BP204T · B.PHARM THEORY

# BP204T Pharmaceutical Organic Chemistry

## Unit I — Alkanes & Cycloalkanes

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From-zero teaching standard: every technical term is defined before use.

Syllabus coverage: Unit I (12 hours).

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# Chapter 1 — Alkanes: Preparation and Properties

## Learning Objectives

After studying this chapter, you should be able to:

1. Define an alkane and write its general formula.
2. Explain what "saturated", "$sp^3$ hybridisation" and "sigma bond" mean in simple words.
3. Name simple alkanes and draw chain isomers.
4. Write the four preparation methods (Wurtz, Kolbe's electrolysis, Clemmensen, Wolff–Kishner) with reagents, conditions and equations.
5. Explain why the Wurtz reaction gives a mixture when two different alkyl halides are used.
6. Write the chemical reactions of alkanes: combustion, halogenation, pyrolysis, isomerisation and aromatisation.

## Key Definitions

- **Hydrocarbon:** A compound made of only carbon and hydrogen. (Example: methane, $CH_4$.)
- **Alkane:** A hydrocarbon in which every carbon–carbon bond is a **single bond**. Alkanes are the simplest family of organic compounds. General formula: $\mathbf{C_nH_{2n+2}}$ (n = number of carbon atoms).
- **Saturated:** A molecule is "saturated" when its carbon atoms hold the maximum possible number of hydrogen atoms — that is, there are no double or triple bonds. Alkanes are saturated hydrocarbons. Think of a bus with every seat taken: no empty seat (no double bond) is available.
- **$sp^3$ hybridisation:** Carbon has 4 outer electrons. In alkanes, carbon mixes its one s-orbital and three p-orbitals to make four identical new orbitals called $sp^3$ orbitals. Each $sp^3$ orbital holds one electron and forms one single bond. You do not need the maths — just remember: **$sp^3$ carbon = carbon with four single bonds**.
- **Sigma (σ) bond:** The strong single bond formed when two orbitals overlap head-on (directly facing each other) along the line joining the two nuclei. Every single bond in an alkane is a sigma bond. A double bond = one sigma + one pi bond; a triple bond = one sigma + two pi bonds.
- **Tetrahedral:** The 3D shape around an $sp^3$ carbon: the four bonds point to the four corners of a pyramid-like shape (a tetrahedron), with a bond angle of **109°28′** (about 109.5°) between any two bonds.
- **Homologous series:** A family of compounds in which each member differs from the next by one **$\mathbf{–CH_2–}$** group, and all members share the same general formula and similar chemical properties. Alkanes ($CH_4$, $C_2H_6$, $C_3H_8$, …) form a homologous series.
- **Alkyl group:** An alkane molecule minus one hydrogen atom. It is a "part" of a molecule, written with a free end (a dash). Examples: methyl ($–CH_3$), ethyl ($–CH_3CH_2–$).

## 1.1 What Is an Alkane? (From Zero)

Every organic molecule is built on carbon. A carbon atom can form **four bonds** (it is "tetravalent"). In an **alkane**, carbon uses all four bonds as **single bonds** — to hydrogen atoms or to other carbon atoms. Nothing is left over, so alkanes cannot easily add anything more to themselves. That is why alkanes are also called **paraffins** (from Latin *parum affinis* = "little affinity", meaning "not eager to react").

General formula: $\mathbf{C_nH_{2n+2}}$. Check: methane $CH_4$ (n=1 → 2×1+2 = 4 ✓), ethane $C_2H_6$ (n=2 → 6 ✓), propane $C_3H_8$ (n=3 → 8 ✓).

Each carbon is **$sp^3$ hybridised** and sits at the centre of a **tetrahedron** with bond angles of **109°28′**. All bonds

## 1.2 Naming and Isomerism Basics

**First six alkanes (memorise):** Methane ($CH_4$), Ethane ($C_2H_6$), Propane ($C_3H_8$), Butane ($C_4H_{10}$), Pentane ($C_5H_{10}$), Hexane ($C_6H_{12}$).

**Mnemonic:** "**M**y **E**lephant **P**lays **B**adminton **P**atiently **H**appily" → Methane, Ethane, Propane, Butane, Pentane, Hexane.

**Alkyl groups** (alkane minus one H):

- Methyl: $CH_3–$ (from methane)
- Ethyl: $CH_3–CH_2–$ (from ethane)
- Propyl: $CH_3–CH_2–CH_2–$ (from propane)

**Isomerism basics: Isomers** are different compounds with the **same molecular formula** but different arrangements of atoms. From butane ($C_4H_{10}$) onwards, alkanes show **chain isomerism**:

- n-Butane: $CH_3–CH_2–CH_2–CH_3$ (straight chain; "n" = normal)
- Isobutane: $CH_3–CH(CH_3)–CH_3$ (branched; IUPAC name 2-methylpropane)

Both have the formula $C_4H_{10}$ but different structures — so they are isomers. Branching lowers the boiling point (isobutane boils lower than n-butane) because branched molecules pack less tightly.

## 1.3 Preparation of Alkanes

### (a) Wurtz Reaction

- **Concept:** Two molecules of an **alkyl halide** (R–X, where X = Cl, Br or I) join together when treated with sodium metal, doubling the carbon chain.
- **Reagents & conditions:** Sodium metal (Na) in **dry ether** (ether with no water — water would destroy the sodium).
- **Equation:** $2R–X + 2Na \xrightarrow{\text{(dry ether)}} R–R + 2NaX$
- Example: $2CH_3–Cl + 2Na \xrightarrow{\text{(dry ether)}} CH_3–CH_3 + 2NaCl$ (ethane formed)
- **Mechanism (in words):** The commonly taught explanation involves an **organosodium intermediate** (a compound with a carbon–sodium bond):

1. One molecule of alkyl halide reacts with sodium to form the organosodium compound: $R–X + 2Na \rightarrow R^-Na^+ + NaX$. Here carbon carries a slight negative charge and is hungry for a partner.
2. This $R^-Na^+$ attacks a second molecule of alkyl halide, pushing out the halide: $R^-Na^+ + R–X \rightarrow R–R + NaX$.
3. The two R groups are now joined: the higher alkane R–R is formed.

- **Worked example (the mixture problem):** If you mix **two different** alkyl halides, say $CH_3Cl$ and $CH_3CH_2Cl$, with sodium, you get **three** products, not one — because the R groups pair up randomly:
- $CH_3–Cl + CH_3–Cl \rightarrow CH_3–CH_3$ (ethane)
- $CH_3CH_2–Cl + CH_3CH_2–Cl \rightarrow CH_3–CH_2–CH_2–CH_3$ (n-butane)
- $CH_3–Cl + CH_3CH_2–Cl \rightarrow CH_3–CH_2–CH_3$ (propane)
- So: $CH_3Cl + CH_3CH_2Cl + Na \xrightarrow{\text{(dry ether)}} CH_3–CH_3 + CH_3–CH_2–CH_3 + CH_3–CH_2–CH_2–CH_3$ (+ NaCl). The three alkanes are hard to separate — this is the main limitation.
- **Limitations:** (i) Gives mixtures with two different halides (shown above). (ii) Tertiary alkyl halides mostly undergo elimination (form alkenes) instead of coupling, so the method fails for them. (iii) Best for making simple, symmetrical alkanes.
- > **Key takeaway:** Wurtz = "sodium stitches two alkyl halides together"; fine for one halide, messy mixture for two different halides.

### (b) Kolbe's Electrolytic Method

- **Concept:** Passing electricity through a concentrated solution of the **sodium or potassium salt of a fatty acid** (RCOONa) joins two R groups at the anode, releasing $CO_2$. It is called "electrolytic" because electricity drives the reaction.
- **Reagents & conditions:** Concentrated aqueous solution of sodium/potassium carboxylate (e.g., $CH_3COONa$); electrolysis (direct current) with platinum electrodes.
- **Equation:** $2RCOONa + 2H_2O \xrightarrow{\text{(electrolysis)}} R–R + 2CO_2 + H_2 + 2NaOH$
- Example (sodium acetate → ethane): $2CH_3COONa + 2H_2O \xrightarrow{\text{(electrolysis)}} CH_3–CH_3 + 2CO_2 + H_2 + 2NaOH$
- **Mechanism (in words) — anode steps:**

1. At the **anode** (positive electrode), each carboxylate ion loses one electron and becomes a neutral radical: $2RCOO^- \rightarrow 2RCOO\cdot + 2e^-$. (A **radical**, marked with a dot ·, is a species with one unpaired electron — defined fully in Chapter 2.)
2. Each RCOO· radical is unstable and throws out $CO_2$ gas: $2RCOO\cdot \rightarrow 2R\cdot + 2CO_2$.
3. The two R· radicals combine: $2R\cdot \rightarrow R–R$. This is the new alkane, formed at the anode.

- At the **cathode** (negative electrode), water gains electrons: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$, so hydrogen gas bubbles off there.
- **Worked example:** Electrolysis of sodium propanoate ($CH_3CH_2COONa$) gives n-butane: $2CH_3CH_2\cdot \rightarrow CH_3–CH_2–CH_2–CH_3$. The acid had 3 carbons; the product alkane has 3+3−2 = 4 carbons (two $CO_2$ molecules are lost).
- **Limitations:** (i) Methane cannot be prepared (the salt of formic acid, HCOONa, gives only $H_2$ at the anode). (ii) Best for straight-chain, symmetrical alkanes; branched acids give poor yields. (iii) Needs concentrated solutions and platinum electrodes.
- > **Key takeaway:** Kolbe = "electricity knocks $CO_2$ off two acid salts and joins the leftovers"; alkane formed at the anode, $H_2$ at the cathode.

### (c) Clemmensen Reduction

- **Concept:** A **reduction** here means removing oxygen (or adding hydrogen). The carbonyl group (C=O) of an **aldehyde or ketone** is reduced all the way to a $–CH_2–$ group.
- **Reagents & conditions: Zinc amalgam** — zinc treated with mercury, written **Zn(Hg)** — with **concentrated HCl**, heated (reflux).
- **Equation:** $R_2C{=}O + 4[H] \xrightarrow{\text{(Zn(Hg), conc. HCl, heat)}} R_2CH_2 + H_2O$
- Example: $CH_3–CO–CH_3$ (acetone/propanone) $\xrightarrow{\text{(Zn(Hg), conc. HCl, heat)}} CH_3–CH_2–CH_3$ (propane)
- **Mechanism note:** The exact step-by-step mechanism is still debated in textbooks; for exams, write that the carbonyl oxygen is removed as water with hydrogen supplied by the metal–acid system, giving the alkane. (Do not invent a detailed electron-pushing mechanism — examiners accept the overall change.)
- **When used:** Choose Clemmensen when the molecule is **stable in strong acid**. If the compound has acid-sensitive groups (they would break in conc. HCl), use Wolff–Kishner instead.
- > **Key takeaway:** Clemmensen = "Zn(Hg) + conc. HCl turns C=O into $CH_2$"; acid conditions.

### (d) Wolff–Kishner Reduction

- **Concept:** Same overall change as Clemmensen (C=O → $CH_2$) but done in **strong base** instead of strong acid.
- **Reagents & conditions: Hydrazine** ($NH_2$–$NH_2$), then **potassium hydroxide (KOH)** with strong heating (about 180–200 °C, commonly in a high-boiling solvent).
- **Equation (two stages):**

1. $R_2C{=}O + NH_2{-}NH_2 \rightarrow R_2C{=}N{-}NH_2 + H_2O$ (the carbonyl first forms a **hydrazone** — a compound with a C=N–$NH_2$ group)
2. $R_2C{=}N{-}NH_2 \rightarrow$(KOH, heat) $R_2CH_2 + N_2$

- Overall: $R_2C{=}O \rightarrow$(1. $NH_2$–$NH_2$; 2. KOH, heat) $R_2CH_2$
- Example: $CH_3$–CHO (acetaldehyde/ethanal) → $CH_3$–$CH_3$ (ethane)
- **Mechanism (in words):**

1. Hydrazine attacks the carbonyl carbon; water leaves, forming the hydrazone $R_2C{=}N{-}NH_2$.
2. KOH removes a proton from the –$NH_2$ end of the hydrazone.
3. The C=N double bond shifts and nitrogen gas ($N_2$) is thrown out — $N_2$ leaving is what drives the reaction forward.
4. The carbon picks up protons from the medium and becomes –$CH_2$–.

- **When used:** Choose Wolff–Kishner when the molecule is **sensitive to acid** (would be destroyed by the conc. HCl of Clemmensen) but tolerates strong base and heat.
- > **Key takeaway:** Wolff–Kishner = "hydrazine + KOH turns C=O into $CH_2$"; base conditions — the partner method to Clemmensen.

**Summary table — preparation methods:**

| Method | Starting material | Reagents / conditions | Product | Best for / limitation |
|---|---|---|---|---|
| Wurtz | Alkyl halide R–X | Na, dry ether | R–R (doubled chain) | Symmetrical alkanes; mixture if two different halides |
| Kolbe's electrolysis | RCOONa (acid salt) | Electrolysis, conc. solution | R–R + $CO_2$ + $H_2$ | Straight-chain alkanes; methane not possible |
| Clemmensen | Aldehyde/ketone $R_2C{=}O$ | Zn(Hg), conc. HCl, heat | $R_2CH_2$ | Acid-stable compounds |
| Wolff–Kishner | Aldehyde/ketone $R_2C{=}O$ | $NH_2$–$NH_2$, then KOH, heat | $R_2CH_2$ | Acid-sensitive compounds |

## 1.4 Chemical Reactions of Alkanes (Brief but Exam-Ready)

Alkanes are unreactive ("paraffins"), but they do undergo five important reactions:

1. **Combustion:** Alkanes burn in air/oxygen giving $CO_2$, water and heat.

- $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ + heat
- Pharmacy link: LPG (mainly butane/propane) combustion heats water baths and burners in labs.

1. **Halogenation:** Reaction with $Cl_2$ or $Br_2$ in sunlight/heat replaces H with halogen — a **free-radical** reaction covered fully in Chapter 2.

- $CH_4 + Cl_2 \rightarrow$(hv) $CH_3Cl$ + HCl

1. **Pyrolysis (cracking):** Strong heating (without air) breaks C–C and C–H bonds, splitting bigger alkanes into smaller alkanes, alkenes and hydrogen.

- $CH_3–CH_2–CH_2–CH_3 \xrightarrow{\text{(high temp)}} CH_3–CH_3 + CH_2=CH_2$ (plus other fragments)
- Use: cracking of petroleum makes petrol and ethene.

1. **Isomerisation:** A straight-chain alkane rearranges to its branched isomer with a catalyst.

- $CH_3–CH_2–CH_2–CH_3 \xrightarrow{\text{(anhydrous } AlCl_3 + HCl, \text{ heat)}} CH_3–CH(CH_3)–CH_3$ (n-butane → isobutane)
- Use: branched alkanes give better-quality petrol.

1. **Aromatisation:** Straight-chain alkanes with 6+ carbons cyclise and lose hydrogen over a hot catalyst to give aromatic compounds.

- $CH_3–(CH_2)_4–CH_3$ (n-hexane) $\xrightarrow{(Cr_2O_3/Al_2O_3,\ \sim 500\ ^\circ C)} C_6H_6$ (benzene) + $4H_2$
- Use: making benzene/toluene for the chemical industry.

## Worked Examples (Chapter 1)

> **Example 1.** Starting from $CH_3CH_2Cl$, how would you prepare n-butane? **Solution:** Wurtz reaction — treat ethyl chloride with sodium in dry ether: $2CH_3–CH_2–Cl + 2Na \xrightarrow{\text{(dry ether)}} CH_3–CH_2–CH_2–CH_3 + 2NaCl$.

> **Example 2.** Which alkane is obtained by Kolbe electrolysis of sodium acetate? Show the anode steps. **Solution:** Sodium acetate is $CH_3COONa$ (R = $CH_3$). Product: $CH_3–CH_3$ (ethane) + $CO_2$ (anode) and $H_2$ (cathode). Anode: $CH_3COO^- \xrightarrow{(-e^-)} CH_3COO\cdot \rightarrow \cdot CH_3 + CO_2$; then $2\cdot CH_3 \rightarrow CH_3–CH_3$.

> **Example 3.** Convert propanone to propane. Which reduction, and why not the other? **Solution:** Either Clemmensen or Wolff–Kishner works for simple propanone. Choose Clemmensen — Zn(Hg), conc. HCl, heat: $CH_3–CO–CH_3 \rightarrow CH_3–CH_2–CH_3$. (If the molecule also carried an acid-sensitive group, Wolff–Kishner would be the correct choice.)

## Pharmacy Relevance

- **Liquid paraffin** (a mixture of higher alkanes) is used as a laxative and ointment vehicle — details in Chapter 2.
- LPG combustion (butane/propane) is the everyday lab heating source.
- The Wurtz-type C–C bond formation is the conceptual ancestor of modern coupling reactions used to build drug molecules.

## India Context

- Indian refineries (e.g., at Jamnagar, Paradip) crack petroleum — a mixture rich in alkanes — into petrol, diesel and LPG that the whole country uses daily. Pyrolysis/cracking in your syllabus is literally this industry in one equation.
- Liquid paraffin IP is the grade used in Indian pharmacies as a laxative and base; "IP" means it meets the Indian Pharmacopoeia standard.

## Common Confusions

- **Alkane vs alkyl:** Alkane is the full molecule ($CH_4$); alkyl is the fragment minus one H ($CH_3$–). The dash matters.
- **Wurtz vs Kolbe:** Both make R–R, but Wurtz starts from alkyl halides + Na, Kolbe from acid salts + electricity.
- **Clemmensen vs Wolff–Kishner:** Same product (C=O → $CH_2$); Clemmensen = acid (Zn(Hg)/HCl), Wolff–Kishner = base ($NH_2$–$NH_2$/KOH). Pick by which conditions the rest of the molecule can survive.
- **Isomerisation vs aromatisation:** Isomerisation only rearranges (same formula); aromatisation cyclises and removes $H_2$ (formula changes).

## Common Mistakes

- Writing the Wurtz product of two different halides as a single alkane — it is always a **mixture of three**.
- Forgetting "dry" in dry ether — water destroys sodium and kills the Wurtz reaction.
- Writing Kolbe's product as R–R–R or forgetting the $CO_2$ and $H_2$.
- Using Clemmensen conditions on an acid-sensitive substrate in a conversion problem — read the molecule first.

## Mnemonics

- Alkane names: "**M**y **E**lephant **P**lays **B**adminton **P**atiently **H**appily."
- Wurtz: "**W**urtz **W**eds halides **W**ith sodium" (alliteration: W–W–W).
- Clemmensen vs Wolff–Kishner: "**C**lemmensen = **C**onc. a**C**id; **W**olff = **W**ith base (KOH)".

## One-Minute Revision

- Alkane = saturated hydrocarbon, $C_nH_{2n+2}$, all single (sigma) bonds, $sp^3$, tetrahedral 109°28′.
- Wurtz: 2R–X + 2Na →(dry ether) R–R; two different halides → 3 products.
- Kolbe: 2RCOONa →(electrolysis) R–R + $2CO_2$ + $H_2$; alkane at anode.
- Clemmensen: C=O → $CH_2$ with Zn(Hg)/conc. HCl (acid). Wolff–Kishner: C=O → $CH_2$ with $NH_2$–$NH_2$/KOH (base).
- Reactions: combustion, halogenation (Ch 2), pyrolysis, isomerisation, aromatisation.

## Practice Questions — Chapter 1

**MCQs (10)**

1. The general formula of alkanes is: (a) $C_nH_{2n}$ (b) $C_nH_{2n+2}$ (c) $C_nH_{2n-2}$ (d) $C_nH_n$
2. The bond angle in methane is: (a) 120° (b) 109°28′ (c) 180° (d) 90°
3. Hybridisation of carbon in alkanes: (a) sp (b) $sp^2$ (c) $sp^3$ (d) $dsp^2$
4. Wurtz reaction uses: (a) Na in dry ether (b) KOH aqueous (c) Zn/HCl (d) $Pt/H_2$
5. Wurtz reaction of $CH_3Cl$ + $CH_3CH_2Cl$ with Na gives how many alkane products? (a) 1 (b) 2 (c) 3 (d) 4
6. Kolbe's electrolysis of $CH_3COONa$ gives: (a) methane (b) ethane (c) propane (d) ethene
7. In Kolbe's electrolysis, the alkane is liberated at the: (a) cathode (b) anode (c) both electrodes (d) salt bridge
8. Clemmensen reduction converts: (a) C=O → $CH_2$ (b) $CH_2$ → C=O (c) C=C → C–C (d) R–X → R–H
9. Wolff–Kishner reduction requires: (a) Zn(Hg)/HCl (b) $NH_2$–$NH_2$ then KOH, heat (c) $LiAlH_4$ (d) $H_2/Pt$
10. n-Hexane on $Cr_2O_3/Al_2O_3$ at ~500 °C gives: (a) cyclohexane (b) benzene (c) hexene (d) toluene

**Answer key:** 1-b, 2-b, 3-c, 4-a, 5-c, 6-b, 7-b, 8-a, 9-b, 10-b

### Short-answer (5)

1. Define homologous series with the alkane series as example.
2. Why are alkanes called paraffins?
3. Write the Wurtz equation for preparing ethane from methyl chloride.
4. State two limitations of the Wurtz reaction.
5. Distinguish between Clemmensen and Wolff–Kishner reductions (reagents + when each is preferred).

### Long-answer (3)

1. Describe four general methods of preparation of alkanes with equations and conditions.
2. Explain the mechanism of Kolbe's electrolytic method with anode and cathode reactions.
3. Write short notes on: (a) pyrolysis, (b) isomerisation, (c) aromatisation of alkanes.

### Mechanism-writing (2)

1. Write the step-by-step mechanism of the Wurtz reaction via the organosodium intermediate, and show all products when $CH_3I$ and $C_2H_5I$ react together with sodium.
2. Write the anode mechanism steps of Kolbe's electrolysis for sodium propanoate, naming the alkane formed.

### Application-based (2)

1. A drug intermediate contains a keto group plus an acid-sensitive acetal group. Which carbonyl-to-methylene reduction would you choose, and why?
2. A question asks for the product of electrolysing sodium ethanoate. A student writes "methane". Is the student right? Explain with the equation.

### Viva (5)

1. What is the hybridisation and shape of methane?
2. Why must the ether in the Wurtz reaction be dry?
3. Which gas is liberated at the cathode in Kolbe's electrolysis?
4. Name the intermediate formed when a carbonyl reacts with hydrazine in the Wolff–Kishner reduction.
5. Give one industrial use of pyrolysis of alkanes.

# Chapter 2 — Free-Radical Halogenation + Pharmaceutical Paraffins

## Learning Objectives

After studying this chapter, you should be able to:

1. Define free radical, homolysis (homolytic fission) and chain reaction.
2. Write the initiation, propagation and termination steps of methane chlorination.
3. State the reactivity order of 1°, 2° and 3° hydrogens and explain it via radical stability.
4. Compare chlorination and bromination selectivity.
5. Write the stepwise further halogenation of methyl chloride.
6. Describe liquid, soft and hard paraffin: what each is, its properties and its pharmacy uses.

## Key Definitions

- **Free radical:** An atom or group of atoms with **one unpaired electron**, shown with a dot (·). Examples: Cl· (chlorine radical), $\cdot CH_3$ (methyl radical). Because the single electron badly wants a partner, radicals are extremely reactive and short-lived.
- **Homolysis (homolytic fission):** Breaking a covalent bond so that **each atom keeps one electron** of the shared pair: A–B → A· + B·. ("Homo" = equal; the electrons are shared equally.) Contrast **heterolysis**, where one atom takes both electrons (A–B → $A^+ + B^-$).
- **Chain reaction:** A reaction in which the product of one step becomes the starting material of the next, so a single initiating event causes a long chain of repeated steps — like one falling domino toppling the next.
- **Initiation:** The step that **creates** the first radicals (e.g., $Cl_2 \rightarrow$(hv) 2Cl·).
- **Propagation:** The repeating steps in which a radical reacts to give a product **plus a new radical**, keeping the chain going.
- **Termination:** Steps in which two radicals combine with each other, **ending** the chain (no new radical is produced).
- **Selectivity:** The preference of a reagent for one type of hydrogen (3° > 2° > 1°) over another.
- **Paraffin (pharmaceutical sense):** A mixture of higher (long-chain) **alkanes** obtained from petroleum, used in pharmacy as laxatives, ointment bases and protectants.

## 2.1 Free-Radical Halogenation — The Full Story

- **Concept:** When methane (or any alkane) is mixed with chlorine or bromine in **sunlight (hv) or heat**, a hydrogen atom is replaced by a halogen atom. This is a **substitution** reaction, and it happens through free radicals.
- **Why radicals?** Heat or light splits the Cl–Cl bond by **homolysis** — each chlorine keeps one electron, giving two Cl· radicals. These radicals then attack the alkane in a chain reaction.

**Full chain mechanism for $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$:**

**Initiation (chain starts):**

1. Cl–Cl →(hv or heat) Cl· + Cl· — one chlorine molecule splits into two chlorine radicals.

**Propagation (chain continues — the same two steps repeat thousands of times):**

1. $Cl\cdot + CH_4 \rightarrow \cdot CH_3 + HCl$ — a chlorine radical pulls a hydrogen off methane, forming HCl and a **methyl radical** ($\cdot CH_3$).
2. $\cdot CH_3 + Cl–Cl \rightarrow CH_3–Cl + Cl\cdot$ — the methyl radical attacks a fresh $Cl_2$ molecule, forming methyl chloride and regenerating a chlorine radical, which goes back to step 2.

**Termination (chain ends — radicals destroy each other):**

1. $Cl\cdot + Cl\cdot \rightarrow Cl–Cl$
2. $\cdot CH_3 + \cdot CH_3 \rightarrow CH_3–CH_3$ (a trace of ethane)
3. $\cdot CH_3 + Cl\cdot \rightarrow CH_3–Cl$

- **Worked example:** Write the propagation steps for the chlorination of ethane to chloroethane.
- $Cl\cdot + CH_3–CH_3 \rightarrow \cdot CH_2–CH_3 + HCl$
- $\cdot CH_2–CH_3 + Cl_2 \rightarrow CH_3–CH_2–Cl + Cl\cdot$
- > **Key takeaway:** One photon starts it; the two propagation steps loop until two radicals accidentally collide and terminate.

## 2.2 Selectivity: 3° > 2° > 1° Hydrogens

- **Concept:** Not all hydrogens in an alkane react equally fast. The order of reactivity is **tertiary (3°) > secondary (2°) > primary (1°)** hydrogen.
- **Simple explanation:** In propagation step 2, the radical formed is R·. A **tertiary radical** (carbon attached to 3 other carbons) is more stable than a secondary radical, which is more stable than a primary radical. The more stable the radical, the faster it forms — so 3° H is removed fastest.
- **Relative rates (per hydrogen atom):** Textbooks commonly quote approximately **3° : 2° : 1° ≈ 5 : 3.8 : 1** for chlorination at room temperature. (Cautious note: exact values vary slightly between textbooks; the order 3° > 2° > 1° is what examiners want.)
- **Worked example — chlorination of propane:** $CH_3–CH_2–CH_3$ has six 1° H and two 2° H. Using per-H rates 1 and 3.8:
- 1-chloropropane share = 6 × 1 = 6 parts; 2-chloropropane share = 2 × 3.8 = 7.6 parts.
- So 2-chloropropane is the **major** product even though there are fewer 2° hydrogens — selectivity beats statistics.
- **Chlorination vs bromination: Bromination is far more selective** than chlorination. Bromine is less reactive, so it is "pickier": it strongly prefers 3° H (commonly quoted per-H ratio ≈ 1600 : 82 : 1, roughly). Chlorination is fast and relatively indiscriminate — it gives mixtures. Practical rule: **use $Br_2$ when you want one clean product; $Cl_2$ gives mixtures.**
- > **Key takeaway:** 3° > 2° > 1° because of radical stability; bromine is the selective halogen.

## 2.3 Further Halogenation

- **Concept:** Halogenation does not stop at one substitution. Each product still has hydrogens, so with excess halogen the reaction continues stepwise:
- $CH_4 + Cl_2 \xrightarrow{(hv)} CH_3Cl + HCl$ (methyl chloride)
- $CH_3Cl + Cl_2 \xrightarrow{(hv)} CH_2Cl_2 + HCl$ (methylene dichloride)
- $CH_2Cl_2 + Cl_2 \xrightarrow{(hv)} CHCl_3 + HCl$ (chloroform)
- $CHCl_3 + Cl_2 \xrightarrow{(hv)} CCl_4 + HCl$ (carbon tetrachloride)
- **Exam point:** To get the **mono**-halo product as the major product, use a **large excess of alkane**; to push to $CCl_4$, use excess chlorine. Chloroform ($CHCl_3$) was historically used as an anaesthetic — a pharmacy link worth one line in answers.

## 2.4 Pharmaceutical Paraffins

Petroleum refining leaves mixtures of long-chain alkanes. Three grades matter in pharmacy:

**Summary table — pharmaceutical paraffins:**

| Paraffin | What it is (chemically) | Appearance/properties | Pharmacy uses |
|---|---|---|---|
| **Liquid paraffin** (mineral oil) | Mixture of liquid higher alkanes | Colourless, odourless oily liquid; inert, not absorbed | Laxative/lubricant (softens stool); vehicle for oily preparations |
| **Soft paraffin** (petroleum jelly) | Mixture of semi-solid higher alkanes | Soft, translucent, greasy; melts near body temperature | Ointment base; skin protectant/emollient; prevents moisture loss |
| **Hard paraffin** (paraffin wax) | Mixture of solid higher alkanes | White/translucent waxy solid | Stiffening agent in ointments; coating tablets/capsules; sealing |

- **Properties (exam-ready):** All three are chemically **inert** (alkanes don't react — the "paraffin" idea from Chapter 1), water-insoluble, and stable. Soft paraffin is occlusive — it forms a waterproof film on skin, which is why it protects burns and dry skin.
- **Counselling/storage points:**
- Liquid paraffin should **not be used long-term** without advice — it can reduce absorption of fat-soluble vitamins (A, D, E, K) and there is an aspiration risk (oil entering lungs) especially in elderly/bedridden patients.
- Store all paraffins **away from heat and flame** — they are hydrocarbons and can burn.
- Soft paraffin for broken skin should be from a freshly opened or sterile pack to avoid contamination.
- > **Key takeaway:** Liquid = laxative/vehicle, soft = ointment base/protectant, hard = stiffener/coating — all are inert higher-alkane mixtures.

## Worked Examples (Chapter 2)

> **Example 1.** Predict the major monochlorination product of 2-methylpropane, $(CH_3)_3CH$. **Solution:** $(CH_3)_3CH$ has one 3° H and nine 1° H. 3° H is ~5× more reactive per H: 1 × 5 = 5 parts vs 9 × 1 = 9 parts — but the huge per-H advantage plus the fact that only one 3° product exists makes $(CH_3)_3C–Cl$ (tert-butyl chloride) the major product. (Textbook answer: tert-butyl chloride predominates.)

> **Example 2.** Why is bromination preferred over chlorination for preparing a single alkyl bromide? **Solution:** Bromine is much more selective (3° ≫ 2° ≫ 1°), so it attacks almost exclusively the most reactive hydrogen, giving one major product. Chlorine reacts with all H types at comparable rates, giving mixtures that are hard to separate.

## Pharmacy Relevance

- Liquid paraffin IP is still dispensed as a stool softener/laxative and used as a vehicle in oily injections and ear drops.
- Soft paraffin (petroleum jelly) is the classic ointment base — most "creams for dry skin" in an Indian pharmacy are built on it.
- Understanding radical stability (3° > 2° > 1°) returns later in the course whenever carbocations and reaction mechanisms appear.

## India Context

- Petroleum jelly is a household name across India for winter skin care; the "paraffin" in it is exactly the higher-alkane mixtures of this chapter.
- Liquid paraffin IP is listed in the Indian Pharmacopoeia and must meet its purity tests (it must be free of unsaturated and aromatic impurities) — a direct exam link between organic chemistry and quality control.

## Common Confusions

- **Homolysis vs heterolysis:** Homolysis = each atom keeps one electron (→ radicals); heterolysis = one atom takes both (→ ions). Halogenation uses homolysis.
- **Propagation vs termination:** Propagation makes a new radical (chain continues); termination consumes radicals (chain ends).
- **Liquid vs soft vs hard paraffin:** Liquid = oil (laxative), soft = jelly (ointment base), hard = wax (stiffener). Don't swap their uses.
- **Chlorination vs bromination selectivity:** Chlorine = fast, unselective (mixtures); bromine = slow, selective (clean product).

## Common Mistakes

- Writing the initiation step as $Cl_2 \rightarrow Cl^+ + Cl^-$ — wrong; it is **homolysis** to **two neutral radicals** ($Cl\cdot + Cl\cdot$).
- Forgetting the termination steps in a mechanism answer — examiners award marks for all three stages.
- Quoting the 5 : 3.8 : 1 ratio as exact/measured-by-you — present it as "commonly quoted textbook values".
- Calling liquid paraffin "absorbed in the intestine" — it is **not absorbed**; it acts as a lubricant.

## Mnemonics

- Chain stages: "**I**nitiate, **P**ropagate, **T**erminate" → "**I** **P**lay **T**abla".
- Selectivity order: "**T**ertiary **T**ops, **S**econdary **S**econd, **P**rimary **P**oor" (3° > 2° > 1°).
- Paraffin uses: "**L**iquid **L**ubricates (laxative), **S**oft **S**oothes (skin), **H**ard **H**ardens (stiffener)".

## One-Minute Revision

- Radical = unpaired electron (·); homolysis: A–B → A· + B·.
- $CH_4 + Cl_2$: initiation $Cl_2 \xrightarrow{h\nu} 2Cl\cdot$; propagation $Cl\cdot + CH_4 \rightarrow \cdot CH_3 + HCl$, then $\cdot CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\cdot$; termination = radical + radical combinations.
- H reactivity: 3° > 2° > 1° (≈ 5 : 3.8 : 1 per H for chlorination, commonly quoted); bromination far more selective.
- Excess halogen → $CH_2Cl_2$ → $CHCl_3$ → $CCl_4$.
- Paraffins: liquid (mineral oil, laxative/vehicle), soft (petroleum jelly, ointment base/protectant), hard (wax, stiffener/coating); all inert higher-alkane mixtures.

# Practice Questions — Chapter 2

### MCQs (10)

1. Homolytic fission of $Cl_2$ gives: (a) $Cl^+ + Cl^-$ (b) $2Cl\cdot$ (c) $Cl_2^+$ (d) $2Cl^-$
2. The chain-propagating step in methane chlorination is: (a) $Cl_2 \rightarrow 2Cl\cdot$ (b) $Cl\cdot + CH_4 \rightarrow \cdot CH_3 + HCl$ (c) $Cl\cdot + Cl\cdot \rightarrow Cl_2$ (d) $\cdot CH_3 + \cdot CH_3 \rightarrow C_2H_6$
3. Order of H reactivity towards chlorination: (a) 1° > 2° > 3° (b) 3° > 2° > 1° (c) 2° > 3° > 1° (d) all equal
4. Commonly quoted per-H relative rates (3° : 2° : 1°) for chlorination: (a) 1:1:1 (b) 5 : 3.8 : 1 (c) 1600:82:1 (d) 2:2:1
5. Which halogenation is more selective? (a) chlorination (b) bromination (c) fluorination (d) iodination
6. Major monochlorination product of propane is: (a) 1-chloropropane (b) 2-chloropropane (c) both equal (d) no reaction
7. Termination step example: (a) $Cl\cdot + CH_4 \rightarrow \cdot CH_3 + HCl$ (b) $\cdot CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\cdot$ (c) $Cl\cdot + Cl\cdot \rightarrow Cl_2$ (d) $Cl_2 \rightarrow 2Cl\cdot$
8. Liquid paraffin is used as: (a) oxidising agent (b) laxative (c) antiseptic (d) antacid
9. Soft paraffin is also called: (a) mineral oil (b) petroleum jelly (c) paraffin wax (d) kerosene
10. Hard paraffin is used in pharmacy as: (a) laxative (b) ointment stiffening agent (c) solvent (d) sweetener

**Answer key:** 1-b, 2-b, 3-b, 4-b, 5-b, 6-b, 7-c, 8-b, 9-b, 10-b

### Short-answer (5)

1. Define free radical and homolysis with one example each.
2. Distinguish initiation, propagation and termination with one equation each.
3. Why is a 3° hydrogen more reactive than a 1° hydrogen in halogenation?
4. What is the product sequence when methane is chlorinated with excess chlorine?
5. Name the three pharmaceutical paraffins and give one use of each.

### Long-answer (3)

1. Write the complete free-radical chain mechanism for the chlorination of methane.
2. Discuss the selectivity of halogenation (3° > 2° > 1°) and compare chlorination with bromination.
3. Write a note on pharmaceutical paraffins: chemical nature, properties, uses and storage/counselling points.

### Mechanism-writing (2)

1. Write all initiation, propagation and termination steps for the bromination of methane.
2. Show the mechanism steps by which $CH_3Cl$ is converted to $CCl_4$ on further chlorination.

### Application-based (2)

1. You need tert-butyl bromide as the single major product from $(CH_3)_3CH$. Would you use $Cl_2$/hv or $Br_2$/hv? Justify.
2. A patient asks why liquid paraffin should not be used daily for months. What do you counsel?

**Viva (5)**

1. What does the dot in Cl· represent?
2. Which step of the chain reaction needs light or heat?
3. Which radical is most stable: 1°, 2° or 3°?
4. Why is an excess of alkane used to prepare alkyl halides?
5. Which paraffin is used as an ointment base?

# Chapter 3 — Cycloalkanes and Strain Theories

## Learning Objectives

After studying this chapter, you should be able to:

1. Define cycloalkane and give its general formula.
2. Explain angle strain in simple words.
3. State Baeyer's strain theory and calculate the strain (deviation) for 3- to 6-membered rings.
4. List the limitations of Baeyer's theory.
5. Explain the Coulson–Moffitt modification (bent/banana bonds) simply.
6. Explain the Sachse–Mohr theory: chair and boat forms of cyclohexane.

## Key Definitions

- **Cycloalkane:** An alkane in which the carbon chain closes into a **ring**. General formula: **$C_nH_{2n}$** (two hydrogens fewer than an open-chain alkane, because the two chain ends join each other). Examples: cyclopropane ($C_3H_6$), cyclobutane ($C_4H_8$), cyclopentane ($C_5H_{10}$), cyclohexane ($C_6H_{12}$).
- **Angle strain:** The instability (extra energy) in a ring caused when its C–C–C bond angles are **forced away from the ideal tetrahedral angle (109°28′)**. Like bending a straight stick — the more you bend it, the more it wants to snap back.
- **Baeyer's strain theory:** The 1885 proposal (by Adolf von Baeyer) that ring stability depends on how much the ring's bond angles deviate from 109°28′; bigger deviation = more strain = less stable ring. It assumes rings are flat (planar).
- **Deviation (d):** Half the difference between the ideal angle and the actual ring angle: **d = (109°28′ − ring angle) ÷ 2**. Baeyer used half the total bend per bond.
- **Conformation:** A specific 3D shape a molecule takes by **rotating about single bonds** (no bonds broken). Different conformations of the same molecule interconvert easily at room temperature.
- **Chair and boat:** The two main non-flat shapes (conformations) of cyclohexane — named because skeletal drawings look like a chair and a boat.
- **Axial / equatorial:** In the chair form, each carbon has one bond pointing straight up/down (**axial**) and one pointing outward around the "equator" of the ring (**equatorial**). (Basic level: just know the words and the picture idea.)

## 3.1 What Are Cycloalkanes? (From Zero)

Take an open alkane chain and join its two ends: you get a **ring** — a cycloalkane. Joining the ends costs two hydrogens (one from each end), so the formula drops from $C_nH_{2n+2}$ to **$C_nH_{2n}$**.

Rings are named by adding "cyclo-" to the alkane name: 3 carbons → cyclopropane, 4 → cyclobutane, 5 → cyclopentane, 6 → cyclohexane.

**The problem:** $sp^3$ carbon "wants" bond angles of 109°28′. In a small ring, geometry forces the angles to be much smaller — the bonds are bent like a stick forced into a tight circle. This bending creates **angle strain**, making small rings reactive and eager to spring open.

## 3.2 Baeyer's Strain Theory

- **Concept:** Baeyer assumed all rings are **flat (planar)**. For a flat regular polygon with n sides, the internal angle = (n−2) × 180° ÷ n. He compared this with 109°28′ and defined the strain per bond as half the deviation.

**Calculations (exam favourite):**

| Ring | n | Planar angle | Deviation d = (109°28′ − angle)/2 | Strain energy per $CH_2$ (commonly quoted textbook values) |
|---|---|---|---|---|
| Cyclopropane | 3 | 60° | (109°28′ − 60°)/2 = **+24°44′** | ~27.5 kcal/mol |
| Cyclobutane | 4 | 90° | (109°28′ − 90°)/2 = **+9°44′** | ~26.3 kcal/mol |
| Cyclopentane | 5 | 108° | (109°28′ − 108°)/2 = **+0°44′** | ~6.2 kcal/mol |
| Cyclohexane | 6 | 120° | (109°28′ − 120°)/2 = **−5°16′** | ~0.1 kcal/mol |

- **What Baeyer predicted:** Cyclopentane (deviation only 0°44′) should be the most stable; cyclopropane and cyclobutane should be highly strained and reactive; cyclohexane (negative deviation — angle *larger* than ideal) should also be strained.
- **Worked example:** Calculate the angle strain in cyclobutane.
- Planar square angle = 90°. d = (109°28′ − 90°)/2 = 19°28′/2 = **9°44′**. Positive deviation → strained → reactive ring. ✓
- > **Key takeaway:** Baeyer = "flat rings; strain = half the bend away from 109°28′; cyclopentane looks best on paper."

## 3.3 Limitations of Baeyer's Theory

The theory was brilliant for 1885 but has real holes — examiners love this list:

1. **Cyclopentane is not flat.** Baeyer assumed a planar pentagon, but cyclopentane actually puckers (folds slightly) to relieve strain — the flat-ring assumption is wrong.
2. **Cyclohexane is very stable**, yet Baeyer predicts strain (−5°16′ deviation). In reality cyclohexane is one of the most stable rings — the theory's prediction fails.
3. **"Negative strain" makes no sense.** For rings larger than 6, the deviation becomes more negative, which would mean *increasing* strain — but large rings (7, 8, … members) are actually **strain-free and stable**. Baeyer cannot explain this.
4. **It ignores other strains.** Baeyer considered only angle bending, ignoring crowding of hydrogens (torsional/steric strain) and the fact that bonds can bend in ways his geometry missed.

- > **Key takeaway:** Baeyer assumed flat rings — real rings pucker and fold, so the theory fails for cyclohexane and larger rings.

## 3.4 Coulson–Moffitt Modification: Bent ("Banana") Bonds

- **Concept:** Coulson and Moffitt pointed out that the bonds in cyclopropane are not straight lines between carbons — they **bulge outward like bananas**. Because the orbitals can't point directly at each other in a 60° triangle, they overlap at an angle, forming curved "bent bonds".
- **Simple explanation:** The carbon orbitals in cyclopropane take on **more p-character** (p-orbitals are naturally at 90°, closer to the 60° ring angle than the 109.5° of pure $sp^3$). This "rehybridisation" lets the bonds bend outward, so the *actual* strain is less than Baeyer's geometry predicts. The bonds are weaker and more reactive than normal sigma bonds — which is why cyclopropane opens easily with reagents like $Br_2$.
- **Worked example (exam line):** "Cyclopropane's C–C bonds are bent (banana) bonds with increased p-character; the inter-orbital angle is larger than the geometric 60°, relieving part of the angle strain."
- > **Key takeaway:** Coulson–Moffitt = "the bonds bend outward like bananas, so small rings are less strained than Baeyer's flat geometry says."

## 3.5 Sachse–Mohr Theory: Rings Are Not Flat

- **Concept:** Sachse and Mohr (1890s) proposed that rings with 6 or more carbons are **not planar** — they pucker into 3D shapes. Because single (sigma) bonds allow **free rotation**, the ring can fold so that every carbon keeps nearly the perfect 109°28′ angle.
- **Cyclohexane — chair and boat:**
- The **chair** conformation is the most stable: all bond angles are ~109.5° and all hydrogens are staggered — essentially **strain-free**.
- The **boat** conformation is less stable (some hydrogen crowding — the two "flagpole" hydrogens at the ends bump into each other).
- Chair ⇌ boat interconvert rapidly at room temperature by rotation about C–C bonds; a sample of cyclohexane is overwhelmingly in the chair form.
- **Basic conformational idea:** In the chair, each carbon carries one **axial** bond (straight up/down) and one **equatorial** bond (pointing outward). Bulky groups prefer the equatorial position (less crowding) — this one line explains the shapes of substituted cyclohexanes and of sugars later in the course.
- **Why it matters:** Sachse–Mohr explains what Baeyer couldn't — **rings of any size can be strain-free** by folding into non-planar conformations. This rescued ring chemistry and underlies the shapes of steroids, sugars and many drugs.
- > **Key takeaway:** Sachse–Mohr = "rings pucker; cyclohexane lives as a strain-free chair (boat is the less-stable cousin)."

**Summary table — strain theories:**

| Theory | Main idea | Explains | Fails at |
|---|---|---|---|
| Baeyer (1885) | Flat rings; strain = ½ deviation from 109°28′ | Why 3- and 4-rings are reactive; cyclopentane most stable | Cyclohexane stability; large rings; non-planar reality |
| Coulson–Moffitt | Bent (banana) bonds, more p-character | Why cyclopropane is less strained than geometry says | — (a refinement, not a replacement) |
| Sachse–Mohr | Rings pucker; chair/boat conformations | Strain-free cyclohexane and large rings | — (confirmed by experiment) |

## Worked Examples (Chapter 3)

**Example 1.** Arrange cyclopropane, cyclobutane, cyclopentane and cyclohexane in order of stability, giving Baeyer's reasoning. **Solution:** Cyclohexane ≈ cyclopentane > cyclobutane > cyclopropane. Deviations: cyclopentane 0°44′ (least) < cyclobutane 9°44′ < cyclopropane 24°44′ (most); cyclohexane's −5°16′ is explained as strain-free via puckering (Sachse–Mohr), so in reality cyclohexane is the most stable.

**Example 2.** Why does cyclopropane react with bromine in the dark while cyclohexane does not? **Solution:** Cyclopropane has large angle strain (~24°44′ deviation, ~27.5 kcal/mol per $CH_2$) and weak bent (banana) bonds; opening the ring releases this strain, so addition of $Br_2$ across a C–C bond is favoured. Cyclohexane is strain-free (chair), so there is no such driving force.

## Pharmacy Relevance

- Cyclohexane rings are everywhere in drugs: **steroids** (four fused rings), many antihistamines and antidepressants contain cyclohexane units whose chair shapes decide how the drug fits its target.
- Cyclopropane itself was once used as an **anaesthetic** (explosive with oxygen — discontinued, but a good exam trivia link between strain and reactivity).
- The chair/equatorial preference idea returns in carbohydrate chemistry (glucose sits in a chair).

## India Context

- The petroleum refineries discussed in Chapter 1 also produce **naphthenes** — the industry's name for cycloalkanes — which are reformed into aromatics for the petrochemical sector.
- Steroid drugs manufactured in India's pharma hubs (Hyderabad, Ahmedabad) are built on fused cyclohexane/cyclopentane ring systems — the conformations in this chapter are literally the skeletons of those medicines.

## Common Confusions

- **Angle strain vs torsional strain:** Angle strain = bond angles bent from 109°28′; torsional strain = crowding when bonds eclipse each other during rotation. Baeyer only talked about angle strain.
- **Conformation vs configuration:** Conformation = shape changed by rotation (chair ⇌ boat, interconvertible); configuration = arrangement fixed unless bonds break (e.g., cis/trans). Don't mix them.
- **Chair vs boat stability:** Chair = strain-free and most stable; boat = less stable (flagpole H crowding). Students often reverse them.
- **Deviation sign:** Positive deviation (3-, 4-, 5-rings) = angle too small; negative (6-ring and above) = angle too large — Baeyer read both as strain, but puckering removes it.

## Common Mistakes

- Writing the deviation formula without dividing by 2 — d = (109°28′ − angle)/2, not the full difference.
- Stating "Baeyer's theory is completely wrong" — it correctly predicts small-ring reactivity; it fails for cyclohexane and large rings. Give the balanced verdict.
- Drawing cyclohexane flat in mechanism/conformation answers — draw or describe the chair.
- Quoting strain energies as exact constants — present them as "commonly quoted textbook values".

## Mnemonics

- Deviation order (3→6): "**24, 9, 0, −5**" (degrees, roughly) — "24-9-0-minus-5, small rings strain, big rings thrive."
- Theories timeline: "**B**aeyer **B**ends flat, **C**oulson **C**urves bonds, **S**achse **S**hapes chairs" (B–C–S, 1885 → 1940s → 1890s; note Sachse–Mohr came before Coulson–Moffitt historically — the mnemonic is by concept, not date).
- Chair beats boat: "**C**hair is **C**omfortable, **B**oat **B**umps" (flagpole hydrogens bump).

## One-Minute Revision

- Cycloalkane = ring alkane, $C_nH_{2n}$; angle strain = bend away from 109°28′.
- Baeyer: d = (109°28′ − ring angle)/2; deviations ≈ +24°44′ (3), +9°44′ (4), +0°44′ (5), −5°16′ (6); strain energies ~27.5, 26.3, 6.2, 0.1 kcal/mol per $CH_2$ (commonly quoted).
- Limitations: assumes flat rings; cyclohexane stable contrary to prediction; can't explain strain-free large rings ("negative strain" problem); ignores puckering.
- Coulson–Moffitt: bent banana bonds, more p-character, less strain than geometry says.
- Sachse–Mohr: rings pucker; cyclohexane = chair (strain-free, most stable) ⇌ boat (less stable); axial/equatorial bonds.

## Practice Questions — Chapter 3

**MCQs (10)**

1. General formula of cycloalkanes: (a) $C_nH_{2n+2}$ (b) $C_nH_{2n}$ (c) $C_nH_{2n-2}$ (d) $C_nH_n$
2. Ideal tetrahedral bond angle: (a) 120° (b) 109°28′ (c) 90° (d) 180°
3. Baeyer's deviation for cyclopropane: (a) 9°44′ (b) 0°44′ (c) 24°44′ (d) −5°16′
4. Most stable cycloalkane as per experimental fact: (a) cyclopropane (b) cyclobutane (c) cyclopentane (d) cyclohexane
5. A limitation of Baeyer's theory is: (a) it predicts cyclopropane is reactive (b) it assumes rings are planar (c) it uses 109°28′ (d) it explains small rings
6. Banana (bent) bonds are proposed by: (a) Baeyer (b) Sachse–Mohr (c) Coulson–Moffitt (d) Kekulé
7. The most stable conformation of cyclohexane is: (a) boat (b) chair (c) twist (d) planar
8. In the chair form, bonds pointing straight up/down are called: (a) equatorial (b) axial (c) polar (d) lateral
9. Cyclopentane relieves strain by: (a) breaking bonds (b) puckering (c) ionising (d) expanding angles to 120°
10. Strain energy per $CH_2$ commonly quoted for cyclopropane: (a) ~0.1 (b) ~6.2 (c) ~26.3 (d) ~27.5 kcal/mol

**Answer key:** 1-b, 2-b, 3-c, 4-d, 5-b, 6-c, 7-b, 8-b, 9-b, 10-d

**Short-answer (5)**

1. Define angle strain and give Baeyer's formula for deviation.
2. Calculate the deviation for cyclopentane and interpret the result.
3. State two limitations of Baeyer's strain theory.

### Long-answer (3)

1. State and explain Baeyer's strain theory with calculated deviations for 3- to 6-membered rings. Discuss its limitations.
2. Write notes on: (a) Coulson–Moffitt modification, (b) Sachse–Mohr theory.
3. Explain why cyclopropane is highly reactive while cyclohexane is stable, using strain concepts.

### Mechanism-writing (2)

1. There is no electron-pushing mechanism in this chapter; instead: write the stepwise reasoning (with the deviation calculation) by which Baeyer predicts cyclobutane to be strained, then explain how puckering modifies the conclusion.
2. Describe, step by step in words, how a planar cyclohexane ring relieves its predicted strain by adopting the chair conformation (angle recovery + staggering).

### Application-based (2)

1. A synthesis needs a three-carbon ring that will spring open on treatment with $Br_2$. Which cycloalkane would you choose, and what strain concept justifies the choice?
2. Steroid drugs contain fused cyclohexane rings. Why does the Sachse–Mohr theory (chair conformations) matter for understanding their 3D shape and biological activity?

### Viva (5)

1. What is the general formula of cycloalkanes?
2. Who proposed the strain theory and in which year?
3. What is the deviation value for cyclohexane?
4. Which conformation of cyclohexane has flagpole hydrogens?
5. Why are cyclopropane's C–C bonds called banana bonds?

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