DAY TWENTY SEVEN

General Organic Chemistry

Learning & Revision for the Day

- Bonding in Organic Compounds
- Classification of Organic Compounds
- Functional Group
- Homologous Series
- IUPAC System
- Isomerism
- Fission of a Covalent Bond
- Electronic Displacement Effect in a Covalent Bond
- Types of Organic Reactions
- 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

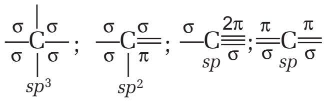
- Carbon is the essential element of all organic molecules and its electronic configuration is 2,4. It always form covalent bonds. The tetravalency of carbon can be explained by the excited state concept, i.e. by moving one of the paired $2s$ electron to empty $2p$ orbital by gaining energy from the 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. A single bond contains only one σ-bond. Whereas, there are one σ and one π-bond in case of a double bond and one σ and two π-bonds in case of a triple bond.

Tetravalency of Carbon

(Shapes of Simple Molecules and Hybridisation)

- Hybridisation is the intermixing of orbitals of almost similar energy to form the same number of orbitals of exactly similar energy.
- The carbon atoms show three types of hybridisations 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.

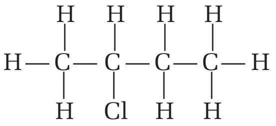
  Usually saturated hydrocarbons are sp^3-hybridised while unsaturated hydrocarbons may be sp^2 or sp-hybridised.



e.g. But-1-en-3-yne (C_4H_4) consists of 7σ-bonds and 3π-bonds. π-bonds give no contribution to hybridisation.

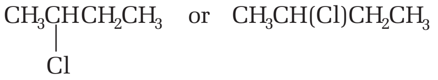
An organic compound can be represented by the following ways :

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



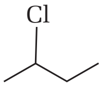
2-chlorobutane

(ii) In **condensed formula**, all the bonds are not shown clearly.



$CH_3\underset{\substack{| \\ Cl}}{C}HCH_2CH_3$ or $CH_3CH(Cl)CH_2CH_3$

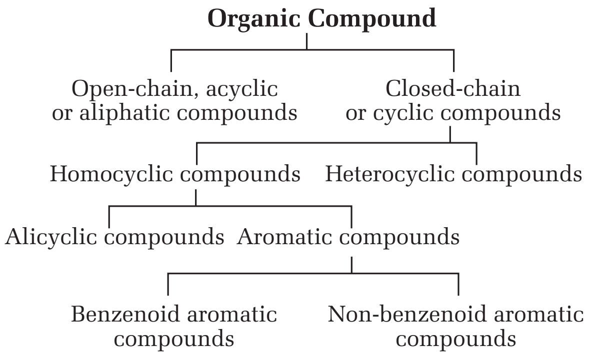
(iii) In **bond line formula**, every fold and free terminal represents a carbon and lines represent the bond.



Classification of Organic Compounds

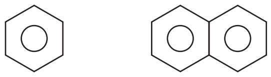
The organic compounds have been classified **on the basis of carbon skeleton (structure)** or functional groups or the concept of homology.

On this basis the organic compounds are classified as :

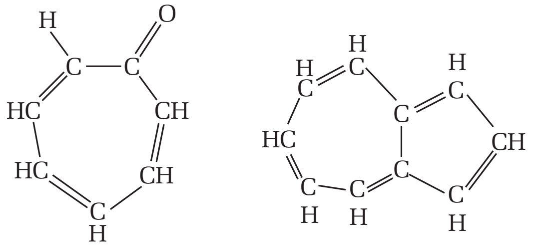


e.g.

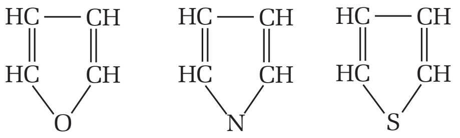
Cyclopropane
(Alicyclic compound)



Benzene Naphthalene
(Benzenoid aromatic compounds)



Tropolone Azulene
(Non-benzenoid aromatic compounds)



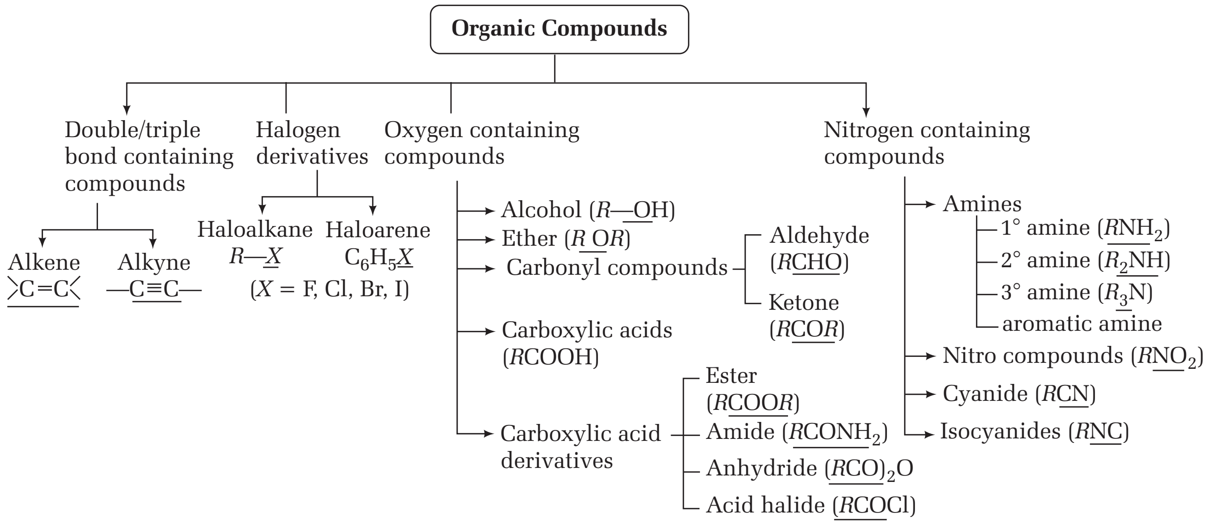
Furan Pyrrole Thiophene

(Heterocyclic compounds)
Compounds having hetero atom in the ring

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.

- **On the basis of functional groups**, organic compounds are classified into following families or homologous series.

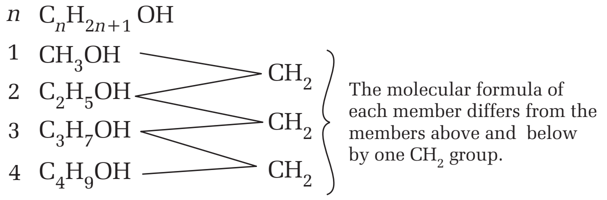


Homologous Series

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:

(i) All compounds in the series can be represented by one general formula, e.g. the homologous series of monohydric alcohols can be represented by the general formula, $C_nH_{2n+1}OH$.

The formula of various homologous can be written by giving the values 1, 2, 3, ... to *n*.



(ii) The molecular mass of every two adjacent members differ by 14 $(CH_2 = 12 + 2 \times 1 = 14)$.

(iii) All compounds in the series have similar chemical properties because of the presence of same functional group.

(iv) 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.

IUPAC System

In trivial system, name was assigned at the wish of discoverer and had no system. These names are also called **common names.** In 1957, the International Union of Pure and Applied Chemistry (IUPAC) 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.

An IUPAC name consist of prefixes and suffixes to indicate the substituent or functional group present in compound.

Some functional groups are always indicated by the prefixes instead of secondary suffixes.

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

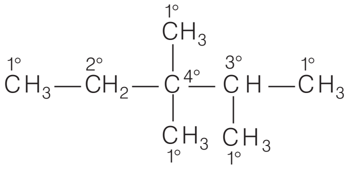
Secondary suffix is used to indicate the functional group in the organic compounds.

Family of Compound	Suffix	IUPAC Name of the Family
Alcohols (—OH)	—ol	Alkanol
Amines $(—NH_2)$	—amine	Alkanamine
Aldehydes (—CHO)	—al	Alkanal
Ketones $(>C=O)$	— one	Alkanone
Carboxylic acids (—COOH)	— oic acid	Alkanoic acid
Amides $(—CONH_2)$	—amide	Alkanamide
Acid halides (—COX)	—oyl halide	Alkanoyl halide
Esters (—COOR)	—oate	Alkyl alkanoate
Nitriles $(—C \equiv N)$	— nitrile	Alkane nitrile

Classification of Carbon and Hydrogen Atoms

- **Primary Carbon Atom** When carbon atom is attached with only one other carbon atom.
- **Secondary Carbon Atom** When carbon atom is attached with two other carbon atoms.
- **Tertiary Carbon Atom** When carbon atom is attached with three other carbon atoms.
- **Quarternary Carbon Atom** When carbon atom is attached with four other carbon atoms.
  Reactivity order of carbon atoms is as follows:

$$3^\circ > 2^\circ > 1^\circ$$



$$\overset{1^\circ}{CH_3}—\overset{2^\circ}{CH_2}—\overset{\overset{1^\circ}{CH_3}\,|}{\underset{|\,\underset{1^\circ}{CH_3}}{C^{4^\circ}}}—\overset{3^\circ}{\underset{|\,\underset{1^\circ}{CH_3}}{CH}}—\overset{1^\circ}{CH_3}$$

- 1°**-hydrogen** (primary) ⟶ attached to 1°-carbon.
- 2°**-hydrogen** (secondary) ⟶ attached to 2°-carbon.
- 3°**-hydrogen** (tertiary) ⟶ attached to 3°-carbon.
- **α-carbon** Carbon which is directly attached to the functional group.
- **β-carbon** Carbon which is directly attached to the α-carbon.
- **α-hydrogen** (s) Hydrogens which are attached to α-carbon atom.
- **β-hydrogen** (s) Hydrogens which are attached to β-carbon atom.

e.g. $\overset{\beta}{CH_3}—\overset{\alpha}{CH_2}—Cl$, $\overset{\beta}{CH_3}—\overset{\alpha}{CH_2}—COOH$

$\overset{\beta}{CH_3}—\overset{\alpha}{CH_2}—CHO$

Rules for IUPAC Nomenclature

Rules for IUPAC nomenclature are as follows :

- First of all, the longest carbon chain in the molecule is identified.
- Numbering is started from the terminal carbon from which branching is nearest.
- If the two substituents are found at 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 (priority wise) as the principal functional group and the compound is then named on that basis.

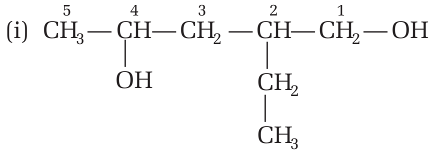
The order of decreasing priority for some functional groups are as follows:

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

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

Some examples are described below:

(i)

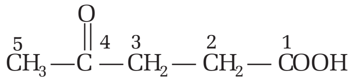


$$\overset{5}{CH_3}-\underset{\underset{OH}{|}}{\overset{4}{CH}}-\overset{3}{CH_2}-\underset{\underset{\underset{\underset{CH_3}{|}}{CH_2}}{|}}{\overset{2}{CH}}-\overset{1}{CH_2}-OH$$

2–ethylpenta-1, 4-diol (IUPAC name)

Maximum number of functional group should be present in longest carbon chain.

(ii)

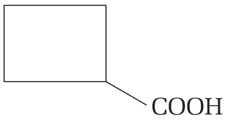


$$\overset{5}{CH_3}-\overset{\overset{O}{\|}}{C}\,{}^{4}-\overset{3}{CH_2}-\overset{2}{CH_2}-\overset{1}{COOH}$$

4-ketopentanoic acid (IUPAC name)

(Numbering according to principal functional group).

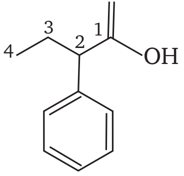
(iii)



Cyclobutane carboxylic acid (IUPAC name)

(Carbon containing functional group is not considered with cyclic ring).

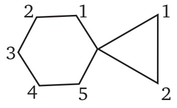
(iv)



2-phenylbutanoic acid (IUPAC name)

If functional group is not directly attached to benzene ring, the ring is considered as branching and known as phenyl.

(v) In spirocyclic compounds, the common atom is designated as spiro atom. Spiro prefix is written before the alkane.



Spiro [2,5] octane

(vi) In bicyclo compounds, the bicyclic systems having two or more atoms in common, are named by prefixing 'bicyclo' to the name of parent hydrocarbon.

Isomerism

The compounds having same molecular formula but differ in properties are known as isomers and the phenomenon is called isomerism. Isomerism can be of the following two types :

(i) Structural Isomerism

(ii) Stereoisomerism

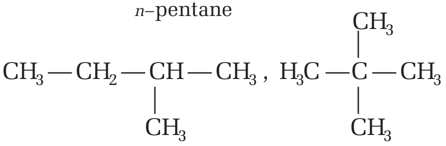
1. Structural Isomerism

In this type of isomerism, compounds have same molecular formula but different structures. Different types of structural isomerism are as follows :

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

$CH_3-CH_2-CH_2-CH_2-CH_3$

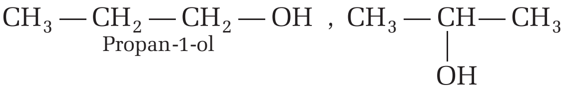
n–pentane



$$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3\ ,\quad H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

iso-pentane *neo*-pentane

(ii) When two or more compounds have same molecular formula but different position of functional groups or substituents then they are called position isomers and phenomenon is called **position isomerism,** e.g. C_3H_8O.



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

Propan-1-ol Propan-2-ol

(iii) When two or more compounds have the same molecular formula but different functional group then they are called functional isomers and phenomenon is called **functional isomerism**, e.g. C_3H_6O represents an aldehyde and a ketone as

$$CH_3-CH_2-CHO,\quad CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

Aldehyde Ketone

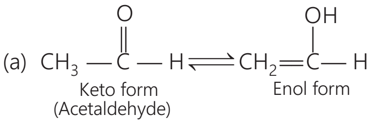
C_2H_6O represents an alcohol and an ether

$$\underset{\text{Alcohol}}{CH_3-CH_2-\ddot{\underset{\cdot\cdot}{O}}H}, \quad \underset{\text{Ether}}{CH_3-\ddot{\underset{\cdot\cdot}{O}}-CH_3} \text{ etc.}$$

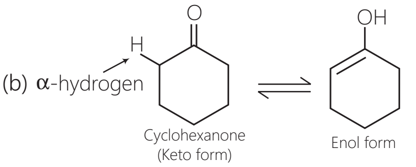
(iv) Metamerism arises due to different alkyl chains on either side of the same functional group in the molecule. e.g. $C_4H_{10}O$

$$CH_3-\ddot{\underset{\cdot\cdot}{O}}-C_3H_7, C_2H_5-\ddot{\underset{\cdot\cdot}{O}}-C_2H_5$$

NOTE **Tautomerism** is a special type of functional isomerism arises in carbonyl compounds containing $\alpha-H$ atom. e.g.



$$\text{(a)}\ \underset{\substack{\text{Keto form}\\\text{(Acetaldehyde)}}}{CH_3-\overset{\overset{\large O}{\|}}{C}-H} \rightleftharpoons \underset{\text{Enol form}}{CH_2=\overset{\overset{\large OH}{|}}{C}-H}$$



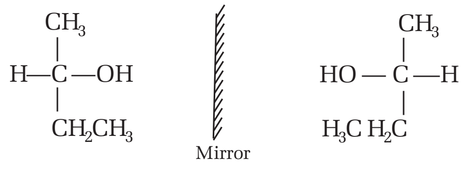
Cyclohexanone (Keto form)

Enol form

2. Stereoisomerism

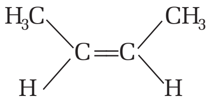
The compounds having same molecular formula but different spatial arrangement of atoms or groups are called stereoisomers and the phenomenon is called stereoisomerism. Stereoisomerism is of two types:

(i) 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.

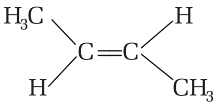


Butan-2-ol

(ii) 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-but-2-ene



trans-but-2-ene

NOTE
- The compound that consists of at least one asymmetric C-atom are capable of showing the phenomenon of optical isomerism.
- Conformational isomerism is not a type of stereoisomerism. These are called conformations that have spatial arrangement of atoms which can be converted into one another by rotation around a C — C single bond. These are non-separable.

Fission of a Covalent Bond

The organic reactions began with the breakage of covalent bond and this breakage or fission is of two types

1. 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.

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

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

2. In **heterolytic fission**, the bond breaks in such a fashion that the shared pair of electrons goes with one of the fragments.

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

It 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. It requires larger energy than homolytic fission. Heterolytic fission is favoured in acid or base catalysed reaction while homolytic fission is favoured in gas phase reactions.

Electrophiles (Electron Deficient Species)

- All non-metal cations and metal cations which have vacant *d*-orbitals. 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.
- Non-metal acidic oxides, e.g. CO_2, SO_2 etc.
- The electrophile attacks at nucleophilic centre and receives electron pair from nucleophile when the two undergoes bonding interaction.
- In case of same nucleophilic site, nucleophilicity parallels basicity, i.e. as the basicity of nucleophile increases, its strength also increases.
- If attacking atoms are different, nucleophilicity varies inversely with electronegativity.

Nucleophiles (Electron Rich Species)

- All anions behaves as nucleophiles, e.g. Cl^-, NH_2^-, OH^- etc.
- Lewis bases, e.g. $:NH_3$, H_2O, $R-\ddot{\underset{\cdot\cdot}{O}}-R$, $-\ddot{\underset{\cdot\cdot}{O}}H$ etc.
- Compounds containing C — C multiple bonds behave as nucleophiles. e.g. Benzene, alkenes etc.
- During a polar organic reaction, a nucleophile attacks an electrophilic centre of the substrate which is that part of the electrophile that is electron deficient.
- Nucleophilicity order is $H^- > CH_3^- > NH_2^- > RO^- > OH^-$.

- Organic compounds such as HCHO and CH_3CN having a multiple bond between carbon and more electronegative atom act as nucleophile as well as electrophile.

Reaction Intermediates

Most of the chemical reactions require certain chemical species to occur. These species are generally short lived, highly reactive and are called reactive intermediates. e.g. free radicals, carbocations, carbanions, carbenes, nitrenes etc. These are discussed as follows :

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

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

2. **Carbocation** Carbon containing chemical species bearing a positive charge on carbon and carry 6 electrons in its valence shell are called **carbocation**. The carbocations follow the following order of stability

$$(C_6H_5)_3\overset{+}{C} > (C_6H_5)_2\overset{+}{C}H > (CH_3)_3\overset{+}{C} > C_6H_5\overset{+}{C}H_2 > 2° > \text{allyl} > 1° > \overset{+}{C}_6H_5 > \text{vinyl}$$

   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.

3. **Carbanion** Carbon containing chemical species bearing a negative charge on carbon atom and carrying 8 electrons in its valence shell is called **carbanion**.

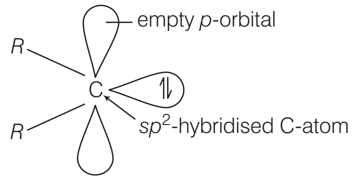
   The order of stability of carbanions is as

$$(C_6H_5)_3C^- > (C_6H_5)_2\bar{C}H > C_6H_5\bar{C}H_2 > \text{allyl} > \bar{C}H_3$$

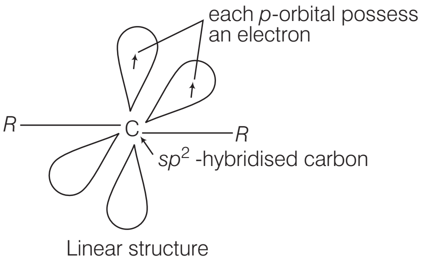
$$(1° > 2° > 3° \text{ carbanions})$$

4. **Carbines** 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. Carbenes are of two types:

   (i) **Single carbene**



   (ii) **Triplet carbene**



Linear structure

   Triplet carbene acts as diradical and it is always more stable than a singlet carbene.

5. **Nitrenes** Neutral monovalent nitrogen species in which nitrogen has two unshared pair of electrons with a monovalent atom or group attached is called **nitrenes,** i.e.

$$\underline{\sigma}\,\ddot{N}:$$

   Nitrenes are produced by thermolysis of azides and are very reactive.

Electronic Displacement in a Covalent Bond

Presence of some atom or group in a molecule or presence of attacking reagent may lead to electronic displacement in a covalent bond. The factors that create the centres of different electron densities are discussed below.

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

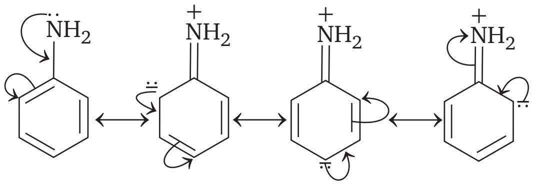
  This is a permanent effect and propagates through carbon chain. The effect decreases rapidly as the number of intervening bonds increases and becomes vanishingly small after three bonds, e.g. $\overset{+\delta\delta\delta}{CH_3} \rightarrow \overset{+\delta\delta}{CH_2} \rightarrow \overset{+\delta}{CH_2} \rightarrow \overset{-\delta}{Cl}$

  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. Therefore, 3°– alkyl halide will be most reactive due to more + *I* effect.
- Electron donating groups (EDG) such as 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.

Resonance Effect

- It involves interaction of two π-bonds or a π-bond and lone pair of electron. This effect may be of +*R* type or –*R* type.
- Electron donating group with respect to conjugate system shows +*R* effect. Central atom of functional group should be more electronegative than the surrounding atoms or groups to show +*R* effect.

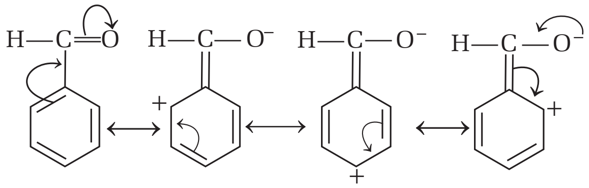
  e.g. halogens, —OH, —O*R*, —OCO*R*, —NH_2, — NHCO*R* etc. This effect in aniline is shown as



- 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. Central atom of functional group should be less electronegative than surrounding atoms or groups to show $-R$ effect.

  e.g. —COOH, —COOR, —CHO, —CN, —NO_2 etc.

  In benzaldehyde, this electron displacement can be depicted as:



- Electron withdrawing group (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.

Relation between Resonance and Bond Order

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

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

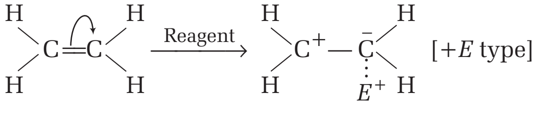
NOTE Resonance energy is the energy lost when a molecule acquires resonance hybrid formula.

(i) Number of π bonds $\propto$ contributing structures $\propto$ resonance energy $\propto$ stability.

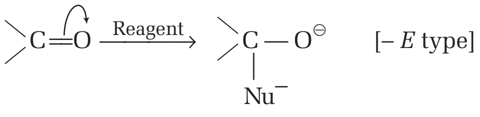
(ii) In benzene, resonance energy is 36 kcal/mol.

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.
- This may be of $+E$ type (when displacement of electron pair is away from the atom or group) or of $-E$ type (when the displacement is towards the atom or group), e.g.



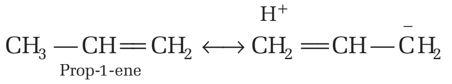
[+E type]



[– E type]

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.



$$\underset{\text{Prop-1-ene}}{CH_3—CH{=}CH_2} \longleftrightarrow \overset{H^+}{CH_2{=}CH—\bar{C}H_2}$$

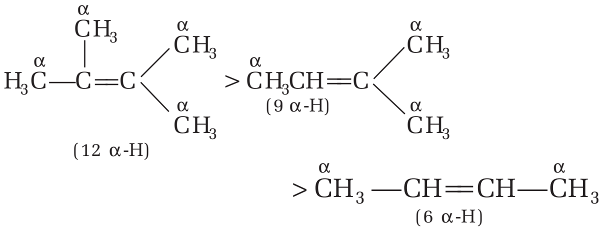
Requirements for structure of hyperconjugation are as follows:

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

(b) 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, the greater is the stability.

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

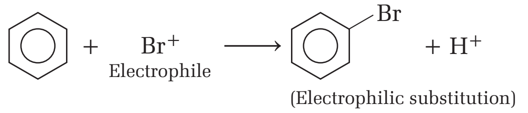
Types of Organic Reactions

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.

1. **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.

   In nucleophilic substitution, the reagent is a nucleophile (base) whereas in an electrophilic substitution, the reagent is an electrophile (acid). e.g.

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



(Electrophilic substitution)

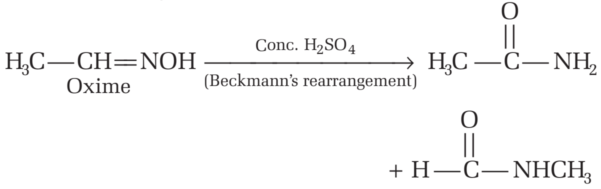
2. **Addition reaction** is a type of reaction in which atoms or group of atoms from the reagent add to the substrate generally without losing any atoms from the substrate.

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

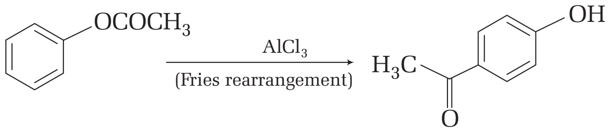
3. **Elimination reaction** removes two atoms or two group of atoms from the substrate, giving the product a multiple bond or, in some cases, causing it to form a ring.

$$\text{e.g.}\quad (CH_3)_3COH \xrightarrow[\text{Heat}]{\text{(i) } H_3O^+} \underset{\text{2-methylprop-1-ene}}{(CH_3)_2C{=}CH_2} + H_2O$$

4. **Rearrangement reactions** involve the migration of an atom or a group from one atom to another within the same molecule. These reactions usually occur in the presence of a catalyst or under special thermodynamic conditions. e.g.



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



Methods for Purification of Organic Compounds

The common techniques used for purification are as follows:

1. **Sublimation process** is employed for those solid substances that directly changes into vapour phase. This method is used to separate sublimable compounds from non-sublimable impurities.
2. **Crystallisation** is one of the most commonly used techniques 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.
3. **Distillation** is used to separate
   (a) volatile liquids from non-volatile impurities.
   (b) the liquids having sufficient difference in their boiling points. Liquids having different boiling points vaporise at different temperatures.

   Several distillation methods employed to separate mixture are as follows :

   (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 spentlye in soap industry by this method.
   (ii) **Fractional distillation** The separation of volatile components of different boiling points in a mixture by the gradual increase of temperature and the separate collection of each component.
   (iii) **Steam distillation** This method is used when substances are steam volatile and immiscible with water.

   - In steam distillation, steam from a steam generator is passed through a heated flask containing the liquid to be distilled. The mixture of steam and the volatile organic compound so obtained is condensed and collected. The compound is later separated from water using a separating funnel.
   - Aniline, nitrobenzene, sandal wood oil, bromobenzene, *o*-nitrophenol, *o*-hydroxy acetophenone are obtained or purified by steam distillation method.
4. **Differential extraction** is used to separate organic compound 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.
5. **Chromatography** is an important technique extensively used to separate mixtures into their components. In this technique, the mixture of substances is applied onto 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.

   Based on the principle involved, chromatography is classified into different categories. Two of these are:
   (a) Adsorption chromatography
   (b) Partition chromatography.
6. **Adsorption chromatography** is based on the fact that different compounds are adsorbed on an adsorbent to different degrees. When a mobile phase is allowed to move over a stationary phase (adsorbent), the components of the mixture move by varying distances over the stationary phase.
   - Following are two main types of chromatographic techniques based on the principle of differential adsorption.
     (a) Column chromatography
     (b) Thin layer chromatography
   - In **partition chromatography** the stationary phase is liquid.

Qualitative Analysis

The qualitative analysis of an organic compound implies the detection of all the major elements which can be present in it with the help of suitable chemical tests.

1. **Detection of Carbon and Hydrogen** It is done with the help of CuO test. Here, 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).
2. Nitrogen, sulphur, halogens and phosphorus present in an organic compound are detected by Lassaigne's test. In Lassaigne's test, the elements present in the organic compound are converted from covalent form into the ionic form by fusing the compound with sodium metal.

$$\mathrm{Na + C + N \xrightarrow{\Delta} NaCN}$$

$$\mathrm{2Na + S \xrightarrow{\Delta} Na_2S}$$

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

2. **Detection of Nitrogen** To detect the presence of nitrogen, freshly prepared $FeSO_4$ solution is added to the Lassaigne's extract and contents are warmed. To this, drops of $FeCl_3$ solutions are then added and solution is acidified with conc. HCl. Appearance of Prussian blue colour confirms presence of nitrogen.

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

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

3. **Detection of Sulphur** To detect the presence of sulphur, sodium nitroprusside solution are added to a part of Lassaigne's extract. The appearance of purple colouration confirms its presence.

$$\mathrm{Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow \underset{\text{Purple colour}}{Na_4\,[Fe(CN)_5NOS]}}$$

Lead acetate test is also used to test its presence. Formation of black precipitate is the final observation.

$$\mathrm{Na_2S + (CH_3COO)_2Pb \longrightarrow PbS\downarrow + 2CH_3COO^-Na^+}$$

4. **Detection of Halogen** To detect the presence of halogens, sodium fusion extract is acidified with nitric acid and then treated with silver nitrate.

$$X^- + \mathrm{Ag^+} \longrightarrow \mathrm{Ag}X\downarrow + \mathrm{NaNO_3}$$

X represents a halogen — Cl, Br or I.

AgCl-white ppt, AgBr-dull yellow ppt, AgI-bright yellow ppt.

5. **Detection of Phosphorus** To detect the presence of phosphorus compound, compound is heated with an oxidising agent (like sodium peroxide), then the phosphorus present in the compound is oxidised to phosphate. The solution is boiled with nitric acid and then treated with ammonium molybdate. 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.

1. **Estimation of Carbon and Hydrogen** The **carbon and hydrogen** are estimated by **Leibig method**.

Percentage of carbon

$$= \frac{12 \times \text{mass of CO}_2}{44 \times \text{mass of organic compound}} \times 100$$

Percentage of hydrogen

$$= \frac{2}{18} \times \frac{\text{mass of H}_2\text{O}}{\text{mass of organic compound}} \times 100$$

2. **Estimation of Nitrogen** Nitrogen can be estimated by the following two methods.

(a) **Dumas' Method** Let the mass of organic compound $= m$g, volume of nitrogen collected $= V_1$ mL, Room temperature $= T_1$ K

$$\text{Volume of nitrogen at STP} = \frac{p_1 V_1 \times 273}{760 \times T_1} \quad (\text{Let it be } V\,\text{mL})$$

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

$$V \text{ mL N}_2 \text{ at STP weighs} = \frac{28 \times V}{22400}\ \text{g}$$

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

(b) **Kjeldahl's Method** Let the mass of organic compound taken $= m$ g, volume of H_2SO_4 of molarity, M taken $= V$ mL and volume of NaOH of molarity $M = V_1$mL

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

Kjeldahl's method is not applicable to compounds containing nitrogen as nitro and azo groups.

3. **Estimation of Halogens** Halogens can be estimated by **carius method**

Let the mass of organic compound $= w$ g

Mass of AgX formed $= w_1$ g

Percentage of halogen

$$= \frac{\text{atomic mass of } X \times \text{mass of Ag}X}{\text{molecular mass of Ag}X \times m} \times 100$$

4. **Estimation of Sulphur** Sulphur be estimated by **Carius method**.

Percentage of sulphur

$$= \frac{32 \times \text{mass of BaSO}_4 \times 100}{233 \times \text{mass of organic compound}}$$

5. **Estimation of Phosphorus** For the estimation of phosphorus weighed amount of organic is heated with conc. HNO_3 in a Carius tube.

Percentage of phosphorus

$$= \frac{62 \times \text{mass of Mg}_2\text{P}_2\text{O}_7}{222 \times \text{weight of organic compound}} \times 100$$

Percentage of phosphorus

$$= \frac{31 \times \text{mass of (NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3}{1877 \times \text{mass of organic compound}} \times 100$$

Calculation of Empirical and Molecular Formulae

Empirical formula expresses the relative number of atoms present in the molecule. It is calculated from percentage composition of the compound.

Molar mass = (empirical formula mass) × n

$$n = \frac{\text{Molar mass}}{\text{Empirical formula mass}}$$

Eudiometry is an excellent method to determine the molecular formula of a gaseous hydrocarbon.

DAY PRACTICE SESSION 1

FOUNDATION QUESTIONS EXERCISE

1 Electronegativity of carbon atoms depend upon their state of hybridisation. In which of the following compounds, the carbon marked with asterisk 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) $CH_3 - CH_2 - CH = {*}CH_2$

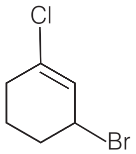
2 Which of the following compounds contain only primary hydrogen atoms?

(a) Isobutene (b) 2, 3 - dimethylbut - 2 - ene
(c) Cyclohexane (d) Propyne

3 The IUPAC name of neopentane is ➞ AIEEE 2009

(a) 2-methylbutane
(b) 2, 2- dimethylpropane
(c) 2-methylropane
(d) 2, 2-dimethylbutane

4 The IUPAC name of the compound shown below is



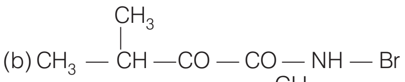
(a) 2-bromo-6-chlorocyclohex-1-ene
(b) 6-bromo-2-chlorocyclohexene
(c) 3-bromo-1-chlorocyclohexene
(d) 1-bromo-3-chlorocyclohexene

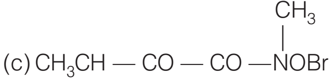
5 Which of the following compounds represents 2,2,3 - trimethyl hexane?

(a) $CH_3C\,(CH_3)_2\ CH_2CH_2CH(CH_3)_2$
(b) $CH_3C\,(CH_3)_2\ CH_2CH\,(CH_3)_2CH_2CH_3$
(c) $CH_3C\,(CH_3)_2\ CH\,(CH_3)CH_2\ CH_2CH_3$
(d) $CH_3C\,(CH_3)_2\ CH_2C\,(CH_3)_2CH_3$

6 The structural formula of 2-oxo-3-methyl-(N-bromo) butanamide is

(a) $CH_3 - CH_2 - CO - CO - NH - Br$

(b) 
$CH_3 - \overset{\overset{CH_3}{|}}{CH} - CO - CO - NH - Br$

(c) 
$CH_3CH - CO - CO - \overset{\overset{CH_3}{|}}{N}OBr$

(d) $(CH_3)_3C - CO - CO - NH\,Br$

7 The maximum number of isomer for an alkene with the molecular formula C_4H_8 is

(a) two (b) three
(c) four (d) five

8 In which of the following functional group isomerism is not possible?

(a) Alcohols (b) Aldehydes
(c) Alkyl halides (d) Cyanides

9 Identify the compound that exhibits tautomerism

(a) 2-butene (b) lactic acid
(c) 2-pentanone (d) ethane

10 The number of stereoisomers possible for a compound of the molecular formula

$CH_3 - CH = CH - CH(OH)$ Me is

(a) 3 (b) 2 (c) 4 (d) 6

11 3-methylpent-2-ene on reaction with HBr in presence of peroxide forms an addition product. The number of possible stereoisomers for the product is ➞ JEE Main 2017

(a) six (b) zero
(c) two (d) four

12 Which of the following compound will exhibit geometrical isomerism?

(a) 1- phenyl-2-butene (b) 3 - phenyl-1-butene
(c) 2 - phenyl-1-butene (d) 1,1- diphenyl-1-propane

13 Which of the following compounds will show metamerism?

(a) $CH_3COOC_2H_5$ (b) $C_2H_5 - S - C_2H_5$
(c) $C_2H_5 - O - C_2H_5$ (d) $CH_3 - O - C_2H_5$

14 Nitroethane can exhibit one of the following kind of isomerism.

(a) Metamerism (b) Optical activity
(c) Tautomerism (d) Position isomerism

15 The correct order of nucleophilicity is

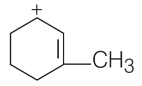
(a) $I^- > Br^- > Cl^- > F^-$ (b) $Cl^- > F^- > Br^- > I^-$
(c) $F^- > Cl^- > Br^- > I^-$ (d) $I^- > Cl^- > Br^- > F^-$

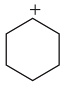
16 How many chiral compounds are possible on monochlorination of 2-methylbutane? ➞ AIEEE 2012

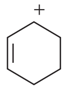
(a) 8 (b) 2
(c) 4 (d) 6

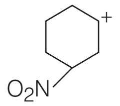
17 Which one of the following is most stable?

➞ JEE Main (Online) 2013

(a) 

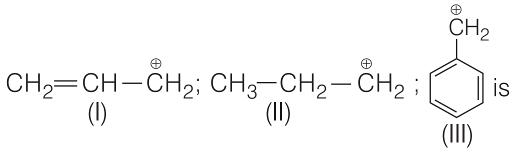
(b) 

(c) 

(d) 

18 The order of stability of the following carbocations

➞ JEE Main (Online) 2013

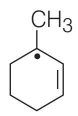


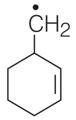
$\overset{}{CH_2}=CH-\overset{\oplus}{C}H_2$; $CH_3-CH_2-\overset{\oplus}{C}H_2$; is

(I) (II) (III)

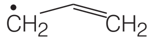
(a) III > II > I (b) II > III > I (c) I > II > III (d) III > I > II

19 Which among the following free radical is most stable?

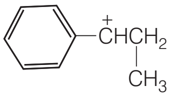
(a) 

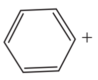
(b) 

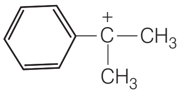
(c) $\dot{C}H_3$

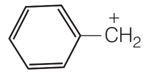
(d) 

20 Which is the most stable carbocation?

(a) 

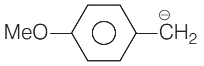
(b) 

(c) 

(d) 

21 The most stable carbanion is

(a) $Ph\overset{\ominus}{C}H_2$

(b) 

(c) 

(d) $PhCH_2\overset{\ominus}{C}H_2$

22 The most stable free radical is

(a) $PhCH_2\dot{C}H_2$ (b) $Me\dot{C}H_2$ (c) $Me_2\dot{C}H$ (d) $Ph\dot{C}HMe$

23 Correct order of nucleophilicity is

(a) $CH_3^- < NH_2^- < OH^- < F^-$ (b) $F^- < OH^- < CH_3^- < NH_2^-$

(c) $OH^- < NH_2^- < F^- < CH_3^-$ (d) $F^- < OH^- < NH_2^- < CH_3^-$

24 The correct order of increasing basicity of the given conjugate bases ($R = CH_3$) is ➞ AIEEE 2010

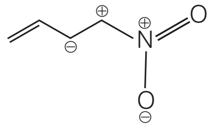
(a) $RCO\bar{O} < HC\equiv\bar{C} < \bar{R} < \bar{N}H_2$

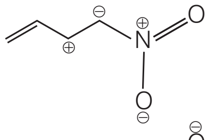
(b) $\bar{R} < HC\equiv\bar{C} < RCO\bar{O} < \bar{N}H_2$

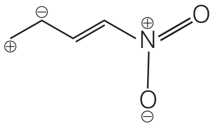
(c) $RCO\bar{O} < \bar{N}H_2 < HC\equiv\bar{C} < \bar{R}$

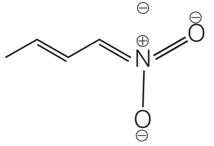
(d) $RCO\bar{O} < HC\equiv\bar{C} < \bar{N}H_2 < \bar{R}$

25 Among the following, the least stable resonance structure is

(a) 

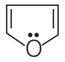
(b) 

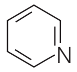
(c) 

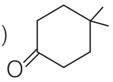
(d) 

26 Which of the following molecules is least resonance stabilised? ➞ JEE Main 2017

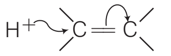
(a) 

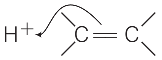
(b) 

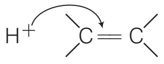
(c) 

(d) 

27 The addition of HCl to an alkene proceeds in two steps. The first step is the attack of H^+ ion to portion which can be shown as

(a) 

(b) 

(c) 

(d) All of these

28 The most suitable method for separation of 1 : 1 mixture of *ortho* and *para*-nitrophenols is

(a) sublimation (b) chromatography

(c) crystallisation (d) steam distillation

29 Two solids *A* and *B* have appreciably different solubilities in water but their melting points are very close. The mixture of *A* and *B* can be separated by

(a) sublimation (b) fractional crystallisation

(c) distillation (d) Both (b) and (c)

30 The distillation technique most suited for separating glycerol from spent lye in the soap industry is

➞ JEE Main 2016

(a) fractional distillation

(b) steam distillation

(c) distillation under reduced pressure

(d) simple distillation

31 The compound that does not give a blue colour in Lassaigne's test is

(a) aniline (b) glycine (c) hydrazine (d) urea

32 The Lassaigne's extract is boiled with dil. HNO_3 before testing for halogens because

(a) Ag_2S is insoluble in HNO_3

(b) AgCN is soluble in HNO_3

(c) Na_2S and NaCN are decomposed by HNO_3

(d) silver halides are soluble in HNO_3

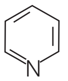
33 In Carius method of estimation of halogens 250 mg of an organic compound gave 141mg of AgBr. The percentage of bromine in the compound is

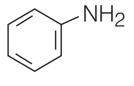
(at. mass Ag = 108, Br = 80) ➞ JEE Main 2015

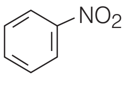
(a) 24 (b) 36 (c) 48 (d) 60

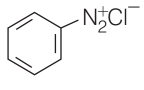
34 Which of the following compounds will be suitable for Kjeldahl's method for nitrogen estimation?

➞ JEE Main 2018

(a) 

(b) 

(c) 

(d) 

35 Match the following and choose the correct option.

	Column I		Column II
A.	Dumas method	1.	$AgNO_3$
B.	Kjeldahl's method	2.	Silica gel
C.	Carius method	3.	Nitrogen gel
D.	Chromatography	4.	Ammonium Sulphate

Codes

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

36 For the estimation of nitrogen, 1.4 g of an organic compound was digested by Kjeldahl's method and the evolved ammonia was absorbed in 60 mL of $\frac{M}{10}$ sulphuric acid. The unreacted acid required 20 mL of $\frac{M}{10}$ sodium hydroxide for complete neutralisation. The precentage of nitrogen in the compound is → JEE Main 2014

(a) 6% (b) 10% (c) 3% (d) 5%

37 29.5 mg of an organic compound containing nitrogen was digested according to Kjeldahl's method and the evolved ammonia was absorbed in 20 mL of 0.1 M HCl solution. The excess of the acid required 15 mL of 0.1 M NaOH solution for complete neutralisation. The percentage of nitrogen in the compound is → AIEEE 2010

(a) 59.0 (b) 47.4 (c) 23.7 (d) 29.5

38 A gaseous hydrocarbon gives upon combustion 0.72 g of water and 3.08 g of CO_2. The empirical formula of the hydrocarbon is → JEE Main (Online) 2013

(a) C_2H_4 (b) C_3H_4 (c) C_6H_5 (d) C_7H_8

39. 60 g of organic compound on analysis gave following results C = 24 g; H = 4 g and O = 32 g.

The compound can be

(a) CH_2O_2 (b) C_2H_2O (c) $C_2H_2O_4$ (d) CH_2O

Direction (Q. Nos. 40-41) *In the following questions Assertion (A) followed by Reason (R) is given.Choose the correct option out of the choices given below.*

(a) Assertion and Reason both are correct statements and Reason is the correct explanation of the Assertion
(b) Assertion and Reason both are correct statements but Reason is not the correct explanation of the Assertion
(c) Assertion is correct incorrect and Reason is incorrect
(d) Both Assertion and Reason are incorrect

40 **Assertion** (A) Simple distillation can help in separating a mixture of propan-1-ol (boiling point 97°C) and propanone (boiling point 56°C).

Reason (R) Liquids with a difference of more than 20°C in their boiling points can be separated by simple distillation.

41 **Assertion** (A) Sulphur present in an organic compound can be estimated quantitatively by Carius method.

Reason (R) Sulphur is separated easily from other atoms in the molecule and gets precipitated as light yellow solid.

42 **Assertion** (A) Cyclopentadienyl anion is much more stable than allyl anion.

Reason (R) Cyclopentadienyl anion is aromatic in nature.

43 **Assertion** (A) Phenol is more reactive than benzene towards electrophilic substitution reaction.

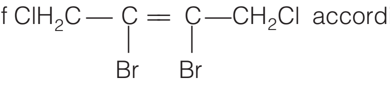
Reason (R) In case of phenol, the intermediate carbocation is more resonance stabilised.

DAY PRACTICE SESSION 2

PROGRESSIVE QUESTIONS EXERCISE

1 The bond between carbon atom (1) and carbon atom (2) in compound $N \equiv \overset{1}{C} — \overset{2}{C}H = CH_2$ involves respectively the hybrid orbitals

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

2 The name of  $ClH_2C — \underset{Br}{\underset{|}{C}} = \underset{Br}{\underset{|}{C}} — CH_2Cl$ according to IUPAC nomenclature system is

(a) dichloro dibromobutene
(b) dichloro dibromobutane
(c) 1,4- dichloro- 2,3- dibromobut- 2- ene
(d) 2,3- dibromo -1,4- dichlorobut- 2- ene

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

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

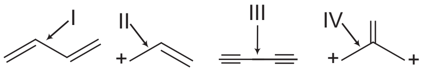
4 Arrange the following free radicals in order of decreasing stability.

Methyl (I), Vinyl (II), Allyl (III), Benzyl (IV)

Codes

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

5 On the basis of hybridisation and resonance effect, the correct order of bond length of the following is



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

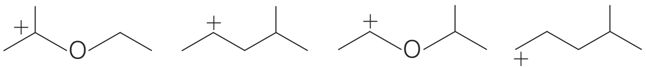
6 Which of the following order is true regarding the acidic nature of COOH ?

(a) Formic acid > acetic acid > propanoic acid
(b) Formic acid > acetic acid < propanoic acid
(c) Formic acid < acetic acid > propanoic acid
(d) Formic acid < acetic acid < propanoic acid

7 Out of the following the alkene that exhibits optical isomerism is

(a) 3-methyl-2-pentene
(b) 4-methyl-1-pentene
(c) 3-methyl-1-pentene
(d) 2-methyl-2-pentene

8 The correct stability order for the following species is



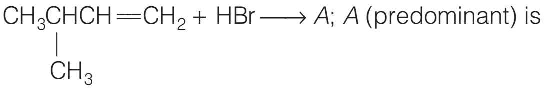
(I) (II) (III) (IV)

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

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

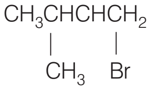
(a) $\overset{\ominus}{C}H_2-CH=CH-CH=\overset{\oplus}{O}-CH_3$
(b) $CH_2=CH-\overset{\ominus}{C}H-CH=\overset{\oplus}{O}-CH_3$
(c) $\overset{\ominus}{C}H_2-\overset{\oplus}{C}H-CH=CH-O-CH_3$
(d) $CH_2=CH-\overset{\ominus}{C}H-\overset{\oplus}{C}H-O-CH_3$

10 Consider the following reaction :



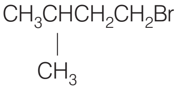
$CH_3\underset{\substack{|\\ CH_3}}{C}HCH=CH_2 + HBr \longrightarrow A$; *A* (predominant) is

(a)



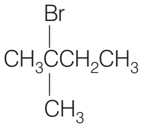
$CH_3\underset{\substack{|\\ CH_3}}{C}H\underset{\substack{|\\ Br}}{C}HCH_2$

(b)



$CH_3\underset{\substack{|\\ CH_3}}{C}HCH_2CH_2Br$

(c)

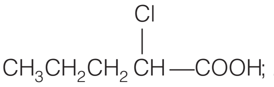


$CH_3\overset{\substack{Br\\ |}}{\underset{\substack{|\\ CH_3}}{C}}CH_2CH_3$

(d) None of these

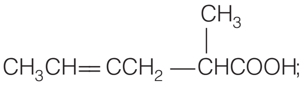
11 Which of the following compounds is wrongly named?

(a)



$CH_3CH_2CH_2\overset{\substack{Cl\\ |}}{C}H-COOH$; 2–chloropentanoic acid

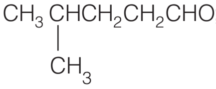
(b)



$CH_3CH=CCH_2-\overset{\substack{CH_3\\ |}}{C}HCOOH$; 2–methylhex–3–enoic acid

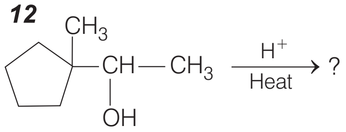
(c) $CH_3CH_2CH=CHCOCH_3$; Hex-3-en-2-one

(d)



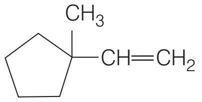
$CH_3\underset{\substack{|\\ CH_3}}{C}HCH_2CH_2CHO$; 4-methylpentanal

12

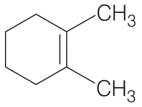


Consider the above written reaction. The product is

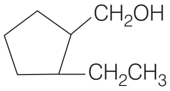
(a)



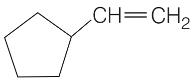
(b)



(c)

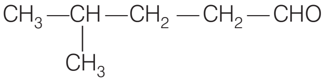


(d)



13 Indicate the wrongly named compound.

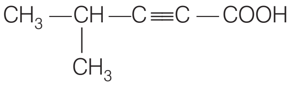
(a)



$CH_3-\underset{\substack{|\\ CH_3}}{C}H-CH_2-CH_2-CHO$

(4-methyl-1-pentanal)

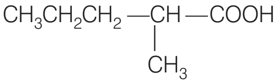
(b)



$CH_3-\underset{\substack{|\\ CH_3}}{C}H-C\equiv C-COOH$

(4-methyl-2-pentyn-1-oic acid)

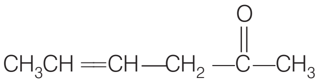
(c)



$CH_3CH_2CH_2-\underset{\substack{|\\ CH_3}}{C}H-COOH$

(2-methyl-1-pentanoic acid)

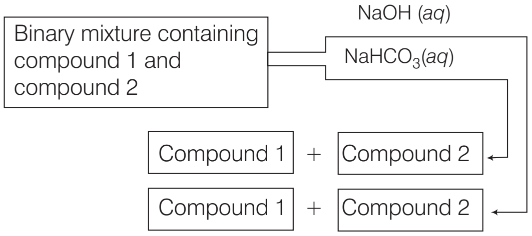
(d)



$CH_3CH=CH-CH_2-\overset{\substack{O\\ \|}}{C}-CH_3$

(3-hexen-2-one)

14 Identify the binary mixtures that can be separated into individual compounds, by differential extraction, as shown in the given scheme.



(a) C_6H_5OH and C_6H_5COOH
(b) C_6H_5COOH and $C_6H_5CH_2OH$
(c) $C_6H_5CH_2OH$ and C_6H_5OH
(d) $C_6H_5CH_2OH$, C_6H_5CHO

15 Which of the following statement is wrong?

(a) Using Lassaigne's test nitrogen or sulphur present in an organic compound can be tested
(b) Using Beilstein's test the presence of halogen in a compound can be tested
(c) Lassaigne's test fails to identify nitrogen in diazo compound
(d) In the estimation of carbon an organic compound is heated with CuO in a combustion tube

16 Which of the following orders is not correct regarding –*I* -effect of the substitutents?

(a) $—I < —Cl < —Br < —F$ (b) $—\overset{+}{N}R_3 < —\overset{+}{O}R_2$

(c) $—\overset{+}{N}R_2 < —OR < —F$ (d) $—SR < —OR < —\overset{+}{O}R_2$

17 Consider the following carbocations.

I. $C_6H_5\overset{+}{C}H_2$ II. $C_6H_5CH_2\overset{+}{C}H_2$

III. $C_6H_5\overset{+}{C}H\,CH_3$ IV. $C_6H_5\overset{+}{C}(CH_3)_2$

The correct sequence of the stability of these carbocation is

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

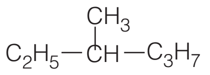
(c) III<I<II<IV (d) IV<III<I<II

18 In Kjeldahl's method, the gas evolved from 1.325 g sample of fertiliser is passed into 50.0 mL of 0.2030 N H_2SO_4. 25.32 mL of 0.1980 N NaOH are required for the titration of unused acid. What will be the percentage of nitrogen in fertiliser?

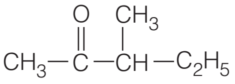
(a) 2.50 % (b) 5.43 %

(c) 6.48 % (d) 12.02 %

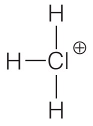
19. Among the following four structure I and IV

(I) 

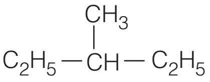
$C_2H_5—\overset{CH_3}{\overset{|}{C}}H—C_3H_7$

(II) 

$CH_3—\overset{O}{\overset{\|}{C}}—\overset{CH_3}{\overset{|}{C}}H—C_2H_5$

(III) 

$H—\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{Cl}}{}^{\oplus}$

(IV) 

$C_2H_5—\overset{CH_3}{\overset{|}{C}}H—C_2H_5$

It is true that

(a) all four are chiral compounds

(b) only I and II are chiral compounds

(c) only III is a chiral compound

(d) only II and IV are chiral compounds

ANSWERS

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

Hints and Explanations

SESSION 1

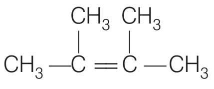
1 Electronegativity of carbon atom depends on their state of hybridisation.More the *s*-character, more is the electronegativity.

$$sp^2 < sp^2 < sp$$

s-character 25% 33% 50%

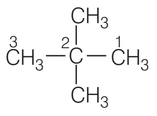
Thus, *sp*- carbon has the highest electronegativity, i.e. option (c) ($CH_3—CH_2—C \equiv {}^*CH$) is correct.

2 2,3-dimethylbut-2-ene contain only primary hydrogen atoms



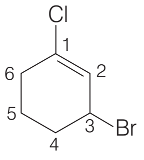
$$CH_3—\overset{CH_3}{\overset{|}{C}}=\overset{CH_3}{\overset{|}{C}}—CH_3$$

3 The neopentane



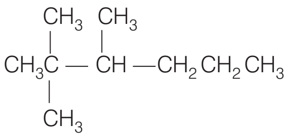
$$\overset{3}{C}H_3—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\overset{2}{C}}}—\overset{1}{C}H_3$$

IUPAC name : 2, 2-dimethylpropane

4 

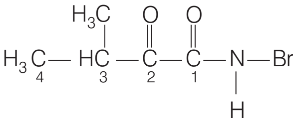
Unsaturation, i.e. double bond is at priority over halogen. So, the correct IUPAC name is 3-bromo-1-chlorocyclohexene.

5 2.2,3-trimethylhexane is represented by



$$CH_3\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—\overset{\overset{CH_3}{|}}{C}H—CH_2CH_2CH_3$$

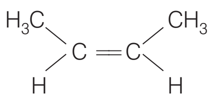
6 2-oxo-3-methyl-(N-bromo) butanamide is

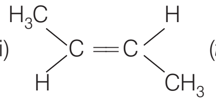


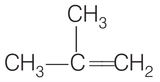
$$\underset{4}{H_3C}—\underset{3}{\overset{\overset{H_3C}{|}}{HC}}—\underset{2}{\overset{\overset{O}{\|}}{C}}—\underset{1}{\overset{\overset{O}{\|}}{C}}—\underset{\underset{H}{|}}{N}—Br$$

7 The maximum number of isomer for an alkene with molecular formula C_4H_8 is four.

(i) $CH_3CH_2CH{=}CH_2$ (But-1-ene)

(ii)  (*cis* but-2-ene)

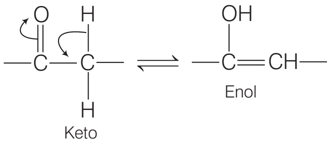
(iii)  (*trans* but-2-ene)

(iv)  (2-methylpropene)

$CH_3{-}\overset{CH_3}{C}{=}CH_2$

8 Alkyl halides do not show functional group isomerism.

9 Tautomerism is due to spontaneous interconversion of two isomeric forms with different functional groups into each other. The term tautomer means constitutional isomers that undergo such rapid interconversion so that they cannot be independently isolated.

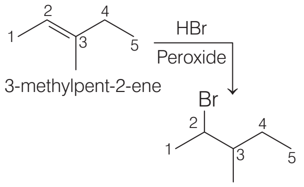


Thus, (c) 2-pentanone exhibit tautomerism.

10 For the given compound $(CH_3{-}CH{=}CH{-}CH(OH)Me$, the total number of stereoisomers are four.

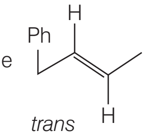
11 The number of stereoisomers in molecules which are not divisible into two equal halves and have *n* number of asymmetric C-atoms $= 2^n$.

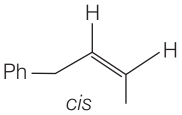
3-methyl pent-2-ene on reaction with HBr in presence of peroxide forms an addition product, i.e. 2-bromo-3-methyl pentane. It has two chiral centres. Therefore, 4 stereoisomers are possible



Anti-Markownikoff's addition
Four stereoisomers are possible
(As molecule has two chiral centres and is asymmetric).

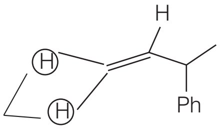
12 Alkene in which different groups are attached with the double bonded carbon atoms exhibit geometrical isomerism.

1-phenyl- 2-butene  ,

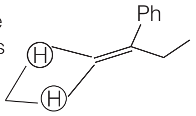


It will show geometrical isomerism.

3-phenyl-1-butene
Same group, does not show geometrical isomerism.



2-phenyl-1-butene
Same group, does not show geometrical isomerism.

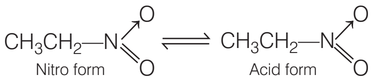


1,1-diphenyl -1-propane being an alkane (saturated compound does show geometrical isomerism.)

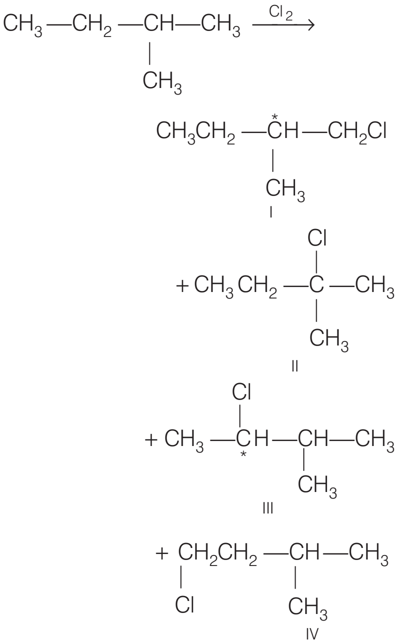
13 Metamerism is possible in ethers, thioethers, secondary amines, esters etc. The metamers belong to the same family but differ in the nature of alkyl groups, e.g.

So, $CH_3COOC_2H_5$ ethyl acetate will not show metamerism.

14 Nitroethane exhibits tautomerism



15 The correct order of nucleophilicity is
$I^- > Br^- > Cl^- > F^-$

16 

$CH_3{-}CH_2{-}\underset{CH_3}{CH}{-}CH_3 \xrightarrow{Cl_2}$

$CH_3CH_2{-}\underset{CH_3}{\overset{*}{C}H}{-}CH_2Cl$ (I)

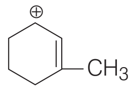
$+\ CH_3CH_2{-}\underset{CH_3}{\overset{Cl}{C}}{-}CH_3$ (II)

$+\ CH_3{-}\underset{*}{\overset{Cl}{C}H}{-}\underset{CH_3}{CH}{-}CH_3$ (III)

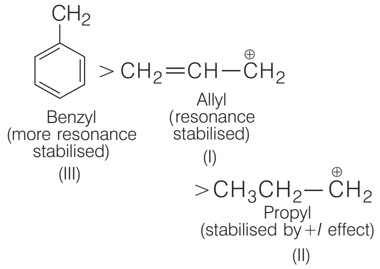
$+\ \underset{Cl}{CH_2}CH_2{-}\underset{CH_3}{CH}{-}CH_3$ (IV)

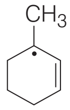
I and III compound are chiral. Therefore, two chiral compounds are possible on monochlorination of 2-methylbutane.

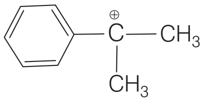
17 Due to the presence of electron releasing group ($-CH_3$) and resonance effect,

 is most stable.

18 The order of stability of carbocation is



19 Among the given free radicals, allyl free radical  is stabilised by resonance, Hence, is more stable.

20 

3° carbocation is more stable.

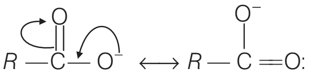
21 EWG stabilises carbanion, $-NO_2$ is EWG both by $-I$ and $-R$. Hence, (c) is the most stable.

22 The most stable free radical is 2° benzyl radical. (PhCHMe) due to resonance.

23 Nucleophilicity

$$\propto \frac{1}{\text{electronegativity of atom bearing negative charge}}$$

So, the correct order is
$F^- < OH^- < NH_2^- < CH_3^-$.

24 

In carboxylate ion, the negative charge is present on oxygen, a most electronegative element here, thus it is resonance stabilised. In $HC{\equiv}C^-$, carbon is *sp*-hybridised so its electronegativity is much higher than nitrogen.

In $\bar{N}H_2$, nitrogen is more electronegative than sp^3-hybridised C-atom. Thus, the order of the stability of conjugated bases is

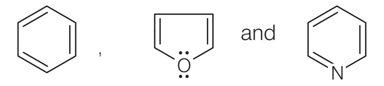
$$RCOO^- > HC \equiv C^- > \bar{N}H_2 > R^-$$

and higher is the stability of conjugated bases, lower will be basic character. Hence, the order of basic character is as

$$RCOO^- < HC \equiv C^- < \bar{N}H_2 < R^-$$

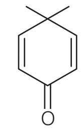
25 The least stable resonance structure is (a). Here, two positive charges present at the adjacent place, elevates the energy, thus lowers the stability.

26 Aromatic compounds are stable due to resonance while non-aromatics are not. According to Huckel's rule (or $4n + 2$ rule), "For a planar, cyclic compound to be aromatic, its π cloud must contain $(4n + 2)\pi$ electrons, where, n is any whole number." Thus,



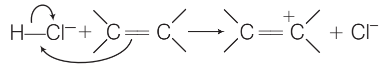
($6\pi e^-$ system) ($4\pi e^- + 2e^-$ system) ($6\pi e^-$ system)

Above given compounds are aromatic and stabilised by resonance. They follow Huckel's rule.



is non-aromatic, hence, least stabilised by resonance.

27 The first step in addition of HCl to an alkene proceeds as



28 *o*-nitrophenol exists as monomer because of chelation and hence steam volatile. Thus, steam distillation method is used for separation of 1 : 1 mixture.

29 Fractional crystallisation is used to separate two solids *A* and *B* having appreciable different solubilities in water but their melting points are very close.

30 Glycerol with high boiling point (290°C) can be separated from spent lye by distillation under reduced pressure. This process is used to purify liquids having very high boiling points. By this process, liquid is made to boil at lower temperature than its boiling point by lowering the pressure on its surface.

31 Hydrazine does not give a blue colour in Lassaigne's, since it does not contain carbon.

32 In order to decompose unreacted sulphide and cyanide, HNO_3 is added.

33 Weight of organic compound = 250 mg

Weight of AgBr = 141 mg

∴ According to formula of % of bromine by Carius method

$$\% \text{ of Br} = \frac{\text{Atomic mass of Br}}{\text{Molecular mass of AgBr}} \times \frac{\text{mass of AgBr}}{\text{mass of organic bromide}} \times 100$$

$$\therefore \quad \% \text{ of Br} = \frac{80}{188} \times \frac{141}{250} \times 100 = \frac{1128000}{47000} = 24\%$$

34 Estimation of nitrogen through Kjeldahl's method is not suitable for organic compounds containing nitrogen in ring or nitrogen in nitro or azo groups. It is because of the fact that nitrogen of these compounds does not show conversion to ammonium sulphate $(NH_4)_2SO_4$ during the process. Hence, among the given compounds only aniline can be used suitably for estimation of nitrogen by Kjeldahl's method.

35 $A \longrightarrow 3$; $B \longrightarrow 4$; $C \longrightarrow 1$; $D \longrightarrow 2$

Dumas' method - Nitrogen gel

Kjeldahl's method - Ammonium sulphate

Carius method - $AgNO_3$

Chromatography- Silica gel

36 Mass of organic compound = 1.4g

Let it contain x mmole of N-atom.

$$\text{Organic compound} \longrightarrow \underset{x \text{ mmol}}{NH_3}$$

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4 \quad \ldots\text{(i)}$$

$$H_2SO_4 + \underset{\substack{\text{6 mmol}\\\text{initially}\\\text{taken}}}{2NaOH} \longrightarrow Na_2SO_4 + 2H_2O \quad \ldots\text{(ii)}$$

2 mmoles of NaOH reacted.

Hence, mmoles of H_2SO_4 reacted in Eq. (ii) = 1

$\Rightarrow$ mmoles of H_2SO_4 reacted from Eq. (i) = 6 – 1 = 5 mmol

$\Rightarrow$ mmoles of NH_3 in Eq. (i)

$= 2 \times 5 = 10$ mmol

$\Rightarrow$ mmoles of N-atom in the organic compound = 10 mmol

$\Rightarrow$ Mass of N $= 10 \times 10^{-3} \times 14$

$= 0.14$g % of N

$$= \frac{\text{Mass of N present in organic compound}}{\text{Mass of organic compound}} \times 100$$

$$\Rightarrow \% \text{ of N} = \frac{0.14}{1.4} \times 100 = 10\%$$

37 Weight of organic compound = 29.5 mg

$$NH_3 + HCl \longrightarrow NH_4Cl$$

$$\underset{\text{(Remaining)}}{HCl} + \underset{\substack{15 \times 0.1 \text{ M}\\= 1.5 \text{ mmol}}}{NaOH} \longrightarrow NaCl + H_2O$$

Total millimole of HCl = 2

Millimole used by $NH_3 = 2 - 1.5 = 0.5$

Weight of $NH_3 = 0.5 \times 17 \text{ mg} = 8.5 \text{ mg}$

Weight of nitrogen

$= \frac{14}{17} \times 8.5 \text{ mg} = 7 \text{ mg}$

$$\% \text{ Nitrogen} = \frac{7}{29.5} \times 100 = 23.7\%$$

38 18 g H_2O contains 2 g hydrogen

∴ 0.72 g H_2O contains 0.08 g H. 44 g CO_2 contains 12 g C

∴ 3.08 g CO_2 contains 0.84 g C

$\therefore C : H = \frac{0.84}{12} : \frac{0.08}{1} = 0.07 : 0.08$

$= 7 : 8$

∴ Empirical formula = C_7H_8

39 Moles of C is 24 g $= \frac{24\text{g}}{12\text{g}} = 2$

Moles of H is 4 g $= \frac{4\text{g}}{16\text{g}} = 4$

Moles of O is 32 g $= \frac{32\text{g}}{16\text{g}} = 2$

So, molecular formula of compound is $C_2H_4O_2$, i.e. CH_2O

40 Simple distillation can be used to separate a mixture of two liquids which do not react and have boiling point difference of more than 20°C.Hence, a mixture of propan-1-ol and propanone can be separated.

41 S (sulphur) present in an organic compound can be estimated quantitatively by Carius method.In this method, a known weight of organic compound is heated with fuming HNO_3, S present in it gets converted into H_2SO_4. On adding $BaCl_2$,H_2SO_4 gets precipitated as $BaSO_4$ which may be of light yellow or white in colour. If light yellow colour is obtained, it means some impurities are present. It is then filtered, washed, purified and then dried and finally pure $BaSO_4$ of white colour is obtained.

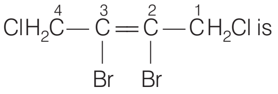
42 Cyclopentadienyl anion is more stable than allyl anion as the former is aromatic and is stabilised by resonance.

43 —OH group is electron donating group, thus activates the benzene ring for electrophilic substitution reaction. Due to more resonance stabilisation of phenoxide ion, it gives more stable carbocation (intermediate).

SESSION 2

1 The bond between carbon atom (1) and carbon atom (2) in compound $N \equiv \overset{1}{C}—\overset{2}{C}H = CH_2$ involves *sp* and sp^2 hybrid orbitals.

2 The IUPAC name of



$$Cl H_2\overset{4}{C}—\underset{Br}{\overset{3}{C}}=\underset{Br}{\overset{2}{C}}—\overset{1}{C}H_2Cl$$ is

2, 3-dibromo-1,4-dichlorobut-2-ene

3 Presence of electron withdrawing groups stabilises the carbanions. Thus, the order of stability is

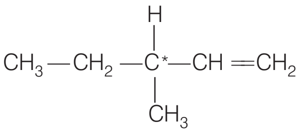
$$\overset{-}{C}Cl_3 > C_6H_5\overset{-}{C}H_2 > (CH_3)_2\overset{-}{C}H > (CH_3)_3\overset{-}{C}.$$

4 On the basis of conjugative and hyperconjugative structure. The correct order for the stability of free radical is benzyl (IV) > allyl (III) > methyl (I) > vinyl (II).

5 As the *p*-character increases, bond length also increases. Resonance effect also cause a change in bond length. Thus, the order of bond length is II > IV > III > I.

6 The correct order for the acidic nature of —COOH group is formic acid > acetic acid > propanoic acid

7



$$CH_3—CH_2—\underset{CH_3}{\overset{H}{C^*}}—CH=CH_2$$

3-methyl-1-pentene

(It has one chiral centre)

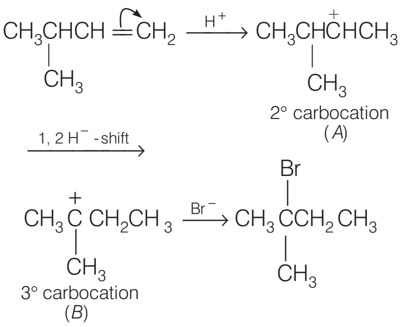
8 Carbocation (I) is stabilised by + *R* effect, (effect of O) as well as + *I* effect of two CH_3 groups. Carbocation (II) is stabilised by + *I* effect of CH_3 and $CH_2CH(CH_3)_2$ groups.

Carbocation (III) is stabilised by + *R* effect of O and +*I* effect of one CH_3 group. Carbocation (IV) is stabilised by +*I* effect of $CH_3CH_2CH(CH_3)_2$ group. Thus, decreasing order of stability of these carbocations is I > III > II > IV

9 The least stable resonating structure of 1-methoxy-1,3-butadiene is $\overset{\ominus}{C}H_2—\overset{\oplus}{C}H—CH=CHOCH_3$. The octet of all atoms are complete in structures (a) and (b). The molecule in which all the atoms have complete octet is more stable than the molecules in which atom have incomplete octet.

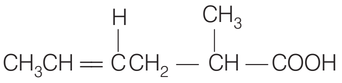
In structure (d), the electron deficiency of positive charged carbon is duly compensated by lone pair of electrons of adjacent oxygen atoms while such neighbour group support is not available in structure (c). Hence, structure (c) is least stable in comparison to structure (d).

10



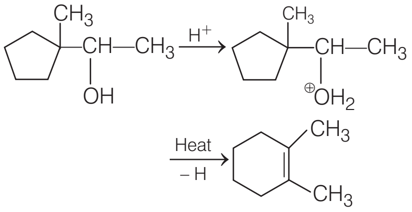
$$\underset{CH_3}{CH_3CHCH}=CH_2 \xrightarrow{H^+} CH_3\underset{CH_3}{CH}\overset{+}{C}HCH_3 \xrightarrow{1,\,2\,H^-\text{-shift}} CH_3\underset{CH_3}{\overset{+}{C}}CH_2CH_3 \xrightarrow{Br^-} CH_3\underset{CH_3}{\overset{Br}{C}}CH_2CH_3$$

11 The correct IUPAC name of the given structure is 2-methyl hex-2-en-1-oic acid.

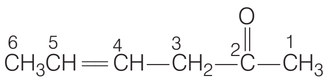


$$CH_3CH=\overset{H}{C}CH_2—\overset{CH_3}{CH}—COOH$$

12 It is the elimination reaction with ring expansion.



13 The correct IUPAC name is



$$\overset{6}{C}H_3\overset{5}{C}H=\overset{4}{C}H—\overset{3}{C}H_2—\overset{O}{\overset{\|}{\overset{2}{C}}}—\overset{1}{C}H_3$$

(hex-4-en-2-one)

14 For separation of mixture compound III and IV are notchiral due to presence of same group on carbon atom by differential extraction one of the component must form salt with the given base so that the salt will be extracted in aqueous layer leaving other component in organic layer.

(a) Both phenol and benzoic acid forms salt with NaOH but not with $NaHCO_3$ hence, this mixture cannot be separated.

(b) Benzoic acid forms salt with NaOH and $NaHCO_3$ both while benzyl alcohol does not hence, the mixture can be separated using NaOH or $NaHCO_3$.

(c) Neither benzyl alcohol nor phenol form salt with $NaHCO_3$, so mixture cannot be separated by using $NaHCO_3$.

(d) Both $C_6H_5CH_2OH$ and C_6H_5CHO cannot form salt.

15 In estimation of C, organic compound is burnt in the presence of excess of oxygen and CuO.

$$2CuO + C \longrightarrow 2Cu + CO_2$$

16 The correct order regarding —I effect of the substituents is –I< – Br < –Cl < – F

These groups have the ability to withdraw electron density toward themselves.

17 The correct sequence of carbocation is II < I < III < IV. Electron releasing stabilises the carbocation by dispersal of positive charge. More the number of alkyl groups, the greater the dispersal of positive charge and the more stable is the carbocation.

18 Meq. of acid taken

$= 0.2030 \times 50 = 10.15$

Meq. of acid used by NaOH

$= 0.1980 \times 25.32 = 5.013$

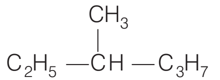
$\therefore$ Meq. of acid used for NH_3

$= 10.15 - 5.013 = 5.137$

or Meq. of NH_3 (i.e.) $NV = 5.137$

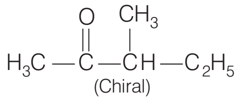
$$\therefore \quad \%\ N = \frac{1.4 \times 5.137}{1.325} = 5.43\%$$

19 Only (I) and (II) are chiral compounds as all the four attached substituents are different.



$$C_2H_5—\overset{CH_3}{C}H—C_3H_7$$

(Chiral)



$$H_3C—\overset{O}{\overset{\|}{C}}—\overset{CH_3}{C}H—C_2H_5$$

(Chiral)