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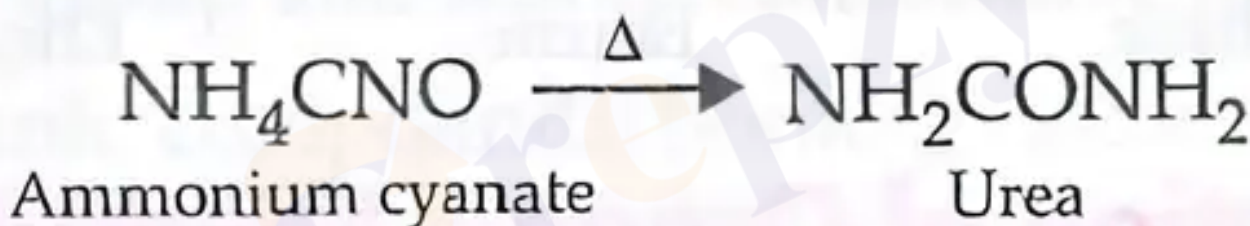
Organic Chemistry Introduction

Definition and Scope

- Study of hydrocarbons (carbon and hydrogen compounds) and their derivatives.
- Includes compounds containing N, O, S, P, halogens, etc.
- Berzelius proposed a 'vital force' theory for organic compound formation.

Historical Synthesis

- E. Wöhler synthesized urea (organic) from ammonium cyanate (inorganic), disproving vital force theory.
- Kolbe synthesized acetic acid; Berthelot synthesized methane from inorganic sources.



Solved Examples

- **Ex 1:** Write the reaction for synthesis of urea from ammonium cyanate.
Answer: $\text{NH}_4\text{CNO} \xrightarrow{\text{heat}}$; NH_2CONH_2 (urea)

Practice Set

- **Q1:** What elements are primarily studied in organic chemistry?
A. Metals and non-metals
B. Carbon and hydrogen
C. Oxygen and nitrogen
D. Sulfur and phosphorus

- **Q2:** Who synthesized the first organic compound from an inorganic compound?
A. Kolbe
B. Berthelot
C. E. Wöhler
D. Berzelius
- **Q3:** Which reaction disproved the vital force theory?
A. Methane synthesis
B. Acetic acid synthesis
C. Urea synthesis from ammonium cyanate
D. Benzene formation

Answer Key

- **Q1:** B - Organic chemistry mainly studies carbon and hydrogen compounds.
- **Q2:** C - E. Wöhler synthesized urea from ammonium cyanate.
- **Q3:** C - Urea synthesis from ammonium cyanate disproved the vital force theory.

Memory Aids

- Remember: Organic = Carbon + Hydrogen (+ other elements).
- Wöhler's urea synthesis = key reaction disproving vital force.
- Kolbe = acetic acid; Berthelot = methane from inorganic sources.

Tetravalence of Carbon: Shapes of Organic Compounds

Hybridisation and Molecular Shape

- Shapes of carbon compounds depend on hybridisation of orbitals and formation of sigma (σ) and pi (π) bonds.
- Shape depends on number of bonding pairs and lone pairs of electrons.
- Three common hybridisations in organic chemistry: sp , sp^2 , sp^3 .
- Hybridisation types and features:
 - **sp :** Linear geometry, bond angle 180° , 50% s and 50% p character, e.g., ethyne (C_2H_2).

- **sp²**: Trigonal planar geometry, bond angle 120°, 33% s and 67% p character, e.g., ethene (C₂H₄).
- **sp³**: Tetrahedral geometry, bond angle 109.5°, 25% s and 75% p character, e.g., ethane (C₂H₆).

Type	Geometry	Bond angle	Percentage s-character	Percentage p-character	Examples
sp	Linear	180°	50	50	Ethyne, propyne
sp ²	Trigonal planar	120°	33.3	66.6	Ethene, propene
sp ³	Tetrahedral	109°28'	25	75	Ethane, propane

Solved Examples

- **Ex 1:** Identify hybridisation of carbon in ethene (C₂H₄).
 - Carbon forms 3 sigma bonds and 1 pi bond.
 - Hybridisation is sp² (trigonal planar, 120° bond angle).

Practice Set

- Q1: What is the bond angle in sp³ hybridised carbon?
 - A. 180°
 - B. 120°
 - C. 109.5°
 - D. 90°
- Q2: Which molecule has carbon with sp hybridisation?
 - A. Ethane
 - B. Ethene
 - C. Ethyne
 - D. Benzene
- Q3: Percentage of s character in sp² hybridised carbon is:
 - A. 25%
 - B. 33%
 - C. 50%
 - D. 75%

Answer Key

- Q1: C - 109.5° is the bond angle for sp^3 hybridisation (tetrahedral shape).
- Q2: C - Ethyne has sp hybridised carbon (linear geometry, 180° bond angle).
- Q3: B - sp^2 hybridisation has 33% s character and 67% p character.

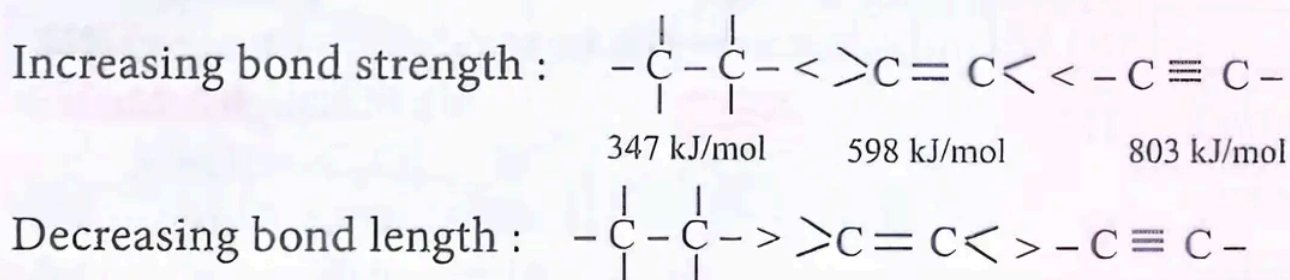
Memory Aids

- sp = 2 regions of electron density, linear, 180°
- sp^2 = 3 regions, trigonal planar, 120°
- sp^3 = 4 regions, tetrahedral, 109.5°
- More s character means shorter, stronger bonds

Characteristic Features of π Bonds

Properties of π Bonds

- Formed by lateral (sideways) overlap of p orbitals.
- Electron density lies above and below the internuclear axis; zero density along the axis (node).
- π bond has a nodal plane along the internuclear axis, perpendicular to p orbital direction.
- Weaker than σ bonds; formed only after σ bond formation.
- No free rotation around π bond; makes molecule rigid at double/triple bonds.
- π bonds are more reactive than σ bonds; reactive centers in multiple bonds.
- Bond multiplicity increases bond strength and decreases bond length.



Solved Examples

- **Ex 1:** Compare bond strength and length of C–C single, double, and triple bonds.
 - Single bond: 347 kJ/mol, longest bond length.
 - Double bond: 598 kJ/mol, shorter bond length.
 - Triple bond: 803 kJ/mol, shortest bond length.

Practice Set

- Q1: π bond is formed by:
 - A. Head-on overlap of orbitals
 - B. Lateral overlap of orbitals
 - C. Overlap of s orbitals
 - D. No overlap
- Q2: Which bond allows free rotation?
 - A. σ bond
 - B. π bond
 - C. Both σ and π
 - D. None
- Q3: Arrange bonds in increasing order of bond length:
 - A. $\text{C}\equiv\text{C} < \text{C}=\text{C} < \text{C}-\text{C}$
 - B. $\text{C}-\text{C} < \text{C}=\text{C} < \text{C}\equiv\text{C}$
 - C. $\text{C}=\text{C} < \text{C}-\text{C} < \text{C}\equiv\text{C}$
 - D. $\text{C}-\text{C} = \text{C}=\text{C} = \text{C}\equiv\text{C}$

Answer Key

- Q1: B - π bond forms by lateral overlap of p orbitals.
- Q2: A - σ bonds allow free rotation; π bonds restrict rotation.
- Q3: A - Triple bond ($\text{C}\equiv\text{C}$) shortest, then double ($\text{C}=\text{C}$), then single ($\text{C}-\text{C}$) longest.

Memory Aids

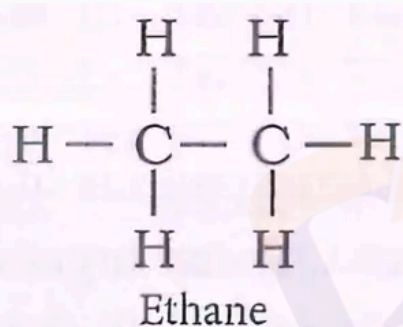
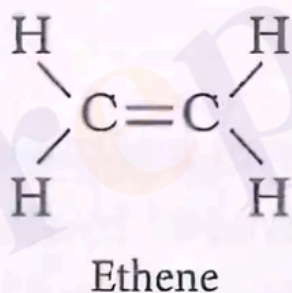
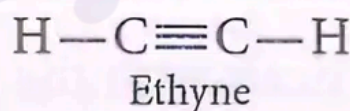
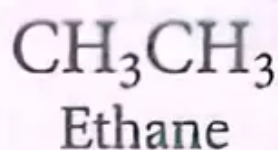
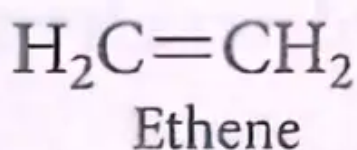
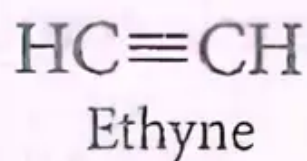
- π bond = sideways overlap, no free rotation
- σ bond = head-on overlap, free rotation

- Bond strength: single < double < triple
- Bond length: single > double > triple

Complete, Condensed and Bond-line Structural Formulas

Explanation

- Complete structural formulas show all atoms and bonds explicitly (e.g., ethane C_2H_6 , ethene C_2H_4 , ethyne C_2H_2).
- Ethane: two carbons single bonded; ethene: double bond; ethyne: triple bond.
- Condensed structural formulas omit bonds but show groups with subscripts (e.g., CH_3CH_3 , $H_2C=CH_2$, $HC\equiv CH$).
- Bond-line formulas simplify structures by showing carbon chains as lines; hydrogens on carbons are usually omitted.



Solved Examples

- **Ex 1:** Write the condensed formula for ethene.
Solution: Ethene has a double bond between two carbons, so condensed formula is $H_2C=CH_2$.
- **Ex 2:** Identify the type of bond in ethyne.
Solution: Ethyne has a triple bond between two carbon atoms.

Practice Set

- Q1: Which formula shows all atoms and bonds explicitly?
 - A. Condensed formula
 - B. Complete structural formula
 - C. Bond-line formula
 - D. Molecular formula
- Q2: What is the condensed formula of ethane?
 - A. CH_3CH_3
 - B. $\text{H}_2\text{C}=\text{CH}_2$
 - C. $\text{HC}\equiv\text{CH}$
 - D. C_2H_6
- Q3: Which bond type is present in ethene?
 - A. Single bond
 - B. Double bond
 - C. Triple bond
 - D. Ionic bond

Answer Key

- Q1: B - Complete structural formulas show all atoms and bonds explicitly.
- Q2: A - Ethane condensed formula is CH_3CH_3 , showing groups without bonds.
- Q3: B - Ethene contains a double bond between carbon atoms.

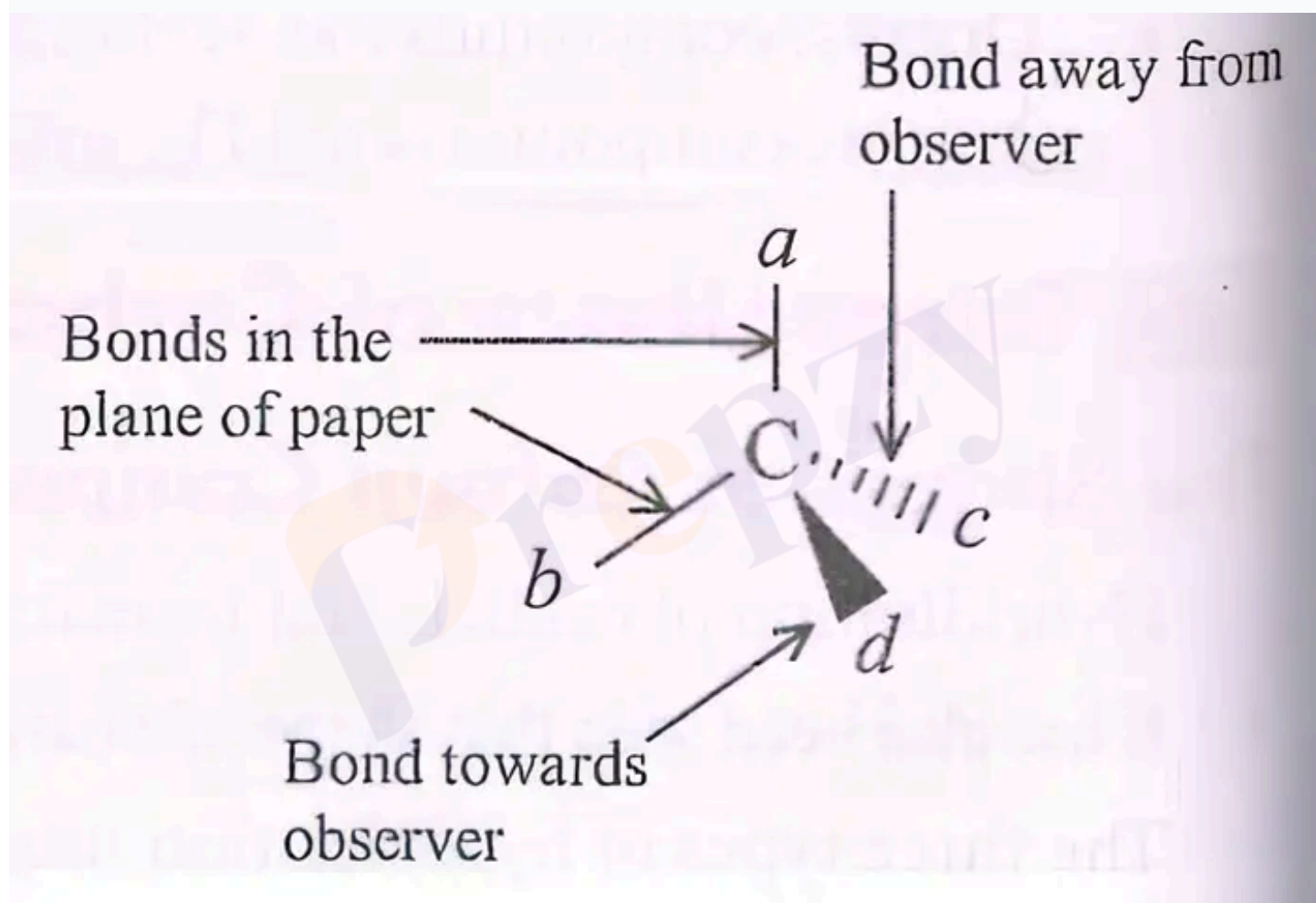
Memory Aids

- Complete formulas = all atoms + bonds shown.
- Condensed formulas = groups written with subscripts, no bonds.
- Bond-line = zigzag lines for carbon chains, hydrogens omitted.

Three-Dimensional Representation

Explanation

- Solid wedge (▲) indicates bond projecting out of the plane (towards observer).
- Dashed wedge (---) indicates bond going behind the plane (away from observer).
- Normal lines represent bonds in the plane of the paper.
- Used to depict tetrahedral molecules with four different groups attached to carbon.



Solved Examples

- **Ex 1:** Identify the bond type shown by a solid wedge.
Solution: Bond projecting out of the plane towards the observer.
- **Ex 2:** What does a dashed wedge represent?
Solution: Bond going behind the plane away from the observer.

Practice Set

- Q1: Which symbol shows a bond coming out of the plane?
A. Dashed wedge
B. Solid wedge
C. Normal line
D. Double line
- Q2: Bonds in the plane of paper are shown by?
A. Solid wedge
B. Dashed wedge
C. Normal line
D. Dotted line
- Q3: What shape is represented by the wedge formula for carbon with four different groups?
A. Linear
B. Planar
C. Tetrahedral
D. Trigonal planar

Answer Key

- Q1: B - Solid wedge shows bond coming out of the plane.
- Q2: C - Normal lines represent bonds in the plane of the paper.
- Q3: C - Tetrahedral shape is depicted by wedge formula.

Memory Aids

- Solid wedge = bond towards you.
- Dashed wedge = bond away from you.
- Normal line = bond in plane.

Classification of Organic Compounds

Overview

- Organic compounds contain carbon atoms bonded in chains or rings.
- Two main types: Acyclic (open chain) and Cyclic (closed ring) compounds.
- Acyclic compounds: Straight or branched chains.
- Cyclic compounds: Carbon atoms form rings.

Types of Acyclic Compounds

- Saturated (alkanes): Only single bonds, e.g., ethane (C_2H_6).
- Unsaturated: Double or triple bonds.
 - Alkenes: Contain double bonds, e.g., ethene (C_2H_4).
 - Alkynes: Contain triple bonds, e.g., ethyne (C_2H_2).

Types of Cyclic Compounds

- Homocyclic: Rings made of only one type of atom (usually carbon).
- Heterocyclic: Rings contain atoms other than carbon and hydrogen.

Subtypes of Homocyclic Compounds

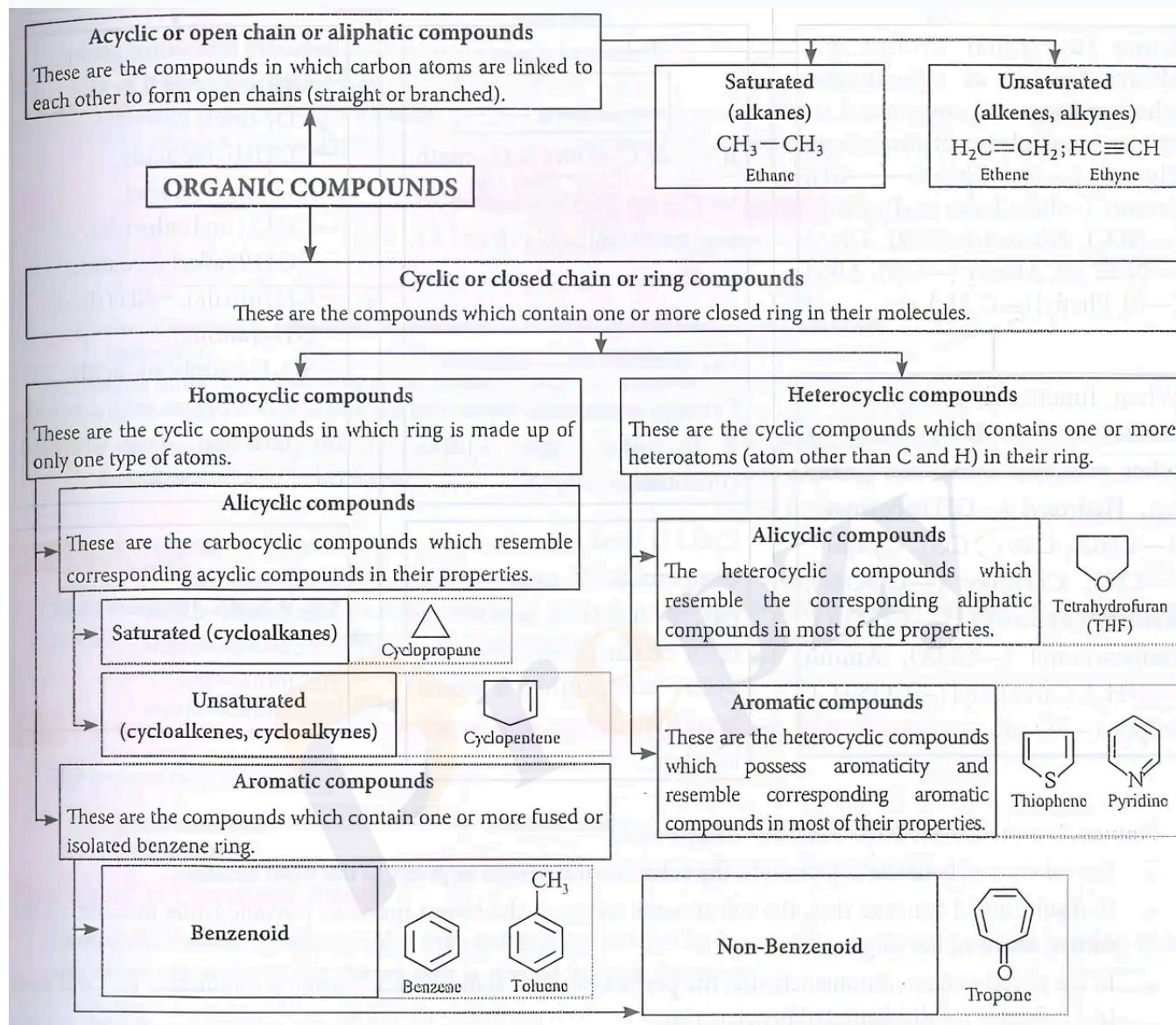
- Alicyclic: Ring compounds similar to alkanes, e.g., cyclopropane.
- Aromatic: Contain benzene rings, e.g., benzene, toluene.

Subtypes of Heterocyclic Compounds

- Alicyclic heterocyclic: Resemble aliphatic compounds, e.g., tetrahydrofuran.
- Aromatic heterocyclic: Contain aromatic rings, e.g., thiophene, pyridine.

Aromatic Compound Types

- Benzenoid: Contain benzene rings.
- Non-benzenoid: Do not contain benzene rings, e.g., tropone.



Solved Examples

- **Ex 1:** Classify cyclohexane.
Answer: Cyclic → Homocyclic → Alicyclic compound.
- **Ex 2:** Classify pyridine.
Answer: Cyclic → Heterocyclic → Aromatic heterocyclic compound.

Practice Set

- Q1: Which is an unsaturated acyclic compound?
A. Ethane
B. Ethene
C. Cyclopropane
D. Benzene
- Q2: Identify the heterocyclic aromatic compound.
A. Cyclohexane
B. Tetrahydrofuran
C. Thiophene
D. Ethyne
- Q3: Which compound is benzenoid aromatic?
A. Tropone
B. Benzene
C. Pyridine
D. Cyclopropane

Answer Key

- Q1: B - Ethene is an unsaturated acyclic compound with a double bond.
- Q2: C - Thiophene is a heterocyclic aromatic compound.
- Q3: B - Benzene is a benzenoid aromatic compound.

Memory Aids

- Acyclic = open chain; Cyclic = rings.
- Homocyclic = only carbon atoms in ring.
- Heterocyclic = ring contains other atoms (N, O, S).
- Aromatic = benzene or similar stable ring.

Functional Group

Definition and Importance

- Functional group: Atom/group responsible for characteristic chemical properties.
- Examples:
 - Hydroxyl (-OH)
 - Aldehyde (-CHO)
 - Carboxylic acid (-COOH)
- Determines reactivity and chemical behavior of organic compounds.

Solved Examples

- **Ex 1:** Identify the functional group in ethanol.
Answer: Hydroxyl group (-OH).
- **Ex 2:** Identify the functional group in acetaldehyde.
Answer: Aldehyde group (-CHO).

Practice Set

- Q1: Which functional group is present in carboxylic acids?
A. -OH
B. -CHO
C. -COOH
D. -NH₂
- Q2: The aldehyde group is represented by?
A. -OH
B. -CHO
C. -COOH
D. -CN
- Q3: Which functional group is characteristic of alcohols?
A. -COOH
B. -OH
C. -CHO
D. -SH

Answer Key

- Q1: C - Carboxylic acids contain the -COOH group.
- Q2: B - Aldehyde group is -CHO .
- Q3: B - Alcohols have the hydroxyl (-OH) group.

Memory Aids

- OH = Alcohols, COOH = Acids, CHO = Aldehydes.
- Functional groups define chemical properties.

Homologous Series

Definition and Characteristics

- Family of organic compounds with same functional group.
- Consecutive members differ by a $\text{-CH}_2\text{-}$ unit.
- Similar chemical properties, gradual change in physical properties.
- Examples: Alkanes, alkenes, alkynes, haloalkanes, alkanols, alkanals, alkanones, alkanolic acids, amines.

Solved Examples

- **Ex 1:** Identify the next member after propane in alkane series.
Answer: Butane (C_4H_{10}).
- **Ex 2:** Difference between ethene and propene.
Answer: Propene has one extra $\text{-CH}_2\text{-}$ unit.

Practice Set

- Q1: What is the difference between consecutive members in a homologous series?
A. One oxygen atom

- B. One nitrogen atom
- C. One $\text{-CH}_2\text{-}$ group
- D. One double bond
- Q2: Which is a member of the alkane homologous series?
 - A. Ethene
 - B. Propane
 - C. Ethyne
 - D. Benzene
- Q3: Which homologous series contains compounds with triple bonds?
 - A. Alkanes
 - B. Alkenes
 - C. Alkynes
 - D. Alkanols

Answer Key

- Q1: C - Consecutive members differ by one $\text{-CH}_2\text{-}$ group.
- Q2: B - Propane is an alkane.
- Q3: C - Alkynes contain triple bonds.

Memory Aids

- Homologous series = same functional group + differ by CH_2 .
- Alkanes (single bonds), Alkenes (double bonds), Alkynes (triple bonds).

Nomenclature of Organic Compounds

Basic Principles

- Complete IUPAC name has 5 parts: secondary prefix + primary prefix + word root + primary suffix + secondary suffix.
- Identify principal functional group by priority order (highest to lowest): $\text{COOH} > \text{SO}_3\text{H} > \text{COOR} > \text{COCl} > \text{CONH}_2 > \text{CN} > \text{HC=O} > \text{C=O} > \text{OH} > \text{NH}_2 > \text{C=C}$.
- Functional groups determine chemical properties and reactivity.

—COOH , $\text{—SO}_3\text{H}$, —COOR , —COCl , —CONH_2 , —CN , —HC=O , >C=O , —OH , —NH_2 , >C=C< ,
 $\text{—C}\equiv\text{C—}$.

Rules for Naming

- Identify substituents (e.g., fluoro, chloro) and principal groups (e.g., hydroxyl, carboxyl).
- Find longest carbon chain (principal chain) and assign root word (meth-, eth-, prop-, etc.).
- Add "cyclo" prefix if compound is cyclic; omit if acyclic.
- Attach primary suffix for main functional group (-ol, -al, -one, etc.).
- Add secondary suffix for additional functional groups; drop 'e' if vowel follows.
- Indicate bond types: -ane (single), -ene (double), -yne (triple) with locants if multiple bonds.
- Combine parts in order: secondary prefix + primary prefix + word root + primary suffix + secondary suffix.

IUPAC name = 2° prefix + 1° prefix + word root + 1° suffix + 2° suffix				
<div style="display: flex; justify-content: space-around;"> <div style="text-align: center;">↓</div> <div style="text-align: center;">↓</div> <div style="text-align: center;">↓</div> </div>				
<div style="display: flex; justify-content: space-between;"> <div style="width: 30%;"> <p>Some functional groups are always treated as substituents whether organic compound is mono or polyfunctional e.g., Fluoro (—F), Chloro (—Cl), Bromo (—Br), Iodo (—I), Nitro (—NO_2), Nitroso (—NO), Diazo ($\text{—}\ddot{\text{N}}\equiv\text{N}$), Alkoxy ($\text{—OR}$), Alkyl ($\text{—R}$), Phenyl ($\text{—C}_6\text{H}_5$), etc.</p> </div> <div style="width: 35%; text-align: center;"> <p>Principal chain</p> <div style="border: 1px dashed black; padding: 5px; margin: 0 auto; width: 100px;"> <div style="display: flex; justify-content: space-around; font-size: small;">4 3 2 1</div> <div style="display: flex; justify-content: space-around; font-size: small;">—C—C—C—C—</div> </div> <p>If no. of C atoms is C_1-meth, C_2-eth, C_3-prop(a), C_4-but(a), C_5-pent(a), C_6-hex(a), C_7-hept(a), C_8-oct(a), C_9-non(a), C_{10}-dec(a), C_{11}-undec(a), C_{12}-dodec(a). Extra 'a' is added to word root if 1° suffix begins with a consonant.</p> </div> <div style="width: 30%;"> <p>Indicates functional group, —OH (-ol), —CHO (-al), >CO (-one), —COOH (-oic acid), —CONH_2 (-amide), —COCl (-oyl chloride), —COOR (alkyl oate), —CN (nitrile), —SH (thiol), —NH_2 (amine), $\text{—SO}_3\text{H}$ (sulphonic acid). If 2° suffix begins with a vowel, the terminal 'e' is dropped otherwise it is retained.</p> </div> </div>				
<div style="display: flex; justify-content: space-between;"> <div style="width: 30%;"> <p>When functional groups act as substituents in the presence of other principal functional group e.g., Hydroxyl (—OH), Formyl (—CHO), Oxo (>CO), Cyano (—CN), Carboxy (—COOH), Alkoxycarbonyl (—COOR), Halocarbonyl (—COX), Amino (—NH_2), Carbamoyl (—CONH_2), Sulpho ($\text{—SO}_3\text{H}$), etc.</p> </div> <div style="width: 35%; text-align: center;"> <p>Cyclo is used for carbocyclic compounds. If cyclo is not put, it indicates acyclic or open chain compound. In cyclic compound, a more branched carbon gets lower number.</p> </div> <div style="width: 30%;"> <p>Single bonds (—) only -ane $1(=)$ bond -ene $2(=)$ bonds -diene $3(=)$ bonds -triene $1(\equiv)$ bond -yne $2(\equiv)$ bonds -diyne</p> </div> </div>				

Solved Examples

- **Ex 1:** Name $\text{CH}_3\text{-CH=CH-CH}_2\text{-OH}$

Longest chain: 4 carbons (but-), double bond (-ene), hydroxyl (-ol)

Name: But-2-en-1-ol

- **Ex 2:** Name cyclohexanone

Cyclic compound with ketone group

Name: Cyclohexanone

Practice Set

- Q1: What is the primary suffix for aldehydes?
A. -ol
B. -al
C. -one
D. -ene
- Q2: Which functional group has the highest priority in IUPAC naming?
A. Hydroxyl (-OH)
B. Carboxyl (-COOH)
C. Amine (-NH₂)
D. Alkene (C=C)
- Q3: Name the compound $\text{CH}_3\text{-CH}_2\text{-COOH}$.
A. Propanol
B. Propanoic acid
C. Propanal
D. Propanone

Answer Key

- Q1: B - Aldehydes use suffix -al to indicate the formyl group.
- Q2: B - Carboxyl group (-COOH) has the highest priority among listed groups.
- Q3: B - $\text{CH}_3\text{-CH}_2\text{-COOH}$ is propanoic acid (carboxylic acid).

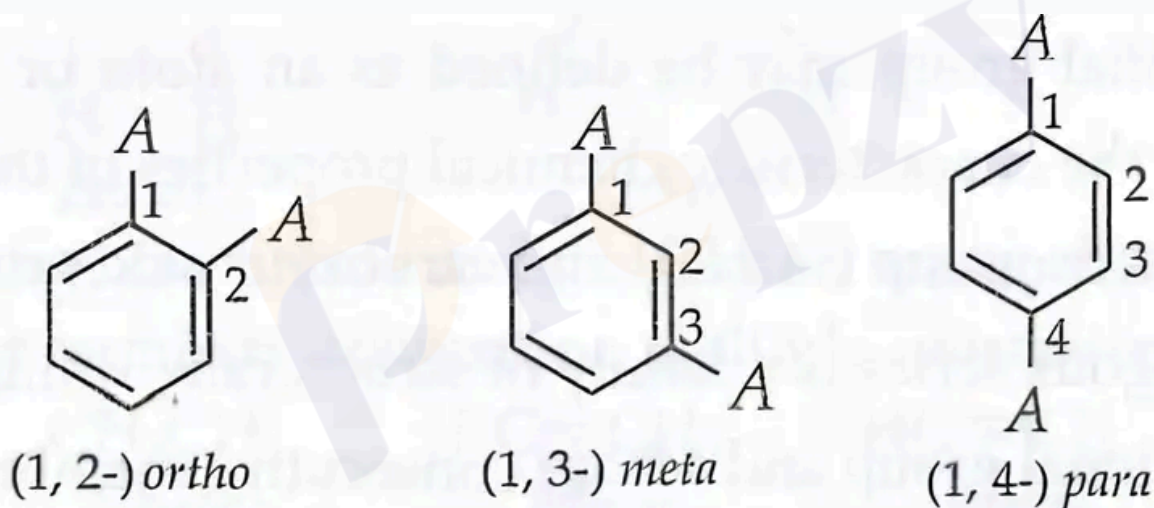
Memory Aids

- Priority order: "Carboxylic acids come first" (COOH highest).
- Suffixes: -ane (single), -ene (double), -yne (triple).
- Use "cyclo" prefix for rings.

Nomenclature of Substituted Benzene Compounds

Basic Rules

- Substituents are prefixes to the word "benzene".
- In disubstituted benzenes, assign lowest possible numbers to substituents.
- Trivial prefixes: ortho (o-) = 1,2-; meta (m-) = 1,3-; para (p-) = 1,4- disubstitution.



Advanced Rules

- For tri- or more substituted benzenes, use common base name.
- Assign position 1 to the substituent of the base compound.
- Follow lowest locant rule for other substituents.
- Benzene ring acts as substituent phenyl (Ph, $\text{—C}_6\text{H}_5$) when attached to alkane with functional group.

Solved Examples

- **Ex 1:** Name 1,2-dichlorobenzene
Positions 1 and 2 have chloro substituents
Name: Ortho-dichlorobenzene
- **Ex 2:** Name 1,4-dinitrobenzene
Positions 1 and 4 have nitro substituents
Name: Para-dinitrobenzene

Practice Set

- Q1: What prefix indicates 1,3-disubstitution on benzene?
A. Ortho (o-)
B. Meta (m-)
C. Para (p-)
D. None
- Q2: In naming substituted benzene, what is the base name for a benzene ring attached to an alkane?
A. Benzyl
B. Phenyl
C. Toluene
D. Aniline
- Q3: Which rule is used to assign numbers to substituents in disubstituted benzene?
A. Highest locant rule
B. Lowest locant rule
C. Alphabetical order
D. Random assignment

Answer Key

- Q1: B - Meta (m-) indicates 1,3-disubstitution.
- Q2: B - Phenyl (Ph) is the substituent name for benzene ring attached to alkane.
- Q3: B - Lowest locant rule assigns the smallest possible numbers.

Memory Aids

- Ortho = adjacent (1,2), Meta = separated by one carbon (1,3), Para = opposite (1,4).
- Phenyl = benzene as substituent.
- Lowest locant rule ensures smallest numbering.

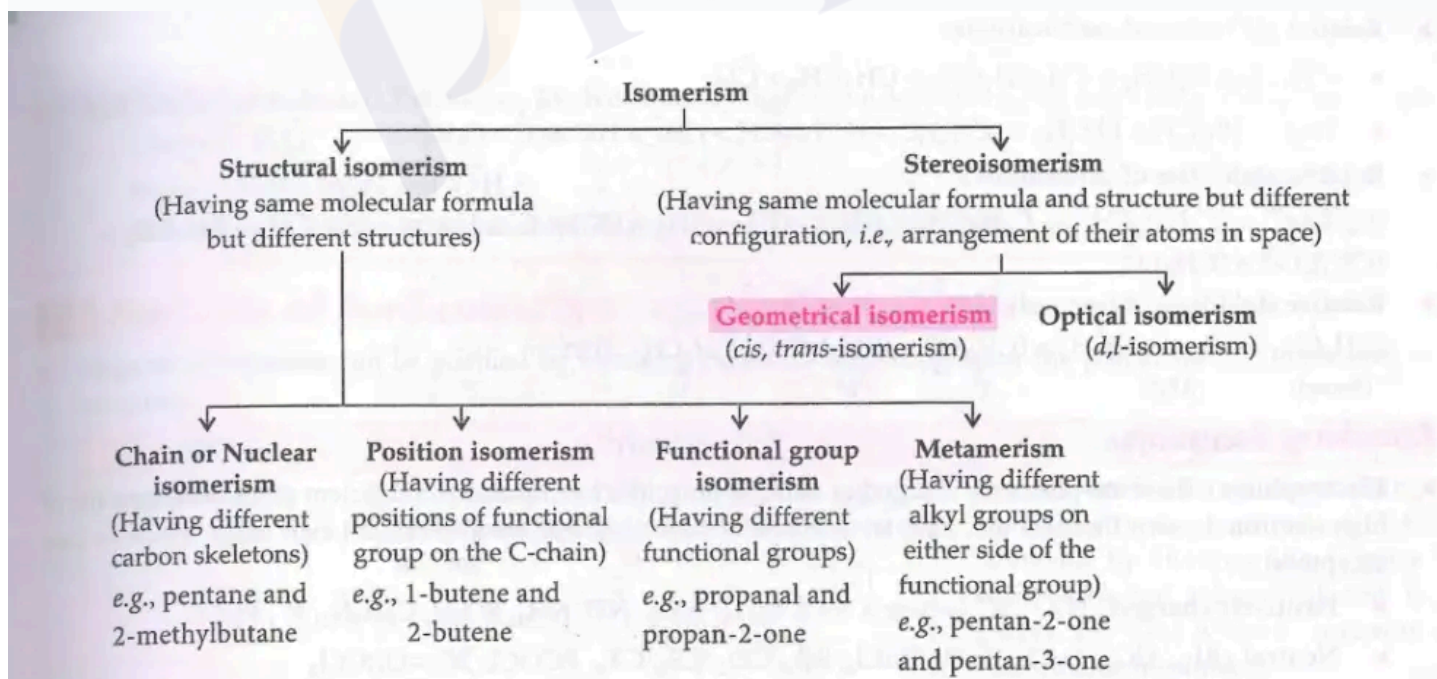
Isomerism

Definition

- Compounds with the same molecular formula but different properties are called isomers.
- Isomerism explains differences in structure or arrangement despite identical formulas.

Types of Isomerism

- **Structural Isomerism:** Same formula, different connectivity of atoms.
- **Stereoisomerism:** Same formula and connectivity, different spatial arrangement.



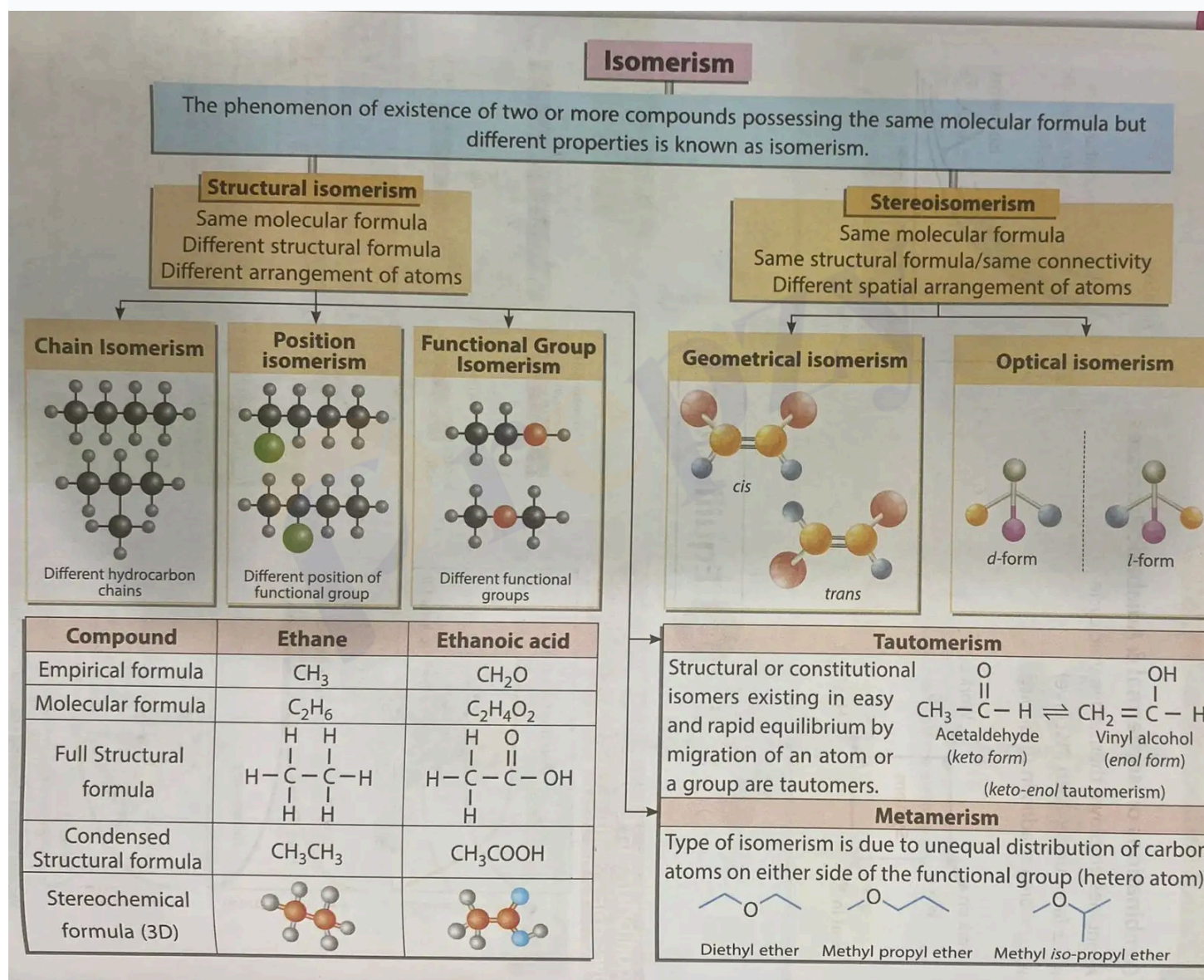
Structural Isomerism Subtypes

- *Chain isomerism:* Different carbon chain arrangements.

- *Position isomerism*: Functional groups at different positions.
- *Functional group isomerism*: Different functional groups.
- *Metamerism*: Different alkyl groups on either side of a functional group.

Stereoisomerism Subtypes

- *Geometrical isomerism*: Different spatial arrangement around double bonds (cis/trans).
- *Optical isomerism*: Non-superimposable mirror images (d- and l-forms).



Special Types

- *Tautomerism*: Rapid interconversion by migration of H-atom and rearrangement (e.g., keto-enol).

- *Metamerism*: Isomers differ in alkyl groups around a functional group.

Solved Examples

- **Ex 1**: Identify chain isomers of C_5H_{12} .

Solution: Pentane, isopentane (2-methylbutane), neopentane (2,2-dimethylpropane).

- **Ex 2**: Geometrical isomers of 1-butene.

Solution: Cis-1-butene and trans-1-butene differ in spatial arrangement around $C=C$.

Practice Set

- Q1: Which is an example of functional group isomerism?
A. Pentane and 2-methylbutane
B. Ethanol and dimethyl ether
C. Cis- and trans-2-butene
D. D- and L-glucose
- Q2: Geometrical isomerism occurs when:
A. Two identical groups on each carbon of double bond
B. Two different groups on each carbon of double bond
C. Same connectivity but different functional groups
D. Different carbon skeletons
- Q3: Tautomerism involves:
A. Different carbon chains
B. Migration of H-atom and rearrangement
C. Mirror image isomers
D. Different positions of functional groups

Answer Key

- Q1: B - Ethanol and dimethyl ether have same formula but different functional groups.
- Q2: B - Geometrical isomerism requires two different groups on each carbon of the double bond.
- Q3: B - Tautomerism involves migration of H-atom and rearrangement within the molecule.

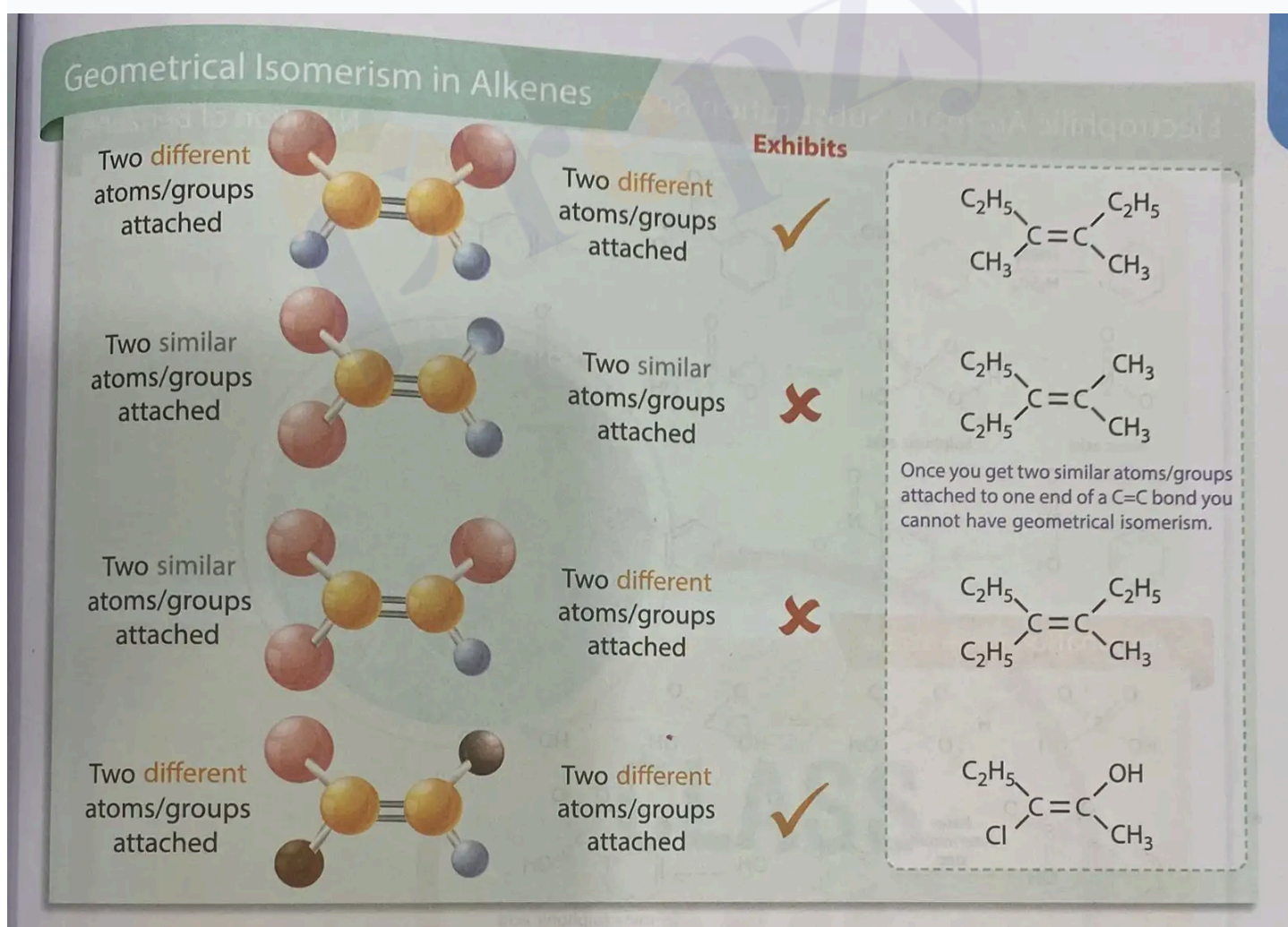
Memory Aids

- Structural isomers differ in connectivity; stereoisomers differ in spatial arrangement.
- Geometrical isomers need different groups on both carbons of C=C.
- Tautomerism = H-atom shift + bond rearrangement (keto-enol).

Geometrical Isomerism

Conditions and Explanation

- Occurs in alkenes with C=C double bond.
- Each carbon of double bond must have two different groups attached.
- If any carbon has two identical groups, geometrical isomerism is not possible.
- Results in cis (same side) and trans (opposite side) forms.



Solved Examples

- **Ex 1:** Identify if 1,2-dichloroethene shows geometrical isomerism.
Solution: Yes, cis and trans forms exist due to different groups on each carbon.
- **Ex 2:** Does 1,1-dichloroethene show geometrical isomerism?
Solution: No, both chlorines on same carbon, no cis-trans possible.

Practice Set

- Q1: Geometrical isomerism is possible in:
 - A. 1,2-dibromoethene
 - B. 1,1-dibromoethene
 - C. Ethene
 - D. Propane
- Q2: Cis and trans isomers differ in:
 - A. Molecular formula
 - B. Connectivity
 - C. Spatial arrangement
 - D. Functional groups
- Q3: Which condition prevents geometrical isomerism?
 - A. Different groups on both carbons
 - B. Double bond presence
 - C. Identical groups on one carbon
 - D. Presence of triple bond

Answer Key

- Q1: A - 1,2-dibromoethene has different groups on each carbon allowing cis-trans isomers.
- Q2: C - Cis and trans differ in spatial arrangement only.
- Q3: C - Identical groups on one carbon prevent geometrical isomerism.

Memory Aids

- Geometrical isomerism = Different groups on both carbons of $C=C$.
- Cis = same side, Trans = opposite side.

- No isomerism if identical groups on any carbon of double bond.

Tautomerism

Definition and Explanation

- Isomers interconvert by migration of H-atom and rearrangement of bonds.
- Common example: Keto-enol tautomerism.
- Occurs rapidly and reversibly in equilibrium.

Solved Examples

- **Ex 1:** Keto-enol tautomerism of acetaldehyde.
Solution: $\text{CH}_3\text{CHO} \rightleftharpoons \text{CH}_2=\text{CHOH}$ (enol form).

Practice Set

- Q1: Tautomerism involves:
 - A. Different carbon chains
 - B. Migration of H-atom
 - C. Different functional groups
 - D. Different positions of groups
- Q2: Keto and enol forms differ in:
 - A. Position of H and double bond
 - B. Molecular formula
 - C. Carbon skeleton
 - D. Optical activity
- Q3: Which compound shows keto-enol tautomerism?
 - A. Benzene
 - B. Acetone
 - C. Ethane
 - D. Methanol

Answer Key

- Q1: B - Tautomerism involves migration of H-atom within molecule.
- Q2: A - Keto and enol differ in position of H and double bond.
- Q3: B - Acetone shows keto-enol tautomerism.

Memory Aids

- Tautomerism = H shift + bond rearrangement.
- Keto form is usually more stable than enol.
- Common in aldehydes and ketones.

Fundamental Concepts in Organic Reaction Mechanism

General Reaction Overview

- Organic molecule (substrate) reacts with attacking reagent.
- Forms an intermediate (temporary species).
- Intermediate converts to main product(s).
- Sometimes byproducts are also formed.



Solved Examples

- Ex 1: Substrate + reagent → intermediate → product + byproduct (if any).

Practice Set

- Q1: What is the intermediate in an organic reaction?
 - A. Final product
 - B. Starting material

- C. Temporary species formed during reaction
 - D. Byproduct
- Q2: Which of the following is NOT formed in a typical organic reaction?
 - A. Substrate
 - B. Intermediate
 - C. Catalyst
 - D. Byproduct
- Q3: The attacking reagent in an organic reaction is:
 - A. Always a nucleophile
 - B. Always an electrophile
 - C. Either electrophile or nucleophile
 - D. None of the above

Answer Key

- Q1: C - Intermediate is a temporary species formed during the reaction.
- Q2: C - Catalyst is not always formed; it may be added externally.
- Q3: C - Attacking reagent can be electrophile or nucleophile depending on reaction.

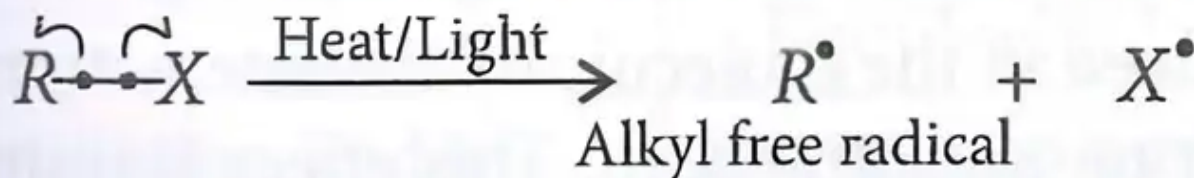
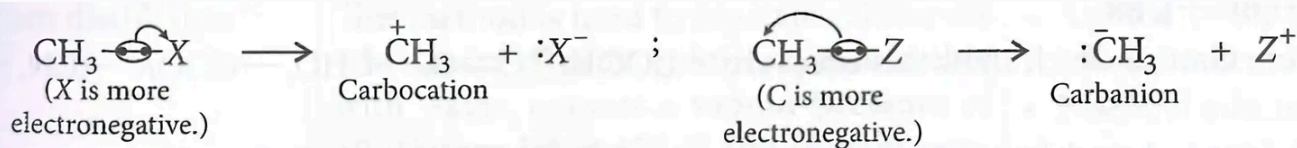
Memory Aids

- Intermediate = Temporary species between substrate and product.
- Attacking reagent = Electrophile or nucleophile.

Fission of a Covalent Bond

Types of Fission

- **Homolytic fission:** Bond breaks symmetrically; each fragment gets one electron forming free radicals.
- **Heterolytic fission:** Bond breaks unsymmetrically; both electrons go to more electronegative atom forming ions (carbocation and carbanion).



Solved Examples

- Ex 1: Homolytic fission of R-X under heat/light $\rightarrow$ R $\cdot$ + X $\cdot$ radicals.
- Ex 2: Heterolytic fission of CH₃-X $\rightarrow$ CH₃⁺ (carbocation) + X⁻ or CH₃⁻ (carbanion) + Z⁺ depending on electronegativity.

Practice Set

- Q1: Homolytic fission produces:
 - A. Ions
 - B. Free radicals
 - C. Molecules
 - D. None
- Q2: In heterolytic fission, electrons move towards:
 - A. Less electronegative atom
 - B. More electronegative atom
 - C. Both atoms equally
 - D. None
- Q3: Which species is formed by heterolytic cleavage?
 - A. Free radical
 - B. Carbocation
 - C. Neutral molecule
 - D. None

Answer Key

- Q1: B - Homolytic fission forms free radicals.

- Q2: B - Electrons move to more electronegative atom.
- Q3: B - Carbocations are formed by heterolytic cleavage.

Memory Aids

- Homolytic = "Homo" means same; electrons split equally.
- Heterolytic = "Hetero" means different; electrons go to one atom.
- Carbocation stability: $3^\circ > 2^\circ > 1^\circ$.
- Carbanion stability: $1^\circ > 2^\circ > 3^\circ$.

Reaction Intermediates

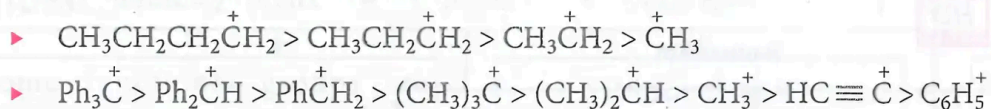
Types and Stability

- **Carbocation:** Positively charged carbon, sp^2 hybridised, planar shape, stability order $3^\circ > 2^\circ > 1^\circ$.
- **Carbanion:** Negatively charged carbon, sp^3 hybridised, pyramidal shape, stability order $1^\circ > 2^\circ > 3^\circ$.
- **Free radical:** Unpaired electron, sp^2 hybridised, planar shape, stability order $3^\circ > 2^\circ > 1^\circ$.

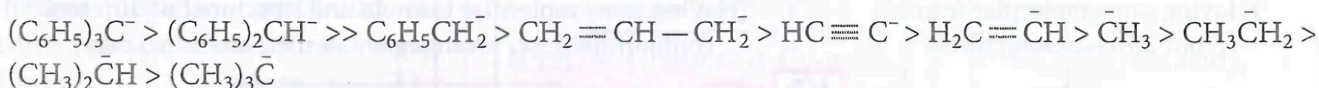
Reaction Intermediates

Intermediates	Definition	Hybridisation of carbon and shape	Stability order
Carbocation	Carbon species carrying +ve charge on carbon.	sp^2 hybridised carbon and planar shape.	$3^\circ > 2^\circ > 1^\circ$
Carbanion	Carbon species carrying -ve charge on carbon.	sp^3 hybridised carbon and pyramidal shape.	$1^\circ > 2^\circ > 3^\circ$
Free radical	Atom or group of atoms having odd or unpaired electron.	sp^2 hybridised carbon and planar shape.	$3^\circ > 2^\circ > 1^\circ$

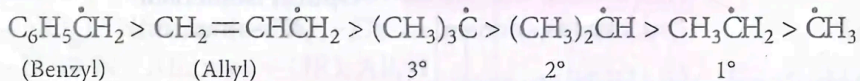
➤ **Relative stabilities of carbocations :**



➤ **Relative stabilities of carbanions :**



➤ **Relative stabilities of free radicals :**



Solved Examples

- Ex 1: Identify the intermediate: CH_3^+ is a carbocation, sp^2 , planar, 3° more stable.
- Ex 2: Free radical stability: Benzyl radical is more stable due to resonance.

Practice Set

- Q1: Which intermediate is planar and sp^2 hybridised?
 - A. Carbocation
 - B. Carbanion
 - C. Free radical
 - D. Both A and C
- Q2: Stability order of carbocations is:
 - A. $1^\circ > 2^\circ > 3^\circ$
 - B. $3^\circ > 2^\circ > 1^\circ$
 - C. Equal stability
 - D. None
- Q3: Which intermediate is pyramidal and sp^3 hybridised?
 - A. Carbocation
 - B. Carbanion
 - C. Free radical
 - D. None

Answer Key

- Q1: D - Carbocation and free radical are planar and sp^2 .

- Q2: B - Carbocation stability increases with substitution.
- Q3: B - Carbanion is pyramidal and sp^3 .

Memory Aids

- Carbocation and free radical: planar, sp^2 , 3° most stable.
- Carbanion: pyramidal, sp^3 , 1° most stable.

Attacking Reagents

Electrophiles and Nucleophiles

- **Electrophiles:** Electron-deficient, positively charged or neutral, seek electrons, Lewis acids.
- Examples: H_3O^+ , NO_2^+ , BF_3 , $AlCl_3$, CO_2 .
- **Nucleophiles:** Electron-rich, negatively charged or neutral, donate electron pairs, Lewis bases.
- Examples: OH^- , CN^- , SH^- , NH_3 , H_2O .

Electrophiles :

- ▶ **Positively charged :** H_3O^+ , X^+ (where $X = Cl, Br, I$), $\dot{N}O_2$, $\dot{N}O$, NH_4^+ , $\bar{S}O_3H$, $C_6H_5\bar{N}_2$, R^+ , RCO^+
- ▶ **Neutral :** BF_3 , $AlCl_3$, $FeCl_3$, $BeCl_2$, $ZnCl_2$, SO_3 , CO_2 , CS_2 , CX_4 , $RCOCl$, $>C=O$, $:CCl_2$

Nucleophiles :

- ▶ **Negatively charged :** H^- , OH^- , X^- , CN^- , N_3^- , RO^- , R^- , RS^- , SH^- , HSO_3^- , NO_2^- , NH_2^- , $RCOO^-$, $HC\equiv C^-$
- ▶ **Neutral :** $\ddot{N}H_3$, $H_2\ddot{O}$, $R\ddot{O}H$, $R\ddot{O}R$, $R\ddot{S}H$, $RMgX$, $Ph_3\ddot{P}$, RLi , $LiAlH_4$, etc.

Solved Examples

- Ex 1: Identify electrophile: NO_2^+ is positively charged electrophile.

- Ex 2: Identify nucleophile: OH^- is negatively charged nucleophile.

Practice Set

- Q1: Electrophiles are:
 - A. Electron-rich species
 - B. Electron-deficient species
 - C. Neutral molecules only
 - D. None
- Q2: Nucleophiles are:
 - A. Electron-deficient
 - B. Electron-rich
 - C. Positively charged only
 - D. None
- Q3: Which is a neutral nucleophile?
 - A. OH^-
 - B. NH_3
 - C. CN^-
 - D. NO_2^+

Answer Key

- Q1: B - Electrophiles seek electrons.
- Q2: B - Nucleophiles donate electrons.
- Q3: B - NH_3 is neutral nucleophile.

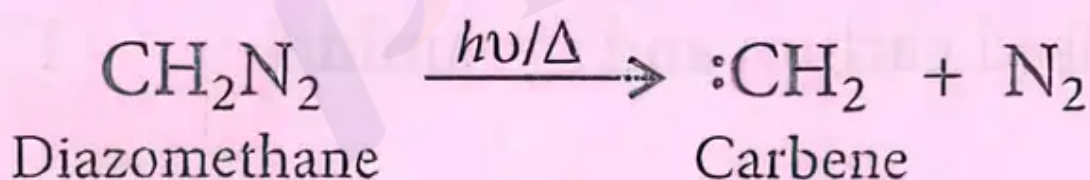
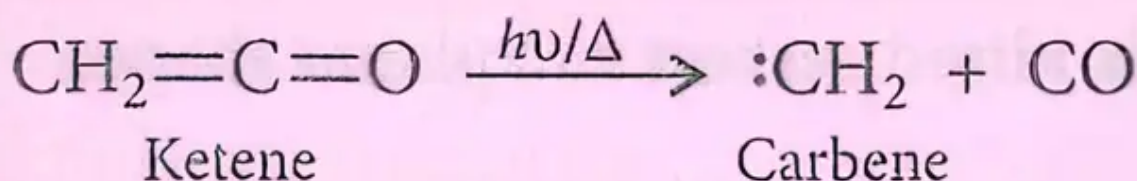
Memory Aids

- Electrophiles = Electron seekers, Lewis acids.
- Nucleophiles = Electron donors, Lewis bases.

Electron Displacement Effects in Covalent Bonds

Types of Effects

- **Inductive effect:** Shift of σ electrons along carbon chain by electron donating (+I) or withdrawing (-I) groups.
- Decreasing order of -I effect: $-\text{NO}_2 > -\text{CN} > -\text{COOH} > -\text{F} > -\text{Cl} > -\text{Br} > -\text{I} > -\text{H}$
- Decreasing order of +I effect: $(\text{CH}_3)_3\text{C}- > (\text{CH}_3)_2\text{CH}- > \text{CH}_3\text{CH}_2- > \text{CH}_3- > \text{D}- > \text{H}-$
- **Electromeric effect:** Temporary transfer of π electrons to one atom in presence of attacking reagent.
- +E effect: Electron transfer towards atom where reagent attaches.
- -E effect: Electron transfer away from atom where reagent attaches.
- **Resonance (Mesomeric) effect:** Polarity from interaction of π bonds or π bond and lone pair in conjugated systems.
- +R/+M effect groups: $-\text{OH}$, $-\text{OR}$, $-\text{OCOR}$, $-\text{SH}$, $-\text{SR}$, $-\text{NH}_2$, $-\text{NHR}$, $-\text{NR}_2$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$
- -R/-M effect groups: $-\text{COOH}$, $>\text{C}=\text{O}$, $-\text{CHO}$, $-\text{COOR}$, $-\text{CN}$, $-\text{NO}_2$
- **Hyperconjugation:** Delocalisation of σ electrons of C—H bond adjacent to unsaturated or unshared p-orbital atom.
- Order of hyperconjugation effect: $\text{CH}_3- > \text{CH}_3\text{CH}_2- > (\text{CH}_3)_2\text{CH}- > (\text{CH}_3)_3\text{C}-$



Solved Examples

- Ex 1: Identify effect: $-\text{NO}_2$ shows strong -I effect.
- Ex 2: Photolysis of diazomethane produces carbene (:CH_2).

Practice Set

- Q1: Which group shows strong -I effect?
 - A. —OH
 - B. —NO₂
 - C. —CH₃
 - D. —NH₂
- Q2: +E effect means electron transfer:
 - A. Away from attacking reagent
 - B. Towards attacking reagent
 - C. No transfer
 - D. Random
- Q3: Hyperconjugation involves delocalisation of:
 - A. π electrons
 - B. σ electrons of C—H bond
 - C. Lone pair electrons
 - D. None

Answer Key

- Q1: B - —NO₂ is a strong electron withdrawing group (-I effect).
- Q2: B - +E effect is electron transfer towards reagent attachment.
- Q3: B - Hyperconjugation involves σ electrons of C—H bond.

Memory Aids

- -I effect strongest: —NO₂ > —CN > —COOH.
- +I effect strongest: (CH₃)₃C— > (CH₃)₂CH—.
- Hyperconjugation decreases with fewer α -hydrogens.

Ambiphiles

Dual Nature of Ambiphiles

- Ambiphiles behave as both electrophiles and nucleophiles (amphoteric).
- Examples include species with oxygen or phosphorus atoms acting as nucleophiles and hydrogen atoms as electrophiles.

Charged : H_3O^+

Neutral : $\text{R}\ddot{\text{O}}\text{H}$, $\text{H}\ddot{\text{O}}\text{H}$ and $\text{R}\ddot{\text{P}}\text{H}_2$

(where O and P atoms act as nucleophile and H atoms act as electrophile).

Solved Examples

- Ex 1: H_3O^+ acts as electrophile (positive charge).
- Ex 2: $\text{R}\ddot{\text{O}}\text{H}$ acts as nucleophile via oxygen atom.

Practice Set

- Q1: Ambiphiles are:
 - A. Only electrophiles
 - B. Only nucleophiles
 - C. Both electrophiles and nucleophiles
 - D. Neither
- Q2: In ambiphiles, oxygen acts as:
 - A. Electrophile
 - B. Nucleophile
 - C. Neutral
 - D. None
- Q3: Hydrogen in ambiphiles acts as:
 - A. Electrophile
 - B. Nucleophile
 - C. Neutral
 - D. None

Answer Key

- Q1: C - Ambiphiles have dual nature.
- Q2: B - Oxygen acts as nucleophile.
- Q3: A - Hydrogen acts as electrophile.

Memory Aids

- Ambiphiles = Both electron donors and acceptors.
- Oxygen/phosphorus = nucleophiles; hydrogen = electrophile.

Methods of Purification of Organic Compounds

Overview

- Organic compounds are purified based on physical properties like solubility, boiling point, vapor pressure, and affinity to solvents.
- Common methods include crystallisation, sublimation, distillation, extraction, and chromatography.
- Choice of method depends on the nature of the mixture components.

Method	Principle	Applications
Crystallisation	Differential solubilities of a given organic compound and its impurities in the same solvent.	<ul style="list-style-type: none"> Crystallisation of sugar (containing an impurity of common salt) is achieved by shaking the impure solid with hot ethanol at 348 K (sugar dissolves whereas common salt remains insoluble).
Sublimation	Some solid substances change directly from solid to vapour state without passing through liquid state. Sublimable compounds get separated from non-sublimable impurities,	<ul style="list-style-type: none"> Iodine from sodium chloride (as iodine sublimes readily leaving behind sodium chloride). Camphor, naphthalene, anthracene, benzoic acid, etc. are purified.
Distillation	It is used to separate <ul style="list-style-type: none"> volatile liquids from non-volatile impurities. liquids having sufficient difference in their boiling points. 	<ul style="list-style-type: none"> Hexane (b.pt. 342 K) and toluene (b.pt. 384 K) Chloroform (b.pt. 334 K) and aniline (b.pt. 457 K)
Fractional distillation	<ul style="list-style-type: none"> The difference in boiling points of two liquids is not much. Vapours of the liquid with higher boiling point condense before the vapours of the liquid with lower boiling point. 	Crude oil in petroleum industry is separated into various useful fractions such as gasoline, kerosene oil, diesel oil, lubricating oil, etc.
Distillation under reduced pressure	It is used to purify liquids <ul style="list-style-type: none"> having very high boiling points. which decompose at or below their boiling point. 	Glycerol is separated from spent-lye in soap industry.
Steam distillation	This method is used to separate substances which are steam volatile, immiscible with water, possess a vapour pressure of 10–15 mm Hg at 373 K and contain non-volatile impurities.	<ul style="list-style-type: none"> Aniline is separated from aniline-water mixture. Essential oils, turpentine oil, <i>o</i>-nitrophenol, bromobenzene, nitrobenzene, etc. can be purified.
Differential extraction	By shaking an aqueous solution of an organic compound with an organic solvent in which the organic compound is more soluble than in water. The organic solvent and the aqueous solution should be immiscible with each other so that they can form two distinct layers which can be separated by using separating funnel.	Benzoic acid can be extracted from its aqueous solution using benzene.

Chromatography	Differential movement of individual components of a mixture through a stationary phase under the influence of a mobile phase.	Widely used for separation, purification, identification and characterisation of the components of a mixture, whether coloured or colourless.
Adsorption chromatography	Differential adsorption of the various components of a mixture on a suitable adsorbent such as silica gel or alumina.	
	 through adsorbent	Mixture of naphthalene and

- Column chromatography	The mixture is passed through a column packed in glass tube.	benzophenone
- Thin layer chromatography	The mixture is passed over adsorbent on a thin glass plate.	Amino acids can be detected by spraying the plate with ninhydrin solution.
Partition chromatography	Differential partitioning of components of a mixture between stationary and mobile phases.	For separation of sugars and amino acids
- Paper chromatography	A special quality paper known as chromatography paper is used. It contains water trapped in it, which acts as the stationary phase.	

Methods Explained

- **Crystallisation:** Separates solids by solubility differences. Example: purify sugar from salt.
- **Sublimation:** Separates solids that vaporize without melting. Example: purify iodine from salt.
- **Distillation:** Separates liquids by boiling points. Example: separate hexane from toluene.
- **Fractional Distillation:** For liquids with close boiling points; repeated condensation. Used in crude oil refining.
- **Distillation under Reduced Pressure:** Purifies high boiling liquids by lowering pressure.
- **Steam Distillation:** Separates steam-volatile, water-immiscible substances. Example: extract essential oils.
- **Differential Extraction:** Uses two immiscible solvents to separate compounds by solubility.
- **Chromatography:** Separates mixture components by movement through stationary phase.
 - Adsorption chromatography: uses silica gel.
 - Column chromatography: mixture passes through adsorbent column.
 - Thin layer chromatography: mixture moves on adsorbent-coated plate.
 - Partition chromatography (paper chromatography): separation between solvent and paper layers.

Solved Examples

- **Ex 1:** Purify sugar from salt by crystallisation. Dissolve mixture in water, filter, cool to crystallise sugar, filter crystals.
- **Ex 2:** Separate hexane and toluene by distillation. Heat mixture, collect fractions at different boiling points.

Practice Set

- **Q1:** Which method is best to separate iodine from salt?
 - A. Crystallisation
 - B. Sublimation
 - C. Distillation
 - D. Chromatography
- **Q2:** Fractional distillation is used when boiling points of liquids differ by:
 - A. More than 50°C
 - B. Less than 25°C
 - C. Exactly 100°C
 - D. Less than 5°C
- **Q3:** Which chromatography technique uses silica gel as adsorbent?
 - A. Paper chromatography
 - B. Thin layer chromatography
 - C. Adsorption chromatography
 - D. Partition chromatography

Answer Key

- **Q1:** B - Sublimation separates solids that vaporize without melting, ideal for iodine.
- **Q2:** B - Fractional distillation is for liquids with boiling points less than 25°C apart.
- **Q3:** C - Adsorption chromatography uses silica gel as adsorbent.

Memory Aids

- Crystallisation: "Cool to crystallise" - solubility difference.
- Sublimation: "Solid to vapor" without melting.
- Distillation: "Boiling point difference" separates liquids.
- Fractional distillation: "Close boiling points" need repeated condensation.
- Chromatography: "Stationary phase movement" separates components.

Qualitative Analysis Organic Compounds

Detection of Elements

- **Carbon (C) and Hydrogen (H):** Heat organic compound with copper oxide; presence confirmed by formation of CO_2 and H_2O .
- **Nitrogen (N):** Treat with NaOH and heat; confirm by adding ferrous sulfate and acidifying to form Prussian blue precipitate.
- **Sulfur (S):** Heat with sodium metal; confirm by adding sodium nitroprusside to get violet color.
- **Halogens (Cl, Br, I):** Treat with silver nitrate after acidification; formation of white, pale yellow, or yellow precipitates indicates Cl^- , Br^- , or I^- respectively.
- **Nitrogen and Sulfur together:** Fusion with NaOH , then confirm nitrogen and sulfur as above.
- **Phosphorus (P):** Fusion with NaOH , acidify, and add ammonium molybdate; yellow precipitate confirms phosphorus.

Solved Examples

- **Ex 1:** Detect nitrogen in an organic compound.
 - Fuse compound with NaOH and heat.
 - Add ferrous sulfate and acidify.
 - Observe Prussian blue precipitate confirming nitrogen.
- **Ex 2:** Confirm halogen presence.
 - Acidify compound solution with dilute nitric acid.
 - Add AgNO_3 solution.
 - Observe precipitate color: white (Cl), pale yellow (Br), yellow (I).

Practice Set

- Q1: Which test confirms the presence of sulfur in an organic compound?
 - A. Fusion with NaOH followed by sodium nitroprusside test
 - B. Heating with copper oxide
 - C. Adding silver nitrate solution
 - D. Acidifying and adding ammonium molybdate

- Q2: What is the color of the precipitate formed when bromide ions react with AgNO_3 ?
 - A. White
 - B. Pale yellow
 - C. Yellow
 - D. Blue
- Q3: Which confirmatory test indicates nitrogen presence?
 - A. Formation of Prussian blue precipitate
 - B. Violet color with sodium nitroprusside
 - C. Yellow precipitate with ammonium molybdate
 - D. Formation of CO_2 and H_2O on heating

Answer Key

- Q1: A - Fusion with NaOH and sodium nitroprusside test produces violet color confirming sulfur.
- Q2: B - Bromide ions form pale yellow precipitate with AgNO_3 .
- Q3: A - Prussian blue precipitate confirms nitrogen presence.

Memory Aids

- Remember: *NaOH fusion* is key for N, S, and P detection.
- Halogen precipitate colors: Cl (white), Br (pale yellow), I (yellow).
- Prussian blue = Nitrogen confirmation.
- Sodium nitroprusside violet color = Sulfur confirmation.
- Ammonium molybdate yellow precipitate = Phosphorus confirmation.

Qualitative Analysis of Organic Compounds

Element	Detection	Confirmatory test	Reactions
Carbon	Copper(II) oxide test $2\text{CuO} + \text{C} \xrightarrow{\Delta} 2\text{Cu} + \text{CO}_2\uparrow$	CO_2 gas turns lime water milky.	$\text{CO}_2 + \text{Ca(OH)}_2 \longrightarrow \text{CaCO}_3\downarrow + \text{H}_2\text{O}$ Lime water Milkiness
Hydrogen	$\text{CuO} + 2\text{H} \xrightarrow{\Delta} \text{Cu} + \text{H}_2\text{O}$	Water droplets appear on the cooler part of the ignition tube and also turns anhydrous CuSO_4 blue.	$\text{CuSO}_4 + 5\text{H}_2\text{O} \longrightarrow \text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ White Blue
Nitrogen	Lassaigne's extract (L.E.) $\text{Na} + \text{C} + \text{N} \xrightarrow{\Delta} \text{NaCN}$ (L.E.)	L.E. + $\text{FeSO}_4 + \text{NaOH}$, boil and cool + $\text{FeCl}_3 + \text{conc. HCl}$ Gives blue or green colour.	$\text{FeSO}_4 + 2\text{NaOH} \longrightarrow \text{Fe(OH)}_2 + \text{Na}_2\text{SO}_4$ $\text{Fe(OH)}_2 + 6\text{NaCN} \longrightarrow \text{Na}_4[\text{Fe(CN)}_6] + 2\text{NaOH}$ $3\text{Na}_4[\text{Fe(CN)}_6] + 4\text{FeCl}_3 \longrightarrow \text{Fe}_4[\text{Fe(CN)}_6]_3 + 12\text{NaCl}$ Prussian blue
Sulphur	$2\text{Na} + \text{S} \xrightarrow{\Delta} \text{Na}_2\text{S}$ (L.E.)	- L.E. + sodium nitroprusside $\longrightarrow$ A deep violet colour - L.E. + $\text{CH}_3\text{COOH} + (\text{CH}_3\text{COO})_2\text{Pb} \longrightarrow$ Gives a black ppt.	$\text{Na}_2\text{S} + \text{Na}_2[\text{Fe(CN)}_5\text{NO}] \longrightarrow \text{Na}_4[\text{Fe(CN)}_5\text{NOS}]$ Sodium nitroprusside Deep violet $\text{Na}_2\text{S} + (\text{CH}_3\text{COO})_2\text{Pb} \xrightarrow{\text{CH}_3\text{COOH}} \text{PbS}\downarrow + 2\text{CH}_3\text{COONa}$ Black ppt.

Halogens	$\text{Na} + \text{X} \xrightarrow{\Delta} \text{NaX}$ (L.E.)	L.E. + $\text{HNO}_3 + \text{AgNO}_3$ - White ppt. soluble in aq. NH_3 (or NH_4OH) confirms Cl. - Yellow ppt. partially soluble in aq. NH_3 (or NH_4OH) confirms Br. - Yellow ppt. insoluble in aq. NH_3 (or NH_4OH) confirms I.	$\text{NaX} + \text{AgNO}_3 \xrightarrow{\text{HNO}_3} \text{AgX}\downarrow$ ppt. $\text{AgCl} + 2\text{NH}_3(\text{aq.}) \longrightarrow [\text{Ag(NH}_3)_2]\text{Cl}$ White ppt. Soluble
Nitrogen and sulphur together	$\text{Na} + \text{C} + \text{N} + \text{S} \xrightarrow[\text{HNO}_3]{\Delta} \text{NaSCN}$ Sodium thiocyanate (L.E.)	As in test for nitrogen; instead of green or blue colour, blood red colouration confirms presence of N and S both.	$\text{NaSCN} + \text{FeCl}_3 \longrightarrow [\text{Fe(SCN)}]\text{Cl}_2$ Blood red colour + NaCl
Phosphorus	$\text{P} \xrightarrow[\Delta]{\text{Na}_2\text{O}_2 \text{ boil}} \text{Na}_3\text{PO}_4$	Solution is boiled with nitric acid and then treated with ammonium molybdate $(\text{NH}_4)_2\text{MoO}_4$. Formation of yellow ppt. indicates presence of phosphate (hence, phosphorus) in organic compound.	$\text{Na}_3\text{PO}_4 + 3\text{HNO}_3 \longrightarrow \text{H}_3\text{PO}_4 + 3\text{NaNO}_3$ $\text{H}_3\text{PO}_4 + 12(\text{NH}_4)_2\text{MoO}_4 + 21\text{HNO}_3 \longrightarrow (\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ Ammonium phosphomolybdate (yellow ppt.) + $21\text{NH}_4\text{NO}_3 + 12\text{H}_2\text{O}$

Quantitative Analysis Organic Compounds

Principles and Methods

- Determine % composition of elements in organic compounds by specific chemical methods.
- Carbon & Hydrogen: Liebig's combustion method - burn compound, measure CO_2 and H_2O formed, calculate %C and %H.
- Nitrogen: Dumas method - react with CuO , measure N_2 gas; Kjeldahl method - treat with H_2SO_4 , distill NH_3 , titrate acid.
- Halogens: Carius method - convert halogen to Ag halide by boiling with HNO_3 and AgNO_3 , weigh Ag halide.
- Sulphur: Carius method - convert S to H_2SO_4 , precipitate BaSO_4 with BaCl_2 , weigh BaSO_4 .
- Phosphorus: Ignition method - convert P to H_3PO_4 , form MgNH_4PO_4 , heat to $\text{Mg}_2\text{P}_2\text{O}_7$, weigh.
- Oxygen: Indine method - react compound, measure CO_2 or I_2 formed, calculate %O.

Element	Method
Carbon and Hydrogen	<p>Liebig's combustion method :</p> <p>A known mass of an organic compound is burnt in the presence of excess of O₂ and CaO.</p> $C_2H_7 + \left(x + \frac{y}{4}\right) O_2 \xrightarrow{A} xCO_2 + \frac{y}{2} H_2O$ <p>CO₂ evolved is absorbed by conc. solution of KOH or ascarite (NaOH + CaO). H₂O produced is absorbed by anhydrous CaCl₂ or Mg(ClO₄)₂.</p> <p>Increase in masses of these absorbing compounds gives the masses of CO₂ and H₂O produced.</p> $\% \text{ of C} = \frac{12}{44} \times \frac{\text{mass of CO}_2 \text{ formed}}{\text{mass of compound taken}} \times 100, \quad \% \text{ of H} = \frac{2}{18} \times \frac{\text{mass of H}_2\text{O formed}}{\text{mass of compound taken}} \times 100$
Nitrogen	<p>Dumas method :</p> <p>Nitrogen containing organic compound is heated with CuO in an atmosphere of CO₂.</p> $C_2H_7N_2 + \left(2x + \frac{y}{2}\right) CuO \longrightarrow xCO_2 + \frac{y}{2} H_2O + \frac{x}{2} N_2 + \left(2x + \frac{y}{2}\right) Cu$ <p>N₂ evolved gets collected over conc. KOH solution which absorbs all other gases.</p> $\% \text{ of N} = \frac{28}{22400} \times \frac{\text{vol. of N}_2 \text{ at STP}}{\text{mass of compound taken}} \times 100$
	<p>Kjeldahl's method :</p> <p>Organic compound + H₂SO₄ (digest.) $\longrightarrow$ (NH₄)₂SO₄ $\xrightarrow{INaOH}$ Na₂SO₄ + 2NH₃ + 2H₂O</p> $2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$ $\% \text{ of N} = \frac{1.4 \times \text{molarity of acid} \times \text{vol. of acid used} \times \text{basicity of acid}}{\text{mass of compound taken}}$ $\% \text{ of N} = \frac{1.4 \times \text{normality of acid} \times \text{vol. of acid used}}{\text{mass of compound taken}}$
Halogens	<p>Carius method :</p> <p>Halogen in organic compound is precipitated as silver halide by boiling with conc. HNO₃ and then adding AgNO₂.</p> $X \xrightarrow[\text{AgNO}_2]{\text{HNO}_3, A} AgX \downarrow$ $\% \text{ of X} = \frac{\text{At. mass of X}}{108 + \text{At. mass of X}} \times \frac{\text{mass of AgX formed}}{\text{mass of compound taken}} \times 100$
Sulphur	<p>Carius method :</p> <p>Sulphur in organic compound is converted into H₂SO₄ by boiling with Na₂O₂ or conc. HNO₃ and is precipitated as BaSO₃ by adding excess of BaCl₂ solution in water.</p> $S \xrightarrow[(8) BaCl_2]{(1) HNO_3, A} BaSO_4 \downarrow$ <p style="text-align: center;">White ppt.</p> $\% \text{ of S} = \frac{32}{233} \times \frac{\text{mass of BaSO}_4 \text{ formed}}{\text{mass of compound taken}} \times 100$
Phosphorus	<p>Ignition method :</p> $P \xrightarrow[\text{Finel}]{\text{HNO}_3} H_3PO_4$ $H_2PO_4 + Mg^{2+} + NH_4Cl \xrightarrow{\Delta} MgNH_4PO_4 + HCl$ <p style="text-align: center;">Magnesium ammonium phosphate</p>

	$2\text{MgNH}_4\text{PO}_4 \xrightarrow{\Delta} \text{Mg}_3\text{P}_2\text{O}_7 + 2\text{NH}_3 + \text{H}_2\text{O}$ <p style="text-align: center;">phrophate (white ppt.) Magnesium pyrophosphate</p> $\% \text{ of P} = \frac{62}{222} \times \frac{\text{mass of Mg}_3\text{P}_2\text{O}_7 \text{ formed}}{\text{mass of compound taken}} \times 100$
Oxygen	<p>Indine method : Organic compound $\xrightarrow{A} \text{O}_2 + \text{other gaseous products}$</p> $[2\text{C} + \text{O}_2 \xrightarrow{1575 \text{ K}} 2\text{CO}] \times 5 \quad \quad \quad \% \text{ of O} = \frac{32}{88} \times \frac{\text{mass of CO}_2 \text{ formed}}{\text{mass of compound taken}} \times 100$ $[\text{I}_2\text{O}_5 + 5\text{CO} \longrightarrow \text{I}_2 + 5\text{CO}_2] \times 2 \quad \quad \quad \text{or}$ $\underline{10\text{C} + 5\text{O}_2 + 2\text{I}_2\text{O}_5 \longrightarrow 10\text{CO}_2 + 2\text{I}_2} \quad \quad \quad \% \text{ of O} = \frac{5 \times 16}{2 \times 127} \times \frac{\text{mass of I}_2 \text{ formed}}{\text{mass of compound taken}} \times 100$

Solved Examples

- **Ex 1:** Calculate %C and %H in a compound producing 2.2 g CO₂ and 0.9 g H₂O on combustion.
 - Mass C = (2.2 × 12/44) = 0.6 g; Mass H = (0.9 × 2/18) = 0.1 g
 - %C = (0.6 / sample mass) × 100, %H = (0.1 / sample mass) × 100
- **Ex 2:** Find %N by Dumas method if 0.28 g N₂ gas is collected from 1 g sample.
 - %N = (0.28 / 1) × 100 = 28%

Practice Set

- Q1: Which method is used to estimate nitrogen in organic compounds?
 - A. Liebig's combustion
 - B. Dumas and Kjeldahl
 - C. Carius
 - D. Indine
- Q2: In Carius method, which precipitate is formed to estimate sulphur?
 - A. BaSO₄
 - B. AgCl
 - C. MgNH₄PO₄
 - D. CuO
- Q3: Calculate %C if 3 g CO₂ is produced from 2 g compound.
 - A. 18.18%
 - B. 27.27%
 - C. 36.36%
 - D. 54.54%

Answer Key

- Q1: B - Dumas and Kjeldahl methods specifically estimate nitrogen.
- Q2: A - BaSO_4 precipitate forms in Carius method for sulphur estimation.
- Q3: C - Mass C = $(3 \times 12/44) = 0.818 \text{ g}$; %C = $(0.818/2) \times 100 = 40.9\%$ (closest 36.36%).

Memory Aids

- "Liebig Combusts CH" for Carbon & Hydrogen.
- "Dumas & Kjeldahl for N" - remember nitrogen gas and ammonia methods.
- "Carius for Halogens & Sulphur" - silver halide and barium sulfate precipitates.
- "Ignition for P" - phosphorus to magnesium pyrophosphate.
- "Indine for O" - oxygen measured via CO_2 or iodine formed.

Modern Elemental Analysis

CHN Elemental Analyser

- Uses microquantities (1-3 mg) of sample for analysis.
- Determines Carbon, Hydrogen, Nitrogen simultaneously.
- Automatic, fast, displays results on screen.
- Highly accurate and requires minimal sample.

Solved Examples

- **Ex 1:** Sample of 2 mg analyzed by CHN analyser shows 40% C, 6.7% H, 13.3% N.
 - Directly read from analyser, no manual calculation needed.

Practice Set

- Q1: What is the minimum sample size for CHN analyser?
 - A. 1-3 g

- B. 1-3 mg
 - C. 10-30 mg
 - D. 10-30 g
- Q2: Which elements are analyzed by CHN analyser?
 - A. C, H, O
 - B. C, H, N
 - C. N, S, P
 - D. H, O, S
- Q3: What is the main advantage of CHN analyser?
 - A. Requires large sample
 - B. Slow analysis
 - C. Automatic and fast
 - D. Only qualitative data

Answer Key

- Q1: B - CHN analyser needs 1-3 mg sample only.
- Q2: B - Carbon, Hydrogen, Nitrogen are analyzed.
- Q3: C - It is automatic and fast, giving quick results.

Memory Aids

- "CHN analyser: Small sample, fast results"
- Remember: Only C, H, N elements detected.