

Aliphatic Saturated Hydrocarbons: Alkanes

LEARNING OBJECTIVES

After studying this chapter, students will be able to:

LO	Cognitive level	Objective
LO 1	Remember	Define alkanes, classify them as straight-chain, branched-chain, and cycloalkanes, recall the general formula C_nH_{2n+2} , and list at least five named examples.
LO 2	Understand	Explain the concept of sp^3 hybridisation in carbon, describe the tetrahedral geometry of methane, and relate bond angles and bond lengths to the structure of alkanes.
LO 3	Apply	Apply IUPAC nomenclature rules to correctly name and draw structures of given straight-chain, branched-chain, and cyclic alkanes.
LO 4	Apply and Analyze	Describe and write balanced equations for the methods of preparation of alkanes (Wurtz reaction, Kolbe's synthesis, Clemmensen's reduction, Wolff-Kishner reduction) and identify the limitations of each method.
LO 5	Analyze	Explain the stepwise free radical mechanism of halogenation of alkanes, differentiate between initiation, propagation, and termination steps, and analyze factors affecting rate and selectivity of halogenation.
LO 6	Evaluate	Evaluate the pharmaceutical significance of liquid paraffin, soft paraffin, and hard paraffin, and justify their use as official pharmaceutical excipients with reference to their physical properties and pharmacopoeial standards.

1.1 INTRODUCTION TO ALKANES

Organic chemistry begins with the simplest class of organic compounds and that is, the hydrocarbons. As the name suggests, hydrocarbons are compounds that contain only two elements: carbon (C) and hydrogen (H). These compounds are the backbone of all organic chemistry and serve as the parent structures from which innumerable other organic molecules are derived.

Among hydrocarbons, the alkanes hold a special place. They are the most fundamental group of saturated, open-chain compounds in which all carbon atoms are joined by single bonds only. Because they have no "extra" bonds that can react easily, alkanes were historically regarded as chemically inert, earning them the name paraffins (from Latin: *parum affinis*, meaning "little affinity"). However, as we shall see, alkanes do undergo important reactions under specific conditions.

For pharmacy students, alkanes are not merely an academic starting point. Their pharmaceutical applications such as, liquid paraffin, soft paraffin (petroleum jelly), and hard paraffin (paraffin wax) do make them directly relevant to drug formulation, cosmetics, and patient care. These materials appear in official pharmacopoeias (IP, BP, USP) as important pharmaceutical excipients and bases.

This chapter covers the complete profile of alkanes: their structure, classification, nomenclature, methods of preparation, physical and chemical properties, the mechanism of free radical halogenation, and their pharmaceutical applications.

1.2 CLASSIFICATION OF ALKANES

The pictorial flowchart given below is self revealing:

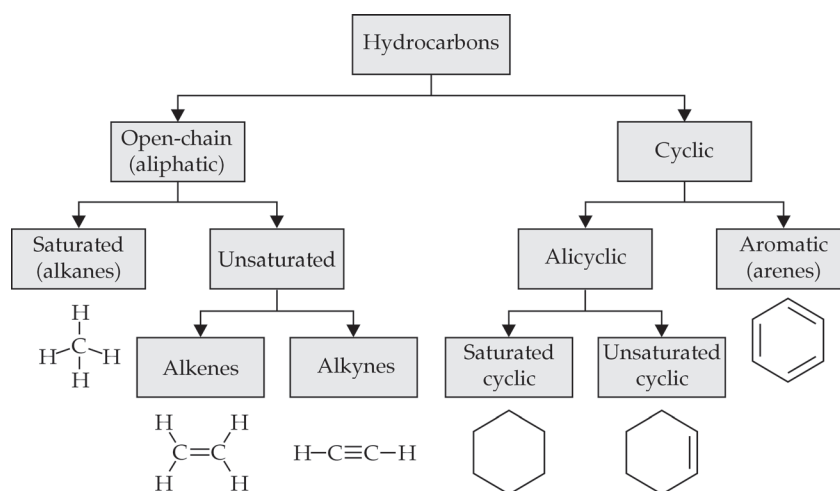


Fig. 1.1: Classification tree of hydrocarbons showing the hierarchy from open-chain to cyclic, and from saturated to aromatic compounds

Alkanes can be classified into three main types based on the arrangement of carbon atoms in their molecular structure:

1.2.1 Straight-chain (Normal) Alkanes

In straight-chain alkanes, all the carbon atoms are arranged in a continuous, unbranched chain. They are also called *n*-alkanes (where '*n*' stands for normal). The general formula for alkanes is C_nH_{2n+2} , where *n* = number of carbon atoms.

Name and structure: Pentane (C_5H_{12})	Chemical formula: $C_nH_{2(n+1)}$
$ \begin{array}{ccccccc} & H & H & H & H & H & \\ & & & & & & \\ H & -C & -C & -C & -C & -C & -H \\ & & & & & & \\ & H & H & H & H & H & \end{array} $	$n = 5$ Substitute the <i>n</i> value: $C_5H_{2(5+1)}$ The formula follows the general chemical formula for alkanes: C_5H_{12}

Fig. 1.2: Extended structural formula of *n*-pentane showing the straight-chain arrangement of carbon atoms

Table 1.1: First ten members of the straight-chain alkane homologous series

<i>n</i> (Carbon atoms)	IUPAC name	Molecular formula	Condensed structural formula
1	Methane	CH ₄	CH ₄
2	Ethane	C ₂ H ₆	CH ₃ -CH ₃
3	Propane	C ₃ H ₈	CH ₃ -CH ₂ -CH ₃
4	Butane	C ₄ H ₁₀	CH ₃ -CH ₂ -CH ₂ -CH ₃
5	Pentane	C ₅ H ₁₂	CH ₃ -(CH ₂) ₃ -CH ₃
6	Hexane	C ₆ H ₁₄	CH ₃ -(CH ₂) ₄ -CH ₃
7	Heptane	C ₇ H ₁₆	CH ₃ -(CH ₂) ₅ -CH ₃
8	Octane	C ₈ H ₁₈	CH ₃ -(CH ₂) ₆ -CH ₃
9	Nonane	C ₉ H ₂₀	CH ₃ -(CH ₂) ₇ -CH ₃
10	Decane	C ₁₀ H ₂₂	CH ₃ -(CH ₂) ₈ -CH ₃

KEY CONCEPT Homologous Series

A homologous series is a group of compounds with the same general formula, differing from each other by a $-\text{CH}_2-$ unit. Successive members differ by 14 mass units. Alkanes form such a series, and each member shares similar chemical properties but shows gradual changes in physical properties.

1.2.2 Branched-chain Alkanes

Branched-chain alkanes have one or more carbon atoms attached as side chains (substituents) to the main carbon chain. They have the same molecular formula as straight-chain alkanes but differ in structure and they are called structural isomers (specifically chain isomers).

Example: Butane (C₄H₁₀) exists in two structural forms:

- *n*-Butane: CH₃-CH₂-CH₂-CH₃ (straight chain)
- Isobutane (2-Methylpropane): CH₃-CH(CH₃)-CH₃ (branched)

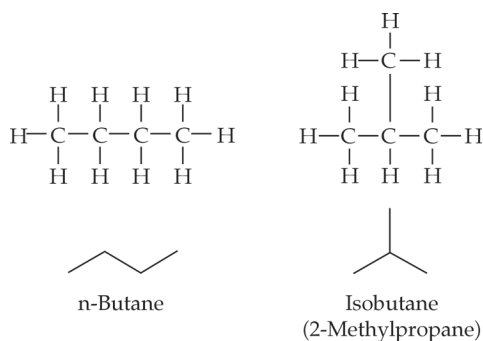


Fig. 1.3: Structural isomers of butane: *n*-butane (left) and isobutane/2-methylpropane (right)

The simplest branched alkanes have common names that are still widely used: *iso*-butane, *iso*-pentane, and *neo*-pentane. However, for systematic work, IUPAC names are preferred.

1.2.3 Cyclic Alkanes (Cycloalkanes)

Cycloalkanes are saturated hydrocarbons in which the carbon atoms are arranged in a ring (closed chain). Their general formula is C_nH_{2n} (**Note:** Two fewer H atoms than the corresponding open-chain alkane because ring formation uses two bonding positions). Common examples include cyclopropane (C_3H_6), cyclobutane (C_4H_8), cyclopentane (C_5H_{10}), and cyclohexane (C_6H_{12}). Cyclohexane is particularly important in pharmaceutical chemistry as it is the basic ring present in many drug molecules.

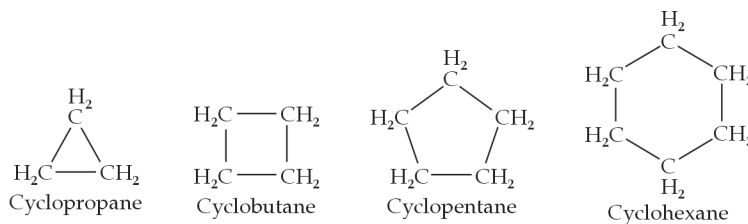


Fig. 1.4: Ring structures of common cycloalkanes—cyclopropane, cyclobutane, cyclopentane, and cyclohexane

Comparison at a Glance

Straight-chain alkanes: C_nH_{2n+2} , unbranched, named with prefix n-

Branched alkanes: C_nH_{2n+2} , same formula as straight-chain isomers, named by IUPAC rules

Cycloalkanes: C_nH_{2n+2} , ring structure, named with prefix cyclo-

1.3 NOMENCLATURE (IUPAC SYSTEM)

The International Union of Pure and Applied Chemistry (IUPAC) has established systematic rules for naming organic compounds. For alkanes, the suffix -ane is always used, preceded by a numerical prefix indicating the number of carbon atoms (meth-, eth-, prop-, but-, pent-, hex-, hept-, oct-, non-, dec-).

1.3.1 Rules for Naming Straight-chain Alkanes

1. Identify the total number of carbon atoms in the chain.
2. Use the appropriate Greek/Latin prefix + 'ane' as the name, e.g. 5 carbons = Pent + ane = Pentane.
3. In condensed formulas, the molecule is written as CH_2 -groups at the ends and $-CH_3$ -groups in between.

1.3.2 Rules for Naming Branched-chain Alkanes

The following rules are used for naming branched-chain alkanes:

1. Select the longest continuous carbon chain as the parent chain. This determines the base name.
2. Number the carbon atoms of the parent chain starting from the end nearer to the first branch point, giving substituents the lowest possible locants (position numbers).
3. Name each substituent as an alkyl group (by dropping -ane and adding -yl): methyl ($-CH_3$), ethyl ($-C_2H_5$), propyl ($-C_3H_7$), etc.

4. Write the name as: [locant-substituent name(s)] + [parent chain name]. If two different substituents are present, list them alphabetically (ignoring multiplying prefixes di-, tri-, etc.).
5. If the same substituent appears more than once, use multiplicative prefixes: di- (2), tri- (3), tetra- (4), etc. each preceded by the relevant locants.
6. If two chains of equal length compete for parent chain status, choose the one with the greater number of substituents.

MEMORY TIP for alphabetical order

Ignore prefixes di-, tri-, tetra- when alphabetising. However, do NOT ignore positional prefixes like *iso-* and *tert-* (e.g. isobutyl comes before methyl; *tert*-butyl comes after ethyl but before isopropyl).

1.3.3 Rules for Naming Cycloalkanes

1. The prefix cyclo- is added before the parent alkane name, e.g. cyclohexane.
2. If a substituent is present, number the ring carbons so that substituents receive the lowest possible locants.
3. If the ring is attached to a chain longer than the ring itself, the ring is named as a substituent (cyclopentyl, cyclohexyl) on the chain.

1.3.4 Worked Examples**Table 1.2: Worked examples of IUPAC nomenclature for alkanes**

Structure/Formula	IUPAC name	Explanation
$\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_3$	Pentane	5-carbon straight-chain
$\text{CH}_3\text{--CH}(\text{CH}_3)\text{--CH}_2\text{--CH}_3$	2-Methylbutane	4C parent chain; methyl at C-2
$\text{CH}_3\text{--C}(\text{CH}_3)_2\text{--CH}_3$	2,2-Dimethylpropane (Neopentane)	3C parent; two methyls at C-2
$\text{CH}_3\text{--CH}_2\text{--CH}(\text{C}_2\text{H}_5)\text{--CH}_2\text{--CH}_3$	3-Ethylpentane	5C parent; ethyl at C-3
Cyclo- C_6H_{12}	Cyclohexane	6-membered ring
Cyclo- $\text{C}_5\text{H}_9\text{--CH}_3$ (methyl at C-1)	Methylcyclopentane	5-membered ring with methyl

1.4 STRUCTURE AND HYBRIDISATION**1.4.1 sp^3 Hybridisation of Carbon**

To understand why alkanes have their characteristic three-dimensional shape, we need to understand how the carbon atom bonds in alkanes. Carbon has atomic number 6, with the electronic configuration: $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^0$ in the ground state.

In the ground state, carbon has only two unpaired electrons and would appear to form only two bonds. However, to form four bonds (as seen in methane and all alkanes), carbon first undergoes excitation: one electron from the 2s orbital is promoted to the empty $2p_z$ orbital, giving the excited configuration: $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$ — now with four unpaired electrons.

These four orbitals (one 2s and three 2p) then mix (hybridise) to form four new, equivalent orbitals called sp^3 hybrid orbitals. This process is called sp^3 hybridisation.

sp^3 Hybridisation—Step-by-Step

Step 1: Ground state: $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^0 \rightarrow$ only 2 unpaired electrons

Step 2: Excited state: $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1 \rightarrow$ 4 unpaired electrons

Step 3: Hybridised: $1s^2 4 \times (sp^3)^1 \rightarrow$ 4 equivalent sp^3 orbitals

Result: 4 equivalent sp^3 hybrid orbitals, each with 25% s-character and 75% p-character

An easy analogy: imagine mixing 1 litre of red paint (the 2s orbital) with 3 litres of blue paint (three 2p orbitals). The result is 4 litres of identical purple paint (four equivalent sp^3 orbitals.)

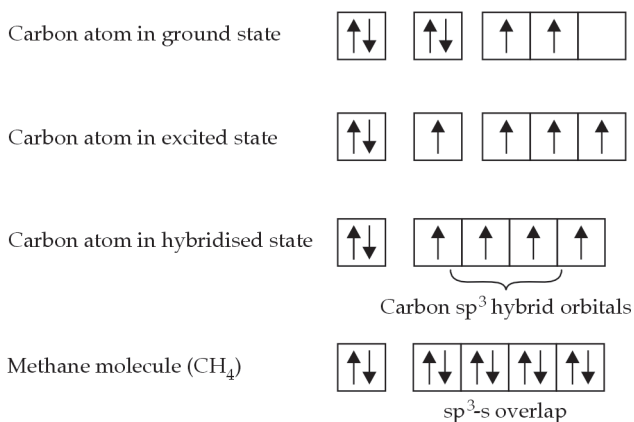


Fig. 1.5: sp^3 Hybridisation of carbon—ground state, excited state, and hybridised state showing formation of four equivalent sp^3 orbitals

The four sp^3 orbitals arrange themselves in space so they are as far apart from each other as possible, minimising electron–electron repulsion. This results in a tetrahedral arrangement, with the carbon nucleus at the centre and the four orbitals pointing towards the corners of a regular tetrahedron.

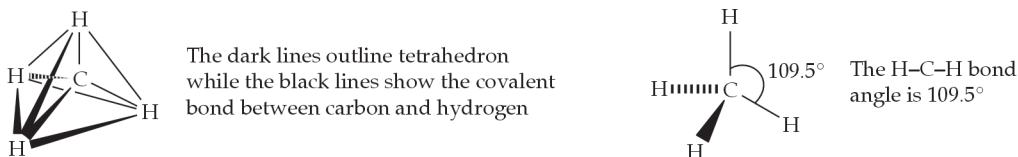


Fig. 1.6: Tetrahedral geometry of methane (CH_4)—four sp^3 orbitals pointing towards the corners of a regular tetrahedron. Bond angle = 109.5°

1.4.2 Bond Lengths and Bond Angles

In an alkane molecule, there are only two types of bonds:

- **C–H bonds:** Formed by overlap of one sp^3 orbital of carbon with the 1s orbital of hydrogen. Bond length = $1.09 \text{ \AA}$ (Angstroms).
- **C–C bonds:** Formed by overlap of two sp^3 orbitals from adjacent carbon atoms. Bond length = $1.54 \text{ \AA}$.

Both types of bonds are sigma (σ) bonds — characterised by direct head-on overlap along the inter-nuclear axis. The bond angle (H-C-H , H-C-C , or C-C-C) is approximately 109.5° (more precisely $109^\circ28'$), as dictated by the tetrahedral geometry.

Table 1.3: Bond parameters in alkanes

Bond type	Formed by	Bond length	Bond angle
C-H (sigma, σ)	$\text{sp}^3(\text{C}) + 1\text{s}(\text{H})$ overlap	1.09 Å	109.5°
C-C (sigma, σ)	$\text{sp}^3(\text{C}) + \text{sp}^3(\text{C})$ overlap	1.54 Å	109.5°

1.4.3 Molecular Geometry

An important consequence of the tetrahedral arrangement is that higher alkanes do not have a truly straight, linear structure, but their carbon atoms are arranged in a *zig-zag* pattern when viewed in three dimensions. This is the most extended (anti) conformation and represents the lowest energy arrangement.

In methane (CH_4), one carbon atom is bonded to four hydrogen atoms—the simplest example of tetrahedral geometry. In ethane (C_2H_6), two tetrahedral carbons are joined, each bearing three H atoms. As the chain grows longer, each additional $-\text{CH}_2-$ unit adds another tetrahedral carbon to the *zig-zag* backbone.

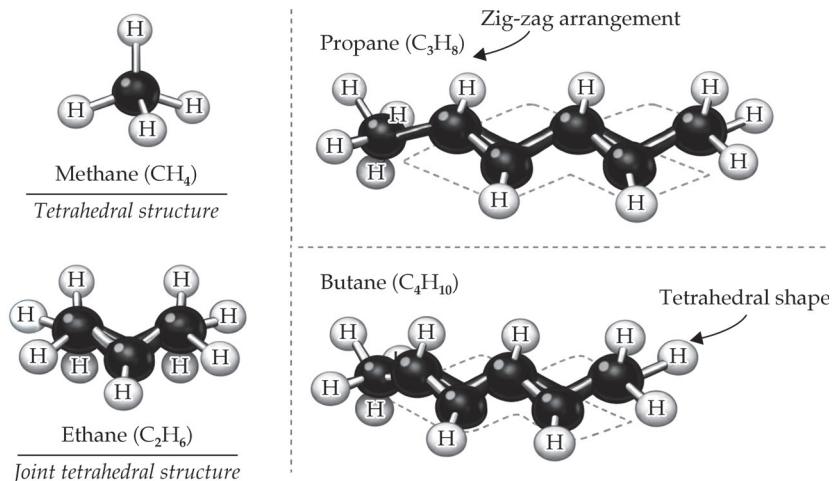


Fig. 1.7: Zig-zag arrangement of carbon atoms in propane and butane, illustrating the three-dimensional tetrahedral structure of alkane chains

1.5 METHODS OF PREPARATION OF ALKANES

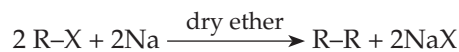
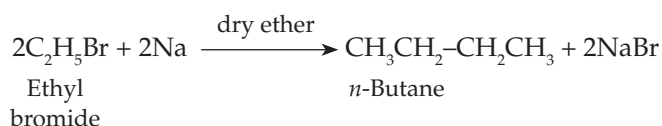
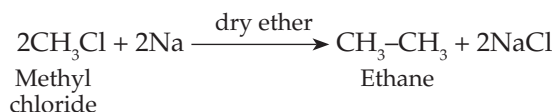
Alkanes can be synthesised in the laboratory and industrially by several methods, mainly the Wurtz reaction, Kolbe's electrolysis, Clemmensen's reduction, and Wolff-Kishner reduction, are described in detail below, along with other important preparative methods.

1.5.1 Wurtz Reaction

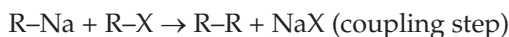
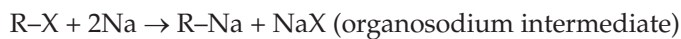
Coupling of two alkyl halide molecules *via* sodium metal to form a symmetrical alkane.

Principle

When two moles of an alkyl halide are treated with sodium metal in dry ether, the carbon skeleton is joined to give a higher alkane with twice the carbon content of the original alkyl halide.

General Reaction**Example****Mechanism**

The reaction proceeds by a nucleophilic mechanism. Sodium reduces one alkyl halide to form an organosodium intermediate (R-Na), which then reacts with the second alkyl halide in a nucleophilic substitution:

**Limitations**

- Best suited for synthesis of symmetrical alkanes (both R groups identical).
- When two different alkyl halides (R-X and R'-X) are used, a mixture of three alkanes is obtained: R-R, R'-R', and R-R'. This makes it unsuitable for pure preparation of unsymmetrical alkanes.
- Methane cannot be prepared by Wurtz reaction (no suitable alkyl halide).
- Alkanes with an odd number of carbons (except methane) require two different halides, giving mixtures.

Exam Tip

Wurtz reaction is best for preparing symmetrical alkanes with **EVEN** number of carbons. Methane **CANNOT** be prepared by this method.

1.5.2 Kolbe's Electrolysis (Kolbe's Synthesis)**Principle**

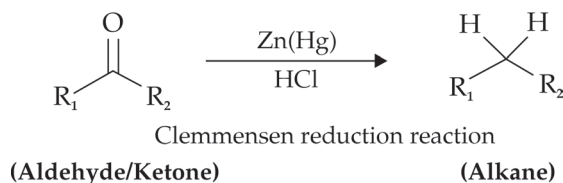
Electrolysis of a concentrated aqueous solution of the sodium (or potassium) salt of a carboxylic acid produces an alkane at the anode. Carbon dioxide is also evolved at the anode, and hydrogen gas is liberated at the cathode.

1.5.3 Clemmensen's Reduction

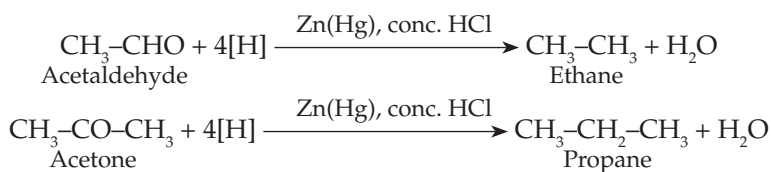
Principle

Aldehydes and ketones (carbonyl compounds) are reduced to alkanes when treated with zinc amalgam (Zn/Hg) and concentrated hydrochloric acid (conc. HCl). The carbonyl group (C=O) is directly reduced to a methylene group (–CH₂–).

General Reaction



Examples



Pharmaceutical Significance

Clemmensen's reduction is particularly important in pharmaceutical synthesis for introducing methylene groups and preparing alkyl side chains in drug molecules. It is preferred for acid-stable substrates.

Limitations

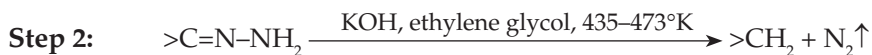
- Not suitable for acid-sensitive compounds (uses conc. HCl, strongly acidic conditions).
- Not used for base-sensitive substrates.

1.5.4 Wolff-Kishner Reduction

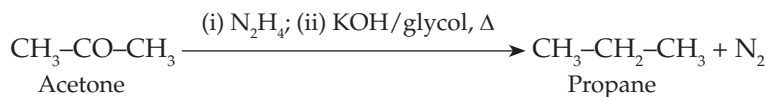
Principle

Aldehydes and ketones are reduced to alkanes using hydrazine (N₂H₄) in the presence of a strong base (KOH or NaOH) at high temperature (about 435–473°K), usually in a high-boiling solvent like ethylene glycol. The reaction proceeds via formation of a hydrazone intermediate.

General Reaction (Two Steps)



Example



KEY COMPARISON**Clemmensen's reduction vs Wolff–Kishner reduction****Clemmensen's reduction:**

Uses acidic conditions (Zn/Hg + conc. HCl) $\longrightarrow$ Preferred for acid-stable, base-sensitive compounds

Wolff–Kishner reduction:

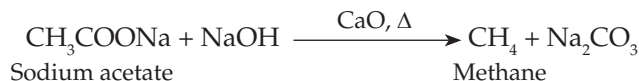
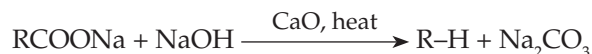
Uses basic conditions (N_2H_4 + KOH) $\longrightarrow$ Preferred for base-stable, acid-sensitive compounds

Advantages

- Particularly suitable for reducing carbonyl groups in acid-sensitive molecules.
- The release of N_2 (an inert gas) acts as a thermodynamic driving force, making the reaction essentially irreversible.

1.5.5 Other Important Methods**Decarboxylation—Sodalime Method**

Sodium or potassium salts of carboxylic acids, when fused with sodalime (a mixture of NaOH + CaO) at high temperature, lose CO_2 and give an alkane with one fewer carbon atom than the parent acid.



Note: CaO in sodalime is hygroscopic and keeps NaOH dry for the reaction.

Table 1.4: Summary of methods of preparation of alkanes

Method	Starting material	Reagent/Conditions	Product	Special feature
Wurtz reaction	Alkyl halide (R-X)	Na, dry ether	Symmetrical alkane (R-R)	Best for even-C alkanes
Kolbe's electrolysis	Sodium carboxylate salt	Electrolysis/aqueous	Alkane (R-R) + CO_2	Anode product; even-C only
Clemmensen reduction	Aldehyde/Ketone (C=O)	Zn/Hg, conc. HCl	Alkane ($-\text{CH}_2-$)	Acidic conditions
Wolff–Kishner reduction	Aldehyde/Ketone (C=O)	N_2H_4 , KOH, glycol,	Alkane ($-\text{CH}_2-$)	Basic conditions; N_2 evolved
Decarboxylation	Sodium carboxylate	Sodalime (NaOH + CaO), heat	Alkane (one C less)	Simple; for lower alkanes

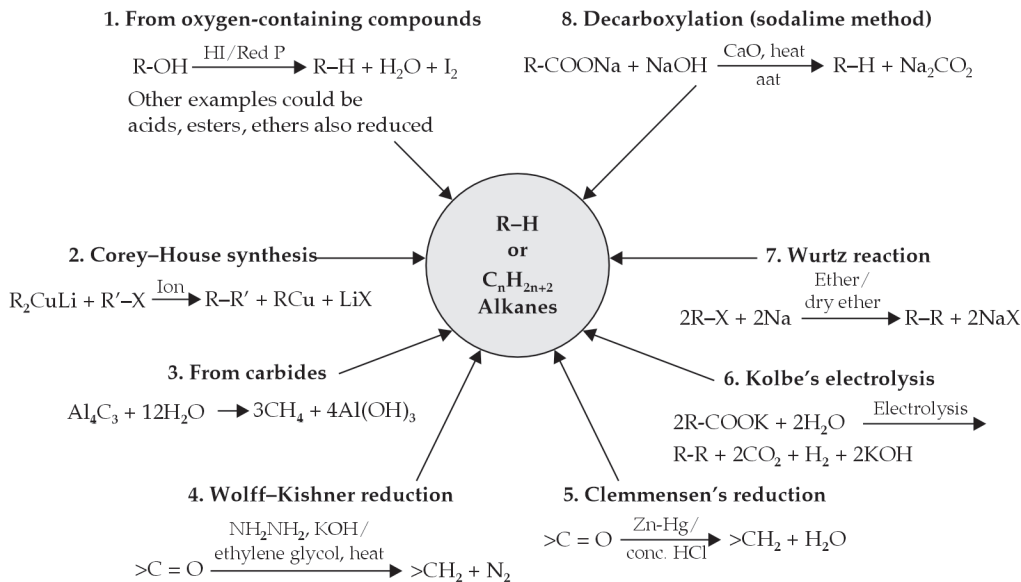


Fig. 1.9: Methods of preparation of alkanes—at a glance

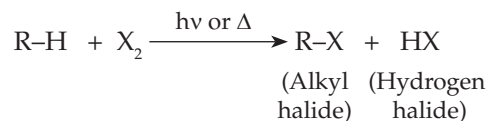
1.6 CHEMICAL REACTIONS OF ALKANES

Despite being called paraffins (inert), alkanes do undergo several important reactions. Because their C–C and C–H bonds are strong and non-polar, alkanes are resistant to attacks by acids, bases, and most polar reagents. Their reactions primarily involve homolytic (free radical) bond cleavage under conditions of high temperature or light.

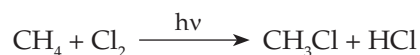
1.6.1 Halogenation

Alkanes react with halogens (Cl_2 , Br_2 , F_2) in the presence of UV light (or heat) to form alkyl halides. This is a substitution reaction—a hydrogen atom is replaced (substituted) by a halogen atom.

General Reaction



Example — Chlorination of Methane



The reaction does not stop at monosubstitution but, further chlorination gives a mixture:

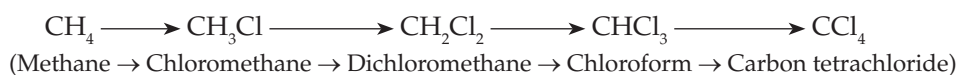
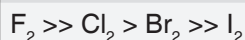
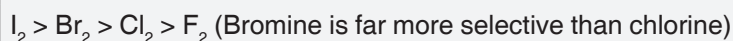
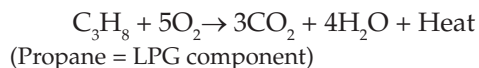
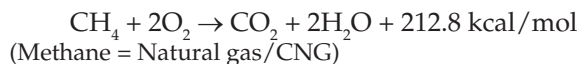
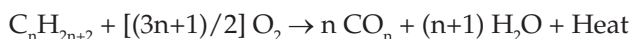


Table 1.5: Comparative reactivity of halogens with alkanes

Halogen	Reactivity	Heat of reaction (kcal/mol)	Comment
Fluorine (F ₂)	Extremely reactive	-116	Reaction is explosive and uncontrollable
Chlorine (Cl ₂)	Reactive (satisfactory)	-27	Requires UV light or heat; controlled reaction
Bromine (Br ₂)	Less reactive than Cl ₂	-10	Slower; more selective for 3°H
Iodine (I ₂)	Essentially unreactive	+13	Reaction is endothermic; does not proceed

Reactivity Order of Halogens:**Selectivity Order (towards specific H type):****1.6.2 Combustion (Oxidation)**

Alkanes are excellent fuels because they undergo complete combustion in excess oxygen to produce carbon dioxide, water, and a large amount of heat energy.

Complete Combustion (Excess Oxygen)**Incomplete Combustion (Limited Oxygen)**

When alkanes burn in an insufficient supply of oxygen, toxic carbon monoxide (CO) is produced, which is a significant health hazard:



Carbon black (soot/lamp black) is formed when combustion is severely oxygen-deficient.

1.6.3 Cracking (Pyrolysis)

Cracking is the thermal or catalytic decomposition of larger alkane molecules into smaller alkanes, alkenes, and hydrogen. It is of enormous industrial importance in petroleum refining to convert heavy oils into petrol (gasoline).

Thermal Cracking

At 500–800°C, C–C bonds break homolytically (free radical mechanism) to give a mixture of smaller alkanes and alkenes:



Catalytic Cracking

Using solid acid catalysts (silica-alumina, zeolites) at lower temperatures, proceeds by carbocation (ionic) mechanism. More selective and gives higher-octane products preferred in modern refining.

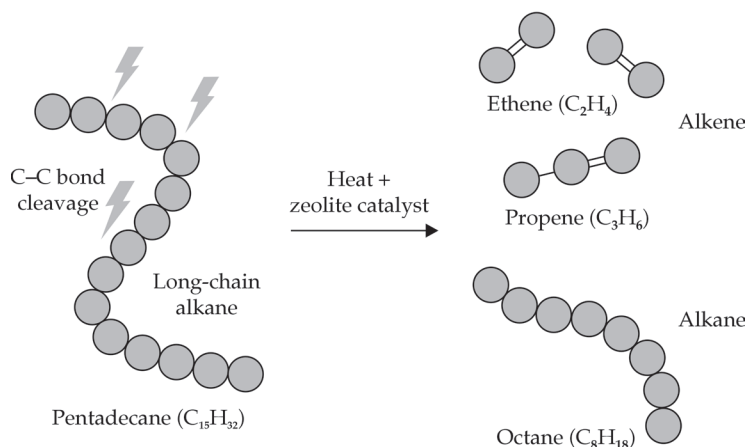
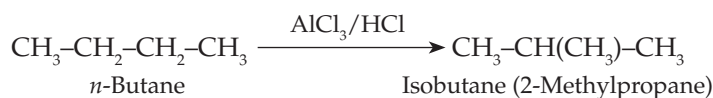


Fig. 1.10: Cracking of alkanes—a large molecule breaking into smaller fragments including alkenes, which are important industrial feedstocks

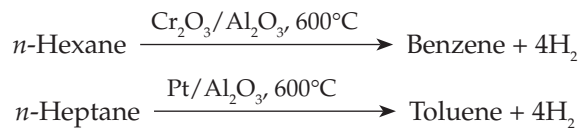
1.6.4 Isomerisation

Straight-chain alkanes can be converted to their branched-chain isomers in the presence of anhydrous aluminium chloride (AlCl_3) and HCl at moderate temperatures. This reaction is important industrially to improve the octane rating of petrol.



1.6.5 Aromatisation (Dehydrogenation and Cyclisation)

Higher alkanes (6 or more carbons) can be converted to aromatic compounds when passed over chromium, vanadium, or molybdenum oxide catalysts at 600°C . This involves simultaneous dehydrogenation and ring cyclisation.



1.7 MECHANISM OF FREE RADICAL SUBSTITUTION (HALOGENATION)

The halogenation of alkanes proceeds by a free radical chain mechanism, which is one of the most fundamental reaction mechanisms in organic chemistry. Understanding it is essential for predicting reaction products and selectivity.

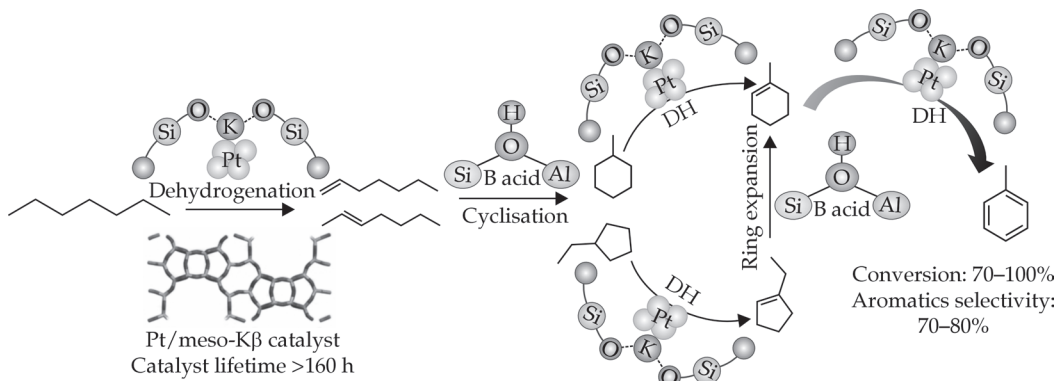


Fig. 1.11: Aromatisation (catalytic reforming) of *n*-hexane to benzene and *n*-heptane to toluene—dehydrogenation and cyclisation reactions of industrial significance in petroleum refining

A free radical is a highly reactive species with one unpaired electron (denoted with a dot, e.g. Cl $\cdot$). Free radicals are formed by homolytic bond cleavage—where each atom in the bond retains one electron.

Homolytic vs Heterolytic Cleavage

Homolytic cleavage: $A:B \rightarrow A\cdot + B\cdot$ (each atom gets one electron — free radicals formed)

Heterolytic cleavage: $A:B \rightarrow A^+ + B^-$ or $A^- + B^+$ (both electrons go to one atom — ions formed)

Halogenation of alkanes = Homolytic cleavage = Free radical mechanism

1.7.1 Step 1: Initiation

The reaction is initiated by ultraviolet (UV) light or heat, which provides the energy to break the halogen–halogen bond homolytically:



Each chlorine atom has one unpaired electron, making it a highly reactive free radical. This step generates the reactive species that drive the chain reaction.

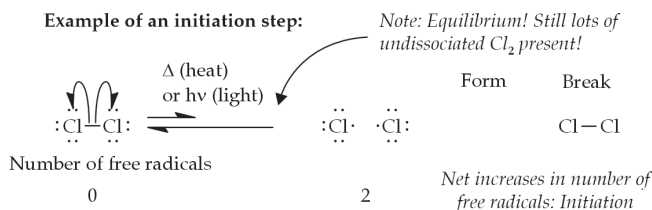
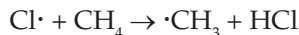


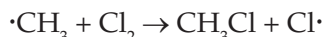
Fig. 1.12: Initiation step—homolytic cleavage of the Cl–Cl bond by UV light to form two chlorine free radicals

1.7.2 Step 2: Chain Propagation

In the propagation steps, free radicals react with stable molecules to generate new free radicals, thereby sustaining the chain reaction. There are two propagation steps.

Propagation Step 2a — H Abstraction

The chlorine radical abstracts (removes) a hydrogen atom from methane, forming a stable HCl molecule and a methyl free radical ($\cdot\text{CH}_3$).

Propagation Step 2b — Halogen Abstraction (Coupling)

The methyl free radical attacks the Cl–Cl molecule, forming chloromethane (the product) and regenerating a chlorine free radical. This radical then re-enters Step 2a, driving the chain reaction.

1.7.3 Step 3: Chain Termination

The chain reaction ends when two free radicals combine to form a stable molecule (no new radical is produced). There are three possible termination events:

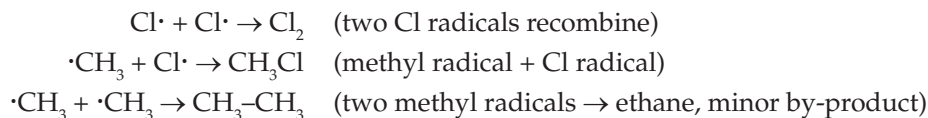


Table 1.6: Summary of free radical chain mechanism for chlorination of methane

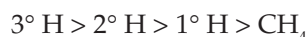
Step	Name	Reaction	Description
Step 1	Initiation	$\text{Cl}_2 \rightarrow 2\text{Cl}\cdot$	UV/heat breaks Cl–Cl; free radicals formed
Step 2a	Propagation	$\text{Cl}\cdot + \text{CH}_4 \rightarrow \cdot\text{CH}_3 + \text{HCl}$	H abstraction; new radical formed
Step 2b	Propagation	$\cdot\text{CH}_3 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{Cl}\cdot$	Halogen abstraction; chain continues
Step 3	Termination	$\text{Cl}\cdot + \text{Cl}\cdot \rightarrow \text{Cl}_2$ etc.	Radicals combine; chain ends

1.7.4 Factors Affecting the Rate and Selectivity of Halogenation**Factor 1: Type of Hydrogen Being Abstracted**

Not all C–H bonds in an alkane molecule are equivalent. Carbon atoms are classified as primary (1°), secondary (2°), or tertiary (3°) based on the number of other carbon atoms they are bonded to:

- **Primary carbon (1°):** Bonded to only one other carbon atom $\rightarrow$ Primary C–H bond
- **Secondary carbon (2°):** Bonded to two other carbons $\rightarrow$ Secondary C–H bond
- **Tertiary carbon (3°):** Bonded to three other carbons $\rightarrow$ Tertiary C–H bond

The ease of hydrogen abstraction follows the order:



Therefore, halogenation preferentially occurs at tertiary positions, followed by secondary, and then primary.

Factor 2: Stability of the Free Radical Formed

The reason for the above preference is directly linked to the stability of the carbon free radical produced. The order of free radical stability is:



Tertiary free radicals are stabilised by hyperconjugation from the three attached alkyl groups. More stable radicals have lower activation energy for their formation, hence form more rapidly and produce the major product.

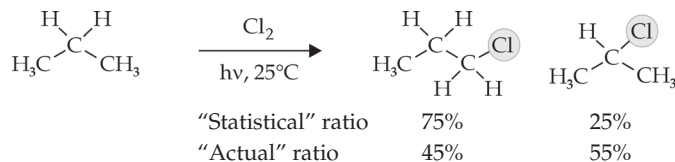


Fig. 1.13: Example of selectivity in chlorination of propane—abstraction of 2° H gives isopropyl chloride (major product) while 1° H abstraction gives *n*-propyl chloride (minor product)

Factor 3: Selectivity of the Halogen

The selectivity of the halogen radical is the inverse of its reactivity:

- **Fluorine (F•):** Extremely reactive; abstracts H atoms indiscriminately; no selectivity. Reaction is explosive.
- **Chlorine (Cl•):** Moderately reactive; some selectivity (prefers 3° over 1°, but not drastically). Selectivity ratio approximately 5:3.8:1 for 3°:2°:1° H at room temperature.
- **Bromine (Br•):** Much less reactive than Cl•, but far more selective. Strongly prefers tertiary positions. Selectivity ratio approximately 1640:82:1 for 3°:2°:1° H. Bromine is used when high selectivity is required.
- **Iodine (I•):** Essentially unreactive with alkanes under normal conditions.

Reactivity–Selectivity Principle

A more reactive halogen radical (like F•) has less selectivity—it reacts with any available C–H bond indiscriminately.

A less reactive halogen radical (like Br•) is more selective—it only reacts with the most easily abstracted (most stable) C–H bonds.

This is the **Reactivity–Selectivity Principle**: High reactivity $\longleftrightarrow$ low selectivity.

1.8 PHARMACEUTICAL APPLICATIONS OF ALKANES

Alkanes and their derivatives have extensive applications in pharmacy, both as drug products and as formulation excipients. The three most important pharmaceutical forms—liquid paraffin, soft paraffin, and hard paraffin, are official in the Indian Pharmacopoeia (IP), British Pharmacopoeia (BP), and United States Pharmacopoeia (USP).

These materials are obtained from petroleum (crude oil) by fractional distillation and subsequent refining and purification. Their pharmaceutical grade must meet strict pharmacopoeial standards for purity, viscosity, melting point, and absence of potentially harmful polycyclic aromatic hydrocarbons (PAHs).

1.8.1 Liquid Paraffin

Pharmaceutical Uses of Liquid Paraffin

- **Laxative (internal use):** Heavy liquid paraffin is used as a lubricant laxative. It lubricates and softens the stool, making bowel movements easier. It is not absorbed from the GI tract, so it acts locally. Official dose: 15–45 ml at night.

Table 1.7: Pharmacopoeial characteristics of liquid paraffin

Attribute	Details
Chemical nature	A mixture of liquid saturated hydrocarbons obtained from petroleum; predominantly C ₁₄ –C ₁₈ alkanes
Pharmacopoeial names	Liquid paraffin (BP/IP); mineral oil (USP/NF)
Appearance	Colourless, transparent, oily liquid with no fluorescence in daylight
Odour/Taste	Practically odourless and tasteless
Density	0.827–0.890 g/ml (light liquid paraffin: lower density; heavy: higher)
Solubility	Practically insoluble in water and ethanol; miscible with most fixed oils
Forms available	Light liquid paraffin (low viscosity) and heavy liquid paraffin (high viscosity)

- **Emollient and skin barrier:** It is used in skin-care preparations, creams, and lotions as an emollient (skin softener) and protective barrier. Prevents transepidermal water loss (TEWL). Useful in dry skin conditions, eczema, and psoriasis.
- **Pharmaceutical solvent/vehicle:** It is used as a vehicle/base for topical formulations and ophthalmic preparations where a non-aqueous, non-polar medium is needed.
- **Ointment base:** Component of many ointment bases, providing smooth consistency, spreadability, and prolonged contact on skin.
- **Oil bath in laboratories:** It is used as a heating medium (oil bath) in pharmaceutical and chemical laboratories for reactions requiring temperatures above 100°C.
- **Diluent in suspensions:** It is used in oral suspensions to disperse poorly water-soluble drugs.

Important Note

Pharmaceutical/medicinal liquid paraffin is not the same as kerosene (paraffin used as fuel). They come from different fractions of petroleum and undergo different levels of refining. Highly refined pharmaceutical-grade liquid paraffin is safe for medicinal use.

1.8.2 Soft Paraffin (Petroleum Jelly/White Soft Paraffin)

Table 1.8: Pharmacopoeial characteristics of soft paraffin (petroleum jelly)

Attribute	Details
Chemical nature	A semi-solid mixture of hydrocarbons obtained from petroleum; carbon range C ₁₆ –C ₃₀
Pharmacopoeial names	White soft paraffin/Yellow soft paraffin (BP/IP); Petrolatum/White petrolatum (USP)
Appearance	White soft paraffin: white or pale yellow; Yellow soft paraffin: yellow. Soft, unctuous (greasy) mass
Consistency	Semi-solid at room temperature; melts on contact with skin
Melting range	38–56°C (IP)
Common brand name	Vaseline® (a commercial petroleum jelly)
Solubility	Practically insoluble in water; slightly soluble in cold alcohol; freely soluble in chloroform, benzene, and light petroleum

Pharmaceutical Uses of Soft Paraffin

- **Ointment base (most important use):** Soft paraffin (petrolatum) is the most widely used oleaginous (hydrocarbon) ointment base in pharmacy. Being inert and non-reactive, it does not interact with most drug molecules. It provides excellent occlusion (prevents evaporation from skin), prolonging drug contact.
- **Emollient for dry skin conditions:** Applied directly as an emollient for chapped lips, dry skin, minor cuts, abrasions, burns, and as a moisturising treatment for eczema and psoriasis.
- **Protective barrier cream:** Forms an occlusive film on skin to protect against irritants, water, and friction (e.g. barrier creams used in wound care and neonatal skin protection).
- **Lubricant:** It is used to lubricate rectal thermometers, catheters, and other medical devices for ease of insertion.
- **Cosmetic applications:** Base for cosmetic creams, cold creams, lip balms, and makeup products.
- **Preservation:** It is used to coat corrosion-prone metal instruments, gun barrels, and as a water repellant.

Difference between White and Yellow Soft Paraffin

Yellow soft paraffin: Contains natural colouring matter from petroleum; less purified.

White soft paraffin: Fully decolorised by treatment with activated charcoal or other decolorising agents; preferred for ophthalmic and dermatological preparations.

1.8.3 Hard Paraffin (Paraffin Wax)

Table 1.9: Pharmacopoeial characteristics of hard paraffin (paraffin wax)

Attribute	Details
Chemical nature	A mixture of solid saturated hydrocarbons (predominantly straight-chain C_{20} – C_{40} alkanes) obtained from petroleum wax distillate
Pharmacopoeial names	Hard paraffin (BP/IP); paraffin wax (NF)
Appearance	White or colourless, translucent, waxy solid
Melting range	50–57°C (BP); can vary by grade
Consistency	Hard, brittle solid at room temperature
Odour	Odourless

Pharmaceutical Uses of Hard Paraffin

- **Ointment base stiffener:** Added to soft paraffin or other ointment bases to increase their melting point and consistency, particularly for use in warm climates where standard ointments may melt.
- **Suppository base:** Paraffin wax is used as a component in suppository formulations to adjust the melting point of the base.
- **Tablet coating:** It is used as a coating material for tablets to provide a polish and to protect them from moisture and atmospheric oxygen.

- **Coating for capsules and pills:** Paraffin wax coating provides protection and a smooth surface finish.
- **Sustained-release matrices:** Incorporated into wax-matrix tablets for modified/sustained drug release, where the drug is embedded in a wax matrix and released slowly.
- **Candle manufacturing:** It is used in the preparation of medicinal candles and aromatic therapeutic candles.
- **Packaging:** It is used to coat paper and cardboard pharmaceutical packaging for moisture protection.

Table 1.10: Comparative overview of the three pharmaceutical paraffins

Paraffin type	Physical state	Carbon range	Melting range	Primary pharmaceutical use
Liquid paraffin	Oily liquid	C ₁₄ –C ₁₈	Liquid at RT	Laxative; ointment base vehicle; emollient
Soft paraffin (petroleum jelly)	Semi-solid	C ₁₆ –C ₃₀	38–56°C	Ointment base; emollient; protective barrier
Hard paraffin (paraffin wax)	Solid	C ₂₀ –C ₄₀	50–57°C	Ointment base stiffener; tablet coating; suppository base



Fig. 1.14: The three pharmaceutical forms of paraffins—liquid paraffin (bottle), soft paraffin (jar), and hard paraffin (block)—showing their consistency and appearance

1.9 SUMMARY

1. Alkanes (C_nH_{2n+2}) are saturated aliphatic hydrocarbons with only C–C and C–H single bonds; also called paraffins due to low reactivity.
2. **Classification:** Straight-chain (*n*-alkanes), branched-chain, and cycloalkanes (C_nH_{2n}).
3. **IUPAC nomenclature:** Select the longest chain as parent; number from the end nearest to the branch; name substituents as alkyl groups alphabetically.
4. **Structure:** All carbons in alkanes are sp³ hybridised—tetrahedral geometry, bond angle 109.5°. C–H bond = 1.09 Å; C–C bond = 1.54 Å.
5. **Methods of preparation:**
 - Wurtz reaction (symmetrical alkanes),
 - Kolbe's electrolysis (even-carbon alkanes from carboxylate salts),
 - Clemmensen's reduction (carbonyl → alkane, acidic conditions),
 - Wolff–Kishner reduction (carbonyl → alkane, basic conditions),
 - decarboxylation, hydrogenation, and Grignard hydrolysis.

6. **Physical properties:** BP and MP increase with molecular weight; decrease with branching. Alkanes are non-polar, insoluble in water, soluble in organic solvents, less dense than water.
7. **Chemical reactions:**
Halogenation (free radical, UV/heat),
Combustion (complete $\rightarrow \text{CO}_2 + \text{H}_2\text{O}$; incomplete $\rightarrow \text{CO}$),
Cracking (thermal/catalytic),
Isomerisation (AlCl_3/HCl),
Aromatisation (600°C , catalyst).
8. **Free radical mechanism of halogenation:**
Three steps:
 - Initiation ($\text{Cl}_2 \rightarrow 2\text{Cl}\cdot$, by UV);
 - Propagation (chain reaction — H abstraction and halogen abstraction);
 - Termination (radical–radical combination).
9. **Selectivity:** $3^\circ \text{H} > 2^\circ \text{H} > 1^\circ \text{H}$ abstracted;
 $\text{Br}\cdot$ more selective than $\text{Cl}\cdot$; Reactivity–Selectivity principle applies.
10. **Pharmaceutical applications:** Liquid paraffin (laxative, emollient, ointment vehicle); Soft paraffin/petroleum jelly (ointment base, skin barrier); Hard paraffin/paraffin wax (tablet coating, suppository base, ointment stiffener).

QUESTION BANK (FOR VIVA VOCE/SYNOPSIS)

A. MULTIPLE CHOICE QUESTIONS (MCQs)

1. The general formula of alkanes is:
(a) C_nH_{2n} (b) $\text{C}_n\text{H}_{2n+2}$ (c) $\text{C}_n\text{H}_{2n-2}$ (d) $\text{C}_n\text{H}_{2n+4}$
2. Which of the following is NOT an alkane?
(a) Propane (b) Cyclohexane (c) Ethene (d) Decane
3. The hybridisation of carbon in methane is:
(a) sp (b) sp^2 (c) sp^3 (d) dsp^2
4. The bond angle in methane is approximately:
(a) 90° (b) 105° (c) 109.5° (d) 120°
5. Which product is formed at the anode in Kolbe's electrolysis of sodium acetate?
(a) CH_4 and CO_2 (b) C_2H_6 and CO_2 (c) CO_2 and H_2 (d) C_2H_4 and CO_2
6. Wurtz reaction is most suitable for the preparation of:
(a) Methane (b) Propane (c) *n*-Butane (d) Benzene
7. In the Clemmensen reduction, the reducing agent used is:
(a) LiAlH_4 (b) $\text{N}_2\text{H}_4/\text{KOH}$
(c) $\text{Zn}/\text{Hg} + \text{conc. HCl}$ (d) H_2/Pd
8. Wolff–Kishner reduction converts which functional group to an alkane?
(a) Alkene (b) Carboxylic acid (c) Carbonyl ($\text{C}=\text{O}$) (d) Alcohol

9. The C–H bond length in alkanes is:
(a) 1.20 Å (b) 1.09 Å (c) 1.54 Å (d) 1.34 Å
10. In free radical halogenation of alkanes, the initiation step involves:
(a) Reaction of alkane with halogen
(b) Homolytic cleavage of X_2 by UV light
(c) Combination of two free radicals
(d) Ionic dissociation of HX
11. The order of stability of carbon free radicals is:
(a) $1^\circ > 2^\circ > 3^\circ$ (b) $3^\circ > 2^\circ > 1^\circ$ (c) $2^\circ > 3^\circ > 1^\circ$ (d) All equal
12. Liquid paraffin is used pharmaceutically as a:
(a) Bactericide (b) Lubricant laxative
(c) Antipyretic (d) Antibiotic
13. Hard paraffin (paraffin wax) is used in pharmacy primarily as a:
(a) Laxative
(b) Ointment stiffener and tablet coating
(c) Antiprotozoal agent
(d) Ophthalmic solvent
14. Which halogen does NOT react with alkanes under normal conditions?
(a) Fluorine (b) Chlorine (c) Bromine (d) Iodine
15. Cracking of alkanes produces:
(a) Only alkanes
(b) Only alkenes
(c) Smaller alkanes and alkenes
(d) Aromatic compounds only
16. The melting range of soft paraffin (petroleum jelly) according to IP is:
(a) 20–35°C (b) 38–56°C (c) 60–80°C (d) 100–120°C
17. What is the by-product formed at the cathode in Kolbe's electrolysis?
(a) CO_2 (b) CO (c) H_2 (d) NaOH only
18. The process of converting straight-chain alkanes to branched-chain isomers using $AlCl_3$ is called:
(a) Aromatisation (b) Hydrogenation
(c) Isomerisation (d) Cracking
19. In halogenation of propane with Cl_2 , the major product is:
(a) 1-Chloropropane (b) 2-Chloropropane
(c) 1,2-Dichloropropane (d) 1,3-Dichloropropane
20. Which of the following methods produces methane?
(a) Wurtz reaction of CH_3Br
(b) Kolbe's electrolysis of sodium acetate
(c) Sodalime decarboxylation of sodium acetate
(d) Both (a) and (b)

21. Soft paraffin (petroleum jelly) is classified pharmacopoeially as:
 (a) A fixed oil
 (b) A hydrocarbon (oleaginous) ointment base
 (c) A water-soluble base
 (d) An emulsifying base
22. Which conformation of alkane is most stable?
 (a) Eclipsed
 (b) Gauche
 (c) Staggered (anti)
 (d) Skew
23. The chain termination step in free radical halogenation involves:
 (a) Cleavage of X_2 bond
 (b) Abstraction of H from alkane
 (c) Combination of two free radicals
 (d) Addition of HX to alkene
24. Aromatisation of *n*-hexane in the presence of Cr_2O_3 at $600^\circ C$ gives:
 (a) Cyclohexane
 (b) Benzene + $4H_2$
 (c) Hexene + H_2
 (d) Toluene + H_2
25. Which paraffin is used as a sustained-release matrix in tablet formulations?
 (a) Liquid paraffin
 (b) Soft paraffin
 (c) Hard paraffin (paraffin wax)
 (d) Microcrystalline wax

ANSWER KEY

1 b	2 c	3 c	4 c	5 b	6 c	7 c	8 c	9 b	10 b
11 b	12 b	13 b	14 d	15 c	16 b	17 c	18 c	19 b	20 c
21 b	22 c	23 c	24 b	25 c					

B. LONG ANSWER QUESTIONS

- Define alkanes. Classify alkanes with suitable examples and give the general formula for each type. Draw structural formulae for five straight-chain alkanes and three branched-chain alkanes.
- Explain the concept of sp^3 hybridisation of carbon in detail. Using methane as an example, describe the electronic configuration changes from ground state to hybridised state, the geometry formed, and the nature of bonds in the methane molecule. Include relevant diagrams.
- Describe, in detail, the Wurtz reaction and Kolbe's electrolysis as methods for the preparation of alkanes. Give the general equation, mechanism (where applicable), one worked example for each, and clearly state the limitations of each method.
- Write a detailed note on Clemmensen's reduction and Wolff-Kishner reduction. Compare the two methods in terms of reagents, conditions, mechanism, and suitability (acid vs base stability of substrate). Give two examples for each.
- Describe, in detail, the mechanism of free radical chlorination of methane, covering all three steps: initiation, propagation, and termination. Explain what would happen if ethane is used instead of methane, and predict the products.

6. Discuss the factors affecting the rate and selectivity of halogenation of alkanes. Explain the concept of reactivity–selectivity principle with reference to chlorination versus bromination. Why does bromination give a more selective product?
7. Explain, in detail, the physical properties of alkanes—state at room temperature, boiling point, melting point, solubility, density, and conductivity—giving scientific reasons for each observed trend.
8. Describe the chemical reactions of alkanes: halogenation, combustion (complete and incomplete), cracking, isomerisation, and aromatisation. Give one example equation for each reaction and state the industrial significance of cracking and aromatisation.
9. Write an essay on the pharmaceutical applications of paraffins (liquid paraffin, soft paraffin, and hard paraffin). For each, describe the chemical nature, pharmacopoeial standards, and at least four pharmaceutical/medicinal uses.
10. Write short notes on:
 - (a) Homologous series of alkanes,
 - (b) IUPAC nomenclature of branched alkanes with five worked examples,
 - (c) Isomerism in alkanes—chain isomerism with examples for C_5H_{12} .

C. SHORT ANSWER QUESTIONS

1. What is the Wurtz reaction? Give one example and state two limitations.
2. Define free radical. Write the initiation step for chlorination of ethane.
3. What is Clemmensen's reduction? Write the reaction for reduction of acetone.
4. Give the IUPAC names for:
 - (a) $CH_3-CH(CH_3)-CH_3-CH_3$
 - (b) $CH_3-C(CH_3)_2-CH_2-CH_3$
 - (c) $CH_3-CH_2-CH(C_2H_5)-CH_2-CH_3$.
5. Explain why alkanes are insoluble in water but soluble in benzene.
6. What is the difference between complete and incomplete combustion of alkanes? Give the equation for each for propane.
7. Write a note on liquid paraffin—its nature, properties, and two pharmaceutical uses.
8. What are the three termination steps in the free radical chlorination of methane?
9. Why do branched alkanes have lower boiling points than their straight-chain isomers?
10. Distinguish between soft paraffin and hard paraffin in terms of physical state, melting range, and pharmaceutical applications (two each).