DAY FIFTEEN

Some Basic Principles and Techniques

Learning & Revision for the Day

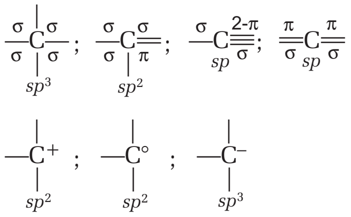
- Bonding in Organic Compounds
- Classification of Organic Compounds
- IUPAC System
- Isomerism
- Fission of a Covalent Bond
- Reaction Intermediates
- Electronic Displacement in a Covalent Bond
- Methods of Purification of Organic Compounds
- Qualitative Analysis
- Quantitative Analysis

The hydrides of carbon (hydrocarbons) and their derivatives are called organic compounds. The branch of chemistry which deals with these compounds is called organic chemistry.

Bonding in Organic Compounds

- Carbon is the essential element of all organic molecules and its electronic configuration is 2,4.
- It is not possible for carbon to accept or donate 4 electrons to achieve inert gas configuration (to achieve stability), due to energy conceptions and thus, carbon always forms covalent bonds.
- The tetravalency of carbon can be explained by the excited state concept, i.e. by moving one of the paired $2s$ electron to empty $2p$ orbital by gaining energy from the system (according to classical concept of bonding) however 4 equivalent C—H bonds in CH_4 is explained on the basis of concept of hybridisation (according to modern concept of bonding). Carbon has a unique property that it can form both σ and π-bonds.
- Carbon atom has unique capacity to form bonds with other carbon atoms. This property of forming bonds with atoms of the same element is called **catenation**.
- **Hybridisation** is the intermixing of orbitals of almost similar energy to form the same number of orbitals of exactly similar energy.
- The carbon atom shows three types of hybridisations (sp, sp^2 or sp^3) depending upon the number of σ-bonds formed in its compounds.

- If there are four σ-bonds, the hybridisation is sp^3 with tetrahedral shape, if three σ-bonds, the hybridisation is sp^2 with trigonal planar shape and if only two σ-bonds, the hybridisation is sp with linear shape.
- Usually saturated hydrocarbons are sp^3 hybridised while unsaturated hydrocarbons may be sp^2 or sp hybridised.



Functional Groups

An atom or group of atoms joined in a specific manner which is responsible for the characteristic chemical properties of the organic compounds e.g. carboxylic acid group (—COOH), aldehydic group (—CHO), etc.

Homologous Series

A homologous series can be defined as a group of compounds in which the members have similar structural features and similar chemical properties and the successive members differ in their molecular formula by $—CH_2$ group.

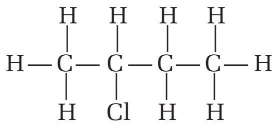
The general characteristics of a homologous series are :

- All compounds in the series can be represented by one general formula e.g. $C_nH_{2n+1}OH$.
- The molecular mass of every two adjacent members differ by 14 ($CH_2 = 12 + 2 \times 1 = 14$).
- All compounds in the series have similar chemical properties because of the presence of same functional group.
- The members of the series show a gradual gradation in their physical properties like solubility, density, melting and boiling points. The physical properties generally increase as the molecular mass increases.

Representation of Different Formulae

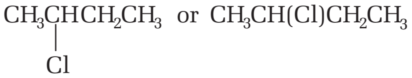
An organic compound can be represented by the following ways:

(i) In structural formula, all the bonds present between any two atoms are shown clearly.



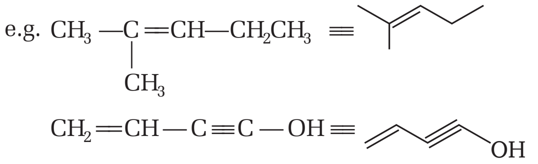
2-chlorobutane

(ii) In condensed formula, type of chemical formula, all the bonds are not shown clearly.



$\underset{\substack{|\\ Cl}}{CH_3CHCH_2CH_3}$ or $CH_3CH(Cl)CH_2CH_3$

(iii) In bond line formula, every fold and free terminal represents a carbon and lines represent the bond.

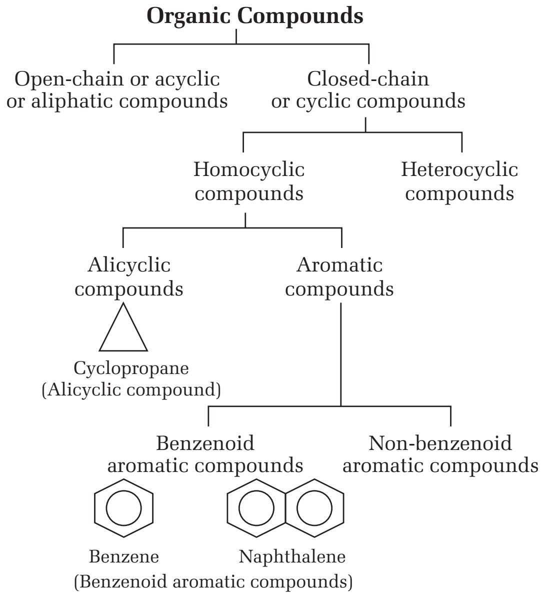


e.g. $CH_3—\underset{\substack{|\\ CH_3}}{C}=CH—CH_2CH_3 \equiv$

$CH_2=CH—C\equiv C—OH \equiv$

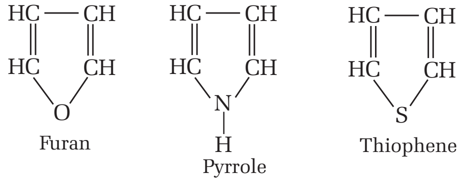
Classification of Organic Compounds

- The organic compounds have been classified on the basis of carbon skeleton (structure) or functional groups or the concept of homology, i.e. the series in which two successive members differ by a $—CH_2$ unit or 14 unit mass.
- On the basis of structure the organic compounds are classified as:



Examples

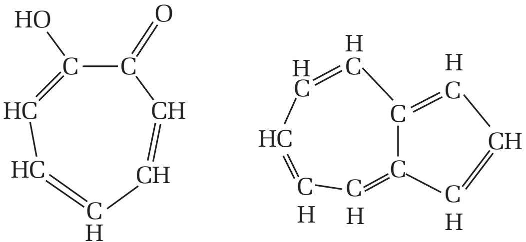
(i)



Furan Pyrrole Thiophene

(Heterocyclic compounds)

(ii)



Tropolone Azulene

(Non-benzenoid aromatic compounds)

- On the basis of functional groups, the organic compounds are classified into various classes, which are given in the following table.

Class	Functional group
Olefins/Alkenes	$>C=C<$
Acetylenes/Alkynes	$-C\equiv C-$
Halides	$-F, -Cl, -Br, -I$ (Halo)
Alcohols	$-OH$ (Hydroxy)
Thiols	$-SH$
Aldehydes	$-\underset{\underset{O}{\|}}{C}-H$ (Aldehydic)
Ketones	$-\overset{\overset{O}{\|}}{C}-$ (Ketonic)
Ethers	$-\overset{\|}{\underset{\|}{C}}-O-\overset{\|}{\underset{\|}{C}}-$ (Alkoxy)
Carboxylic acid	$-\overset{\overset{O}{\|}}{C}-OH$ (Carboxyl)
Sulphonic acid	$-SO_3H$
Amides	$-\overset{\overset{O}{\|}}{C}-NH_2$ (Amide)
Amines	$-N\begin{matrix}H\\H\end{matrix}$ (Amino)
Cyanides/Nitriles	$-C\equiv N$ (Cyano)
Nitro compounds	$-N\begin{matrix}O\\O\end{matrix}$ (Nitro)
Esters	$-\overset{\overset{O}{\|}}{C}-O-\overset{\|}{\underset{\|}{C}}-$ (Ester)
Acid halides	$-\overset{\overset{O}{\|}}{C}-X$ (Acyl halide)

IUPAC System

In 1957, the International Union of Pure and Applied Chemistry evolved a scheme for giving systematic name to organic compounds on the basis of their structure. This is known as the **IUPAC system of nomenclature.**

This system has set of rules for naming organic molecules from their structure.

Rules for IUPAC Nomenclature

- First of all, the longest carbon chain in the molecules is identified.
- Numbering is started from the terminal carbon from where branching is nearest.
- If the two substituents are found in equivalent positions, the numbering is done alphabetically.
- If there are two chains of equal size then that chain is to be selected which contains more number of side chains.
- The longest chain of carbon atoms containing the functional group is numbered in such a way that the functional group is attached at the carbon atom possessing lowest possible number in the chain.
- In polyfunctional compounds, one of the functional group is chosen (prioritywise) as the principal functional group and the compound is then named on that basis.

Some functional groups are always indicated by the prefixes instead of secondary suffixes. They are tabulated with their IUPAC names as

Functional Group	Prefix	Family	IUPAC name
$-NO_2$	Nitro	$R-NO_2$	Nitroalkane
$-OR$	Alkoxy	$R-O-R'$	Alkoxyalkane
$-Cl$	Chloro	$R-Cl$	Chloroalkane
$-Br$	Bromo	$R-Br$	Bromoalkane
$-I$	Iodo	$R-I$	Iodoalkane
$-F$	Fluoro	$R-F$	Fluoroalkane
$-NO$	Nitroso	$R-NO$	Nitrosoalkane

Secondary suffix is used to indicate the functional group in the organic compounds.

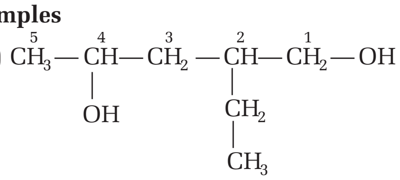
Family of compound	Suffix	IUPAC name of the family
1. Alcohols ($-OH$)	—ol	Alkanol
2. Amines ($-NH_2$)	—amine	Alkanamine
3. Aldehydes ($-CHO$)	—al	Alkanal
4. Ketones ($>C=O$)	— one	Alkanone
5. Carboxylic acids ($-COOH$)	— oic acid	Alkanoic acid
6. Amides ($-CONH_2$)	—amide	Alkanamide
7. Acid halides ($-COX$)	—oyl halide	Alkanoyl halide
8. Esters ($-COOR$)	—oate	Alkyl alkanoate
9. Nitriles ($-C\equiv N$)	— nitrile	Alkane nitrile

The order of decreasing priority for some functional groups are as follows:

$-COOH, -SO_3H, -COOR, -COCl, -CONH_2,$

$-CN, -CHO, >C=O, -OH, -NH_2, >C=C<, -C\equiv C-.$

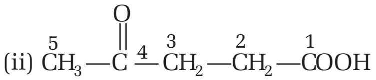
Examples

(i) 

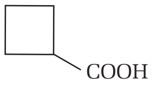
$$\overset{5}{C}H_3-\underset{\underset{OH}{|}}{\overset{4}{C}H}-\overset{3}{C}H_2-\underset{\underset{\underset{\underset{CH_3}{|}}{CH_2}}{|}}{\overset{2}{C}H}-\overset{1}{C}H_2-OH$$

2-ethylpentan-1, 4-diol (IUPAC)

(Maximum number of FG should be present in longest carbon chain).

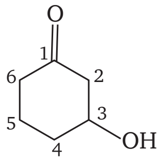
(ii) 
$\overset{5}{C}H_3-\overset{\overset{O}{\|}}{C}\overset{4}{-}\overset{3}{C}H_2-\overset{2}{C}H_2-\overset{1}{C}OOH$

4-ketopentanoic acid (IUPAC)

(iii) 

Cyclobutane carboxylic acid (IUPAC)

(Carbon containing FG is not considered with cyclic ring).

(iv) 

3-hydroxy cyclohexanone (IUPAC)

Isomerism

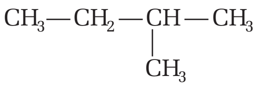
The compound having same molecular formula but differ in properties are known as isomers and the phenomenon is called isomerism. There are of two types:

Structural Isomerism

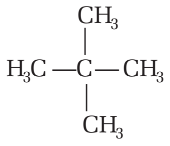
The compounds possess same molecular formula but different structures. It is of following types :

(i) When two or more compounds have similar molecular formula but different carbon skeletons, then these are referred as chain isomers and phenomenon is termed as **chain isomerism**, e.g. C_5H_{12}.

$CH_3-CH_2-CH_2-CH_2-CH_3$
n–pentane


$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$,

iso-pentane

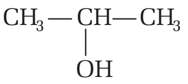

$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

neo-pentane

(ii) When two or more compounds have same molecular formula but different position of functional groups or substituents then these are known as position isomers and phenomenon is called **position isomerism**.

e.g. C_3H_8O

$CH_3-CH_2-CH_2-OH$,
Propan-1-ol

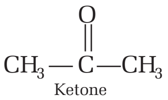

$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$

Propan-2-ol

(iii) When two or more compounds have the same molecular formula but different functional group then these are termed as functional isomers and phenomenon is called functional isomerism.

e.g. C_3H_6O represents an aldehyde and a ketone as:

CH_3-CH_2-CHO,
Aldehyde

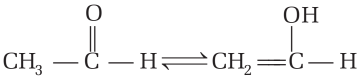

$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

Ketone

(iv) **Metamerism** arises due to different alkyl groups on either side of the same functional group in the molecule.

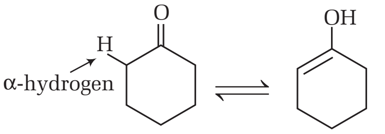
e.g. $C_4H_{10}O, CH_3-\ddot{\underset{\cdot\cdot}{O}}-C_3H_7, C_2H_5-\ddot{\underset{\cdot\cdot}{O}}-C_2H_5$

NOTE Tautomerism is a special type of functional isomerism arises in carbonyl compounds containing α–H (H-attached to the carbon atom adjacent to functional group) atom. e.g.

(a) 
$CH_3-\overset{\overset{O}{\|}}{C}-H \rightleftharpoons CH_2=\overset{\overset{OH}{|}}{C}-H$

Keto form
(Acetaldehyde)

Enol form

(b) 

Cyclohexanone
(Keto form)

Enol form

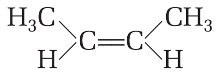
Stereoisomerism

The compounds possess same molecular formula but different spatial arrangement of atoms or groups

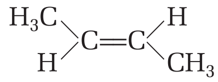
Stereoisomerism is of two types:

(i) The isomers having same molecular formula but different spatial arrangement of atoms about the double bond are known as geometrical isomers and this phenomenon is called **geometrical isomerism**.

e.g.

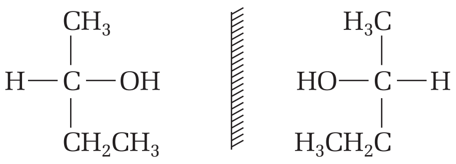


cis-2-butene



trans-2-butene

(ii) Compounds having similar physical and chemical properties but differ only in behaviour towards plane polarised light are called **optical isomers** and property is known as optical isomerism, e.g.



2-butene

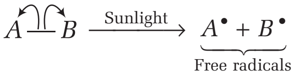
Mirror

NOTE Structures obtained due to free rotation about $C\overset{\sigma}{-}C$ bond are called conformers and phenomenon is called **conformation**. Conformers are not considered as isomers because their separation is not possible.

Fission of a Covalent Bond

The organic reactions begin with the breakage of covalent bond, this breakage is of two types:

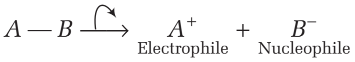
(i) In **homolytic fission**, one of the electrons of the shared pair in a covalent bond goes with each of the bonded atoms. Generally, homolytic fission takes place in non-polar covalent molecules in the presence of sunlight or high temperature.



$$A—B \xrightarrow{\text{Sunlight}} \underbrace{A^\bullet + B^\bullet}_{\text{Free radicals}}$$

e.g. $Cl_2 \xrightarrow{\text{Sunlight}} 2\,Cl^\bullet$

(ii) In **heterolytic fission**, the bond breaks in such a way that the shared pair of electrons goes with one of the fragments, arising positive and negative charges.



$$A—B \longrightarrow \underset{\text{Electrophile}}{A^+} + \underset{\text{Nucleophile}}{B^-}$$

e.g. $H—Cl \longrightarrow H^+ + Cl^-$

Heterolytic fission generally takes place in polar covalent molecules but in non-polar molecules, it takes place in the presence of catalyst like $AlCl_3$ (anhyd.), $FeCl_3$ (anhyd.) etc.

Electrophiles (Electron Deficient Species)

- It is an electron deficient species that attack at nucleophilic centre which is the electron rich centre of the substrate.
- All non-metal cations and metal cations which have vacant *d*-orbitals are electrophiles.
  e.g. Cl^+, NO_2^+, CH_3CO^+, etc.
- Lewis acids (incomplete octet), e.g. BF_3, $ZnCl_2$ (anhydrous), $FeCl_3$ (anhydrous), $AlCl_3$ (anhydrous), $:CH_2$ etc., are electrophiles.
- Non-metal acidic oxides, e.g. CO_2, SO_2, etc., are electrophiles.

Nucleophiles (Electron Rich Species)

- It is an electron rich species that attacks an electrophilic centre of the substrate.
- All anions, e.g. Cl^-, NH_2^-, OH^-, etc.
- Lewis bases, e.g. $:NH_3$, $H_2\underset{\cdot\cdot}{\ddot{O}}$, $R—\underset{\cdot\cdot}{\ddot{O}}—R$, $—\underset{\cdot\cdot}{\ddot{O}}H$, etc.
- Benzene, alkenes, etc.
- Nucleophilicity order is $H^- > CH_3^- > NH_2^- > RO^- > OH^-$
- Generally, strong base is strong nucleophile.

Reaction Intermediates

These are the speciies formed in the intermediate steps of a section.

These species are generally short lived and highly reactive and are called **reactive intermediates**, e.g. free radicals, carbocations, carbanions, carbenes, nitrenes, etc.

(i) **Free radicals** are highly reactive, neutral and electron deficient species. The order of the stability of free radicals is

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

(ii) Carbon containing chemical species bearing a positive charge on carbon and carry **6 electrons** in its valence shell are called **carbocations**.

Carbocations are electron deficient species, seeks electrons during a reaction, i.e. it acts as an electrophile.

The carbocations follow the following order of stability

$$(C_6H_5)_3C^+ > (C_6H_5)_2\overset{+}{C}H > C_6H_5\overset{+}{C}H_2\ (CH_3)_3C^+$$
$$> \text{allyl} > 2° > 1° > \overset{+}{C}_6H_5 > \text{vinyl}$$

Less stable carbocations (1°/2°) can be converted into more stable carbocations (2°/3°) through either 1, 2-hydride shift or 1, 2-methyl shift.

(iii) Carbon containing chemical species bearing a negative charge on carbon atom and carrying **8 electrons** in its **valence shell** is called **carbanion**. Carbanions acts as nucleophile as these are electron rich species.

The order of stability of carbanions is as:

$$(C_6H_5)_3C^- > (C_6H_5)_2\bar{C}H > C_6H_5\bar{C}H_2 > \text{allyl} > \bar{C}H_3$$
$$(1° > 2° > 3° \text{ carbanions})$$

(iv) The neutral divalent carbon species in which two non-bonding electrons are present along with 2 bonding pairs are called **carbenes**. Carbenes act as electrophiles as these are electron deficient species.

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. The factors that results in electronic displacement in a covalent bond are discussed below:

1. Inductive Effect

Inductive effect is just like shifting of shared pair of electrons in polar covalent molecules. If shared pair is more shifted towards the more electronegative atom. The less electronegative atom acquire slight positive charge and more electronegative atom acquire partial negative charge.

e.g. $\overset{+\delta}{CH_3} \rightarrow \overset{-\delta}{Cl}$

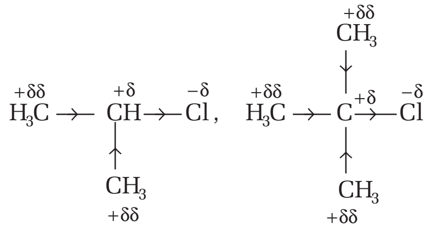
- If an atom or group withdraws electrons away from carbon, this is known as–*I*-effect, while if an atom or a group donates electrons to a carbon, this is known as **+*I* effect**.
- This is a permanent effect and propagates through carbon chain,

  e.g. $\overset{+\delta\delta}{CH_3} \rightarrow \overset{+\delta}{CH_2} \rightarrow \overset{-\delta}{Cl}$, $\overset{+\delta\delta\delta}{CH_3} \rightarrow \overset{+\delta\delta}{CH_2} \rightarrow \overset{+\delta}{CH_2} \rightarrow \overset{-\delta}{Cl}$

  1° alkyl halide

  Here, Cl has –*I*-effect and alkyl group has +*I* effect.
- Greater the number of C-atoms in alkyl groups, greater would be its +*I* effect.

e.g.



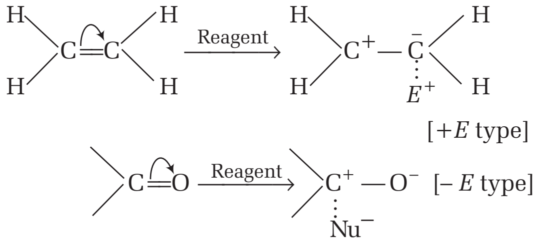
$\overset{+\delta\delta}{H_3C} \rightarrow \underset{\overset{\uparrow}{\underset{+\delta\delta}{CH_3}}}{\overset{+\delta}{CH}} \rightarrow \overset{-\delta}{Cl}$, $\overset{+\delta\delta}{H_3C} \rightarrow \overset{\overset{+\delta\delta}{CH_3}}{\underset{\underset{+\delta\delta}{CH_3}}{\overset{+\delta}{C}}} \rightarrow \overset{-\delta}{Cl}$

2° alkyl halide 3° alkyl halide

- $+I$ effect of alkyl groups enhances $-I$ effect of the halogen atoms. 3°-alkyl halide will be most reactive due to more $+I$ effect.
- **Electron Donating Groups** (EDG) Alkyl groups like $-CH_3$, $-C_2H_5$ etc., produce $+I$ effect.
- **Electron Withdrawing Groups** (EWG) such as $-NO_2$, $-CN$, $-COOH$, $-COOR$, $-OC_6H_5$ etc., produce $-I$-effect.

2. Electromeric Effect

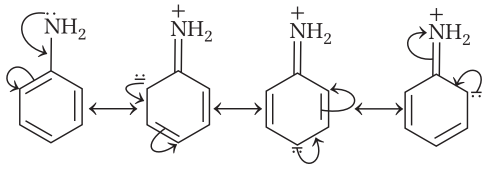
- It is defined as the polarity produced in a multiple bonded compound as a reagent approaches it.
- In the presence of attacking reagent, the two π-electrons are completely transferred to any of the one atom.
- This effect is temporary.



3. Resonance Effect

- It involves delocalisation of π-electrons. This effect may be of $+R$ type or $-R$ type. Electron donating group with respect to conjugate system shows $+R$ effect. e.g. halogens, $-OH$, $-OR$, $-OCOR$, $-NH_2$, $-NHCOR$ etc.

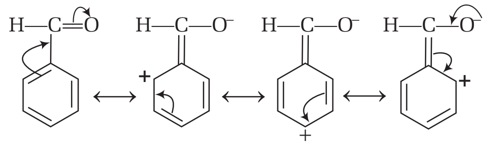
  This effect in aniline is shown as :



- Electron donating groups producing $+R$ effect are *ortho* and *para* directing. They activate the benzene ring towards the electrophilic substitution reactions except halogens. Halogens slightly deactivate the benzene ring towards the electrophilic substitution reaction. More the EDG more is the basic nature.
- Electron withdrawing groups with respect to conjugate system shows $-R$ effect.

  e.g. $-COOH$, $-COOR$, $-CHO$, $-CN$, $-NO_2$ etc.

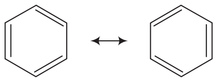
The electron displacenent in benzaldehyde is shown below:



- Electron withdrawing groups (EWG) producing $-R$ effect are *meta* directing. They deactivate the benzene ring towards the electrophilic substitution reaction. More the EWG, more is the acidic nature.
- 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,



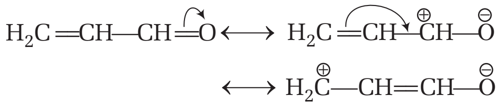
NOTE Resonance energy :

(i) Number of π-bonds ∝ contributing structures ∝ resonance energy ∝ stability

(ii) In benzene, resonance energy is 36 kcal/mol.

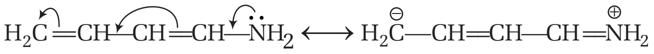
4. Mesomeric Effect

- It is defined as the 'polarity' produced in a molecule due to conjugation. It is a permanent effect and categorised to $+M$ and $-M$ just like inductive effect. e.g.



$$H_2C{=}CH{-}CH{=}O \longleftrightarrow H_2C{=}CH{-}\overset{\oplus}{C}H{-}\overset{\ominus}{O} \longleftrightarrow H_2\overset{\oplus}{C}{-}CH{=}CH{-}\overset{\ominus}{O}$$

- A group or atom is said to show $+M$-effect when the direction of electron displacement is away from it. e.g.

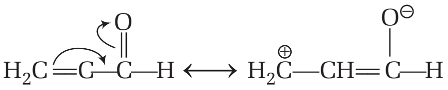


$$H_2C{=}CH{-}CH{=}CH{-}\ddot{N}H_2 \longleftrightarrow H_2\overset{\ominus}{C}{-}CH{=}CH{-}CH{=}\overset{\oplus}{N}H_2$$

Decreasing order of $+M$ power of group are.

$O^- > NH_2 > OH > OR > NHAc >$ alkyl groups $>$ $(CH_3 > 1° > 2° > 3°) >$ phenyl groups

- A group or atom is said to have $-M$ effect when the direction of electron displacement is towards it. e.g.



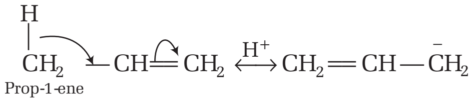
$$H_2C{=}C{-}\overset{\overset{O}{\|}}{C}{-}H \longleftrightarrow H_2\overset{\oplus}{C}{-}CH{=}\overset{\overset{O^{\ominus}}{|}}{C}{-}H$$

Decreasing order of $-M$ power of group are

$\overset{+}{N}H_3 > NO_2 > CX_3 > CN > SO_3H >$ $CHO > COOH > COCl > COOR > CONH_2$

5. Hyperconjugation

It involves delocalisation of σ-electrons of a C—H bond of an alkyl group attached directly to an atom of unsaturated system or to an atom with an unshared p-orbital. e.g.



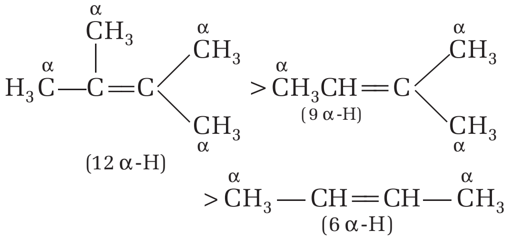
Conditions for hyperconjugation are as follows:

(i) Compounds should have at least one sp^2 hybrid carbon of either alkene, alkyl carbocation or alkyl free radical.

(ii) α-carbon with respect to sp^2 hybrid carbon should have at least one hydrogen. More the number of H—C bonds attached to the unsaturated system, more stable will be the alkene.

The following are the important applications of hyperconjugation.

(i) **Stability of Alkenes** More the number of α-hydrogen atoms, more stable is the alkene.



(ii) **Stability of Carbocation** Greater the number of alkyl groups attached to a positively charged carbon atom, greater is the stability.

$$(CH_3)_3C^+ > (CH_3)_2\overset{+}{C}H > CH_3-\overset{+}{C}H_2 > \overset{+}{C}H_3$$

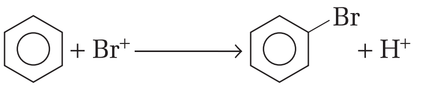
Types of Organic Reactions

Based on the nature of reactants, products and byproducts as well as the mechanism, organic reactions are classified into four major categories, substitution, addition, elimination and rearrangement reactions.

- **Substitution reaction** is a type of reaction in which one atom, or a group of atoms, from the reagent replaces or substitutes itself for one atom or a group of atoms on the substrate.
  (i) In a nucleophilic substitution, the reagent is a nucleophile (base).

$$C_2H_5OH + \underset{\text{Nucleophile}}{Cl^-} \longrightarrow \underset{\text{Nucleophilic substitution}}{C_2H_5Cl + OH^-}$$

  (ii) In an electrophilic substitution, the reagent is an electrophile (acid). e.g.



Electrophile Electrophilic substitution

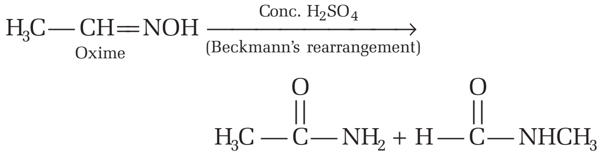
- **Addition reaction** is a type of reaction in which atoms or groups of atoms from the reagent add to the substrate generally without loosing any atoms from the substrate.

  e.g. $CH_2=CH_2 + HBr \longrightarrow CH_3CH_2Br$

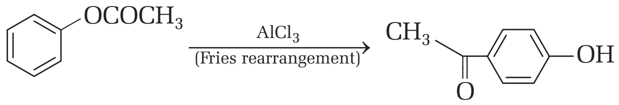
- **Elimination reaction** removes two atoms or two groups of atoms from the substrate, giving the product a multiple bond or, in some cases, causing it to form a ring.

  e.g. $(CH_3)_3COH \xrightarrow[\text{(ii) Heat}]{\text{(i) }H_3O^+} (CH_3)_2C=CH_2 + H_2O$

- **Rearrangement reaction** usually occur in the presence of a catalyst or under special thermodynamic conditions. e.g.



$$\underset{\text{Oxime}}{H_3C-CH=NOH} \xrightarrow[\text{(Beckmann's rearrangement)}]{\text{Conc. }H_2SO_4} H_3C-\overset{O}{\overset{\|}{C}}-NH_2 + H-\overset{O}{\overset{\|}{C}}-NHCH_3$$



Methods of Purification of Organic Compounds

The common techniques used for the purification are as follows:

- **Sublimation** process is employed for those solid substances directly changes into vapour phase. It is used to separate sublimable compounds from non-sublimable compounds.
- **Crystallisation** is one of the most commonly used technique for the purification of solid organic compounds. It is based on the difference in the solubilities of the compound and the impurities in a suitable solvent.
- **Distillation** is used to separate
  (i) volatile liquids from non-volatile impurities.
  (ii) the liquids having sufficient difference in their boiling points. Liquids having different boiling points vaporise at different temperatures (fractional distillation)

It involves the following methods:

(i) **Distillation under reduced pressure** This method is used to purify liquids having very high boiling points and those, which decompose at or below their boiling points. Glycerol can be separated from spent lye in soap industry by this method.

(ii) **Steam distillation** This method is used when substances are steam volatile and immiscible with water.

- **Differential extraction** is used to separate an organic compound which is present in aqueous medium, it is separated by shaking it with an organic solvent, in which it is more soluble than in water.
  The organic solvent and the aqueous solution should be immiscible with each other so that they form two distinct layers which can be separated by separating funnel.
- **Chromatography** is an important technique extensively used to separate mixtures into their components.
  (i) In this technique, the mixture of substances is applied on to a stationary phase (solid or liquid), a pure solvent. A mixture of solvents or a gas is allowed to move slowly over the stationary phase.
  (ii) Based on the principle involved, chromatography is classified into different categories.
    (a) Adsorption chromatography
    (b) Partition chromatography.

(iii) Following are two main types of chromatographic techniques based on the principle of differential adsorption
   (a) Column chromatography
   (b) Thin layer chromatography

Qualitative Analysis

This method involves the conversion of covalently bonded nitrogen, sulphur or halogens present in the organic compounds to corresponding water-soluble ions, in the form of sodium salts.

Detection of Carbon and Hydrogen

Carbon and hydrogen present in organic compound are detected by heating with CuO such that carbon changes into CO_2 (tested with lime water which develops turbidity) and hydrogen to H_2O (tested with anhydrous copper sulphate which turns blue).

Detection of Other Elements

Nitrogen, sulphur, halogens and phosphorus present in an organic compound are detected by Lassaigne's test.

$$\mathrm{Na + C + N \xrightarrow{\Delta} NaCN} \qquad \mathrm{2Na + S \xrightarrow{\Delta} Na_2S}$$

$$\mathrm{Na} + X \xrightarrow{\Delta} \mathrm{Na}\,X, \qquad (X = \mathrm{Cl, Br, I})$$

1. Test for Nitrogen

$$\mathrm{6CN^- + Fe^{2+} \longrightarrow [Fe(CN)_6]^{4-}}$$

$$\mathrm{3[Fe(CN)_6]^{4-} + 4Fe^{3+} \xrightarrow{x\,H_2O} \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3 \cdot xH_2O}}$$

Lassaigne's test is given by compounds carrying nitrogen and carbon. So, hydrazine (NH_2-NH_2) and hydroxyl amine (NH_2OH) do not give this test.

2. Test for Sulphur

(i) $\mathrm{S^{2-} + Pb^{2+} \longrightarrow \underset{\text{Black}}{PbS}}$

(ii) $\mathrm{Na + C + N + S \longrightarrow NaSCN}$

$\mathrm{Fe^{3+} + SCN^- \longrightarrow \underset{\text{Blood red}}{[Fe(SCN)]^{2+}}}$

3. Test for Halogens

The sodium fusion extract is acidified with nitric acid and then treated with silver nitrate.

$$X^- + \mathrm{Ag^+} \longrightarrow \mathrm{Ag}X$$

X represents a halogen — Cl, Br or I. AgCl-white ppt. AgBr-Dull yellow ppt. AgI-bright yellow ppt.

4. Test for Phosphorus

(i) The compound is heated with an oxidising agent (like sodium peroxide), the phosphorus present in the compound is oxidised to phosphate.

(ii) The solution is boiled with nitric acid and then treated with ammonium molybdate.

(iii) A yellow colouration or precipitate indicates the presence of phosphorus.

Quantitative Analysis

The quantitative analysis is carried out to determine the proportions in which different elements are present in an organic compound.

Estimation of Carbon and Hydrogen

The carbon and hydrogen are estimated by Leibig method.

$$\text{Percentage of carbon} = \frac{12 \times \text{wt. of } CO_2}{44 \times \text{wt. of organic compound}} \times 100$$

$$\text{Percentage of hydrogen} = \frac{2}{18} \times \frac{\text{wt. of } H_2O}{\text{wt. of organic compound}} \times 100$$

Estimation of Nitrogen

Nitrogen can be estimated by either of the following two methods:

1. Duma's Method

Let the mass of organic compound $= m$ g, Volume of nitrogen collected $= V_1$ mL, Room temperature $= T_1$ K

$$\text{Volume of nitrogen at STP} = \frac{p_1V_1 \times 273}{760 \times T_1} \quad (\text{Let it be } V \text{ mL})$$

where,
p_1 and V_1 are the pressure and volume of nitrogen.
p_1 = atmospheric pressure – aqueous tension

22400 mL N_2 at STP weighs 28 g of N_2

$$V \text{ mL } N_2 \text{ at STP weighs } = \frac{28 \times V}{22400} \text{ g of } N_2$$

$$\text{Percentage of nitrogen } = \frac{28 \times V \times 100}{22400 \times m}$$

2. Kjeldahl's Method

Let the mass of organic compound taken $= w$ g, Volume of H_2SO_4 of molarity M taken $= V$ mL and

V_1 mL of NaOH of molarity M

$$\text{Percentage of N} = \frac{1.4 \times M \times 2\,(V - V_1/2)}{w}$$

Estimation of Halogens and Sulphur

- Estimation of halogens and sulphur is done by **Carius method** as follows :

  Let, the mass of organic compound $= w$ g

  Mass of AgX formed $= w_1$ g
- Percentage of halogen

$$= \frac{\text{atomic mass of } X \times \text{wt. of Ag}X}{\text{molecular mass of Ag}X \times w} \times 100$$

- Percentage of sulphur $= \dfrac{32 \times \text{mass of } BaSO_4 \times 100}{233 \times \text{mass of organic compound}}$
- Estimation of halogen and sulphur is carried out as follows :

  Percentage of phosphorus

$$= \frac{62 \times \text{mass of } Mg_2P_2O_7}{222 \times \text{wt. of organic compound}} \times 100$$

Or Percentage of phosphorus

$$= \frac{31 \times \text{mass of } (NH_4)_3PO_4 \cdot 12MoO_3}{1877 \times \text{wt. of organic compound}} \times 100$$

DAY PRACTICE SESSION 1

FOUNDATION QUESTIONS EXERCISE

1 A compound with molecular formula C_4H_4O has all the four carbon atoms and the oxygen atom in the ring. It also has two double bonds. The compound is

(a) monocyclic and aromatic
(b) homocyclic and non-aromatic
(c) heterocyclic and aromatic
(d) heterocyclic and non-aromatic

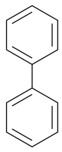
2 Electronegativity of carbon atoms depends upon their state of hybridisation. In which of the following compounds, the carbon marked with a steris *k* is most electronegative?

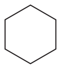
(a) $CH_3—CH_2—{}^*CH_2—CH_3$
(b) $CH_3—{}^*CH=CH—CH_3$
(c) $CH_3—CH_2—C\equiv{}^*CH$
(d) $CH_3—CH_2—CH={}^*CH_2$

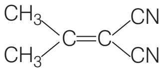
3 Which of the following compounds contain all the carbon atoms in the same hybridisation state?

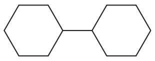
(a) $H—C\equiv C—C\equiv C—H$
(b) $CH_3—C\equiv C—CH_3$
(c) $CH_2=C=CH_2$
(d) $CH_2=CH—C\equiv CH$

4 In which of the following molecules, all atoms are coplanar? **→ NEET 2016 Phase II**

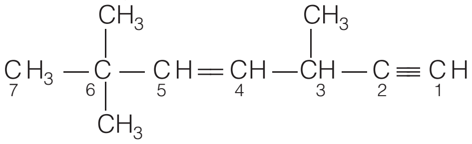
(a)


(b)


(c)


(d)


5 The state of hybridisation of C_2, C_3, C_5 and C_6 of the hydrocarbon,



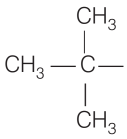
$$\underset{7}{CH_3}-\underset{6}{\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}}-\underset{5}{CH}=\underset{4}{CH}-\underset{3}{\overset{\overset{CH_3}{|}}{CH}}-\underset{2}{C}\equiv\underset{1}{CH}$$

is in the following sequence **→ CBSE-AIPMT 2009**

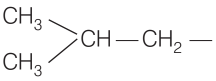
(a) sp, sp^3, sp^2 and sp^3
(b) sp^3, sp^2, sp^2 and sp
(c) sp, sp^2, sp^2 and sp^3
(d) sp, sp^2, sp^3 and sp^2

6 The structure of *iso*-butyl group in organic compound is **→ NEET 2013**

(a) $CH_3—CH—CH_2—CH_3$
(b) $CH_3—CH_2—CH_2—CH_2—$

(c)


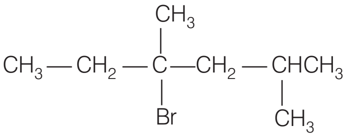
$$CH_3—\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}—$$

(d)


$$(CH_3)_2CH—CH_2—$$

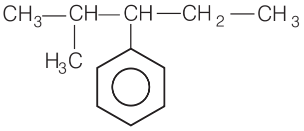
7 Which nomenclature is not according to IUPAC system? **→ CBSE-AIPMT 2012**

(a) $Br—CH_2—CH=CH_2$
1-bromoprop-2-ene

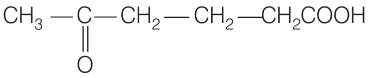
(b)


$$CH_3—CH_2—\overset{\overset{CH_3}{|}}{\underset{\underset{Br}{|}}{C}}—CH_2—\underset{\underset{CH_3}{|}}{CH}CH_3$$

4-bromo-2, 4-dimethylhexane

(c)


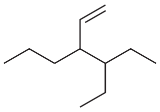
2-methyl-3-phenylpentane

(d)


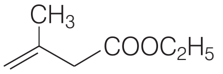
$$CH_3—\underset{\underset{O}{\|}}{C}—CH_2—CH_2—CH_2COOH$$

5-oxohexanoic acid

8 The correct IUPAC name of the compound is

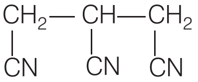


(a) 3-ethyl-4-ethenylheptane
(b) 3-ethyl-4-propylhex-5-ene
(c) 3-(1-ethyl propyl) hex-1-ene
(d) 4-ethyl-3-propylhex-1-ene

9 The IUPAC name of


is

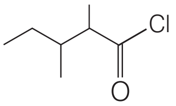
(a) ethyl acetylate
(b) ethyl methyl butenoate
(c) ethyl acetoethanoate
(d) ethyl (3-methyl) but-3-enoate

10 The IUPAC name of


$$\underset{\underset{CN}{|}}{CH_2}—\underset{\underset{CN}{|}}{CH}—\underset{\underset{CN}{|}}{CH_2}$$

is

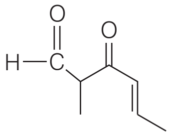
(a) isobutanenitrile
(b) 3-cyano pentan-1, 5-dinitrile
(c) propan-1, 2, 3-tricarbonitrile
(d) 2, 2-bis (cyanomethyl) ethane nitrile

11 The IUPAC name of


is

(a) 3, 4-dimethyl pentanoyl chloride
(b) 1-chloro-1-oxo-2, 3-dimethyl pentane
(c) 2-ethyl-3-methyl butanoyl chloride
(d) 2, 3-dimethyl pentanoyl chloride

12 The IUPAC name of the compound **➞ NEET 2017**



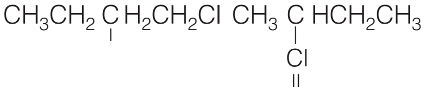
is ....

(a) 3-keto-2-methylhex-4-enal
(b) 5-formylhex-2-en-3-one
(c) 5-methyl-4-oxohex-2-en-5-al
(d) 3-keto-2-methylhex-5-enal

13 The number of isomer for the compound with the molecular formula $C_2BrClFI$ is

(a) 3 (b) 4
(c) 5 (d) 6

14 Consider the following structure

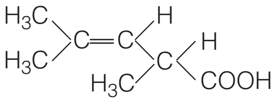


$CH_3CH_2\underset{\text{I}}{C}H_2CH_2Cl \quad CH_3\underset{\underset{\text{II}}{Cl}}{\underset{|}{C}}HCH_2CH_3$

Type of isomerism shown by I and II is

(a) chain (b) position
(c) Both (a) and (b) (d) None of the above

15 The following compound can exhibit

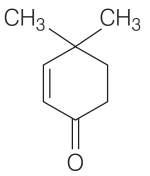


(a) geometrical isomerism
(b) geometrical and optical isomerism
(c) optical isomerism
(d) tautomerism

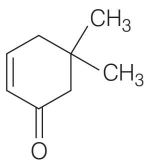
16 Which of the following acids does not exhibit optical isomerism? **➞ CBSE-AIPMT 2012**

(a) Maleic acid (b) α-amino acids
(c) Lactic acid (d) Tartaric acid

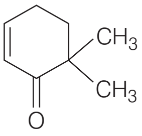
17 Given,



(I)



(II)



(III)

Which of the following can exhibit tautomerism?

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

18 Choose the correct statement?

(a) Tautomeric structures can be isolated easily
(b) Stereoisomers have different molecular structure but same configurations
(c) Melting point of *cis*-isomer is greater than melting point of *trans*-isomer
(d) Solubility of *trans*-isomer is lower than *cis*-isomer

19 Which of the following compounds will exhibit *cis-trans* (geometrical) isomerism? **➞ CBSE-AIPMT 2009**

(a) 2-butene (b) Butanol (c) 2-butyne (d) 2-butenol

20 When CH_3Cl undergoes homolytic bond-fission

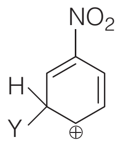
(a) carbon undergoes a geometric change from tetrahedral to planar
(b) hybridisation changes from sp^3 to sp^2
(c) Both of these takes place
(d) None of the above takes place

21 Correct the increasing order of acidity is as

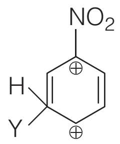
(a) H_2O, C_2H_2, H_2CO_3, phenol
(b) C_2H_2, H_2O, H_2CO_3, phenol
(c) phenol, C_2H_2, H_2CO_3, H_2O
(d) C_2H_2, H_2O, phenol and H_2CO_3

22 Which of the following carbocations is expected to be most stable? **➞ NEET 2018**

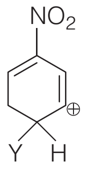
(a)



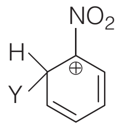
(b)



(c)



(d)



23 Arrange the following carbocations in order of stability.

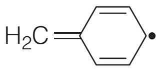
Benzyl	Allyl	Methyl	Vinyl
I	II	III	IV

Choose the correct option.

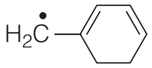
(a) IV > III > II > I (b) I > II > III > IV
(c) II > I > IV > III (d) III > I > II > IV

24 Which of the following is incorrect representation?

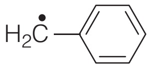
(a)



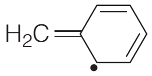
(b)



(c)

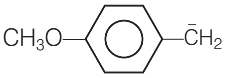


(d)

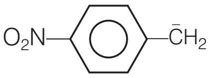


25 Consider the following carbanions :

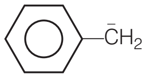
1.



2.



3.



Correct order of stability is

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

26 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 to their decreasing stability

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

27 Which of the following is correct with respect to $-I$ effect of the substituents? (R = alkyl) **➞ NEET 2018**

(a) $—NH_2 > —OR > —F$ (b) $—NR_2 < —OR < —F$
(c) $—NH_2 < —OR < —F$ (d) $—NH_2 > —OR > —F$

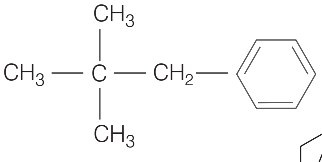
28 In which of the following, the substituent does not event its resonance effect?

(a) $C_6H_5NH_2$ (b) $C_6H_5\overset{+}{N}H_3$ (c) C_6H_5OH (d) C_6H_5Cl

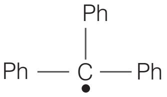
29 Hyperconjugation involves delocalisation

(a) electrons of carbon-hydrogen bond of an alkyl group directly linked to an atom of unsaturated system
(b) electrons of carbon-hydrogen bond of alkyl group directly attached to the negatively charged carbon atom
(c) π-electrons of carbon-carbon bond
(d) one pair of electrons

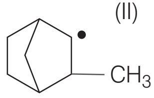
30 Consider the following compounds



(I)



(II)



(III)

Hyperconjugation occurs in **➞ CBSE-AIPMT 2015**

(a) Only I (b) Only II (c) Only III (d) Both I and III

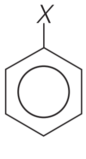
31 The correct order of decreasing acidic strength of trichloroacetic acid (A), trifluoroacetic acid (B), acetic acid (C) and formic acid (D) is **➞ CBSC-AIPMT 2012**

(a) $B>A>D>C$ (b) $B>D>C>A$ (c) $A>B>C>D$ (d) $A>C>B>D$

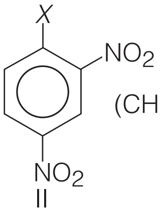
32 The correct order of reactivity towards the electrophilic substitution of the compounds aniline (I), benzene (II) and nitrobenzene (III) is **➞ CBSE-AIPMT 2003**

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

33 The correct order of increasing reactivity of $C—X$ bond towards nucleophile in the following compounds is **➞ CBSE-AIPMT 2010**



I



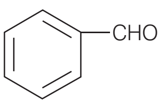
II

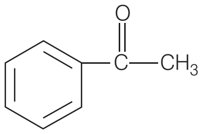
$(CH_3)_3C—X$ III

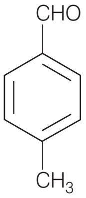
$(CH)_2CH—X$ IV

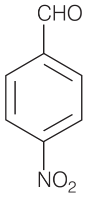
(a) I< II< IV< III (b) II< III< I< IV
(c) IV< III< I< II (d) III< II< I< IV

34 Which one is most reactive towards nucleophilic addition reaction? **➞ CBSE-AIPMT 2014**

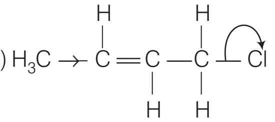
(a)


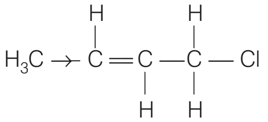
(b)


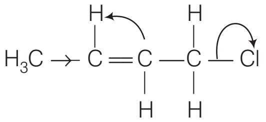
(c)


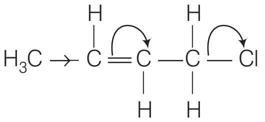
(d)


35 Which of the following is the most correct electron displacement for a nucleophilic reaction to take place? **➞ CBSE-AIPMT 2015**

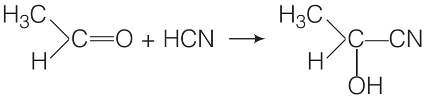
(a)

$H_3C \rightarrow \overset{H}{C}=\underset{H}{C}-\overset{H}{\underset{H}{C}}-Cl$

(b)

$H_3C \rightarrow \overset{H}{C}=\underset{H}{C}-\overset{H}{\underset{H}{C}}-Cl$

(c)

$H_3C \rightarrow \overset{H}{C}=\underset{H}{C}-\overset{H}{\underset{H}{C}}-Cl$

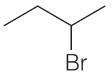
(d)

$H_3C \rightarrow \overset{H}{C}=\underset{H}{C}-\overset{H}{\underset{H}{C}}-Cl$

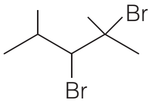
36 Select the correct statement(s) for the following reaction.

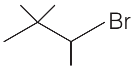


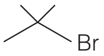
(a) Addition takes place at the carbonyl compound and thus, addition is regioselective
(b) A chiral carbon is produced and recemic mixture is formed
(c) Geometry of the reactant is different from that of the product
(d) All of the above statements are true

37 Which of the following is alkyl halides would be most likely to give a rearranged product under S_N1 conditions?

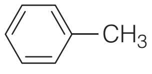
(a)


(b)


(c)


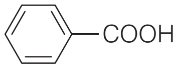
(d)


38 Increasing order of the following for electrophilic substitution reaction is



(I)

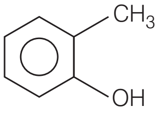
(II)

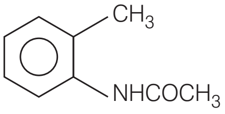


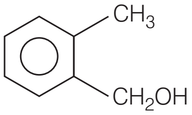
(III)

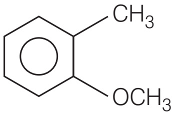
(a) I<II<III
(b) III<II<I
(c) II<III<I
(d) I<III<II

39 Which one of the following is the most reactive towards electrophilic reagent? **➞ CBSE-AIPMT 2011**

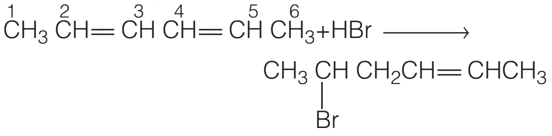
(a)


(b)


(c)


(d)


40 In the following reaction,



$$\overset{1}{CH_3}\,\overset{2}{CH}=\overset{3}{CH}\,\overset{4}{CH}=\overset{5}{CH}\,\overset{6}{CH_3}+HBr \longrightarrow CH_3\,\underset{\underset{Br}{|}}{CH}\,CH_2CH=CHCH_3$$

addition is called

(a) 2, 3-addition (b) 1, 2-addition
(c) 1, 4-addition (d) 4, 5-addition

41 Dehydrohalogenation of an alkyl halide is

(a) nucleophilic substitution reaction
(b) elimination reaction
(c) rearrangement reaction
(d) Both (a) and (b)

42 Impure naphthalene is purified by

(a) fractional crystallisation (b) fractional distillation
(c) solvent extraction (d) sublimation

43 Fractional distillation is useful in the distillation of

(a) petroleum (b) coal tar
(c) crude alcohol (d) All of these

44 Impure glycerine can be purified by

(a) steam distillation (b) simple distillation
(c) vacuum distillation (d) extraction with a solvent

45 The sodium extract of an organic compound on acidification with acetic acid and addition of lead acetate solution gives a black precipitate. The organic compound contains

(a) nitrogen (b) halogen (c) sulphur (d) phosphorus

46 In an organic compound, phosphorus is estimated as

(a) $Mg_2P_2O_7$ (b) $Mg_3(PO_4)_2$
(c) H_3PO_4 (d) P_2O_5

47 In the Kjeldahl's for estimation of nitrogen present in a soil sample, ammonia evolved from 0.75 g of sample neutralised 10 mL of 1 M H_2SO_4. The percentage of nitrogen in the soil is **➞ CBSE-AIPMT 2014**

(a) 37.33 (b) 45.33
(c) 35.53 (d) 43.33

48 In Duma's method of estimation of nitrogen, 0.35 g of an organic compound gave 55 mL of nitrogen collected at 300 K temperature and 715 mm pressure. The percentage composition of nitrogen in the compound would be **➞ CBSE-AIPMT 2011**

(Aqueous tension at 300 K = 15 mm)

(a) 16.45 (b) 17.45
(c) 14.45 (d) 15.45

Direction (Q. Nos. 49-50) *Each of these questions contains two statements : Assertion and Reason. Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes* (a), (b), (c) and (d) *given below.*

(a) Assertion is true, Reason is true; Reason is the correct explanation for Assertion
(b) Assertion is true, Reason is true; Reason is not the correct explanation for Assertion
(c) Assertion is true, Reason is false
(d) Assertion is false, Reason is true

49 **Assertion** In the E2 elimination, β-H and leaving group should be antiperiplanar.

Reason In the E2 elimination, base always abstracts unhindered β-H.

50 **Assertion** A mixture of plant pigments can be separated by chromatography.

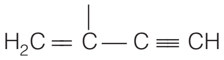
Reason Chromatography is used for the separation of coloured substances into individual components.

DAY PRACTICE SESSION 2

PROGRESSIVE QUESTIONS EXERCISE

1 Which of the following represent the given mode of hybridisation of $sp^2 - sp^2 - sp - sp$ from left to right?

(a) $H_2C=CH-C\equiv N$

(b)


$H_2C=\overset{\overset{H}{|}}{C}-C\equiv CH$

(c) $H_2C=C=C=CH_2$

(d)


2 What is the decreasing order of strength of the bases?

OH^-, NH_2^-, $H-C\equiv C^-$ and $CH_3-CH_2^-$

(a) $CH_3-CH_2^- > NH_2^- > H-C\equiv C^- > OH^-$
(b) $H-C\equiv C^- > CH_3-CH_2^- > NH_2^- > OH^-$
(c) $OH^- > NH_2^- > H-C\equiv C^- > CH_3-CH_2^-$
(d) $NH_2^- > H-C\equiv C^- > OH^- > CH_3-CH_2^-$

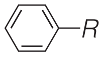
3 The decreasing order of the stability of the ions

$\underset{I}{CH_3-\overset{+}{C}H-CH_3}$ $\underset{II}{CH_3-\overset{+}{C}H-OCH_3}$

$\underset{III}{CH_3-\overset{+}{C}H-COCH_3}$

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

4 In the following benzyl/allyl system

$R-CH{=}CH_2$ or  (R is alkyl group)

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

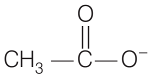
5 $CH_3Br + Nu^- \longrightarrow CH_3-Nu + Br^-$

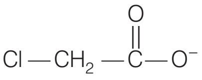
The decreasing order of the rate of the above reaction with nucleophiles (Nu^-) A to D is

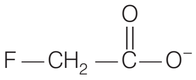
[Nu^- = (A) PhO^-, (B) CH_3COO^-, (C)HO^-, (D) CH_3O^-]

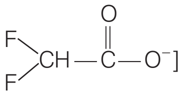
(a) D > C > A > B
(b) D > C > B > A
(c) A > B > C > D
(d) B > D > C > A

6 Ionic species are stabilised by the dispersal of charge. Which of the following carboxylate ion is the most stable?

(a) 
$CH_3-\overset{O}{\overset{\|}{C}}-O^-$

(b) 
$Cl-CH_2-\overset{O}{\overset{\|}{C}}-O^-$

(c) 
$F-CH_2-\overset{O}{\overset{\|}{C}}-O^-$

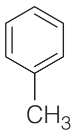
(d) 

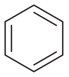
7 The order for ease of heterolysis of following t-butyl compounds is

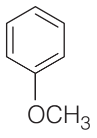
$(CH_3)_3\underset{I}{C}-OH$; $(CH_3)_3\underset{II}{C}-OAc$; $(CH_3)_3\underset{III}{C}-Cl$

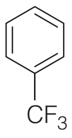
(a) I < II < III
(b) III < II < I
(c) I < III < II
(d) II < I < III

8 Among the following compounds, the decreasing order of reactivity towards electrophilic substitution is


I

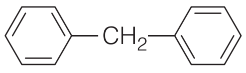

II


III


IV

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

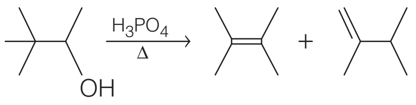
9 The molecular formula of diphenyl methane

 is $C_{13}H_{12}$

How many structural isomers are possible when one of the hydrogen is replaced by a chlorine atom?

(a) 6 (b) 4 (c) 8 (d) 7

10 Consider the following reaction,

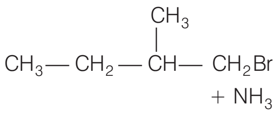


Which response contains all the correct statements about this process?

I. Dehydration II. Carbon skeleton migration
III. E2 mechanism
IV. Formation of most stable carbocation forms

(a) Both I and III (b) I, II and III
(c) I, II and IV (d) I, III and IV

11 Match the reactions of Column I with their names in Column II and choose the correct code given below.

	Column I		Column II
A.	 $CH_3-CH_2-\overset{CH_3}{\overset{\mid}{C}H}-CH_2Br + NH_3$	1.	Nucleophilic addition
B.	$CH_3CHO + NaHSO_3$	2.	Electrophilic substitution
C.	$C_6H_6 + CH_3Cl$	3.	Electrophilic addition
D.	$CH_2{=}CHCH_3 + HBr$	4.	Nucleophilic substitution

Codes

	A	B	C	D		A	B	C	D
(a)	1	2	4	3	(b)	3	2	1	4
(c)	4	1	2	3	(d)	3	1	2	4

12 During hearing of a court case, the judge suspected that some changes in the documents had been carried out. He asked the forensic department to check the ink used at two different places. According to you which technique can give the best results?

(a) Column chromatography (b) Solvent extraction
(c) Distillation (d) Thin layer chromatography

13 Electronegativity of carbon atoms depends upon their state of hybridisation. In which of the following compounds, the carbon marked the asterisk is most electronegative?

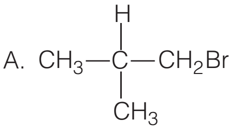
(a) $CH_3-CH_2-\overset{*}{C}H_2-CH_3$

(b) $CH_3-\overset{*}{C}H{=}CH-CH_3$

(c) $CH_3-CH_2-C{\equiv}\overset{*}{C}H$

(d) $CH_3-CH_2-CH{=}\overset{*}{C}H_2$

14 Arrange the following alkyl halide in decreasing order of the rate of β-elimination reaction with alcoholic KOH

A. 

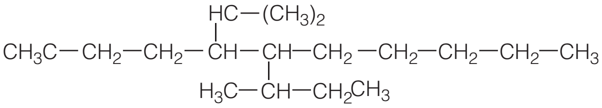
$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-CH_2Br$$

B. CH_3-CH_2-Br

C. $CH_3-CH_2-CH_2-Br$

(a) $A > B > C$ (b) $C > B > A$ (c) $B > C > A$ (d) $A > C > B$

15 Which is the correct IUPAC name of the following compound?



$$CH_3C-CH_2-CH_2-\overset{\overset{HC-(CH_3)_2}{|}}{CH}-\underset{\underset{H_3C-CH-CH_2CH_3}{|}}{CH}-CH_2-CH_2-CH_2-CH_2-CH_3$$

(a) 5-butyl-4-isopropyldecane
(b) 5-ethyl-4-propyldecane
(c) 5-*sec* -butyl-4-*tert*-propyldecane
(d) 4-(1-methylethyl) -5-(1 – methylpropyl)-decane

16 Select the incorrect statement.

(a) Electron withdrawing inductive effect of the carbonyl group in —COOH group weakens the O—H bond and favours ionisation of a carboxylic and compared with an alcohol

(b) Aniline is a weaker base than ammonia

(c) Inductive effect of the chlorine destabilises the acid and stabilises the conjugate base

(d) Phenol is weaker acid than water

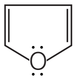
ANSWERS

SESSION 1	**1** (c)	**2** (c)	**3** (a)	**4** (a)	**5** (a)	**6** (d)	**7** (a)	**8** (d)	**9** (d)	**10** (c)
	11 (d)	**12** (a)	**13** (d)	**14** (b)	**15** (c)	**16** (a)	**17** (a)	**18** (a)	**19** (a)	**20** (c)
	21 (d)	**22** (a)	**23** (b)	**24** (b)	**25** (c)	**26** (c)	**27** (b,c)	**28** (b)	**29** (a)	**30** (c)
	31 (a)	**32** (b)	**33** (a)	**34** (d)	**35** (d)	**36** (d)	**37** (c)	**38** (b)	**39** (a)	**40** (b)
	41 (b)	**42** (d)	**43** (d)	**44** (c)	**45** (c)	**46** (a)	**47** (a)	**48** (a)	**49** (c)	**50** (b)
SESSION 2	**1** (b)	**2** (a)	**3** (d)	**4** (a)	**5** (a)	**6** (d)	**7** (a)	**8** (b)	**9** (b)	**10** (a)
	11 (c)	**12** (d)	**13** (c)	**14** (d)	**15** (d)	**16** (d)				

Hints and Explanations

SESSION 1

1 The compound is heterocyclic because oxygen atom is in the ring. As it has two double bonds and four carbon atoms. The structure is

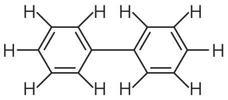


2 As the state of hybridisation changes from sp^3 to sp^2- sp, electronegativity of C-atom increases. Therefore, sp-hybridised C-atom is most electronegative.

3 (a) $H-\overset{sp}{C}\equiv\overset{sp}{C}-\overset{sp}{C}\equiv C-H$ (b) $\overset{sp^3}{C}H_3-\overset{sp}{C}\equiv\overset{sp}{C}-\overset{sp^3}{C}H_3$

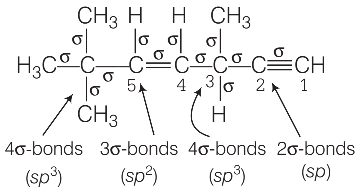
(c) $\overset{sp^2}{C}H_2=\overset{sp}{C}=\overset{sp^2}{C}H_2$ (d) $\overset{sp^2}{C}H_2=\overset{sp^2}{C}H-\overset{sp}{C}\equiv\overset{sp}{C}H$

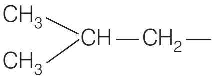
4 The molecule in which all the carbon atoms are sp^2-hybridised will be coplanar. Thus, in option (a), i.e.



all carbons are sp^2-hybridised.

5 If number of σ bonds = 2; hybridisation is sp.
If number of σ bonds = 3; hybridisation is sp^2,
If number of σ bonds = 4; hybridisation is sp^3.

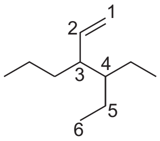


6 The *iso*-butyl group is 

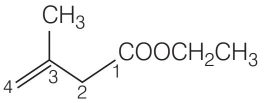
$$\begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>CH-CH_2-$$

7 In IUPAC system of nomenclature, preference is given to multiple bond than halogen substituent, so the correct name of $Br-\overset{3}{C}H_2-\overset{2}{C}H=\overset{1}{C}H_2$ is 3-bromoprop-1-ene

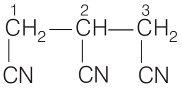
8



4-ethyl-3-propylhex-1-ene

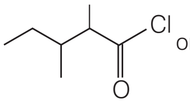
9 

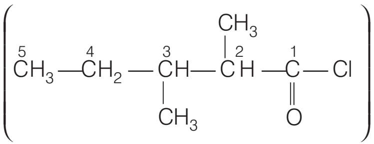
Ethyl (3-methyl) but-3-enoate

10 

$$\begin{array}{ccccc}\overset{1}{CH_2} & - & \overset{2}{CH} & - & \overset{3}{CH_2}\\ | & & | & & |\\ CN & & CN & & CN\end{array}$$

Propan-1,2,3-tricarbonitrile

11 

or 

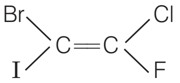
$$\left(\overset{5}{CH_3}-\overset{4}{CH_2}-\underset{\displaystyle CH_3}{\overset{3}{CH}}-\overset{\displaystyle CH_3}{\overset{2}{CH}}-\underset{\displaystyle O}{\overset{1}{C}}-Cl\right)$$

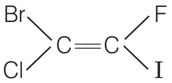
2,3-dimethyl pentanoyl chloride

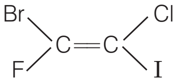
12 —CHO group gets higher priority over $>C=O$ and $>C=C<$ group in numbering of principal carbon chain.

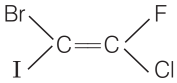
IUPAC name = 3- keto-2-methyl hex-4-enal

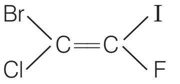
13 The possible isomer of $C_2BrClFI$ are as:

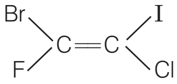
(i) 

(ii) 

(iii) 

(iv) 

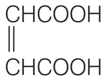
(v) 

(vi) 

14 When two or more compounds have same molecular formula but the position of functional group gets differ, than these are called position isomerism and phenomenon is called position isomerism.

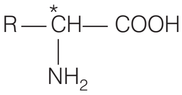
15 The given compound will show optical isomerism as geometrical isomerism is not possible due to attachment of same groups.

16 Only those compounds exhibit optical isomerism, which have chiral centre and/or absence of symmetry elements. (Chiral carbon is the carbon in which all the four valencies of which are satisfied by four different groups.)

(a) 

$$\begin{array}{c}CHCOOH\\ \|\\ CHCOOH\end{array}$$

Maleic acid
(no chiral centre,
so, optically inactive)

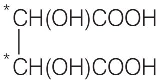
(b) 

$$R-\underset{\displaystyle NH_2}{\underset{|}{\overset{*}{C}H}}-COOH$$

α-amino acids
(one chiral centre
so, optically active)

(c) $CH_3\overset{*}{C}H(OH)COOH$

Lactic acid
(one chiral centre,
so, optically active)

(d) 

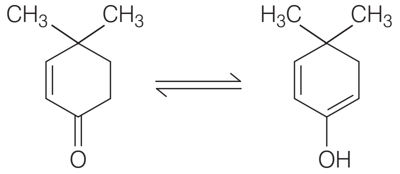
$$\begin{array}{l}{}^{*}CH(OH)COOH\\ |\\ {}^{*}CH(OH)COOH\end{array}$$

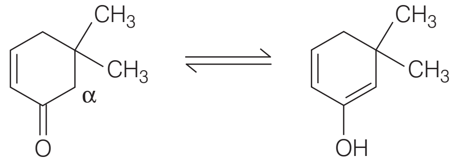
Tartaric acid
(two chiral carbon,
so,optically active)

Thus, maleic acid does not exhibit optical isomerism.

Note If $R = H$, the α-amino acid is achiral.

17 In keto-enol tautomerism keto form should have α-hydrogen (structure I and II).

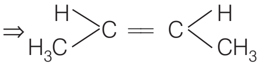
I. 

II. 

18 b. Stereoisomers have same molecular but different configurations.

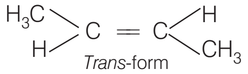
c. Melting point of *trans*–isomers is greater than melting point of *cis*-isomers.

d. Solubility of *trans*–isomer is higher than *cis*–isomer.

19 $CH_3CH = CHCH_3 \Rightarrow$ 

2 -butene

Cis-form

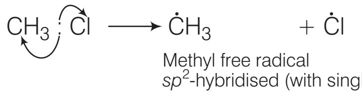


Trans-form

$CH_3CH_2CH_2CH_2OH \Rightarrow$ no geometrical isomers
Butanol

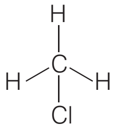
$CH_3C \equiv CCH_3 \Rightarrow$ no geometrical isomers

$CH_3CH_2C(OH) = CH_2 \Rightarrow$ no geometrical isomers

20 

$$CH_3 \vdots \dot{C}l \longrightarrow \dot{C}H_3 + \dot{C}l$$

Methyl free radical
sp^2-hybridised (with singly
occupied *p*-orbital)



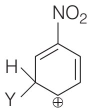
Bond angle 120°
with three coplanar (C–H)
bonds

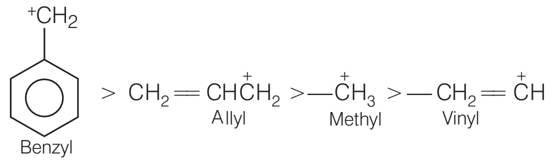
(sp^3-hybridised carbon)
tetahedral bond angle
109°28

21 C_2H_2 have acidic nature but it is less acidic than water. Phenol is more acidic than water due to resonance stabilisation of phenoxide ion H_2CO_3 is most acidic due to resonating stabilisation of carbonate ion (CO_3^{2-})

Thus, correct order is $C_2H_2 < H_2O <$ phenol $< H_2CO_3$

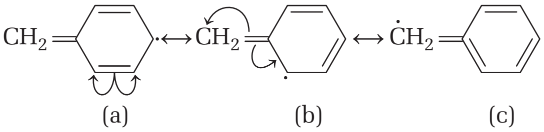
22 $—NO_2$ group is an electron withdrawing group and exhibit $-I$ effect. This effect increases with decrease in distance of positive charge present on C-atom and hence lesser is the stability of carbocation. In option (a), the positive charge is at maximum distance to NO_2 group, so $-I$ effect due to NO_2 group will be minimum and stability will be maximum.



23 

$$\text{Benzyl} > CH_2{=}CH\overset{+}{C}H_2 > —\overset{+}{C}H_3 > —CH_2{=}\overset{+}{C}H$$

(Stabilised on the basis of conjugative and hyperconjugative structures)

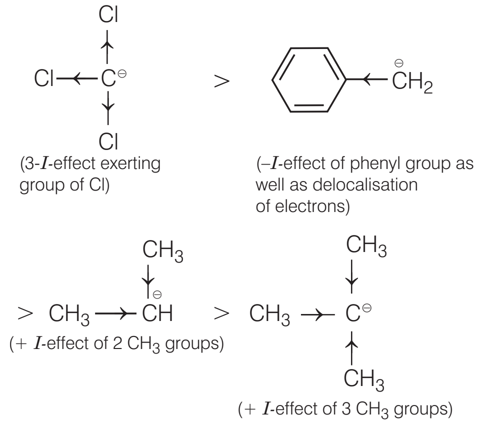
24 

Hence, option (b) is incorrect representation of radical.

25 — NO_2 group shows –*M*-effect, while CH_3O— group shows + *M*-effect (–*M*-effect stabilises an anion).

26 – *I*-effect [e^- withdrawing] exerting groups stabilises carbanion by the dispersal of their negative charge, while + *I*-effect exerting [e^- releasing] groups destabilises the carbanion by increasing electron density on them. On the other hand, resonance stabilised carbanion are stable due to the involvement of their lone pair of electron with the delocalisation of π-electrons of attached phenyl group.

Thus,



(3-*I*-effect exerting group of Cl)

(–*I*-effect of phenyl group as well as delocalisation of electrons)

(+ *I*-effect of 2 CH_3 groups)

(+ *I*-effect of 3 CH_3 groups)

27 –*I* effect is related to the ability of substituent for the electron attraction capacity, from the attached carbon atom. i.e. it is based on electronegativity of an atom. This effect increases with increase in the electronegativity of an atom. From above we can conclude that options (b) and (c) are correct.

—N*R*$_2$ < —O*R* < —F (–*I* effect)

—NH_2 < —O*R* < —F (–*I* effect)

Also, option (a) and (d) shows the order of + *I* effect

—NH_2 > —O*R* > —F (+*I* effect)

—N*R*$_2$ > —O*R* > —F (+*I* effect)

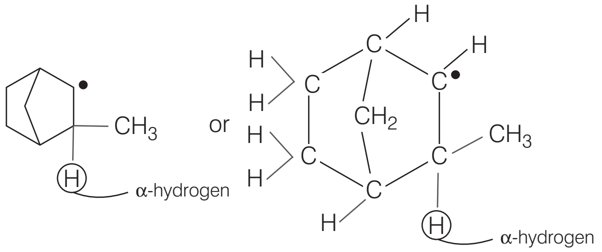
28 $C_6H_5\overset{+}{N}H_3$ does not exerts the resonance effect as lone pair of nitrogen is not available for delocalisation.

29 In hyperconjugation electrons of CH bond of an alkyl group undergo delocalisation with unsaturated system.

30 Hyperconjugation occurs through the H-atoms present on the carbon atom next to the double bond, i.e. α-hydrogen atoms.

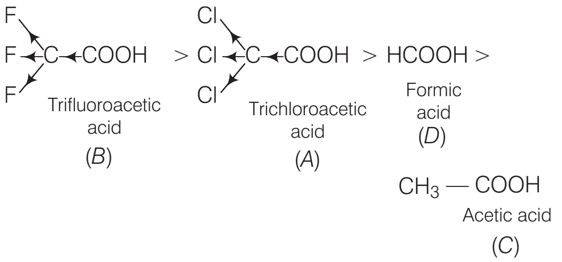
There is no α-H in the structures I and II.

So, hyperconjugation occurs in structure III only



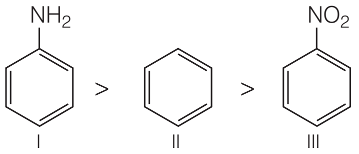
31 If an electron withdrawing group (–*I*-showing group) is present, e.g. —CF_3 has more (–*I*-effect) withdrawing power than —CCl_3, it makes the removal of proton more easy by stabilising the remaining carboxylate ion and thus, makes the acid more acidic.

The order of acidity of given compounds is



Trifluoroacetic acid (*B*) > Trichloroacetic acid (*A*) > Formic acid (*D*) > $CH_3—COOH$ Acetic acid (*C*)

32 In aniline, —NH_2 group is attached with benzene ring. —NH_2 group shows +M-effect. So, it activates the benzene ring. Hence, rate of electrophilic substitution is increased due to increase in the electron density at o/p-position. In case of nitrobenzene, (—NO_2) –*M*-effect deactivates the benzene ring. So in nitrobenzene, rate of electrophilic substitution is lower than benzene. Hence, order of S_E reaction is



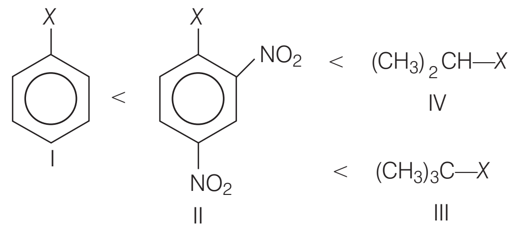
33 Alkyl halides are more reactive towards nucleophilic substitution. Reactivity depends upon the stability of carbocation intermediate formed.

Among the given halides, aryl halide (C_6H_5X) is least reactive towards nucleophile, due to the four possible reason :

(i) Resonance effect
(ii) Hybridisation
(iii) Unstability of phenyl cation
(iv) Double bond character

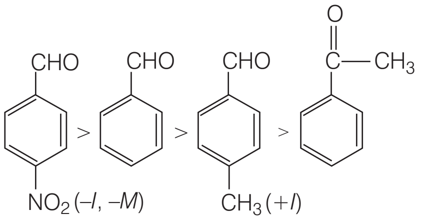
C—*X* bond acquires some double bond character due to resonance. Presence of electron withdrawing groups like — NO_2 at *ortho* and *para*-positions facilitate the nucleophilic displacement of —*X* of aryl halide.

Among alkyl halides, 3° halides are more reactive as compared to 2° halides due to the formation of more stable carbocation. Hence, the order of reactivity of C — *X* bond towards nucleophile is as

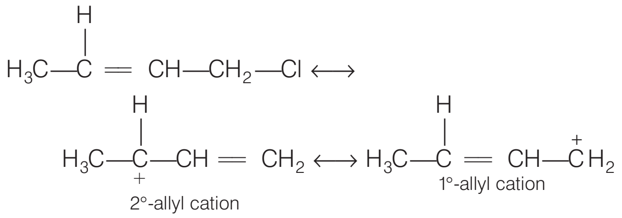


34. Reactivity of carbonyl compounds towards nucleophilic addition reactions depends on the presence of substituted group.

Electron withdrawing (–*I*) group increase reactivity towards nucleophilic addition reactions. Thus, correct order is



35 Allylic and benzylic halides show high reactivity towards S_N1 reaction. Further, due to greater stabilisation of allyl and benzyl carbocations intermediates by resonance, primary allylic and primary benzylic halides show higher reactivity in S_N1 reactions than other simple primary halides.

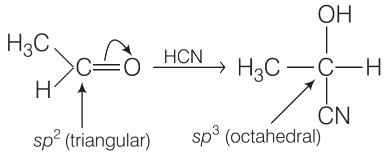


$$H_3C—\overset{H}{\overset{|}{C}}=CH—CH_2—Cl \longleftrightarrow$$

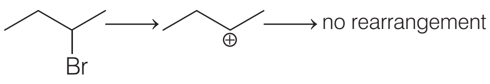
$$\underset{\text{2°-allyl cation}}{H_3C—\underset{+}{\overset{H}{\overset{|}{C}}}—CH=CH_2} \longleftrightarrow \underset{\text{1°-allyl cation}}{H_3C—\overset{H}{\overset{|}{C}}=CH—\overset{+}{C}H_2}$$

Hence, it undergoes nucleophilic reaction readily.

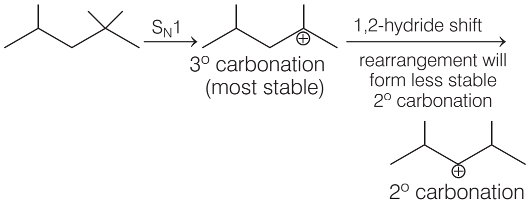
36



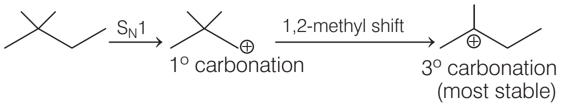
37 (a)



(b)

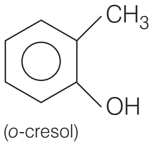


(c)



38 — CH_3 is an activating group, — COOH is deactivating group. Thus, order is III<II<I.

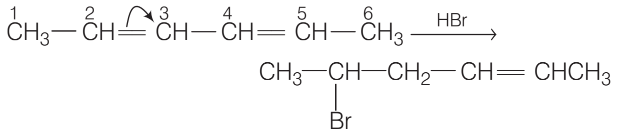
39



(*o*-cresol)

Due to +*M*-effect of —OH group and hyperconjugation of — CH_3 group, the benzene of *o*-cresol is highly reactive ring towards electrophilic substitution.

40



$$\overset{1}{C}H_3—\overset{2}{C}H=\overset{3}{C}H—\overset{4}{C}H=\overset{5}{C}H—\overset{6}{C}H_3 \xrightarrow{HBr} CH_3—\underset{Br}{\underset{|}{C}H}—CH_2—CH=CHCH_3$$

41 Dehydrohalogenation of alkyl halide in the presence of alc. KOH is the example of elimination reaction.

$$RCH_2—CH_2Cl + \underset{\text{Alc.}}{KOH} \xrightarrow{\Delta} RCH=CH_2 + KCl + H_2O$$

42 Impure naphthalene is purified by sublimation.

43 Fractional distillation is useful in distillation of petroleum, coaltar and crude alcohol.

44 Impure glycerine can be purified by vacuum distillation as it has tendency to decompose at a temperature below their boiling point.

45 $Na_2S + (CH_3COO)_2Pb \longrightarrow \underset{\substack{\text{Black}\\ \text{ppt.}}}{PbS\downarrow} + 2CH_3COONa$

46 In Carius method, the weighed organic compound (containing phosphorus) is heated with conc. HNO_3 followed by $MgCl_2$ in the presence of NH_4Cl and NH_4OH. By this, magnesium ammonium phosphate, $MgNH_4PO_4$ is formed which on ignition gives magnesium pyrophosphate ($Mg_2P_2O_7$).

From the amount of magnesium pyrophosphate, the percentage of phosphorus is calculated as

$$\% \text{ of } P = \frac{62}{222} \times \frac{\text{weight of } Mg_2P_2O_7}{\text{weight of substance taken}} \times 100$$

47 Percentage of nitrogen $= \dfrac{1.4 \times N \times V}{W}$

where, N = Normality of consumed acid

V = Quantity of consumed acid in millilitre

W = Weight of sample $= \dfrac{1.4 \times 10 \times 2}{0.75} = 37.33\%$

48 $\dfrac{p_1V_1}{T_1} = \dfrac{p_2V_2}{T_2}$

where, p_2 = pressure of N_2 at STP = 760 mm

T_2 = Temperature of N_2 at STP = 273 K

V_2 = ?

Volume of N_2 at STP (By gas equation)

$$\left(\frac{p - p_1}{t + 273}\right) V_1 \times \frac{273}{760} = V_2$$

where, $p_1 = p - p_1$

p = 715 mm (pressure at which N_2 collected).

p_1 = aqueous tension of water = 15 mm

$T_1 = t + 273 = 300$ K

V_1 = 55 mL

= volume of moist nitrogen in nitrometer

$$\therefore \qquad V_2 = \frac{(715-15)\times 55}{300}\times\frac{273}{760} = 46.098 \text{ mL}$$

$$\% \text{ of nitrogen in given compound} = \frac{28}{22400}\times\frac{V_2}{W}\times 100$$

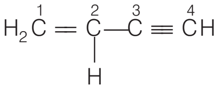
$$= \frac{28}{22400}\times\frac{46.098}{0.35}\times 100 = 16.45\%$$

49 In E2 elimination, β-H and leaving group are in the same plane but anti-conformation. Base can abstract hindered β-H. Thus, Reason is false.

50 Chromatography is used to separate almost any given mixture, whether coloured or colourless into its constituents and to test the purity of these constituents.

SESSION 2

1 As pi (π)-bonds do not go for hybridisation. For option (b), the hybridisation of C-atoms are in order $sp^2 \rightarrow sp^2 \rightarrow sp \rightarrow sp$, i.e.



$$H_2\overset{1}{C}=\underset{\underset{\displaystyle H}{|}}{\overset{2}{C}}-\overset{3}{C}\equiv\overset{4}{C}H$$

(i) C_1 is sp^2 due to presence of one pi (π)-bond between C_1 and C_2 carbon atoms

(ii) C_2 is also sp^2 hybrid due to presence of one pi (π)-bond between C_1 and C_2 carbon atoms.

(iii) C_3 and C_4 are sp hybrid due to presence of two pi (π)-bonds between C_3 and C_4 carbon atoms

2 Basic strength depends on the ability to donate lone pair of electrons and stability of conjugate ion (i.e. base).

Thus, more acidic be the species, more stable is its conjugate.

(i) OH^- is conjugate of H_2O, which is amphoteric in nature.

(ii) NH_2^- has lone pair of electrons over N-atom, thus is highly basic.

(iii) $H-C\equiv C^-$ is the conjugate of $HC\equiv CH$, in which both the C-atoms are sp hybrid, thus is acidic and therefore its conjugate is a base

(iv) Due to (+) *I* effect of $-CH_3$ group, bonded with $-CH_2^-$, $CH_3-CH_2^-$ is most basic.

Hence, correct order for basic strength is

$CH_3-CH_2^- > NH_2^- > H-C\equiv C^- > OH^-$

3 Electron releasing groups [i.e. (+) *I*-groups] increases the stability of carbcations, while electron withdrawing groups [i.e. (–) *I*-effect groups] decreases the stability.

∵ $-OCH_3$ and $-CH_3$ show (+) *I*-effect and (+) *I*-effect of $-OCH_3$ is more pronounced than in $-CH_3$, while $-COCH_3$ show (–) *I*-effect.

Thus, order of stability will be II > I > III.

4 Alkyl-group (*R*) is an electron-releasing group and will show (+) *I*-effect.

More be number of such groups, more will be the (+) *I*-effect, thus more be the inductive effect.

Hence, correct order is

$(CH_3)C- > (CH_3)_2CH- > CH_3-CH_2-$

5 The reaction

$CH_3Br + Nu^- \longrightarrow CH_3-Nu + Br^-$ is an example of S_N2 reaction.

Thus, stronger be the $N\ddot{u}$, faster is the rate of reaction.

∵ (A) PhO^- is stabilised through resonance, thus is least reactive.

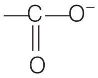
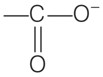
(B) CH_3COO^- is also stabilised by resonance but to lesser extent than of PhO^-.

[∵ PhO^- show more no. of resonance structures]

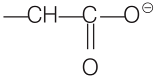
(c) OH^- and CH_3O^- does not show resource, but *I*-effect of (*D*) is more than of (*C*).

Hence correct order of reactivity will be

D < *C* < *B* < *A* or *D* > *C* > *A* > *B*

6 Electron withdrawing groups, [i.e (–) *I*-groups] attached with the  $-\underset{\underset{\displaystyle O}{\|}}{C}-O^-$ group, increases the stability of carboxylate ion. while electron releasing groups [i.e. (+) *I*-groups] decreases the stability of the carboxylate group. More be number of (–) *I*-groups or they are closer to the  $-\underset{\underset{\displaystyle O}{\|}}{C}-O^-$ group.

More is the stability of carboxylate ion.

Thus, due to presence of two fluorine (F) atoms, bonded with the  $-CH-\underset{\underset{\displaystyle O}{\|}}{C}-O^{\ominus}$ group, (d) is the most stable species.

7 Electron withdrawing groups, make the heterolysis easier than electron releasing groups for *t*-butyl compounds.

Between $(CH_3)_3-C-OH$ and $(CH_3)_3-C-OAc$ groups, $(CH_3)_3-C-OAc$ is better for heterolysis due to presence of $-OAc$ group.

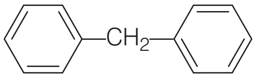
Thus, order for case of heterolysis will be III > II > I

8 Electron releasing groups (i.e. (+) *I*-groups) make the electrophilic substitution easy, while electron withdrawing groups make the electrophilic substitution difficult due to decrease in electron density at *ortho* and *para* positions.

Between $-OCH_3$ and $-OH$ groups, $-OCH_3$ is a better Nu, thus can show better electrophilic substitution than $-OH$ group. While in structure (II) we have no group. Thus order of reactivity towards electrophilic substitution will be

III > I > II > IV

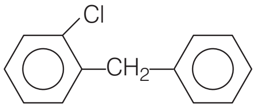
9 The molecular formula of diphenyl methane having structure.



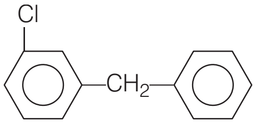
Show (4) structural isomers;

Which are as follows:

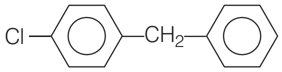
(i) *ortho* substituted structure



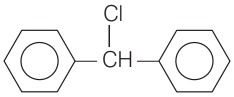
(ii) *meta* substituted structure



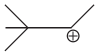
(iii) *para* substituted structure



(iv) Cl is substituted with one H-atom of —CH_2 group; i.e



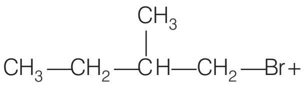
10 When  $\xrightarrow[\Delta]{H_3PO_4}$ is heated in the presence of H_3PO_4. In first step protonation occurring H-atom of H_3PO_4 and go for dehydration, with the formation of carbocation:



(carbocation)

In next step, one of the H-atom (adjacent to C^+-center) go for elimination *via* E_2 mechanism and give the corresponding alkene. Hence, option (a) is the correct answer.

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

(A) 

$CH_3—CH_2—\overset{CH_3}{\overset{|}{C}}H—CH_2—Br + NH_3 \rightarrow$ Show nucleophilic substitution.

(B) $CH_3CHO + NaHSO_3 \rightarrow$ Show nucleophillic substitution

(C) $C_6H_6 + CH_3Cl \rightarrow$ Show electrophilic substitution

(D) $CH_2 = CH \cdot CH_3 + HBr \rightarrow$ Show electrophilic addition

12 To check the ink used at two different places, the results we can get by using 'Thin Layer-Chromatography.

13 More be the *s*-character of the hybrid C-atom, more is its electronegativity.

(a) marked C-atom is sp^3 hybrid due to formation of 4 sigma (σ) bonds.

(b) marked C-atom is sp^2 hybrid due to presence of one pi (π) bond.

∴ Has 33.33% *s*-character.

(c) marked C-atom is *sp*-hybrid, due to presence of two pi (π) bonds.

∴ Has 50% *s*-character.

(d) Marked C-atom is sp^2 hybrid due to presence of one pi (π) bond.

Hence, option (c) is the correct answer.

14 β-elimination reactions depend on the degree of C-atom, with which the leaving group is attached.

More be the degree of C-atom, easier is the β-elimination.

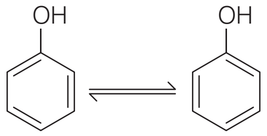
Also, after the removal of Br, (*A*) can form 3° carbo-cation, (*B*) can form 1° carbocation, while (*C*) can form 2° carbocation.

More be the stability of carbocation, more reactive is the species towards β-elimination and order of stability for carbcation is → $3° > 2° > 1°$.

Hence, correct order of β-elimination will be $A > C > B$.

15 The correct IUPAC of the given compound is →
4-(1-methyl ethyl)-5-(1-methyl propyl)-decane.

16 The structures, that can show resonance and having acidic —H, are stronger acids than of water. As water can not show any resonance.



Therefore, phenol is stronger acid than water.

Hence, statement (d) is incorrect, while all other are correct statements.