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CHAPTER NOTES

Hydrocarbons Class 11 Notes | CBSE Chemistry Chapter 12

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Hydrocarbons Class 11 Notes | CBSE Chemistry Chapter 12

Hydrocarbons is Chapter 12 of CBSE Class 11 Chemistry — the chapter where organic chemistry stops being abstract and starts making sense. Everything from cooking gas (LPG) to petrol, from polythene bags to naphthalene balls, is a hydrocarbon. Master classification, the named reactions, and the substitution mechanisms here, and a huge slice of NEET, JEE, and your board organic paper becomes routine scoring.

By the end of these notes you will be able to name any alkane, alkene, or alkyne by IUPAC rules, predict the product of Markovnikov, anti-Markovnikov, ozonolysis, and Friedel-Crafts reactions, explain benzene's aromaticity, and apply the directive influence of groups in electrophilic substitution. This is a high-weightage chapter carrying roughly 6–8 marks in boards, and the launchpad for the entire Class 12 organic syllabus.

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Key Concepts

1. Classification of Hydrocarbons

Hydrocarbons are compounds made of only carbon and hydrogen. The way the carbon atoms are joined decides everything about their behaviour, so we classify them first.

- **Saturated (alkanes):** only C–C single bonds. General formula C_nH_{2n+2}. Example: methane CH_4, ethane C_2H_6.
- **Unsaturated (alkenes & alkynes):** contain C=C or C≡C. Alkenes C_nH_{2n} (ethene C_2H_4); alkynes C_nH_{2n-2} (ethyne C_2H_2).
- **Aromatic:** contain a benzene ring (or fused rings) with delocalised π electrons. Example: benzene C_6H_6.

[DIAGRAM: A tree — Hydrocarbons branching into Aliphatic (acyclic + alicyclic) and Aromatic; aliphatic further splitting into saturated alkanes and unsaturated alkenes/alkynes.]

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2. Alkanes — Nomenclature and Isomerism

Alkanes are saturated open-chain hydrocarbons (C_nH_{2n+2}) in which carbon is sp^3 hybridised with bond angles of 109.5°. They are also called paraffins because of their low reactivity.

IUPAC naming: pick the longest chain (root word), number it so substituents get the lowest locants, name substituents alphabetically as prefixes, and end with "-ane".

For example, $(CH_3)_2CHCH_2CH_3$ is **2-methylbutane** — a four-carbon main chain with a methyl branch at C-2.

Chain (Structural) Isomerism

Alkanes from butane onward show **chain isomerism** — same molecular formula, different skeletons. C_4H_{10} has two isomers (n-butane and isobutane); C_5H_{12} has three; C_6H_{14} has five.

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3. Conformations of Alkanes

Conformations are the different spatial arrangements obtained by rotation about a C–C single bond. They are not isomers because they interconvert freely and cannot be isolated.

- **Staggered:** hydrogen atoms of the two carbons are as far apart as possible — minimum repulsion, most stable.
- **Eclipsed:** hydrogen atoms directly overlap — maximum torsional strain, least stable.

For ethane the energy difference between staggered and eclipsed forms is only about 12.5 kJ/mol, so rotation is essentially free at room temperature.

[DIAGRAM: Newman projections of ethane — staggered (back H's at 60° to front H's) versus eclipsed (back H's directly behind front H's).]

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4. Preparation of Alkanes

Alkanes are made by adding hydrogen to unsaturated compounds or by removing functional groups.

- **Hydrogenation (Sabatier–Senderens):** alkene + H_2 → alkane, using Ni/Pt/Pd catalyst.
- **Wurtz reaction:** 2R–X + 2Na → R–R + 2NaX (gives symmetrical alkanes with an even number of carbons).
- **Decarboxylation:** sodium salt of a carboxylic acid + soda lime → alkane with one less carbon. $CH_3COONa + NaOH \rightarrow CH_4 + Na_2CO_3$.
- **Kolbe's electrolysis:** electrolysis of aqueous sodium carboxylate gives an alkane at the anode.

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5. Properties of Alkanes & Mechanism of Halogenation

Alkanes are non-polar, insoluble in water, and generally unreactive. Their most important reaction is **free-radical substitution** with halogens in sunlight (UV light).

$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$ (continues to CH_2Cl_2, $CHCl_3$, CCl_4)

Free-Radical Mechanism (Chlorination of Methane)

- **Initiation:** $Cl_2 \rightarrow 2Cl\bullet$ (homolytic cleavage by UV light).
- **Propagation:** $Cl\bullet + CH_4 \rightarrow \bullet CH_3 + HCl$; then $\bullet CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\bullet$.
- **Termination:** radicals combine — $Cl\bullet + Cl\bullet \rightarrow Cl_2$, $\bullet CH_3 + Cl\bullet \rightarrow CH_3Cl$, $\bullet CH_3 + \bullet CH_3 \rightarrow C_2H_6$.

Reactivity order of halogens: $F_2 > Cl_2 > Br_2 > I_2$. Fluorination is explosive; iodination is reversible and slow.

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6. Alkenes — Structure and Nomenclature

Alkenes (C_nH_{2n}) contain at least one C=C double bond. The doubly bonded carbons are sp^2 hybridised with bond angles near 120°; the double bond is one strong σ bond plus one weaker π bond.

IUPAC names end in "-ene" and the chain is numbered to give the double bond the lowest locant. For example $CH_3–CH=CH–CH_3$ is **but-2-ene**.

Geometrical (cis–trans) Isomerism

Because rotation about C=C is restricted, alkenes can show **geometrical isomerism** when each doubly bonded carbon carries two different groups.

- **cis:** identical groups on the same side.
- **trans:** identical groups on opposite sides (usually more stable).

But-2-ene exists as cis- and trans- forms; but-1-ene does not (one carbon carries two H atoms).

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7. Preparation and Properties of Alkenes

Alkenes are made by **elimination** reactions that introduce a double bond.

- **Dehydrohalogenation:** alkyl halide + alc. KOH → alkene + KX + H_2O.
- **Dehydration of alcohols:** alcohol + conc. H_2SO_4 (heat) → alkene + H_2O.
- **Dehalogenation:** vicinal dihalide + Zn → alkene.

Their characteristic chemistry is **electrophilic addition** across the electron-rich double bond: addition of H_2, X_2, HX, H_2O, etc.

Baeyer's test: alkenes decolourise cold dilute alkaline $KMnO_4$ (purple → colourless), giving a vicinal glycol — a test for unsaturation.

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8. Markovnikov & Anti-Markovnikov (Peroxide Effect)

When an unsymmetrical reagent like HBr adds to an unsymmetrical alkene, the orientation matters.

Markovnikov's rule: the negative part of the reagent adds to the carbon bearing the *fewer* hydrogen atoms (the H goes to the carbon already having more H's). This is because the more stable carbocation forms preferentially.

$CH_3–CH=CH_2$ + HBr → **$CH_3–CHBr–CH_3$** (2-bromopropane).

Anti-Markovnikov Addition (Kharasch / Peroxide Effect)

In the presence of organic **peroxides**, HBr (only HBr) adds against Markovnikov's rule, via a free-radical mechanism.

$CH_3–CH=CH_2$ + HBr (peroxide) → **$CH_3–CH_2–CH_2Br$** (1-bromopropane).

Note: HCl and HI do not show the peroxide effect.

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9. Ozonolysis of Alkenes

Ozonolysis is the cleavage of a C=C double bond by ozone to locate its position. The alkene reacts with O_3 to form an ozonide, which on reductive cleavage (Zn/H_2O) gives two carbonyl compounds.

$CH_3–CH=CH_2$ → CH_3CHO + HCHO (ethanal + methanal)

By identifying the aldehydes/ketones formed, we can pinpoint where the double bond was in the original alkene — a favourite reasoning question.

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10. Alkynes — Preparation and Acidic Character

Alkynes (C_nH_{2n-2}) contain a C≡C triple bond; the carbons are sp hybridised, linear, with 180° bond angles. The triple bond is one σ and two π bonds.

Preparation

- Ethyne from calcium carbide: $CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2$.
- Double dehydrohalogenation of vicinal/geminal dihalides with alc. KOH.

Acidic Character of Terminal Alkynes

The H attached to a triply bonded (sp) carbon is **acidic** because the sp carbon, with 50% s-character, holds the bonding electrons tightly. Terminal alkynes therefore react with sodium and ammoniacal $AgNO_3/Cu_2Cl_2$.

$HC≡CH + Na \rightarrow HC≡C^-Na^+ + ½H_2$; $HC≡CH + 2[Ag(NH_3)_2]^+ \rightarrow Ag–C≡C–Ag$ (white ppt) — a test for terminal alkynes.

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11. Addition Reactions of Alkynes

Like alkenes, alkynes undergo electrophilic addition, but in two stages (across each π bond).

- **Hydrogenation:** with $Pd/BaSO_4$ (Lindlar's catalyst) gives cis-alkene; with Ni gives the alkane.

- **Addition of water:** $C_2H_2 + H_2O$ (dil. H_2SO_4, $HgSO_4$) → CH_3CHO (acetaldehyde), via an unstable enol.
- **Polymerisation:** 3 ethyne molecules cyclise (red-hot tube) to give **benzene**.

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12. Aromatic Hydrocarbons — Benzene Structure & Aromaticity

Aromatic hydrocarbons (arenes) contain the benzene ring. Benzene (C_6H_6) is a flat, regular hexagon with all C–C bond lengths equal (139 pm), intermediate between single and double bonds.

Each carbon is sp^2 hybridised; the six unhybridised p-orbitals overlap to form a **delocalised π electron cloud** above and below the ring — this delocalisation gives benzene its unusual stability (resonance energy ≈ 152 kJ/mol).

Hückel's Rule (Aromaticity)

A compound is **aromatic** if it is planar, cyclic, fully conjugated, and contains **(4n + 2) π electrons** (n = 0, 1, 2…). Benzene has 6 π electrons (n = 1), so it is aromatic.

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13. Electrophilic Substitution in Benzene

Because the π cloud is electron-rich but stable, benzene prefers **substitution** over addition — it keeps the ring intact. The general mechanism has three steps.

- **Generation of electrophile (E^+).**
- **Attack of E^+ on the ring** → arenium ion (carbocation, σ-complex), resonance stabilised.
- **Loss of H^+** restoring aromaticity → substituted benzene.

Reaction	Reagents	Electrophile	Product
Nitration	conc. HNO_3 + conc. H_2SO_4	NO_2^+ (nitronium ion)	Nitrobenzene
Sulphonation	fuming H_2SO_4 (SO_3)	SO_3 / $^+SO_3H$	Benzenesulphonic acid
Halogenation	X_2 + anhyd. FeX_3 / AlX_3	X^+	Halobenzene
Friedel–Crafts alkylation	R–X + anhyd. $AlCl_3$	R^+ (carbocation)	Alkylbenzene
Friedel–Crafts acylation	RCOCl + anhyd. $AlCl_3$	RCO^+ (acylium ion)	Aryl ketone

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14. Directive Influence of Substituents

A group already present on the ring decides *where* the next group goes and whether reaction is faster or slower.

- **Ortho/para-directing, activating:** –OH, $–NH_2$, –OR, $–CH_3$, –alkyl. They release electrons, speed up substitution, and direct the new group to the 2- and 4- positions.

- **Meta-directing, deactivating:** $-NO_2$, –COOH, –CHO, $-SO_3H$, –CN. They withdraw electrons, slow substitution, and direct to the 3- position.
- **Exception:** halogens (–Cl, –Br) are deactivating but still ortho/para-directing.

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15. Carcinogenicity and Toxicity

Benzene and polynuclear aromatic hydrocarbons are not just exam topics — they are health hazards. **Polynuclear hydrocarbons** such as benz[a]pyrene, formed by incomplete combustion of tobacco, coal, and petrol, are **carcinogenic** (cancer-causing).

These compounds enter the body, get metabolised, and damage DNA, which can trigger cancer. This is why prolonged exposure to vehicle exhaust and cigarette smoke is dangerous.

Weightage in Board & Entrance Exams

Exam	Typical Weightage	Most-Tested Areas
CBSE Board (Class 11)	6–8 marks	IUPAC naming, Markovnikov, mechanisms, directive influence
JEE Main / Advanced	2–3 questions	Ozonolysis, peroxide effect, aromaticity, reaction sequences
NEET	2–3 questions	Named reactions, acidic character of alkynes, aromatic substitution

[TABLE: Question-type split — VSA (1 mark): definitions & reagents; SA (2–3 marks): mechanisms, Markovnikov products, conformations; LA (5 marks): full electrophilic substitution mechanism, directive influence reasoning.]

Important Definitions

Term	Definition
Hydrocarbon	A compound containing only carbon and hydrogen
Alkane	Saturated hydrocarbon with only C–C single bonds: C_nH_{2n+2}
Alkene	Unsaturated hydrocarbon with a C=C double bond: C_nH_{2n}
Alkyne	Unsaturated hydrocarbon with a C≡C triple bond: C_nH_{2n-2}
Conformation	Spatial arrangement from rotation about a C–C single bond (e.g. staggered, eclipsed)
Markovnikov's rule	Negative part of HX adds to the carbon with fewer H atoms (more stable carbocation)
Peroxide effect	Anti-Markovnikov addition of HBr to alkenes in presence of peroxides
Ozonolysis	Cleavage of C=C by ozone to give carbonyl compounds, locating the double bond
Aromaticity	Extra stability of planar, cyclic, conjugated rings with (4n+2) π electrons (Hückel's rule)
Electrophilic substitution	Replacement of a ring H by an electrophile, keeping aromaticity intact

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Solved Examples

Example 1

Write the IUPAC name of $(CH_3)_3C–CH_2–CH_3$.

Answer: Longest chain = pentane (5 C); two methyl groups on C-2. Name: **2,2-dimethylbutane** (main chain is butane, with two methyls at C-2).

Example 2

Predict the product when propene reacts with HBr (a) without peroxide and (b) with peroxide.

Answer: (a) Markovnikov → **2-bromopropane** ($CH_3CHBrCH_3$). (b) Anti-Markovnikov (peroxide effect) → **1-bromopropane** ($CH_3CH_2CH_2Br$).

Example 3

An alkene on ozonolysis gives only acetone (propanone). Identify the alkene.

Answer: Two acetone units join at the carbonyl carbons → $(CH_3)_2C=C(CH_3)_2$, i.e. **2,3-dimethylbut-2-ene**.

Example 4

Why is ethyne more acidic than ethene and ethane?

Answer: The acidic H is on an **sp** carbon (50% s-character) in ethyne, which holds the electron pair closer to the nucleus, stabilising the carbanion. Order of acidity: ethyne (sp) > ethene (sp^2) > ethane (sp^3).

Example 5

Name the electrophile in the nitration of benzene and write the reagents used.

Answer: Electrophile = **nitronium ion, NO_2^+**; reagents = conc. HNO_3 + conc. H_2SO_4 (nitrating mixture). Product = nitrobenzene.

Example 6

Toluene (methylbenzene) is nitrated. Predict the major products and explain.

Answer: $-CH_3$ is an **ortho/para-directing, activating** group, so nitration gives mainly **o-nitrotoluene and p-nitrotoluene**, and the reaction is faster than for benzene.

Important Questions for Board Exams

1-Mark Questions (VSA)

1. Write the general formula of alkanes, alkenes, and alkynes.
2. Why does benzene undergo substitution rather than addition?
3. Name the catalyst used to convert an alkyne to a cis-alkene.
4. What is the electrophile in Friedel–Crafts acylation?
5. Which alkene shows geometrical isomerism — but-1-ene or but-2-ene? Why?

2–3-Mark Questions (SA)

1. State Markovnikov's rule and illustrate with the addition of HBr to propene.
2. Explain the peroxide effect with a suitable example and mechanism outline.
3. Draw and compare the staggered and eclipsed conformations of ethane; state which is more stable and why.
4. Explain why terminal alkynes are acidic but alkenes and alkanes are not.

5-Mark Questions (LA)

1. Describe the free-radical mechanism of chlorination of methane (initiation, propagation, termination).
2. Explain the mechanism of electrophilic substitution in benzene, taking nitration as an example.

3. Discuss the directive influence of substituents in benzene with examples of ortho/para- and meta-directing groups.

Quick Revision Points

- Alkanes C_nH_{2n+2} (sp^3, 109.5°); alkenes C_nH_{2n} (sp^2, 120°); alkynes C_nH_{2n-2} (sp, 180°)
- Conformations: staggered (stable) vs eclipsed (least stable); not isomers
- Alkane prep: hydrogenation, Wurtz, decarboxylation, Kolbe's electrolysis
- Halogenation of alkanes = free-radical substitution (UV); $F_2 > Cl_2 > Br_2 > I_2$
- Markovnikov: negative part to C with fewer H; peroxide effect = anti-Markovnikov (HBr only)
- Ozonolysis locates C=C → gives two carbonyl compounds
- Terminal alkyne H is acidic (sp carbon); gives white ppt with ammoniacal $AgNO_3$
- 3 C_2H_2 → benzene; benzene is aromatic by Hückel's (4n+2) rule, 6 π electrons
- Electrophiles: nitration NO_2^+, sulphonation SO_3, halogenation X^+, F–C R^+/RCO^+
- –OH, $–NH_2$, $–CH_3$ are o/p-directing activators; $–NO_2$, –COOH are m-directing deactivators; halogens o/p but deactivating
- Polynuclear aromatics (e.g. benz[a]pyrene) are carcinogenic

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Next Chapter: Chapter 14 — Environmental Chemistry