accept an electron pair in a reaction, is called an electrophile)

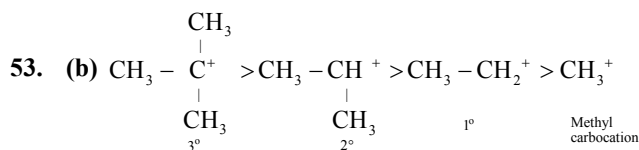
51. (b) Stability of carbonium ions.
tertiary alkyl > secondary alkyl > primary alkyl > methyl.
More the number of alkyl groups, the greater the dispersal of positive charge and therefore, more the stability of carbonium ion is observed.



triphenylmethyl cation

Dispersal of positive charge increases with the increase in the number of benzene ring.

52. (a) C–C bond length in benzene is $1.39\text{\AA}$ which is in between C–C ($1.54\text{\AA}$) and C = C ($1.34\text{\AA}$) because of resonance.



Greater the no. of alkyl groups, greater would be the dispersal of the charge and hence more stable will be the carbonium ion.

54. (b) 3° alcohol on dehydrogenation gives most stable carbonium ion.

55. (b) The reaction of an alkyl halide or aryl halide with benzene in the presence of a Lewis acid, generally AlCl_3 is known as Friedel Craft's reaction.

56. (a) Due to delocalisation of π -electrons benzene has resonance.

57. (d) Resonance structure of molecule does not have identical bonding.

58. (a) Triphenyl methyl cation has three benzene resonating ring so it is most stable compound.

59. (a) It is nucleophilic substitution reaction which is in first order.

60. (d) All cations are expected to act as Lewis acid since they are electron deficient in nature. However cation such as Na^+ , K^+ etc. (Inert gas configuration) have a very little tendency to accept electrons. Therefore they do not act as Lewis acids in Friedel Craft's reaction.

61. (d) When methane gas is treated with chlorine in the presence of sunlight, one hydrogen of methane replaced by the chlorine atom and forms methyl chloride. The mechanism involved in this reaction is free radical mechanism. So it is an example of free radical substitution reaction.

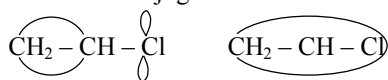
62. (a) Electron deficient species (in complete octet) acts as an electrophile *i.e.* BCl_3 .

63. (d) Phenol will undergo electrophilic substitution more readily than benzene.

64. (d) CH_3O^- is the strongest nucleophile which is capable of acting as donor of electron pair.

65. (d) The non reactivity of the chlorine atom in vinyl chloride may be explained from the molecular orbital point of view as follows. If the chlorine atom has sp^2 hybridization the C–Cl bond will be a σ -bond and the two lone pairs of electron would occupy the other two sp^2 orbitals. This would leave a p -orbital containing a lone

pair and this orbital could not conjugate with the π bond of the ethylenic link. Thus two M.O.S. will be required to accommodate these four π electrons. Furthermore since chlorine is more electronegative than carbon, the electron will tend to be found in the chlorine atom has now lost full control of the one pair and so, is less negative than it would have been had there been no conjugation. Since two carbon atoms have acquired a share in the lone pair, each atom acquires a small negative charge. Hence, owing to delocalisation of bonds (through conjugation), the vinyl chloride molecule has an increased stability. Before the chlorine atom can be displaced by some other group the lone pair must be localised again on the chlorine atom. This requires energy and so the chlorine is more firmly bound than has no conjugation occurred.



66. (d) Halogenation of alkanes takes place in presence of light (sunlight or UV) or at elevated temperature via free radical.

67. (d) All the given species undergo nucleophilic substitution reaction. This reactivity can be explained in terms of the nature of C-X bond which is highly polarised covalent bond due to large difference in the electro negativities of carbon and halogen atoms.



68. (c) Increasing + I effect



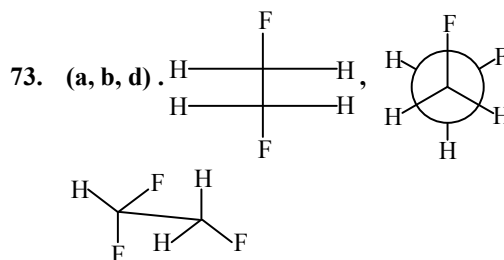
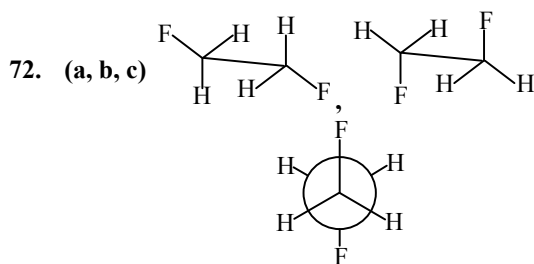
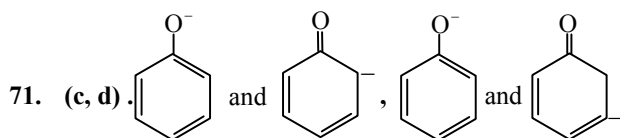
69. (c) $\text{CH} \equiv \text{CH} + \text{H}_2 \longrightarrow \text{CH}_2 = \text{CH}_2$

That is called addition reaction.

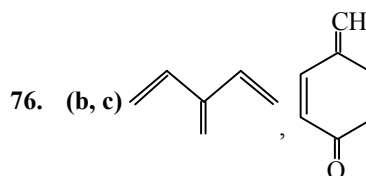
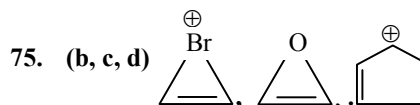
70. (d) It is SN^2 type of reaction.

NCERT Exemplar Problems

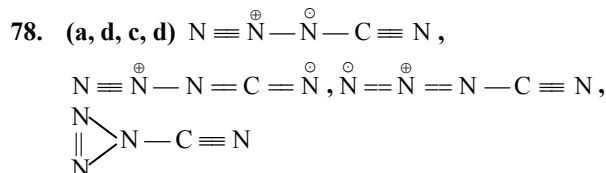
More than One Answer



74. (a, c, d) They (ABMO) have higher energy than atomic orbital, They (ABMO) are formed out phase overlap subtraction, Atomic orbital's which are in the plane as shown below can form AMBO



77. (b, c, d) The atoms 1, 2, 6, 7 and sp^2 hybridized, The atoms 1, 2, 3, 5, 6, 7 and 8 all lie in the same plane, The 3, 4, 5 and 8 are sp^3 hybridized



79. (a, c, d) 'p' is aromatic. The sulfur is sp^2 -hybridized. One of the lone pairs of electrons is in sp^2 and the other lone pair is in a p-orbital parallel to the p-orbital of the carbons. If 'r' is planar, the system is anti-aromatic, 's' is aromatic even though it does not obey Huckel's rule

Assertion and Reason

80. (d) Here both assertion and reason are incorrect because cis-1, 3-dihydroxy cyclohexane exist in chair conformation and in chair conformation hydrogen bonding is present.

81. (a) The assertion that on keeping benzyl bromide in acetone water it produces benzyl alcohol is correct. Because $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ hydrolysed to produce $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$. This conversion is of SN^2 mechanism.

82. (b) Catenation property of carbon is primarily due to its small size. Electronic configuration and unique strength of carbon-carbon bonds.

83. (b) Less reactivity of saturated hydrocarbons are due to presence of single bonds between carbon atoms.

84. (b) Glucose is insoluble in ether.
85. (a) An alkyl group attached to the positively charged carbon of a carbonium ion tends to release electrons towards that carbon; thus the positive charge gets dispersed as the alkyl group becomes somewhat positively charged itself. More the number of alkyl groups, the greater is the dispersal of positive charge and therefore more easily it will be formed.
86. (b) Heterolytic fission occurs when the two atoms differ considerably in their electro negativities and shared pair of electrons is carried by more electronegative atom.
87. (d) The order of reactivity of carbonium ions is $1^\circ > 2^\circ > 3^\circ$. Carbon atom in carbonium ion is in sp^2 state of hybridisation. The three hybridized orbitals lie in the same plane and are involved in the formation of three σ bonds with three atoms or groups while the unhybridised p-orbital remains vacant.
88. (b) Since free radicals contain odd electrons, so they are short lived and they readily try to pair up the odd electrons to form neutral molecules, that is why they are highly reactive.
89. (b) Each carbon atom in ethylene is attached to two hydrogen atoms by single covalent bonds and to another carbon atoms by a double bond. Since each carbon is attached to three other atoms, it uses sp^2 hybrid orbitals and an unhybridised p_z orbital to form its bond. Each C-H bond is a σ bond resulting from the overlap of $1s$ orbital of hydrogen atom and sp^2 orbital of a carbon atom. One C-C bond results from the linear overlap of sp^2 orbitals one from each carbon atom. One π bond results from the lateral overlap of two unhybridised p_z orbitals, one from each carbon atom.

Comprehension Based

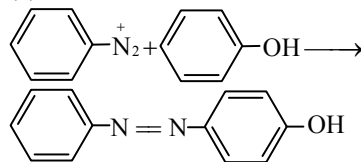
90. (d) $\text{>C}-\text{C}<\xrightarrow{\text{bond fission}}\text{>C}^+ + \text{>C}^-$ Heterolytic
 $\text{>}\dot{\text{C}} + \dot{\text{C}}<$
91. (c) $\text{>C=O} \rightleftharpoons \text{>C}^+-\text{O}^-$ or $\text{>C=O} \rightleftharpoons \text{>C}^+-\text{O}^-$
92. (c) Resonance and +I effect in $\text{C}_6\text{H}_5\text{C}^+(\text{CH}_3)_2$
93. (b) $\text{HNO}_3 + \text{H}_2\text{SO}_4 \xrightarrow[\text{Acid}]{\text{Base}} \text{NO}_2^+ + \text{HSO}_4^- + \text{H}_3\text{O}^+$
94. (c) This is against the characteristics of $\text{S}_{\text{N}}2$
95. (a) The simplest alkane with chirality is $\text{C}_3\text{H}_7-\text{CH}-\text{C}_2\text{H}_5$

96. (a) It can neither accept electron pair nor can donate.

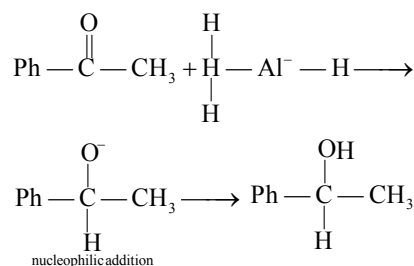
Match the Column

97. (a) A→2, B→3, C→1, D→4

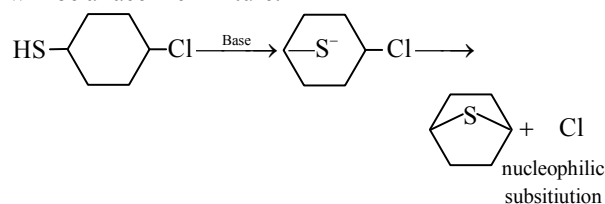
98. (a) A→3,4, B→5, C→1-2, D→3



This is an example of electrophilic substitution at para position of phenol, giving a coupling product.

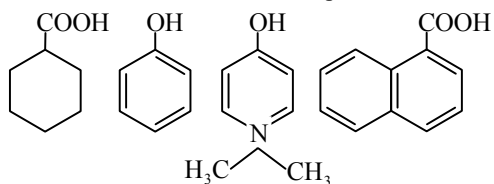


Pianacol-pinacolone rearrangement, occur through carbocation intermediate. Nucleophilic addition occur at (planar) carbon, generating chiral centre, hence, product will be a racemic mixture.

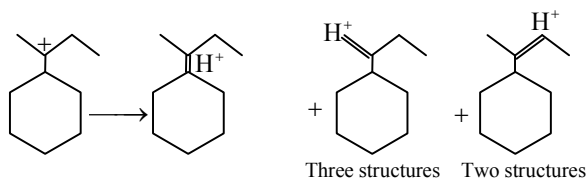


Integer

99. (4) Aromatic alcohols and carboxylic acids forms salt with NaOH, will dissolve in aqueous NaOH.



100. (6) These are total 6α -H to sp^2 carbon and they all can participate in hyperconjugation.



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