

## Organic Chemistry

### Key Points

1. The nature of the covalent bonding in organic compounds can be described in terms of orbitals hybridization concept, according to which carbon can have  $sp^3$ ,  $sp^2$  and  $sp$  hybridized orbitals. The  $sp^3$ ,  $sp^2$  and  $sp$  hybridized carbons are found in compounds like methane, ethene and ethyne respectively.
2. The chemical properties of an element depend on the electronic configuration of the outer shell.
3. Hydrogen bond a particularly strong intermolecular attraction between a non-bonding pair of electrons and an electrophilic O—H or N—H hydrogen. Hydrogen bonds have bond energies of about 5 kcal/mol (21 kJ/mol), compared with about 100 kcal/mol (about 400 kJ/mol) for typical C—H bonds.
4. This mixing and redistribution of energy is called hybridisation and the resultant orbitals are called hybrid orbitals.
5. Organic reaction mechanism concepts are based on the structure of the substrate molecule, fission of a covalent bond, the attacking reagents, the electron displacement effects and the conditions of the reaction.
6. The hydrogen bond is an electrostatic attractive force between covalently bonded hydrogen atom of one molecule and an electronegative atom (such as F, O, and N) of another molecule.
7. A covalent bond may be cleaved in heterolytic or homolytic fashion. A heterolytic cleavage yields carbocations or carbanions, while a homolytic cleavage gives free radicals as reactive intermediate.
8. Reactions proceeding through heterolytic cleavage involve the complimentary pairs of reactive species. These are electron pair donor known as nucleophile and an electron pair acceptor known as electrophile.

9. Organic compounds can also be classified on the basis of functional groups, into families or homologous series.
10. Organic chemistry deals with millions of compounds. In order to clearly identify them, a systematic method of naming has been developed and is known as the IUPAC (**I**nternational **U**nion of **P**ure and **A**ppplied **C**hemistry) system of nomenclature.
11. Inductive effect is donation or withdrawal of electron density through sigma bonds.
12. A molecule or ion can be expressed in two or more valid lewis structures can be drawn, differing only in the placement of valence electrons. These lewis structures are called resonance forms. Individual resonance forms do not exist, but we can estimate their relative energies. The more important (lower –energy) structures are called major contributors, and the less important (higher-energy) structures are called minor contributors. When a charge is spread over two or more atoms by resonance, it is said to be delocalized, and the molecule is said to be resonance stabilized.
13. Electromeric effect is defined as the complete transfer of a shared pair of  $\pi$ -electrons to one of the atoms joined by a multiple bond on the demand of an attacking reagent.
14. Compounds containing carbon and hydrogen only are called hydrocarbons. A hydrocarbon is termed saturated if it contains only carbon-carbon single bonds.
15. Hyperconjugation involves delocalization of s electrons of C – H bond of an alkyl group directly attached to an atom of unsaturated system or to an atom with an unshared p orbital. The s-electrons of C – H bond of the alkyl group enter into partial conjugation with the attached unsaturated system or with the unshared p orbital. Hyper conjugation is a permanent effect.
16. Unsaturated hydrocarbons are those, which contain at least one carbon-carbon double or triple bond.

17. The inductive, resonance, electromeric and hyperconjugation effects may help in the polarization of bond making certain carbon atom or other atom positions as places of low or high electron densities.
18. Organic reactions can be broadly classified into following types: substitution, addition elimination and rearrangement reactions.
19. The order of decreasing priority for some functional groups is:  
—SO<sub>3</sub>H, —COOH, —COOR (R = alkyl group), —COCl, —CONH<sub>2</sub>, —CN,  
—HC = O, >C = O, —OH, —NH<sub>2</sub>, >C=C<, —C — C—.
20. Reactive intermediate is a short-lived species that is never present in high concentration because it reacts as quickly as it is formed.
21. Isomers are different compounds with the same molecular formula.
22. Isomers are grouped into two broad classes: constitutional isomers and stereoisomers. Constitutional isomers (structural isomers) differ in their bonding sequence; their atoms are connected differently. **Stereoisomers** have the same bonding sequence, but they differ in the orientation of their atoms in space. **Stereochemistry** is the study of the structure and chemistry of stereoisomers.
23. Electrophilic reagent can be of two types, namely  
(i) Positive electrophiles and (ii) Neutral electrophiles.
24. **Negative Nucleophiles:** Species which carry an excess of electron pair and are negatively charged.
25. Alkanes show conformational isomerism due to free rotation along the C — C sigma bonds. Out of staggered and the eclipsed conformations of ethane, staggered conformation is more stable as hydrogen atoms are farthest apart. Alkenes exhibit geometrical (cis-trans) isomerism due to restricted rotation around the carbon-carbon double bond.

26. Certain compounds rotate the plane polarized light (produced by passing ordinary light through Nicol prism) when it is passed through their solutions. Such compounds are called optically active compounds.
27. The angle by which the plane polarized light is rotated is measured by an instrument called polarimeter. If the compound rotates the plane polarized light to the right, i.e., clockwise direction, it is called dextrorotatory (Greek for right rotating) or the d-form and is indicated by placing a positive (+) sign before the degree of rotation. If the light is rotated towards left (anticlockwise direction) the compound is said to be laevorotatory or the l-form and a negative (−) sign is placed before the degree of rotation. Such (+) and (−) isomers of a compound are called optical isomers and the phenomenon is termed as optical isomerism.
28. Homolytic fission results in the formation of free radicals.
29. The objects which are non-superimposable on their mirror image (like a pair of hands) are said to be chiral and this property is known as chirality. While the objects, which are, superimposable on their mirror images are called achiral.
30. The stereoisomers related to each other as non superimposable mirror images are called enantiomers. Enantiomers possess identical physical properties namely, melting point, boiling point, solubility, refractive index, etc. They only differ with respect to the rotation of plane polarized light. If one of the enantiomer is dextro rotatory, the other will be laevo rotatory.
31. The ions of carbon, known as carbanions and carbonium ions, are of special importance in organic chemistry.
32. Homolytic chemistry is the chemistry of the odd electron; Heterolytic chemistry is the chemistry of the electron pair.
33. A mixture containing two enantiomers in equal proportions will have zero optical rotation, as the rotation due to one isomer will be cancelled by the rotation due to the other isomer. Such a mixture is known as racemic mixture or racemic modification. A racemic mixture is represented by prefixing dl or ( $\pm$ ) before the

name, for example ( $\pm$ ) butan-2-ol. The process of conversion of enantiomer into a racemic mixture is known as racemisation.

34. Diastereomers are stereoisomers which are not mirror images.
35. A molecule as a whole is asymmetric if it does not possess any element of asymmetry such as
  - i) Plane of symmetry
  - ii) Centre of symmetry
  - iii) Axis of symmetry
  - iv) Alternating axis of symmetry
36. Inductive effect is denoted by the symbol I and represented by a straight arrow ( $\rightarrow$ ), the arrow head pointing towards the source.
37. The inductive effect causes certain degree of polarity in the bond which in turn renders the bond much more liable to be attached by other charged atoms (or) group.
38. Thus inductive effect may be defined as the permanent displacement of electron forming a covalent bond towards the more electronegative element or group.
39. The plane of symmetry of a molecule represents a plane bisecting the molecule such that each half of the molecule is the mirror image of the other half. The plane of symmetry is called a sigma ( $\sigma$ ) plane or a mirror plane.
40. The centre of symmetry is defined as that point (atom) in a molecule from which if a straight line is drawn from any part of the molecule through that point (atom) and extended to an equal distance by a straight line on the other side, a like point (atom) is encountered. It is symbolized as  $C_i$  and is also called the centre of inversion.
41. Configurations are the two possible spatial arrangements around a chirality centre or other stereocentre.
42. If a molecule or ion can be shown by two (or) more structures differing only in the distribution of electrons, but none of these structures truly explains all the properties

of that molecule (or) ion, these structures are called resonating (or) contributing or canonical structures and this phenomenon is called resonance.

43. This kind of polarizability of multiple bonds is known as electromeric effect. Electromeric effect causes complete transfer of the loose electrons from one carbon to the other consequently, one end is positively charged and the other negatively charged which aid the reagent to attack.
44. D-L configurations (Fischer-Rosanoff convention) D has the same relative configuration as (+)-glyceraldehyde. L has the same relative configuration as (–)-glyceraldehyde.
45. The configuration of a chiral centre is specified by Cahn-Ingold-Prelog notational system using the descriptors R and S.
46. Hyper conjugation involves delocalization of C—H sigma electrons into an adjacent pi system.
47. Fischer projection formula is line notation used to indicate absolute configuration in two-dimensional sense.
48. Stability of Carbonium ions: The order of stability of carbonium ions is as follows  $(\text{CH}_3)_3\text{C}^+ > (\text{CH}_3)_2\text{CH}^+ > \text{CH}_3\text{CH}_2^+$   
Above order of stability can be explained by hyper conjugation.
49. Resolution refers to method of separating a racemic mixture into two pure enantiomers.
50. The maximum possible number of stereoisomers for n centres of chirality is equal to  $2^n$ . However, this rule does not hold when the molecule contains two or more analogous centres of chirality. In such compounds with  $n = 2$ , only three stereoisomers are formed—a d, l pair and a meso compound.
51. Carbocations are the key intermediates in several reactions and particularly in nucleophilic substitution reactions.
52. The greater stability of alkyl substituted carbocations is sometimes partly ascribed to the phenomenon of hyperconjugation.

53. Carbanions are anions of carbon, generated by the removal of one of the groups attached to a carbon without removing the bonding electrons.
54. The configuration of simple carbanions such as the methyl anion thus appears to be pyramidal just like that of ammonia with which the methyl anion is isoelectronic.
55. Carbenes can be defined as neutral, divalent carbon intermediates in which a carbon is covalently bonded to two atoms and has two non-bonding orbitals containing two electrons between them.
56. Nitrenes are electron-deficient monovalent nitrogen species in which the nitrogen atom has a sextet of electrons in its outer shell.
57. Arynes may be defined as aromatic compounds containing a formal carbon-carbon triple bond.
58. Compounds which possess the same molecular formula but differ in bonding arrangement of atoms (or) groups within the molecule i.e. differ in structure
59. The conversion of a keto form into an enol form is known as enolisation and the enolisation of a compound has been found to depend upon various factors such as structural factor, temperature and nature of solvent.