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CUET · CHEMISTRY · CLASS XI · CODE 306

Hydrocarbons

CUET unit: Hydrocarbons

By **UniDrill** · NCERT-grounded study material

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📌 Snapshot

- Hydrocarbons (compounds of C and H only) are classified into saturated (alkanes, cycloalkanes), unsaturated (alkenes, alkynes) and aromatic; petroleum and natural gas are the main industrial sources (NCERT §9.1, p. 295–296).
- Each class has its own preparation routes, physical trends and named chemical reactions — Wurtz, Kolbe, decarboxylation and hydrogenation for alkanes; Markovnikov/Kharasch, ozonolysis and Baeyer's test for alkenes; Lindlar/Na-liquid NH_3 reductions, acidity of 1-alkynes and Reppe polymerisation for alkynes; electrophilic aromatic substitution and directive effects for arenes.
- Conformations of ethane (staggered vs eclipsed, $\Delta E \approx 12.5$ kJ mol^{-1}) and geometrical isomerism of alkenes (cis–trans) are the stereochemistry anchors (NCERT §9.2.4, p. 305; §9.3.3, p. 308).
- Benzene's structure is explained via Kekulé → resonance → MO delocalisation, and aromaticity by Hückel's $(4n+2)\pi$ rule (NCERT §9.5.2–9.5.3, p. 319–321).
- CUET typically asks Markovnikov product, ozonolysis fragments, EAS mechanism and o/p- vs m-directing influence — all covered here.

📖 Detailed Notes

2.1 Core concepts

- Hydrocarbons are classified by C–C bond type: saturated open-chain (alkanes, C_nH_{2n+2}), saturated cyclic (cycloalkanes), unsaturated (alkenes C_nH_{2n}, alkynes C_nH_{2n-2}) and aromatic arenes; methane (sp^3, all H–C–H = 109.5°) is the simplest alkane (NCERT §9.1–9.2, p. 295–296).
- Alkane nomenclature: longest chain, lowest locants, alphabetical substituent order; isomerism is chain (skeletal) — C_4H_{10} has 2, C_5H_{12} has 3, C_6H_{14} has 5, $C_{10}H_{22}$ has 75 isomers (NCERT §9.2.1, p. 297–298).
- Alkane preparation: (a) catalytic hydrogenation of alkenes/alkynes over Pt/Pd/Ni (eqs 9.1–9.3), (b) reduction of alkyl halides with Zn/dil. HCl (eq 9.4) — fluorides excluded, (c) Wurtz reaction — alkyl halide + Na in dry ether → higher alkane with even number of C (eq 9.7–9.8), (d) decarboxylation of sodium salt of carboxylic acid with sodalime giving an alkane with one C less (eq 9.9-context), (e) Kolbe electrolysis of aqueous sodium/potassium carboxylate giving an alkane with even number of C

atoms at the anode — methane cannot be made this way (NCERT §9.2.2, p. 300–301).

- Alkane physical properties: non-polar, weak van der Waals; C1–C4 gases, C5–C17 liquids, $\geqslant$C18 solids; b.p. rises with molecular mass but branching lowers b.p. (n-pentane 309.1 K > isopentane > neopentane) (NCERT §9.2.3, p. 301–302).
- Alkane chemical reactions: (1) free-radical halogenation in sunlight/UV/heat — initiation (Cl2 homolysis), propagation (Cl· + CH4 → ·CH3 + HCl; ·CH3 + Cl2 → CH3Cl + Cl·), termination (Cl·+Cl·, ·CH3+·CH3 → ethane explains C2H6 by-product) — reactivity F2 > Cl2 > Br2 > I2 (NCERT §9.2.3, p. 302–303); (2) combustion: CnH2n+2 + (3n+1)/2 O2 → nCO2 + (n+1)H2O (eq 9.19); (3) controlled oxidation gives CH3OH (Cu, 523 K, 100 atm), HCHO (Mo2O3), CH3COOH ((CH3COO)2Mn), and 3°-H alkanes → 3° alcohols with KMnO4 (eqs 9.21–9.24); (4) isomerisation of n-hexane to methylpentanes with anhyd. AlCl3/HCl (eq 9.25); (5) aromatisation/reforming: n-alkanes with $\geqslant$6 C at 773 K / 10–20 atm over V/Mo/Cr–Al2O3 → benzene/toluene (eq 9.26); (6) reaction with steam (Ni, 1273 K) → CO + 3H2; (7) pyrolysis/cracking — dodecane at 973 K → heptane + pentene (eq 9.29).
- Conformations of ethane: free rotation about C–C σ bond gives infinite conformers; two extremes — staggered (H atoms farthest apart, minimum torsional strain, most stable) and eclipsed (H atoms closest, max strain, least stable); skew = intermediate; ΔE(eclipsed – staggered) ≈ 12.5 kJ mol^{-1}, so rotation is essentially free at room temperature and conformers cannot be isolated; represented by Sawhorse and Newman projections (NCERT §9.2.4, p. 305–306).
- Alkene structure: C=C is one σ (sp^2–sp^2 head-on, 397 kJ mol^{-1}) + one weaker π (2p–2p sideways, 284 kJ mol^{-1}); total C=C bond enthalpy 681 kJ mol^{-1}; C=C bond length 134 pm (< C–C 154 pm); the loosely held π electrons make alkenes susceptible to electrophiles (NCERT §9.3.1, p. 306).
- Alkene nomenclature: longest chain containing C=C, suffix "-ene", number from the end nearer the double bond; alkene isomerism is structural (chain + position) and geometrical (cis–trans) — disubstituted YXC=CXY with two identical groups on the same side is cis, opposite side is trans; cis-but-2-ene μ = 0.33 D, trans-but-2-ene $\mu \approx 0$ (NCERT §9.3.2–9.3.3, p. 306–309).
- Alkene preparation: (a) partial reduction of alkynes — H2/Lindlar (Pd–BaSO4 poisoned with quinoline/S) → cis-alkene; Na in liquid NH3 → trans-alkene (eqs 9.30–9.33); (b) dehydrohalogenation of alkyl halides with alcoholic KOH — β-elimination, reactivity I>Br>Cl, tertiary > secondary > primary (eq 9.34), Saytzeff rule governs orientation (more substituted alkene major); (c) dehalogenation of vicinal dihalides with Zn (eqs 9.35–9.36); (d) acid-catalysed dehydration of alcohols with conc. H2SO4 (eq 9.37) (NCERT §9.3.4, p. 309–310).
- Alkene reactions: (1) H2/Pt-Pd-Ni → alkane; (2) X2 (Cl2, Br2) → vicinal dihalide via cyclic halonium ion — Br2/CCl4 decolourisation is the test for unsaturation (eqs 9.38–9.39); (3) HX (HI>HBr>HCl) addition obeys Markovnikov rule — negative part of addendum goes to the carbon with fewer H; mechanism: H+ forms more stable

secondary carbocation, then Br$^-$ adds, giving 2-bromopropane from propene + HBr; carbocation stability 3° > 2° > 1° > CH3+ (eqs 9.40–9.42); (4) Kharasch peroxide effect — HBr + alkene in presence of peroxides goes anti-Markovnikov via free-radical mechanism giving 1-bromopropane from propene; effect seen only for HBr (HCl bond too strong 430.5 kJ; HI bond too weak so I• recombines) (eq 9.43); (5) cold conc. H2SO4 → alkyl hydrogen sulphate (Markovnikov); (6) H2O / dilute H2SO4 → alcohol (Markovnikov); (7) oxidation: cold dilute alkaline KMnO4 (Baeyer's reagent) → vicinal diol/glycol (decolourisation = unsaturation test); hot acidic KMnO4/ K2Cr2O7 → cleavage to ketones/acids (but-2-ene → 2 CH3COOH); (8) ozonolysis: alkene + O3 → ozonide → Zn/H2O → aldehydes and/or ketones — used to locate the position of C=C (eq 9.51–9.52); (9) polymerisation: nCH2=CH2 → polythene; propene → polypropene (NCERT §9.3.5, p. 310–314).

- Alkyne structure: C≡C is sp-hybridised, one σ + two π bonds; bond length 120 pm, bond enthalpy 823 kJ mol^{-1}; H–C≡C–H is linear, ∠H–C–C = 180°; sp-hybridised C has 50% s-character → most electronegative → terminal H is acidic (NCERT §9.4.2, p. 315).
- Alkyne nomenclature: suffix "-yne"; ethyne (acetylene), propyne, but-1-yne and but-2-yne — position isomers; chain isomers appear from C5H8 onwards (NCERT §9.4.1, p. 314).
- Alkyne preparation: (a) from calcium carbide — CaCO3 → CaO + CO2; CaO + 3C → CaC2 + CO; CaC2 + 2H2O → Ca(OH)2 + C2H2 (eqs 9.55–9.57); (b) from vicinal dihalide via alc. KOH (loss of one HX) → vinyl halide, then NaNH2 → alkyne; from geminal dihalides similarly; (c) Kolbe electrolysis of sodium salt of alkene-dicarboxylates (NCERT §9.4.3, p. 315–316).
- Alkyne physical properties: first three gases, next eight liquids; weakly polar, immiscible in water, soluble in organic solvents (NCERT §9.4.4, p. 316).
- Alkyne reactions: (A) Acidic character of 1-alkynes — terminal H is acidic; HC≡CH + Na → HC≡C$^-$Na+ + ½H2; with NaNH2 → sodium acetylide + NH3; gives white ppt with ammoniacal AgNO3 (Tollens' = silver acetylide) and red ppt with ammoniacal CuCl (cuprous acetylide); but-2-yne does NOT react because no terminal H; acidity order HC≡CH > H2C=CH2 > CH3–CH3; (B) addition reactions go via vinyl cation, Markovnikov in unsymmetrical alkynes: H2/Lindlar gives cis-alkene, Na/liq NH3 gives trans-alkene, full H2/Pt gives alkane; X2 addition (Br2/CCl4 decolourisation test); 2HX → gem-dihalide (propyne + 2HBr → 2,2-dibromopropane); H2O at 333 K with HgSO4/dil H2SO4 → enol tautomerises to carbonyl — ethyne → acetaldehyde (CH3CHO), propyne → acetone (CH3COCH3) (Markovnikov); (C) polymerisation — linear ethyne → polyacetylene (conducting polymer for electrodes); cyclic (Reppe) — 3 C2H2 over red-hot iron tube at 873 K → benzene (eq 9.69) (NCERT §9.4.4, p. 316–318).
- Aromatic hydrocarbons (arenes): benzene C6H6 isolated by Faraday (1825); Kekulé (1865) proposed cyclic hexagonal structure with alternating single and double bonds plus oscillation to explain a single ortho-product; resonance — benzene is hybrid of

two Kekulé structures; all six C–C bonds equal (139 pm, between single 154 pm and double 133 pm); MO picture: six sp^2 C's, each contributes one p-orbital → six π electrons delocalised in two doughnut clouds above and below the planar ring → unusual stability (NCERT §9.5.2, p. 319–321).

- Aromaticity (Hückel rule): planar, cyclic, fully conjugated systems with $(4n+2)\pi$ electrons ($n = 0, 1, 2, \cdots$); benzene has 6 π = $(4\times1+2)$ (NCERT §9.5.3, p. 321).
- Benzene preparation: (i) cyclic polymerisation of ethyne (Reppe), (ii) decarboxylation of sodium benzoate with sodalime, (iii) reduction of phenol vapours over heated Zn dust (eq 9.70–9.71) (NCERT §9.5.4, p. 321–322).
- Benzene reactions — electrophilic aromatic substitution (EAS): nitration (conc. HNO3 + conc. H2SO4 → $NO2^+$); halogenation (Cl2/Br2 with Lewis acid FeCl3/FeBr3/AlCl3 → halobenzene); sulphonation (oleum/fuming H2SO4 → benzenesulphonic acid); Friedel–Crafts alkylation (R–Cl + anhyd. AlCl3 → alkylbenzene; n-PrCl gives isopropylbenzene because of carbocation rearrangement); Friedel–Crafts acylation (R–COCl/acid anhydride + AlCl3 → aryl ketone); excess Cl2/AlCl3 → hexachlorobenzene C6Cl6 (eqs 9.72–9.79); EAS mechanism — (a) electrophile generation, (b) arenium ion (σ-complex, one C is sp^3) stabilised by resonance, (c) proton loss restores aromaticity (NCERT §9.5.5, p. 322–324).
- Addition reactions of benzene (vigorous conditions): H2/Ni high T/P → cyclohexane (eq 9.80); 3 Cl2 / UV light → benzene hexachloride C6H6Cl6 (gammaxane, BHC) (eq 9.81); combustion → CO2 + H2O with sooty flame (eq 9.82).
- Directive influence in monosubstituted benzene: o/p-directing activating groups (electron-donating, EDG) — –OH, –NH2, –NHR, –NHCOCH3, –OCH3, –CH3, –C2H5, etc. — increase ring electron density at o/p positions through +R/resonance; halogens (–Cl, –Br) are o/p-directing but deactivating (strong –I effect lowers overall density but resonance still favours o/p); m-directing deactivating groups (electron-withdrawing, EWG) — –NO2, –CN, –CHO, –COR, –COOH, –COOR, –SO3H — lower density most at o/p, leaving m comparatively richer (NCERT §9.5.6, p. 324–325).
- Carcinogenicity/toxicity: benzene and polynuclear aromatic hydrocarbons with > 2 fused benzene rings (e.g., benzpyrene) are toxic and carcinogenic; formed in incomplete combustion of tobacco, coal and petroleum; they damage DNA and cause cancer (NCERT §9.6, p. 325).

2.2 Definitions to memorise

Term	Definition	Page
Hydrocarbon	A compound of carbon and hydrogen only	295
Alkane	Saturated open-chain hydrocarbon, CnH2n+2, only C–C and C–H single bonds	296
Cycloalkane	Saturated hydrocarbon with a closed ring of C atoms	296
Wurtz reaction		301

Term	Definition	Page
	R–X + 2Na + X–R (dry ether) → R–R + 2NaX; gives higher alkanes with even C atoms	
Kolbe electrolysis	Electrolysis of aqueous sodium/potassium salt of carboxylic acid → alkane (even C) at anode	301
Decarboxylation	Loss of CO2 from sodium salt of acid with sodalime, gives alkane with one C less	301
Conformation	Spatial arrangement of atoms convertible into one another by rotation about a C–C single bond	305
Torsional strain	Repulsive interaction between electron clouds of adjacent bonds that hinders free rotation	305–306
Staggered conformation	Conformation of ethane with H atoms as far apart as possible; lowest energy, most stable	305–306
Newman projection	View along the C–C bond axis; front C as a point, rear C as a circle	305
Markovnikov rule	The negative part of the addendum attaches to the carbon bearing fewer H atoms	311
Kharasch / peroxide effect	Anti-Markovnikov addition of HBr to alkenes in presence of peroxide via free-radical mechanism	312
Baeyer's reagent	Cold dilute alkaline KMnO4; oxidises alkenes to vicinal glycols; test for unsaturation	313
Ozonolysis	Alkene + O3 → ozonide → Zn/H2O → carbonyl compounds; locates C=C position	313
Lindlar's catalyst	Pd/CaCO3 (or Pd/C) partially deactivated by quinoline/sulphur; gives cis-alkene from alkyne	309
Aromatisation	Conversion of n-alkanes (⩾6 C) to benzene/toluene at 773 K, 10–20 atm over V/Mo/Cr–Al2O3	304
Hückel rule	A planar cyclic conjugated system is aromatic if it has (4n+2)π electrons (n = 0, 1, 2⋯)	321
Arenium ion (σ-complex)	Carbocation intermediate in EAS in which one ring carbon becomes sp^3	323
Activating group	Substituent that increases ring electron density (e.g., –OH, –NH2, –CH3); o/p-directing	324
Deactivating group	Substituent that decreases ring electron density; usually m-directing (e.g., –NO2, –COOH)	325
Carcinogenicity	Cancer-causing property of polynuclear aromatic hydrocarbons such as benzpyrene	325

2.3 Diagrams / processes to remember

- Fig. 9.1 — Tetrahedral structure of methane (sp^3, ∠H–C–H = 109.5°), p. 296.
- Fig. 9.2 — Sawhorse projection of eclipsed vs staggered ethane, p. 305.
- Fig. 9.3 — Newman projection of eclipsed vs staggered ethane, p. 305.
- Fig. 9.4–9.5 — Orbital picture of ethene: sp^2 σ-framework; π-bond from lateral 2p–2p overlap; π-cloud above and below the molecular plane, p. 306–307.
- Fig. 9.6 — Orbital picture of ethyne: two sp orbitals on each C give the C–C and C–H σ bonds; two perpendicular π bonds give the cylindrical π cloud, p. 315.
- Fig. 9.7 (a–d) — Benzene: two Kekulé structures, sp^2 hybridisation, the six unhybridised p-orbitals overlapping to give two doughnut π clouds above and below the planar ring, p. 320–321.
- Free-radical chain mechanism of CH_4 chlorination — initiation (Cl_2 homolysis), propagation (Cl· abstracts H, ·CH_3 attacks Cl_2), termination steps yielding CH_3Cl, HCl and C_2H_6 as a by-product, p. 302–303.
- Markovnikov vs Kharasch mechanism diagrams — carbocation pathway (2° more stable than 1°) versus free-radical pathway (2° free radical more stable), p. 311–312.
- EAS mechanism — generation of E^+, arenium-ion intermediate (with three resonance structures) and proton loss to $AlCl_4^-$ / HSO_4^-, p. 322–324.

2.4 Common confusions / NTA trap points

- Wurtz reaction with two different alkyl halides gives a mixture of three alkanes (R–R, R'–R', R–R') and so is not practical for odd-number-of-C alkanes — distractors will offer a single product (NCERT §9.2.2, p. 301; Exercise 9.25).
- Kolbe electrolysis cannot prepare methane because two methyl free radicals would have to come from sodium formate (HCOONa) — but the anode product needs a carboxylate of the form $CH_3(CH_2)_n COO^-$ giving even-C alkanes; methane needs an odd path (NCERT §9.2.2, p. 301).
- Peroxide effect occurs only with HBr, NOT with HCl (bond too strong, 430.5 kJ mol^{-1}) or HI (bond too weak, 296.8 kJ mol^{-1}; I· simply recombines). Common trap: option claims peroxide effect with HCl (NCERT §9.3.5, p. 312).
- Lindlar's catalyst (H_2, poisoned Pd) gives the cis-alkene; Na in liquid NH_3 gives the trans-alkene from the same alkyne — students confuse the two (NCERT §9.3.4, p. 309).
- Halogens (–Cl, –Br) are o/p-directing but deactivating — students often label them activating because they direct ortho/para (NCERT §9.5.6, p. 325).
- In hydration of alkynes with $HgSO_4/H_2SO_4$, the product is a carbonyl (ethyne → acetaldehyde; propyne → acetone) and NOT an enol or alcohol — the enol intermediate tautomerises (NCERT §9.4.4, p. 317).

- Friedel–Crafts alkylation of benzene with n-propyl chloride gives isopropyl benzene (not n-propyl benzene) because the n-propyl cation rearranges to the more stable isopropyl cation (NCERT §9.5.5, p. 322).
- Only terminal alkynes (1-alkynes) show acidic character with Na/NaNH2/AgNO3 ammoniacal/CuCl ammoniacal. But-2-yne has no terminal ≡C–H and is unreactive in these tests — a frequent NTA distractor (NCERT §9.4.4, p. 316).

🎯 Practice MCQs

Q1. **Which of the following hydrocarbons cannot be prepared by Kolbe's electrolytic method?**

A. Ethane

B. Methane

C. Butane

D. Hexane

Q2. **The major product of the reaction of propene with HBr in the absence of peroxide is**

A. 1-Bromopropane

B. 2-Bromopropane

C. 1,2-Dibromopropane

D. 3-Bromopropane

Q3. **In the presence of benzoyl peroxide, propene reacts with HBr to give predominantly**

A. 2-Bromopropane (Markovnikov product)

B. 1-Bromopropane (anti-Markovnikov product)

C. 1,2-Dibromopropane

D. 2,2-Dibromopropane

📊 PYQ Alignment

Hydrocarbons is a high-yield chapter for CUET (UG) Chemistry, with roughly 10–12 MCQs each year across the 2023–25 papers. Recurring question types include identifying the Markovnikov vs anti-Markovnikov product, ozonolysis of a given alkene (or working back from carbonyl fragments to the alkene), Lindlar-versus-Na/liq-NH3 stereochemistry of alkyne reduction, predicting the major product and directive effect in electrophilic aromatic substitution, free-radical mechanism steps of alkane halogenation, and direct factual questions on Hückel's rule and aromaticity criteria.

CUET 2025 — Actual PYQs from this chapter

Q.25 (CUET 2025) Reagents used in hydroboration oxidation of propene: (A) B_2H_6 (B) H_2O (C) H_2O_2 (D) OH^-

- A) — B) — C) — D) —

Tests: Alkene/alkyne reactions **Answer:** Not in extracted key

Q.34 (CUET 2025) In nitration of benzene using conc. H_2SO_4 + conc. HNO_3, the nitrating species is:

- A) NO_2^- B) NO_3^+ C) NO^+ D) NO_2^+

Tests: Hydrocarbons — benzene reactions **Answer:** Not in extracted key

CUET 2024 — Actual PYQs from this chapter

Q.28 (CUET 2024) Match alkenes with products in acidic hydration reaction (diagram-based question).

- A) — B) — C) — D) —

Tests: Alkene chemistry **Answer:** Not in extracted key

Q.22 (CUET 2024) Chlorine is ortho-para directing though electron withdrawing because: (A) –I effect (B) destabilises carbocation (C) accepts electrons by resonance (D) releases electrons by resonance Options given.

- A) — B) — C) — D) —

Tests: EAS — ortho/para directing of halogens **Answer:** Not in extracted key

CUET 2023 — Actual PYQs from this chapter

Q.7 (CUET 2023) Which of the following reactions will not produce ketones?

- A) Hydrolysis of alkynes B) Ozonolysis of substituted alkenes C) Treating nitrite with Grignard reagent D) Stephen's reaction

Tests: Alkene/alkyne reactions **Answer:** Not in extracted key