



# HYDROCARBONS

## Class 11 Chemistry - Chapter 13

### CBSE Board 2025-26 Syllabus

Complete Notes | Tips & Tricks | Case Studies | Expected Questions

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★ ★ ★ COMPREHENSIVE STUDY MATERIAL FOR CLASS 11 CHEMISTRY ★ ★ ★



## CHAPTER OVERVIEW

### What You Will Learn:

- **Classification of Hydrocarbons:** Aliphatic, Aromatic; Open chain and Cyclic
- **Alkanes:** IUPAC nomenclature, isomerism, preparation, physical & chemical properties, free radical mechanism
- **Alkenes:** Structure, IUPAC names, geometrical isomerism, preparation, reactions, electrophilic addition
- **Alkynes:** Structure, IUPAC names, preparation, acidic nature, reactions
- **Aromatic Hydrocarbons (Benzene):** Structure, Kekulé, resonance, aromaticity (Hückel's rule), EAS reactions
- **Carcinogenicity & Toxicity:** Health effects of hydrocarbons

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## 💡 Why This Chapter is Important:

Hydrocarbons are the **backbone of Organic Chemistry!** This chapter sets the stage for all organic reactions in Class 11 and Class 12:

- CBSE Board Exams — 10-15 marks every year
- JEE Main & Advanced — direct mechanism and reaction questions
- NEET — reaction types and products
- Foundation for: Haloalkanes, Alcohols, Aldehydes/Ketones, Carboxylic Acids

**Key Focus Areas:** Free radical mechanism (Alkanes), Markovnikov's rule (Alkenes), Acidic nature (Alkynes), EAS reactions (Benzene)



# CLASSIFICATION OF HYDROCARBONS

## Hydrocarbon Classification Tree

```
HYDROCARBONS (Compounds of C and H only)
|
|----- ALIPHATIC (Open chain)
|
|           |
|           |----- SATURATED → Alkanes (C-C single bond)
|           |
|           |----- UNSATURATED
|           |
|           |----- Alkenes (C=C double bond)
|           |----- Alkynes (C≡C triple bond)
|
|----- AROMATIC (Cyclic, conjugated π system)
|           |
|           |----- Benzene and its derivatives
|
|----- ALICYCLIC (Cyclic but non-aromatic)
|           |----- Cycloalkanes, Cycloalkenes
```



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## General Molecular Formulas

**Alkanes** →  $C_nH_{2n+2}$

**Alkenes** →  $C_nH_{2n}$

**Alkynes** →  $C_nH_{2n-2}$

**Benzene** →  $C_6H_6$  ( $C_nH_{2n-6}$  for arenes)

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## SECTION 1: ALKANES (Saturated Hydrocarbons)

### 1.1 Introduction & Nomenclature

#### What are Alkanes?

Alkanes are **saturated hydrocarbons** — they contain only C–C single bonds and C–H bonds. They are also called *paraffins* (meaning "little affinity") because they are relatively unreactive.

- General Formula:  $C_nH_{2n+2}$
- First member: Methane ( $CH_4$ ,  $n=1$ )
- Each C atom is  **$sp^3$  hybridized** → tetrahedral geometry ( $109.5^\circ$ )

n	Name	Molecular Formula	Structural Formula	No. of Isomers
1	Methane	$CH_4$	$CH_4$	1
2	Ethane	$C_2H_6$	$CH_3-CH_3$	1
3	Propane	$C_3H_8$	$CH_3-CH_2-CH_3$	1
4	Butane	$C_4H_{10}$	n-Butane / Isobutane	2
5	Pentane	$C_5H_{12}$	n-Pentane / Isopentane / Neopentane	3
6	Hexane	$C_6H_{14}$	—	5

## 🔥 IUPAC Naming Rules — "LLPNB" Method:

1. **L**ongest chain → parent name
2. **L**owest locants → number from end closest to branch
3. **P**refixes → name substituents (methyl, ethyl, etc.) alphabetically
4. **N**umber locants → write number before substituent name
5. **B**rackets / commas → use comma between numbers, hyphen between number and letter

**Example:**  $\text{CH}_3\text{-CH}(\text{CH}_3)\text{-CH}_2\text{-CH}_3 \rightarrow 2\text{-methylbutane}$

## 1.2 Conformational Isomerism in Ethane

### 📺 Conformations of Ethane

Rotation about C–C single bond gives different spatial arrangements called **conformations**.

- **Staggered Conformation:** H atoms on adjacent C are as far apart as possible → *minimum energy* → *more stable*
- **Eclipsed Conformation:** H atoms on adjacent C directly overlap → *maximum torsional strain* → *less stable*
- Energy difference between staggered and eclipsed = **12.6 kJ/mol**

*Conformations are not isomers — they interconvert rapidly at room temperature.*

## 1.3 Preparation of Alkanes

### Important Methods

#### 1. Wurtz Reaction

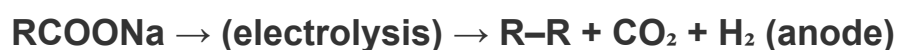


(Gives symmetrical alkane; R is alkyl group; X is halogen)

#### 2. From Unsaturated Hydrocarbons (Hydrogenation)



#### 3. Kolbe's Electrolytic Method



💡 **Trick to Remember Wurtz Reaction:**

**"Wurtz Wins by Doubling the Carbon chain!"**



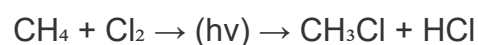
⚠️ Wurtz reaction is *not suitable for mixed alkanes* (gives mixture of products).

## 1.4 Physical Properties of Alkanes

Property	Trend	Reason
Boiling Point	Increases with molecular mass	Stronger van der Waals forces
Boiling Point (isomers)	Branched < Straight chain	Less surface area → weaker forces
State (at 25°C)	C <sub>1</sub> –C <sub>4</sub> : Gas; C <sub>5</sub> –C <sub>17</sub> : Liquid; C <sub>18</sub> + : Solid	Increasing intermolecular forces
Solubility	Insoluble in water; soluble in organic solvents	Non-polar nature
Density	Less dense than water	Low molecular mass, non-polar

## 1.5 Chemical Reactions of Alkanes

### A. Halogenation (Free Radical Substitution Mechanism)



This is the **MOST IMPORTANT reaction** — mechanism is always asked in exams!

## Free Radical Mechanism — Step by Step

### Step 1: Chain Initiation

$\text{Cl}-\text{Cl} \rightarrow (\text{h}\nu) \rightarrow 2\text{Cl}\cdot$  (free radicals formed by homolytic cleavage)

### Step 2: Chain Propagation

$\text{Cl}\cdot + \text{CH}_4 \rightarrow \text{CH}_3\cdot + \text{HCl}$

$\text{CH}_3\cdot + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{Cl}\cdot$

(This cycle repeats thousands of times!)

### Step 3: Chain Termination





$\text{Cl}\cdot + \text{Cl}\cdot \rightarrow \text{Cl}_2$

$\text{CH}_3\cdot + \text{Cl}\cdot \rightarrow \text{CH}_3\text{Cl}$

$\text{CH}_3\cdot + \text{CH}_3\cdot \rightarrow \text{C}_2\text{H}_6$

(Free radicals combine → chain ends)

### Common Mistakes in Free Radical Mechanism:

-  Saying it's electrophilic addition — it's **FREE RADICAL SUBSTITUTION**
-  Confusing homolytic with heterolytic cleavage —  $\text{h}\nu$  causes **homolytic** cleavage (each atom gets 1 electron)
-  Forgetting that  $\text{F}_2$  reacts explosively,  $\text{Br}_2$  is slow,  $\text{I}_2$  does not react normally
-  Not writing the radical ( $\cdot$ ) symbol in initiation/propagation steps

## Reactivity Order of Halogens with Alkanes



(F<sub>2</sub> too violent; I<sub>2</sub> reaction is reversible — practically does not occur)

## B. Combustion of Alkanes



Alkanes are excellent fuels (LPG, CNG, petrol, diesel).

*Incomplete combustion* → CO (poisonous) + soot (carbon)

## C. Isomerisation & Pyrolysis

- **Isomerisation:** n-butane → (AlCl<sub>3</sub>, HCl, heat) → iso-butane
- **Thermal Cracking (Pyrolysis):** Breaking long chain alkanes at high temp into smaller molecules — basis of petroleum refining
- **Reforming:** n-hexane → (Pt, Δ) → cyclohexane + H<sub>2</sub>

## SECTION 2: ALKENES (Unsaturated — One Double Bond)

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### 2.1 Structure & Hybridization

#### Key Features of Alkenes:

- General formula:  $C_nH_{2n}$
- Carbon atoms of double bond: **sp<sup>2</sup> hybridized**
- Bond angles: **120°** (trigonal planar)
- C=C consists of: **one  $\sigma$  bond + one  $\pi$  bond**
- $\pi$  bond is formed by **lateral overlap** of unhybridized p orbitals
- $\pi$  bond is weaker than  $\sigma$  bond → site of chemical reactions
- First member: **Ethene (Ethylene)**  $CH_2=CH_2$

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## 2.2 Geometrical (Cis-Trans) Isomerism

### Condition for Geometrical Isomerism:

Each carbon of the C=C double bond must have **two different groups** attached to it.

**Cis isomer:** Similar groups on same side of double bond

**Trans isomer:** Similar groups on opposite sides of double bond

### Example: But-2-ene ( $\text{CH}_3\text{-CH=CH-CH}_3$ )

Cis-but-2-ene: Both  $\text{CH}_3$  groups on same side  $\rightarrow$  higher boiling point (due to polarity)

Trans-but-2-ene:  $\text{CH}_3$  groups on opposite sides  $\rightarrow$  lower boiling point, more stable

*Note:  $\text{CH}_2=\text{CH}_2$  (ethene) and  $\text{CH}_2=\text{CH-CH}_3$  (propene) do NOT show geometrical isomerism!*

### Quick Rule — E/Z Notation (Modern System):

When groups cannot be named cis/trans, use **E** (Entgegen = opposite) and **Z** (Zusammen = together).

Priority is assigned by **CIP rules** (higher atomic number = higher priority).

- **Z**  $\rightarrow$  higher priority groups on *same* side
- **E**  $\rightarrow$  higher priority groups on *opposite* sides

## 2.3 Preparation of Alkenes

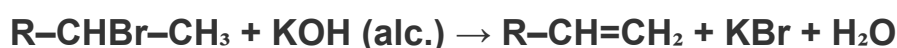
### Important Methods

#### 1. Dehydration of Alcohols (most common in exams)



Order of ease:  $3^\circ > 2^\circ > 1^\circ$  alcohol

#### 2. Dehydrohalogenation ( $\beta$ -elimination)



Follows Saytzeff's rule: more substituted alkene is major product

#### 3. Dehalogenation



#### 💡 Saytzeff's Rule (Must Remember!):

"In elimination reactions, the more substituted (more stable) alkene is the major product."

Example:  $\text{CH}_3\text{-CHBr-CH}_2\text{-CH}_3 + \text{KOH(alc)} \rightarrow$  major product:  $\text{CH}_3\text{-CH=CH-CH}_3$  (but-2-ene, more substituted) rather than  $\text{CH}_3\text{-CH}_2\text{-CH=CH}_2$  (but-1-ene)

## 2.4 Chemical Reactions of Alkenes

### A. Electrophilic Addition (Mechanism — MOST IMPORTANT)

The  $\pi$  bond of alkene acts as an **electron donor** and attracts electrophiles.



#### Example: Addition of HBr to Propene

Step 1:  $\text{H}^+$  attacks  $\pi$  bond  $\rightarrow$  forms **carbocation intermediate** (more stable = secondary > primary)

Step 2:  $\text{Br}^-$  attacks the carbocation  $\rightarrow$  forms product

Result:  $\text{CH}_3\text{-CHBr-CH}_3$  (2-bromopropane) — follows Markovnikov's rule

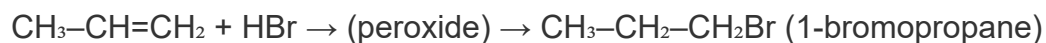
### ★ Markovnikov's Rule (EXAM FAVOURITE)

**"In addition of an unsymmetrical reagent (HX) to an unsymmetrical alkene, the negative part (X) goes to that carbon which has fewer hydrogen atoms (more substituted carbon)."**

OR: "Rich gets richer" — H goes to the carbon that already has more H atoms!

### Anti-Markovnikov (Peroxide Effect / Kharasch Effect):

In presence of peroxide ( $\text{H}_2\text{O}_2$  or  $\text{R}-\text{O}-\text{O}-\text{R}$ ),  $\text{HBr}$  adds opposite to Markovnikov's rule.



*Note: Peroxide effect works ONLY with HBr, NOT HCl or HI!*

Mechanism: Free radical addition (not ionic)

Reaction	Reagent	Product	Type
Hydrogenation	$\text{H}_2$ / Ni, Pt, Pd	Alkane	Electrophilic addition
Addition of HX	HCl, HBr, HI	Alkyl halide (Markovnikov)	Electrophilic addition
Hydration	$\text{H}_2\text{O}$ / $\text{H}_2\text{SO}_4$	Alcohol	Electrophilic addition
Halogenation	$\text{Br}_2$ / $\text{CCl}_4$	Vicinal dihalide	Electrophilic addition
Ozonolysis	$\text{O}_3$ then $\text{Zn}/\text{H}_2\text{O}$	Aldehydes/Ketones	Oxidative cleavage
Oxidation	$\text{KMnO}_4$ (cold, dil.)	Diol (glycol)	Hydroxylation
Polymerisation	High T, P / catalyst	Polyethylene (PE)	Addition polymerisation

⚠ **Common Mistakes with Alkene Reactions:**

- ❌ Applying Markovnikov's rule to *symmetrical* alkenes ( $\text{CH}_2=\text{CH}_2$  — no Markovnikov needed!)
- ❌ Confusing bromine test:  $\text{Br}_2/\text{CCl}_4$  *decolourises* → indicates unsaturation (both alkenes AND alkynes)
- ❌ Forgetting that hot, conc.  $\text{KMnO}_4$  cleaves the double bond; cold, dil.  $\text{KMnO}_4$  gives diol
- ❌ Applying peroxide effect to HCl or HI — it works ONLY for HBr!

## ⚡ SECTION 3: ALKYNES (Unsaturated — One Triple Bond)

### 3.1 Structure & Hybridization

#### Key Features of Alkynes:

- General formula:  $C_nH_{2n-2}$
- Carbon atoms of triple bond: **sp hybridized**
- Bond angle: **180°** (linear geometry)
- $C\equiv C$  consists of: **one  $\sigma$  bond + two  $\pi$  bonds**
- First member: **Ethyne (Acetylene)**  $HC\equiv CH$
- Ethyne bond lengths:  $C-H = 106 \text{ pm}$ ;  $C\equiv C = 120 \text{ pm}$

#### 🎯 Hybridization Comparison (EXAM TRICK):

Type	Hybridization	Bond Angle	Geometry	Formula
Alkane	$sp^3$	$109.5^\circ$	Tetrahedral	$C_nH_{2n+2}$
Alkene	$sp^2$	$120^\circ$	Trigonal Planar	$C_nH_{2n}$
Alkyne	$sp$	$180^\circ$	Linear	$C_nH_{2n-2}$

*Trick: More  $\pi$  bonds  $\rightarrow$  more s-character  $\rightarrow$  smaller bond angle (no! angle increases)  $\rightarrow$  Actually: more s-character  $\rightarrow$  shorter, stronger C-H bond  $\rightarrow$  MORE ACIDIC!*

## 3.2 Acidic Nature of Alkynes

### ★ Why Terminal Alkynes are Acidic (VERY IMPORTANT)

In alkynes ( $sp$  hybridized), the C–H bond has **50% s-character** (vs 25% in  $sp^3$  and 33% in  $sp^2$ ).

Higher s-character  $\rightarrow$  electrons closer to nucleus  $\rightarrow$  more electronegative carbon  $\rightarrow$  **H released more easily as  $H^+$**

**Acidity order:** Alkyne ( $sp$ ) > Alkene ( $sp^2$ ) > Alkane ( $sp^3$ )

$HC\equiv CH + NaNH_2 \rightarrow HC\equiv C^-Na^+ + NH_3$  (sodium acetylide formed)

$HC\equiv CH + AgNO_3$  (amm.)  $\rightarrow HC\equiv C-Ag\downarrow + HNO_3$  (silver acetylide — white ppt)

*This reaction is used to distinguish terminal alkynes from non-terminal alkynes and alkenes!*

## 3.3 Preparation of Alkynes

### Important Methods

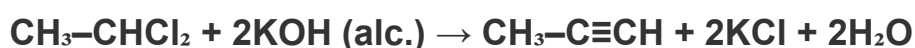
#### 1. From Calcium Carbide (Industrial method for Ethyne)



#### 2. Dehydrohalogenation of Vicinal Dihalides



#### 3. From Alkyl Dihalides (Geminal)



## 3.4 Chemical Reactions of Alkynes

### A. Addition Reactions (Electrophilic Addition)

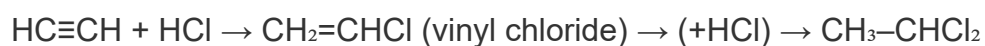
Alkynes undergo addition in two stages (can add 2 moles of reagent).

#### Hydrogenation:



*Lindlar's catalyst (Pd/BaSO<sub>4</sub> + quinoline) gives only cis-alkene (partial hydrogenation)*

#### Addition of HX:



Markovnikov's rule applies at second step!

#### Addition of Water (Hydration):



This is Markovnikov addition — gives *enol* first, which tautomerises to ketone/aldehyde

### Memory Trick for Alkyne Reactions:

#### "Alkynes Add Twice, Acidic at Terminal!"

- Add HX → vinyl halide → gem-dihalide
- Add H<sub>2</sub>O → aldehyde/ketone (via enol tautomerism)
- Terminal alkynes react with AgNO<sub>3</sub>, CuCl to give precipitates (identification test)

## SECTION 4: AROMATIC HYDROCARBONS

### (Benzene)

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#### 4.1 Discovery & Structure of Benzene

##### Historical Background

- **Faraday (1825)** — Isolated benzene from compressed illuminating gas
- **Kekulé (1865)** — Proposed cyclic structure with alternating single and double bonds
- Benzene formula:  $C_6H_6$
- Problem with Kekulé structure: Predicts two types of 1,2-dibromobenzene (but only one exists!)
- **Modern explanation:** Benzene has delocalized  $\pi$  electrons — all C–C bonds are equivalent (bond length = 139 pm, between single 154 pm and double 134 pm)

## Resonance in Benzene

Benzene is best represented as a **resonance hybrid** of two Kekulé structures and other minor contributors.

All 6 carbon atoms: **sp<sup>2</sup> hybridized**

Each carbon has one unhybridized p orbital → together form a **delocalized π electron cloud** above and below the ring

All C–C bond lengths: **139 pm** (equivalent → NOT alternating single/double)

All bond angles: **120°**

Shape: **Planar regular hexagon**

## 4.2 Aromaticity — Hückel's Rule

### ★ Hückel's Rule (MUST REMEMBER)

**A compound is aromatic if it is:**

1. Cyclic
2. Planar
3. Completely conjugated (alternating single and double bonds, or lone pairs)
4. Has **(4n + 2) π electrons** (where n = 0, 1, 2, 3...)

Benzene: 6 π electrons →  $4(1)+2 = 6$  ✓ (n=1) → Aromatic!

### Aromatic vs Anti-aromatic vs Non-aromatic

Compound	$\pi$ electrons	$4n+2?$	Classification
Benzene ( $C_6H_6$ )	6	Yes ( $n=1$ )	Aromatic
Naphthalene ( $C_{10}H_8$ )	10	Yes ( $n=2$ )	Aromatic
Cyclobutadiene	4	No ( $4n$ , $n=1$ )	Anti-aromatic
Cyclooctatetraene	8	No ( $4n$ , $n=2$ )	Non-aromatic (tub shaped)
Pyridine ( $C_5H_5N$ )	6	Yes ( $n=1$ )	Aromatic

## 4.3 Electrophilic Aromatic Substitution (EAS) — KEY REACTIONS

### General Mechanism of EAS

Benzene is electron-rich (due to  $\pi$  cloud)  $\rightarrow$  attacks electrophile ( $E^+$ )

**Step 1:**  $E^+$  attacks benzene  $\rightarrow$  forms *arenium ion / sigma complex / Wheland intermediate*

**Step 2:** Loss of  $H^+$  from sigma complex  $\rightarrow$  restores aromaticity  $\rightarrow$  substituted benzene

*Note: Unlike alkenes (addition), benzene undergoes SUBSTITUTION to preserve aromaticity!*

Reaction	Reagent	Electrophile	Product
Halogenation	$Cl_2$ or $Br_2$ / Lewis acid ( $FeCl_3$ , $AlCl_3$ )	$Cl^+$ or $Br^+$	Chlorobenzene / Bromobenzene
Nitration	Conc. $HNO_3$ + Conc. $H_2SO_4$ ( $55^\circ C$ )	$NO_2^+$ (Nitronium ion)	Nitrobenzene
Sulphonation	Fuming $H_2SO_4$ (Oleum)	$SO_3$ (electrophile)	Benzenesulphonic acid
Friedel-Crafts Alkylation	$R-X$ / $AlCl_3$	$R^+$ (carbocation)	Alkylbenzene
Friedel-Crafts Acylation	$R-CO-X$ / $AlCl_3$	$RCO^+$ (acylium ion)	Aryl ketone

## 4.4 Directing Effects of Substituents

### Ortho/Para vs Meta Directors — KEY FOR EXAMS

**Ortho/Para (o/p) Directors:** Activate the ring → direct incoming group to ortho and para positions

- $-\text{OH}$ ,  $-\text{NH}_2$ ,  $-\text{NHR}$ ,  $-\text{OCH}_3$ ,  $-\text{CH}_3$ ,  $-\text{X}$  (halogens)
- Electron-donating groups (EDG) are generally o/p directors
- Exception: Halogens are deactivators but still o/p directors!

**Meta (m) Directors:** Deactivate the ring → direct incoming group to meta position

- $-\text{NO}_2$ ,  $-\text{CN}$ ,  $-\text{CHO}$ ,  $-\text{COOH}$ ,  $-\text{SO}_3\text{H}$ ,  $-\text{COR}$
- Electron-withdrawing groups (EWG) are meta directors

### Memory Trick for Directors:

**o/p Directors = "OH, NH, alkyl, halogen" (think of them as FRIENDS of benzene)**

**Meta Directors = "NO<sub>2</sub>, CN, CHO, COOH, SO<sub>3</sub>H" (think of them as ENEMIES)**

Friends → ortho/para | Enemies → meta

## 4.5 Carcinogenicity & Toxicity

### ⚠ Health Hazards of Hydrocarbons

- Benzene and polynuclear aromatic hydrocarbons (PAHs like benzo[a]pyrene) are **carcinogenic**
- PAHs are formed during incomplete combustion of organic material
- Found in cigarette smoke, grilled food, vehicle exhaust
- CO from incomplete combustion of alkanes is **toxic** — binds haemoglobin (forms carboxyhaemoglobin)
- Benzene vapours: prolonged exposure causes **leukaemia**

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## CASE-BASED QUESTIONS (New CBSE Pattern)

### Case Study 1: The Miracle Molecule — Methane

Methane (CH<sub>4</sub>) is the simplest alkane and the major component of natural gas (CNG). It is produced naturally in swamps by anaerobic decomposition of organic matter and hence called "marsh gas." Its free radical halogenation with chlorine in sunlight is a chain reaction. Methane is also a potent greenhouse gas — 25 times more effective than CO<sub>2</sub> over 100 years.

**Q1. What type of hybridization do carbon atoms in methane have?**

*Ans: sp<sup>3</sup> hybridization; bond angle = 109.5°; tetrahedral geometry.*

**Q2. Write the chain initiation step for chlorination of methane.**

*Ans: Cl<sub>2</sub> → (hv) → 2Cl• (homolytic cleavage)*

**Q3. What does the term "chain propagation" mean in free radical mechanism?**

*Ans: Steps in which radicals are continuously produced and consumed, sustaining the chain reaction without external energy input.*

**Q4. Name two chain termination steps in the chlorination of methane.**

*Ans: Cl• + Cl• → Cl<sub>2</sub>; CH<sub>3</sub>• + Cl• → CH<sub>3</sub>Cl*

## Case Study 2: Alkenes in Industry

Alkenes are among the most important industrial chemicals. Ethylene (ethene) is the most produced organic chemical in the world — used to make polyethylene, ethanol, and ethylene oxide. The addition reactions of alkenes are the foundation of plastics, pharmaceuticals, and fuel additives. Markovnikov's rule governs the regioselectivity of HX addition, while Saytzeff's rule governs elimination reactions. Ozonolysis is used in structural determination of unknown alkenes.

**Q1. Predict the major product when HBr adds to propene in the absence of peroxide.**

*Ans: 2-bromopropane ( $\text{CH}_3\text{CHBrCH}_3$ ) — Markovnikov's rule*

**Q2. What happens when propene reacts with HBr in the presence of benzoyl peroxide?**

*Ans: 1-bromopropane ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ ) — Anti-Markovnikov (peroxide effect / free radical addition)*

**Q3. Cold dilute  $\text{KMnO}_4$  is added to ethene. Name the product and type of reaction.**

*Ans: Ethylene glycol (ethan-1,2-diol) — Hydroxylation (syn addition); Baeyer's reagent test —  $\text{KMnO}_4$  is decolourised.*

**Q4. What is the significance of Saytzeff's rule?**

*Ans: It predicts that the major product of dehydrohalogenation/dehydration is the most substituted (more stable) alkene.*

### Case Study 3: Benzene and EAS Reactions

Benzene undergoes electrophilic aromatic substitution (EAS) rather than addition, because addition would destroy the aromatic stabilization (resonance energy = 36 kcal/mol). The sigma complex (arenium ion) intermediate loses a proton to regenerate the aromatic ring. Substituents already present on the ring either activate or deactivate the ring and direct the incoming electrophile to specific positions.

#### Q1. Why does benzene prefer substitution over addition reactions?

*Ans: To preserve aromaticity — addition would destroy the delocalized  $\pi$  system and the extra stability (resonance energy) associated with it.*

#### Q2. What is the electrophile in nitration of benzene? How is it generated?

*Ans: Nitronium ion ( $\text{NO}_2^+$ ). Generated by:  $\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{HSO}_4^- + \text{H}_2\text{O}$*

#### Q3. Toluene (methylbenzene) is more reactive than benzene in EAS. Explain.

*Ans:  $-\text{CH}_3$  is an electron-donating (ortho/para directing) group. It increases electron density on the ring, especially at ortho and para positions, making it easier for the electrophile to attack.  $\rightarrow$  Ring is activated.*

#### Q4. In Friedel-Crafts alkylation, why is rearrangement of carbocation a problem?

*Ans: The carbocation ( $\text{R}^+$ ) formed can rearrange to a more stable (more substituted) carbocation before attacking benzene, giving unexpected (rearranged) products.*

# MOST EXPECTED QUESTIONS FOR BOARD EXAM

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## Very Short Answer Questions (1 Mark)

1. Write the general formula for alkynes.
2. State Markovnikov's rule.
3. What is the hybridization of carbon in benzene?
4. Name the product formed when ethyne reacts with water in presence of  $\text{H}_2\text{SO}_4/\text{HgSO}_4$ .
5. What is the electrophile in sulphonation of benzene?
6. Define geometrical isomerism.
7. Write the IUPAC name of  $\text{CH}_3\text{-CH=CH-CH}_3$ .
8. Why do alkynes show acidic character?
9. What is the Lindlar's catalyst used for?
10. State Hückel's rule for aromaticity.

## Short Answer Questions (2–3 Marks)

1. Write the mechanism of free radical chlorination of methane. (3 marks)
2. Distinguish between cis and trans isomers of but-2-ene with examples. (2 marks)
3. Explain why benzene undergoes electrophilic substitution rather than electrophilic addition. (3 marks)
4. What is the Peroxide Effect? Explain with an example. (3 marks)
5. How is ethyne prepared from calcium carbide? Write the balanced equation. (2 marks)
6. What happens when ethene reacts with (a) cold dilute  $\text{KMnO}_4$  and (b) hot conc.  $\text{KMnO}_4$ ? (2 marks)
7. Compare the acidic character of alkynes, alkenes, and alkanes. Explain. (3 marks)
8. Explain the Friedel-Crafts alkylation of benzene with a suitable example. (3 marks)
9. Write the products of ozonolysis of but-2-ene. (2 marks)
10. What are the conditions for a compound to show geometrical isomerism? (2 marks)

## Long Answer Questions (5 Marks)

1. **(a)** Explain the mechanism of electrophilic addition of HBr to propene. **(b)** What is the Anti-Markovnikov product? How is it formed? (5 marks)
2. **(a)** What is aromaticity? State Hückel's rule. **(b)** Describe the structure of benzene on the basis of molecular orbital theory. **(c)** Explain why benzene has equal C–C bond lengths. (5 marks)
3. **(a)** How is nitrobenzene prepared from benzene? Write the reaction mechanism. **(b)** Explain the directing effect of  $-\text{NO}_2$  group in further nitration. (5 marks)
4. **(a)** Explain conformational isomerism in ethane. **(b)** Which conformation is more stable and why? **(c)** What is torsional strain? (5 marks)



## EXAM PREPARATION STRATEGY

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### 30-Day Study Plan for Hydrocarbons:

1. **Days 1–3:** Alkane nomenclature, free radical mechanism — read + write mechanism 5 times
2. **Days 4–6:** Alkene reactions, Markovnikov's rule, geometrical isomerism — practice 10 questions
3. **Days 7–9:** Alkyne structure, acidic nature, preparation — write reactions
4. **Days 10–12:** Benzene structure, resonance, aromaticity (Hückel's rule)
5. **Days 13–16:** All 5 EAS reactions — write mechanism and directing effects
6. **Days 17–20:** Practice board-level questions (short + long answers)
7. **Days 21–25:** Case studies, previous year questions
8. **Days 26–28:** Formula sheet revision, mechanism writing speed practice
9. **Days 29–30:** Last-minute checklist and mock test

### ⚠️ Last Minute Checklist (1 Day Before Exam):

- Know hybridization:  $sp^3$  (alkane),  $sp^2$  (alkene),  $sp$  (alkyne)
- Memorize general formulas:  $C_nH_{2n+2}$ ,  $C_nH_{2n}$ ,  $C_nH_{2n-2}$ ,  $C_6H_6$
- Write free radical mechanism (initiation  $\rightarrow$  propagation  $\rightarrow$  termination)
- Revise Markovnikov's rule and Anti-Markovnikov with examples
- Revise Saytzeff's rule and conditions (KOH/alc.)
- Write all 5 EAS reactions of benzene (reagents + conditions)
- Memorize o/p and meta directors list
- Revise Hückel's rule with examples (aromatic vs anti-aromatic)
- Know Lindlar's catalyst and its use
- Revise acidic nature of alkynes with reaction with  $AgNO_3$  (amm.)

### 🎯 Exam Writing Tips:

1. **Always write balanced equations** with conditions above/below the arrow
2. **Show all steps in mechanism** — draw the intermediate clearly (carbocation, radical, sigma complex)
3. **Use curved arrows** in ionic mechanisms to show electron movement
4. **Label the products** (major/minor when applicable)
5. **State the rule/law** before applying it (Markovnikov's, Saytzeff's, Hückel's)
6. **For structure drawing** — draw clearly with all bond types (single, double, triple)
7. **Include conditions** — temperature, catalyst, solvent are part of the answer!



## Formula & Reactions Sheet — Write This for Quick

## Revision!

Concept	Key Formula / Reaction / Rule
Alkane formula	$C_nH_{2n+2}$ ; $sp^3$ ; $109.5^\circ$
Alkene formula	$C_nH_{2n}$ ; $sp^2$ ; $120^\circ$ ; $C=C$ ( $1\sigma+1\pi$ )
Alkyne formula	$C_nH_{2n-2}$ ; $sp$ ; $180^\circ$ ; $C\equiv C$ ( $1\sigma+2\pi$ )
Markovnikov's Rule	H adds to C with more H; X to more substituted C
Anti-Markovnikov	HBr + peroxide $\rightarrow$ X to less substituted C
Saytzeff's Rule	Elimination $\rightarrow$ more substituted alkene is major product
Hückel's Rule	Aromatic: cyclic, planar, conjugated, $(4n+2)$ $\pi$ electrons
Benzene C–C bond length	139 pm (between single 154 pm & double 134 pm)
Nitration electrophile	$NO_2^+$ (nitronium ion) from $HNO_3 + H_2SO_4$
Friedel-Crafts	$R-X + \text{benzene} + AlCl_3 \rightarrow \text{alkylbenzene}$ ; $R-COCl + AlCl_3 \rightarrow \text{aryl ketone}$
Free Radical Steps	Initiation $\rightarrow$ Propagation $\rightarrow$ Termination
o/p Directors	$-OH$ , $-NH_2$ , $-CH_3$ , $-OCH_3$ , $-X$
Meta Directors	$-NO_2$ , $-CN$ , $-CHO$ , $-COOH$ , $-SO_3H$

**Alkyne acidic test**

**$\text{HC}\equiv\text{CH} + \text{AgNO}_3 \text{ (amm.)} \rightarrow \text{white ppt of silver acetylide}$**

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## QUICK REVISION NOTES

### Key Definitions (Must Know Word-to-Word)

- 1. Hydrocarbons:** Organic compounds containing only carbon and hydrogen atoms.
- 2. Alkanes:** Saturated hydrocarbons with general formula  $C_nH_{2n+2}$ , containing only C–C single bonds.
- 3. Alkenes:** Unsaturated hydrocarbons containing at least one C=C double bond; general formula  $C_nH_{2n}$ .
- 4. Alkynes:** Unsaturated hydrocarbons containing at least one C≡C triple bond; general formula  $C_nH_{2n-2}$ .
- 5. Markovnikov's Rule:** In addition of HX to an unsymmetrical alkene, H attaches to carbon with more hydrogen atoms, and X to carbon with fewer hydrogen atoms.
- 6. Saytzeff's Rule:** In elimination reactions, the alkene with the greater number of alkyl substituents on the doubly bonded carbon (more substituted, more stable) is formed as the major product.
- 7. Aromaticity (Hückel's Rule):** A compound is aromatic if it is cyclic, planar, completely conjugated, and contains  $(4n+2)$   $\pi$  electrons.
- 8. Electrophilic Aromatic Substitution:** A reaction in which an electrophile replaces a hydrogen atom on an aromatic ring, preserving aromaticity.
- 9. Geometrical Isomerism:** Type of stereoisomerism arising due to restricted rotation about C=C bond when each  $sp^2$  carbon carries two different substituents.
- 10. Free Radical:** A species with one unpaired electron (e.g.,  $Cl\cdot$ ,  $CH_3\cdot$ ) formed by homolytic bond cleavage, involved in chain reactions.

## ⚡ One-Line Facts (Speed Revision)

- Alkane C:  $sp^3$  | Alkene C:  $sp^2$  | Alkyne C:  $sp$
- Benzene bond length = 139 pm (equal for all C–C)
- Benzene resonance energy  $\approx$  150 kJ/mol
- Reactivity of halogens:  $F_2 > Cl_2 > Br_2 > I_2$
- Lindlar's catalyst  $\rightarrow$  partial hydrogenation  $\rightarrow$  cis-alkene only
- Na/liq.  $NH_3$  (Birch reduction)  $\rightarrow$  trans-alkene
- $KMnO_4$  (cold, dil.)  $\rightarrow$  diol |  $KMnO_4$  (hot, conc.)  $\rightarrow$  cleavage
- Ozonolysis of terminal alkene  $\rightarrow$  aldehyde + formaldehyde
- Terminal alkynes give white ppt with  $AgNO_3$  (ammoniacal)
- Benzene vapours are carcinogenic  $\rightarrow$  avoid prolonged exposure
- $CaC_2 + H_2O \rightarrow$  acetylene (ethyne) — industrial source
- Wurtz reaction:  $2RX + 2Na \rightarrow R-R + 2NaX$
- Tautomerism of enol  $\rightarrow$  keto form:  $CH_2=CHOH \rightarrow CH_3CHO$
- $NO_2$  group: meta director + deactivator of benzene

## Top 10 Reaction Types (Practice These!)

1. Free radical halogenation of alkanes (write full mechanism)
2. Dehydration of alcohol to alkene
3. Markovnikov addition of HX to alkene
4. Anti-Markovnikov addition of HBr (peroxide)
5. Ozonolysis of alkenes (predict products)
6. Hydration of alkynes to aldehyde/ketone
7. Acidic nature test of terminal alkynes ( $\text{AgNO}_3$  test)
8. Nitration of benzene (mechanism)
9. Friedel-Crafts alkylation/acylation of benzene
10. Predicting o/p vs meta products for substituted benzenes

## Study Material Information

This comprehensive study material on **Hydrocarbons** has been meticulously prepared following the latest CBSE curriculum and examination pattern for Class 11 Chemistry (2025-26 session). The content includes detailed explanations of all topics — classification of hydrocarbons, alkanes (free radical mechanism, conformational isomerism), alkenes (Markovnikov's rule, geometrical isomerism, electrophilic addition), alkynes (acidic nature, preparation), aromatic hydrocarbons (benzene structure, resonance, Hückel's rule, all EAS reactions, directing effects), case-based questions as per new CBSE pattern, and most expected questions for board exams.

### Key Features of This Material:

- Complete Chapter 13 coverage with crystal-clear concepts
- Classification of hydrocarbons: aliphatic, aromatic, alicyclic
- Alkanes: nomenclature, conformations, halogenation mechanism
- Alkenes: geometrical isomerism, Markovnikov's and Saytzeff's rules
- Alkynes: acidic nature, Lindlar's catalyst, hydration to carbonyl
- Benzene: Kekulé structure, resonance, aromaticity (Hückel's rule)
- All 5 EAS reactions with mechanism and directing effects
- Memory tricks and shortcuts for reaction prediction
- 3 complete case studies as per latest CBSE pattern
- Most expected questions with detailed answers
- Common mistakes to avoid
- Exam preparation strategy and last-minute checklist
- Quick revision notes and comprehensive formula sheet

## Why Hydrocarbons is THE Turning Point:

Hydrocarbons is not just a chapter — it's the **gateway to all of Organic Chemistry!** The reaction mechanisms and functional group behavior learned here are used in:

- ✓ Haloalkanes & Haloarenes (Class 12)
- ✓ Alcohols, Phenols & Ethers
- ✓ Aldehydes, Ketones & Carboxylic Acids
- ✓ Amines
- ✓ JEE & NEET (Organic mechanism questions — 5-8 marks every year!)

**Master Hydrocarbons = 60% of Organic Chemistry becomes intuitive!**

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Content is based on NCERT syllabus and CBSE guidelines for 2025-26.

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*Disclaimer: This material is prepared as a comprehensive study aid for Class 11 students. While every effort has been made to ensure accuracy and alignment with CBSE curriculum, students are advised to refer to their NCERT textbooks and official CBSE guidelines for examination preparation. This material covers Chapter 13: Hydrocarbons from Class 11 Chemistry NCERT textbook (Reprint 2025-26). All reactions, mechanisms, and definitions are as per latest NCERT edition.*

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