Organic Chemistry - Some Basic Principles and Techniques

12 Chapter

1 CLASSIFICATION OF ORGANIC COMPOUNDS

Organic Compounds

- Acyclic or open chain
- Cyclic or closed chain
  - Alicyclic compounds
    - Homocyclic or carbocyclic compounds
    - Heterocyclic compounds (non-aromatic)
  - Aromatic compounds
    - Benzenoid compounds
    - Non-benzenoid compounds
  - Heterocyclic aromatic compounds

2 NOMENCLATURE

Abbreviation for alkyl groups

Isopropyl – $CH_3-CH(CH_3)-$

sec-Butyl – $CH_3-CH_2-CH(CH_3)-$

Isobutyl – $(CH_3)_2CH-CH_2-$

tert-Butyl – $(CH_3)_3C-$

Neopentyl – $CH_3-C(CH_3)_2-CH_2-$

Nomenclature of Branched Chain Alkanes: (Rules)

(a) Longest carbon chain is identified

(b) Numbering is done so that branched carbon atoms get the lowest possible numbers

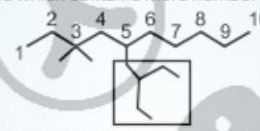
(c) For two substituents present at equivalent positions, the lower number is given to the one coming first in alphabetical listing

(d) For branched alkyl groups, the carbon atom of the branch that attaches to the root alkane is numbered (1) such as

$^{4}CH_3-\underset{CH_3}{^{3}CH}-^{2}CH_2-\underset{CH_3}{^{1}CH}-$ (1, 3-Dimethylbutyl) –

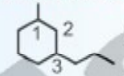
(e) While writing the names of the substituents in alphabetical order, the prefixes iso and neo are considered to be the part of fundamental name of alkyl group but sec- and tert- are not considered to be the part of fundamental name.

(f) If two chains are of equal size then that chain is to be selected which contains more number of side chains



5-(2-Ethylbutyl)-3, 3-dimethyldecane

Nomenclature of Cyclic Compounds



(Alphabetic order of numbering)
1-Methyl-3-propylcyclohexane

Nomenclature of organic compounds having functional groups(s)

(a) The functional group present in the molecule is identified which determines the choice of appropriate suffix.

(b) 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.

(c) The order of decreasing priority for some functional groups:

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

$-HC=O, >C=O, -OH, -NH_2, >C=C<, -C\equiv C-$

$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

Hexane-2, 4-dione

$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-COOH$

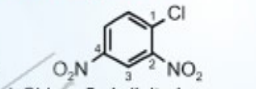
5-Oxohexanoic acid

$CH_2=CH-CH_2-\underset{OH}{CH}-CH_3$

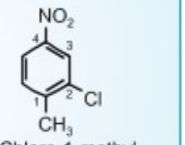
Pent-4-en-2-ol

Cyclohex-2-en-1-ol

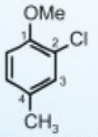
Nomenclature of substituted benzene compounds



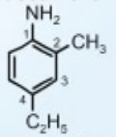
1-Chloro-2, 4-dinitrobenzene



2-Chloro-1-methyl -4-nitrobenzene



2-Chloro-4-methylanisole



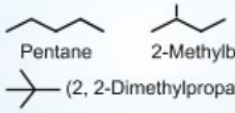
4-Ethyl-2-methylaniline

3 ISOMERISM

(a) Structural Isomerism

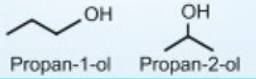
Compounds having the same molecular formula but different structures are classified as structural isomers.

(i) **Chain isomerism:** Example, C_5H_{12} represents three chain isomers



Pentane, 2-Methylbutane, (2, 2-Dimethylpropane)

(ii) **Position isomerism:** Example, C_3H_8O represents two alcohols



Propan-1-ol, Propan-2-ol

(iii) **Functional group isomerism:** Example, C_3H_6O represents an aldehyde and a ketone

propanone propanal

(iv) **Metamerism:**

It arises due to different alkyl chains on either side of the functional group.

Example : $CH_3OC_3H_7$ and $C_2H_5OC_2H_5$ are metamers.

(b) **Stereoisomerism**

The compounds that have the same constitution and sequence of covalent bonds but differ in relative positions of their atoms or groups in space are called stereoisomers. They are classified as

(i) Geometrical isomerism

(ii) Optical isomerism

4 FUNDAMENTAL CONCEPTS IN ORGANIC REACTION MECHANISM

Organic molecule (Substrate) $\xrightarrow{\text{Attacking reagent}}$ [Intermediate] $\rightarrow$ Byproduct(s)

$\downarrow$

Product(s)

(a) **Fission of Covalent bond**

(i) **Heterolytic cleavage** and (ii) **Homolytic cleavage**

(i) **Heterolytic cleavage**

In heterolytic cleavage, the bond breaks in such a fashion that the shared pair of electrons remains with one of the fragments.

- **Carbocations:**
  - A species having a carbon atom possessing sextet of electrons and a positive charge is called carbocation.
  - Alkyl groups directly attached to the positively charged carbon stabilise the carbocations due to inductive and hyperconjugation effects.
    - Stability order:

$(CH_3)_3\overset{+}{C} > (CH_3)_2\overset{+}{C}H > CH_3\overset{+}{C}H_2 > \overset{+}{C}H_3$

- **Carbanions:**
  - A carbon species carrying a negative charge on carbon atom is called carbanion.
  - Carbon in carbanion is generally sp^3 hybridised and its structure is distorted tetrahedral.
    - Stability order:

$\bar{C}H_3 > CH_3\bar{C}H_2 > (CH_3)_2\bar{C}H > (CH_3)_3\bar{C}$

(ii) **Homolytic cleavage:** One of the electrons of the shared pair in a covalent bond goes with each of bonded atoms resulting in formation of free radicals.

- Free radicals : Stability order

$\dot{C}H_3 < CH_3\dot{C}H_2 < (CH_3)_2\dot{C}H < (CH_3)_3\dot{C}$

(b) **Nucleophiles and Electrophiles**

- **Nucleophiles:** A reagent that brings an electron pair to the reactive site is called a nucleophile (Nu:)

Examples: H_2O, NH_3, $CH_3\bar{O}$, $\bar{S}H$

- **Electrophile :** A reagent that takes away an electron pair from reactive site is called electrophile (E^+)

Example: $AlCl_3$, BF_3, $\overset{+}{N}O_2$, Cl^+

(c) **Electron Displacement Effects in Covalent Bonds**

(i) **Inductive effect**

- When covalent bond is formed between atoms of different electronegativity, the electron density is more towards the more electronegative atom.
- It operates through σ-bonds
- The inductive effect is related to the ability of substituent(s) to either withdraw or donate electron density to the attached carbon atom.
- It is a permanent effect
- It is of two types

+I effect : e.g. $-CH_3$, $-CH_2CH_3$ etc.

–I effect : e.g. $-NO_2$, $-CN$, $-CHO$, $-COOH$ etc.

(ii) **Resonance structures**

- Benzene can be represented by energetically identical structures (I) and (II) called resonance structures.

(I) (II)

- Actual structure is resonance hybrid of (I) and (II)
- The resonance structures (canonical structures) are hypothetical and individually do not represent any real molecule.
- The energy of actual structure of the molecule is lower than that of any of the canonical structures.
- The difference in energy between the actual structure and the lowest energy resonance structure is called the resonance energy.

(iii) **Resonance effect**

- It is a permanent effect
- It operates through π-bond(s)
- It is of two types

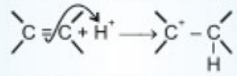
+R effect : Halogens, –OH, –OR, –OCOR, $-NH_2$ etc.

–R effect : –COOH, –CHO, –CN, $-NO_2$ etc.

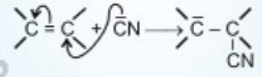
(iv) **Electromeric effect**

- It is a temporary effect
- Organic compounds having multiple bond (a double or triple bond) show this effect in presence of attacking reagent
- It is of two types

Positive electromeric effect (+E effect)

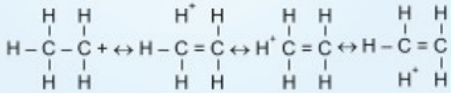


Negative electromeric effect (–E effect)



(v) **Hyperconjugation**

- It involves delocalisation of σ 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



- It is a permanent effect.

5 METHODS OF PURIFICATION OF ORGANIC COMPOUNDS

The common techniques used for purification:

(i) Sublimation (ii) Crystallisation

(iii) Distillation : It is used to separate

(a) Volatile liquids from non-volatile impurities.

(b) The liquids having sufficient difference in boiling points e.g. mixture of chloroform (b.p. 334 K) and aniline (b.p. 457 K) is separated by this method.

(c) Distillation can be achieved by three different ways

- **Fractional Distillation:** This is applicable if boiling points of two liquids is not much, e.g. this is applicable to separate different fractions of crude oil in petroleum industry.

- **Steam Distillation:** This technique is applied to separate substances which are steam volatile and are immiscible with water.
  Example: Aniline is separated by this technique from aniline water mixture.
- **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.
  Example: Glycerol can be separated from spent-lye in soap industry by using this technique.

(iv) **Differential Extraction:**
- When an organic compound is present in an 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.
- They form distinct layer which can be separated by separatory funnel.
- The compound is obtained by evaporating the organic solvent.

(v) **Chromatography:** It is an important technique extensively used to separate mixtures into their components.
Based on the principle involved it is classified into two main categories.
(a) Adsorption chromatography and
(b) Partition chromatography
(a) **Adsorption Chromatography:** It is based on the fact that different compounds are adsorbed on an adsorbent to different degrees. Commonly used adsorbents are silica gel and alumina. It is of two types
- Column chromatography
- Thin layer chromatography

(b) **Partition Chromatography:** It is based on continuous differential partitioning of components of a mixture between stationary and mobile phases. Paper chromatography is a type of partition chromatography.

(6) QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

Nitrogen, sulphur, halogens and phosphorus present in an organic compound are detected by Lassaigne's test. The elements present in the compound are converted from covalent form into the ionic form by fusing compound with sodium metal.

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

$2Na + S \xrightarrow{\Delta} Na_2S$; $Na + X \xrightarrow{\Delta} NaX$ (X = Cl, Br or I)

(A) **Test for nitrogen**

$6\bar{C}N + Fe^{2+} \rightarrow [Fe(CN)_6]^{4-}$

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

(B) **Test of Sulphur**

(i) $S^{2-} + Pb^{2+} \rightarrow$ **PbS (black)**

(ii) $S^{2-} + \underset{\text{Nitroprusside}}{[Fe(CN)_5NO]^{2-}} \rightarrow \underset{\text{Violet}}{[Fe(CN)_5NOS]^{4-}}$

In case, nitrogen and sulphur both are present, sodium thiocyanate is formed

$Na + C + N + S \rightarrow NaSCN$

$Fe^{3+} + S\bar{C}N \rightarrow [Fe(SCN)]^{2+}$ (Blood red)

(C) **Test of Halogen**

$X^- + Ag^+ \rightarrow AgX$
- A white precipitate, soluble in NH_4OH shows presence of chlorine.
- A yellowish precipitate soluble, sparingly soluble in NH_4OH shows presence of Br
- A yellow precipitate insoluble in NH_4OH shows presence of iodine

(D) **Test of Phosphorus**

$\text{Compound} \xrightarrow{Na_2O_2} Na_3PO_4 \xrightarrow{HNO_3} H_3PO_4$

$H_3PO_4 \xleftarrow{(NH_4)_2MoO_4} \underset{\text{(Yellow ppt)}}{(NH_4)_3PO_4 \cdot 12\,MoO_3}$

(7) QUANTITATIVE ANALYSIS

(A) **Nitrogen is estimated by Dumas and Kjeldahl's method**

(i) **Dumas method**

Let volume of nitrogen at STP = V mL

Mass of organic compound = m g

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

(ii) **Kjeldahl's Method**

$\text{Organic compound} + H_2SO_4 \rightarrow (NH_4)_2SO_4$

$(NH_4)_2SO_4 \xleftarrow{H_2SO_4} NH_3 \xleftarrow{NaOH} (NH_4)_2SO_4$

Let mass of organic compound = m g

Volume of H_2SO_4 of molarity M needed for neutralisation of ammonia produced = V mL

$$\% \text{ of nitrogen} = \frac{V \times 2M \times 1.4}{m}$$

- Kjeldahl's method is not applicable to compounds containing nitrogen in nitro and azo groups and nitrogen present in ring (e.g. pyridine).

(B) **Halogens**

Carius method:

$\text{Organic compound} \xrightarrow[AgNO_3\,\Delta]{\text{Fuming } HNO_3} AgX \downarrow$

Let mass of compound = m g

Mass of AgX formed = m_1 g

$$\% \text{ of halogen} = \frac{\text{atomic mass of X} \times m_1 \times 100}{\text{molecular mass of Ag X} \times m} \%$$

(C) **Sulphur**

Carius method:

$\text{Organic compound} \xrightarrow{Na_2O_2} H_2SO_4 \xrightarrow{BaCl_2} BaSO_4 \downarrow$

Let mass of compound = m g

Mass of $BaSO_4$ = m_1 g

$$\% \text{ of sulphur} = \frac{32 \times m_1 \times 100}{233 \times m} \%$$

(D) **Phosphorus**

$\text{Organic compound} \xrightarrow[HNO_3]{\text{Fuming}} H_3PO_4 \xrightarrow{(NH_4)_2MoO_4} (NH_4)_3PO_4 \cdot 12MoO_3 \downarrow$

Let mass of compound = m g

Mass of $(NH_4)_3PO_4 \cdot 12MoO_3$ = m_1 g

Molar mass of $(NH_4)_3PO_4 \cdot 12MoO_3$ = 1877 g

$$\% \text{ of P} = \frac{31 \times m_1 \times 100}{1877 \times m} \%$$

Sharpen Your Understanding

1. Number of σ and π bonds present in the given molecule respectively are

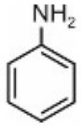
$CH_3 - CH = CH - CH = CH - CN$

[NCERT Pg. 335]

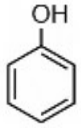
(1) 13 and 3 (2) 13 and 2

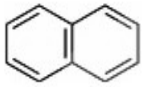
(3) 14 and 4 (4) 13 and 4

2. Which among the following is heterocyclic aromatic compound? [NCERT Pg. 340]

(1) 

(2) 

(3) 

(4) 

3. Isobutyl group among the following is [NCERT Pg. 341]

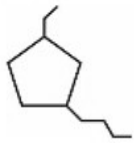
(1) $CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-$

(2) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-$

(3) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-$

(4) $CH_3 - CH_2 - CH_2 - CH_2 -$

4. IUPAC name of the given compound is



[NCERT Pg. 343]

(1) 1-Butyl-3-ethylcyclopentane

(2) 3-Butyl-1-ethylcyclopentane

(3) 1-Butyl-4-ethylcyclopentane

(4) 4-Butyl-1-ethylcyclopentane

5. Propanone and propanal are [NCERT Pg. 349]

(1) Chain isomers

(2) Metamers

(3) Position isomers

(4) Functional group isomers

6. Most stable carbocation among the following is [NCERT Pg. 349]

(1) $Ph-\overset{\oplus}{C}H_2$ (2) $(CH_3)_3\overset{+}{C}$

(3) $(CH_3)_2\overset{+}{C}H$ (4) $CH_3\overset{+}{C}H_2$

7. Consider the following statements. [NCERT Pg. 351]

(a) A reagent that takes away an electron pair is called an electrophile

(b) A nucleophile is electron rich species

(c) In methyl halide, carbon is electrophilic centre

Correct statements are

(1) (a) and (b) only (2) (b) and (c) only

(3) (a), (b) and (c) (4) (a) and (c) only

8. Which among the following is a temporary effect? [NCERT Pg. 355]

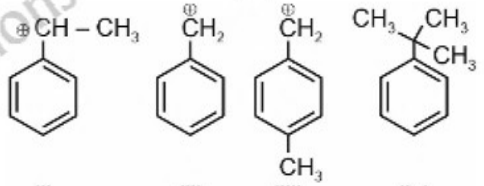
(1) Hyperconjugation

(2) Resonance

(3) Inductive effect

(4) Electromeric effect

9. Consider the following species



(i) (ii) (iii) (iv)

[NCERT Pg. 355]

Hyperconjugation will be observed in

(1) (i) and (ii) only

(2) (ii) and (iii) only

(3) (i) and (iii) only

(4) (i), (ii), (iii) and (iv)

10. The group which shows –I and –R effect is [NCERT Pg. 352, 354]

(1) –Cl (2) –OR

(3) $-NO_2$ (4) –NHCOR

11. Mixture of aniline and chloroform can be easily separated by [NCERT Pg. 357]

(1) Distillation

(2) Fractional distillation

(3) Steam distillation

(4) Sublimation

12. On treating sodium fusion extract with sodium nitroprusside solution blood red colour is obtained. It indicates the presence of which element(s) in the organic compound? [NCERT Pg. 363]

(1) Nitrogen only

(2) Sulphur only

(3) Phosphorous only

(4) Nitrogen and sulphur both

13. Most stable carbanion among the following is [NCERT Pg. 350]

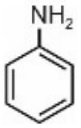
(1) $\overset{\ominus}{C}H_2-NO_2$

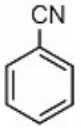
(2) $\overset{\ominus}{C}H_3$

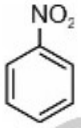
(3) $(CH_3)_2\overset{\ominus}{C}H$

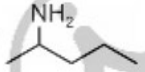
(4) $\overset{\ominus}{C}H_2-Ph$

14. Kjeldahl's method is not applicable to which compound? [NCERT Pg. 366]

(1) 

(2) 

(3) 

(4) 

15. In sulphur estimation 0.25 g of an organic compound gave 0.466 g of barium sulphate. Percentage of sulphur in the compound is [NCERT Pg. 367]

(1) 45.5%

(2) 16.4%

(3) 56.5%

(4) 25.6%

16. The element which cannot be detected by Lassaigne's test is [NCERT Pg. 362]

(1) Nitrogen

(2) Sulphur

(3) Chlorine

(4) Oxygen

17. Commonly used adsorbent(s) in column chromatography is/are [NCERT Pg. 360]

(1) Silica gel

(2) Alumina

(3) Charcoal

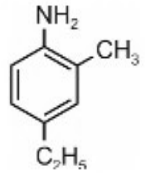
(4) Both (1) and (2)

18. Which among the following is a nucleophile? [NCERT Pg. 351]

(1) BF_3 (2) B_2H_6

(3) $\bar{S}H$ (4) $AlCl_3$

19. IUPAC name of the given compound is



[NCERT Pg. 347]

(1) 4-Ethyl-2-methylaniline

(2) 4-Amino-1-ethyl-3-methylbenzene

(3) 4-Ethyl-6-methylaniline

(4) 4-Amino-1-ethyl-5-methylbenzene

20. Which among the following is a planar molecule? [NCERT Pg. 335]

(1) $CH_2 = CH - CN$

(2) $CH_2 = C = CH_2$

(3) $CH_3 - CH = CH_2$

(4) $CH_3 - CH = CH - CH_3$

Thinking in Context

1. Urea can be synthesised by heating _____. [NCERT Pg. 334]
2. _____ arises due to different alkyl chains on either side of the functional group. [NCERT Pg. 349]
3. Alkyl groups directly attached to the positively charged carbon stabilise the carbocations due to _____ and _____ effects. [NCERT Pg. 349]
4. A reagent that takes away an electron pair is called _____. [NCERT Pg. 351]
5. The _____ structures are hypothetical and individually do not represent any real molecule. [NCERT Pg. 353]
6. The IUPAC group prefix 'formyl' is used for _____. [NCERT Pg. 345]
7. _____ structures have same number of unpaired electrons. [NCERT Pg. 353]
8. _____ is also termed as no bond resonance. [NCERT Pg. 356]
9. In _____ cleavage, radical formation takes place. [NCERT Pg. 349]
10. _____ technique is applied to separate substances which are steam volatile and are immiscible with water. [NCERT Pg. 359]
11. Paper chromatography is a type of _____ chromatography. [NCERT Pg. 362]
12. The sodium fusion extract is boiled with ferrous sulphate and then acidified with concentrated sulphuric acid, formation of Prussian blue colour confirms the presence of _____. [NCERT Pg. 363]
13. Nitrogen, sulphur, halogens and _____ present in an organic compound are detected by Lassaigne's test. [NCERT Pg. 362]
14. Ammonium phosphomolybdate is _____ coloured compound. [NCERT Pg. 363]
15. In quantitative estimation of halogens by Carius method, a known mass of organic compound is heated with fuming nitric acid in presence of _____ in Carius tube. [NCERT Pg. 367]
16. Hyperconjugation involves delocalization of σ electrons of C – H bond of an alkyl group directly attached to an atom of unsaturated system or to an atom with an unshared _____. [NCERT Pg. 355]
17. Methyl propanoate and butanoic acid are _____. [NCERT Pg. 348]
18. The structural unit _____ is called neopentyl group. [NCERT Pg. 341]
19. Glycerol is separated from spent-lye in soap industry by using _____ technique. [NCERT Pg. 358]
20. $[Fe(SCN)]^{2+}$ is _____ in colour. [NCERT Pg. 363]

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