FREE NOTES · NCERT + JEE/NEET LEVEL

Hydrocarbons

Alkanes (preparation, properties, conformations), alkenes (isomerism, preparation, Markovnikov and peroxide effect, ozonolysis), alkynes (acidity, reactions), aromatic hydrocarbons (benzene, aromaticity, electrophilic substitution, directive influence) and carcinogenicity.

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02 Alkanes: preparation
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01 Classification

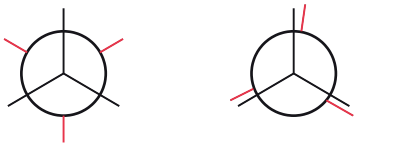
Type	Formula	Bond	Example
Alkane (saturated)	C_nH_{2n+2}	C–C (sp^3)	Methane
Alkene	C_nH_{2n}	C=C (sp^2)	Ethene
Alkyne	C_nH_{2n-2}	C≡C (sp)	Ethyne
Aromatic (arenes)	—	Delocalised ring	Benzene

02 Alkanes: preparation

- **Hydrogenation** of alkenes/alkynes: H_2 + Pt/Pd/Ni.
- **From alkyl halides:** Zn + HCl reduction; **Wurtz**: 2RX + 2Na (dry ether) → R–R (even-carbon alkanes; methane can't be made).
- **Decarboxylation:** RCOONa + NaOH/CaO (soda lime) → R–H + Na_2CO_3 (one C less).
- **Kolbe's electrolysis:** 2RCOONa (aq) → R–R + $2CO_2$ (at anode).

03 Alkanes: properties & conformations

- Non-polar; b.p. rises with size, falls with branching (n-pentane 309 K > isopentane 301 K > neopentane 282.5 K).
- **Halogenation** (free radical, light): $CH_4 + Cl_2 \rightarrow CH_3Cl \rightarrow \ldots \rightarrow CCl_4$. Reactivity $F_2 > Cl_2 > Br_2 > I_2$; H replaced: 3° > 2° > 1°.
- **Combustion**: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$, ΔH very negative (fuel).
- Controlled oxidation, isomerisation ($AlCl_3$/HCl), aromatisation (hexane → benzene, Cr_2O_3/V_2O_5), pyrolysis/cracking.



Newman projections of ethane

Conformations of ethane: rotation about C–C gives staggered (H's far apart, least torsional strain) and eclipsed forms; energy difference only ~12.5 kJ/mol, so they interconvert at room temperature and can't be separated. Representations: sawhorse and Newman.

04 Alkenes: structure & preparation

- C=C = 1σ + 1π (π electrons loosely held ⇒ reactive). Bond length 134 pm.
- **Geometrical isomerism**: cis (same side) and trans (opposite). cis-but-2-ene is polar, higher b.p.; trans is non-polar, higher m.p.
- **From alkynes**: Lindlar's catalyst (Pd/C + quinoline) ⇒ cis-alkene; Na/liquid NH_3 ⇒ trans-alkene.
- **Dehydrohalogenation**: R–X + alc. KOH ⇒ alkene (Saytzeff).
- **Dehalogenation** of vicinal dihalides with Zn.
- **Acidic dehydration** of alcohols: conc. H_2SO_4, heat.

05 Alkenes: reactions

Reagent	Product / rule
H_2 / Ni	Alkane
Br_2 in CCl_4	Vicinal dibromide; **red-brown colour disappears** (test of unsaturation)
HX (unsymmetrical alkene)	**Markovnikov:** H goes to the C with more H (via the more stable carbocation). Propene + HBr → 2-bromopropane
HBr + peroxide	**Anti-Markovnikov** (Kharash, free radical): 1-bromopropane. Only HBr shows this.
Cold dil. $KMnO_4$ (Baeyer's reagent)	Glycol; **pink colour disappears** (test)
Hot acidic $KMnO_4$	Ketones/acids (C=C breaks)
O_3 then Zn/H_2O (ozonolysis)	Aldehydes/ketones; locates the double bond
H_2SO_4 then H_2O	Alcohol (Markovnikov)
Polymerisation	n $CH_2{=}CH_2$ → polythene

06 Alkynes

- C≡C = 1σ + 2π, linear, 120 pm. **Ethyne from CaC_2**: $CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2$. Also from vicinal dihalides + alc. KOH, then $NaNH_2$.
- **Acidic H:** terminal ≡C–H is acidic (sp C has 50% s character). $HC{\equiv}CH + Na \rightarrow HC{\equiv}C^-Na^+ + \frac{1}{2}H_2$. Acidity: $HC{\equiv}CH > CH_2{=}CH_2 > CH_3{-}CH_3$. Terminal alkynes give white ppt with ammoniacal $AgNO_3$ (test vs internal alkynes).
- Addition of H_2, X_2, HX (Markovnikov, twice), water (Hg^{2+}/H_2SO_4 ⇒ ethanal from ethyne; ketones from others).
- **Cyclic polymerisation:** 3 HC≡CH, red-hot Fe tube 873 K ⇒ benzene.

07 Benzene & aromaticity

- C_6H_6, planar, all C sp^2, all C–C bonds equal (139 pm, between single and double) because of resonance (Kekulé structures). Very stable, prefers substitution over addition.
- **Hückel's rule**: planar, cyclic, fully conjugated, with **(4n + 2) π electrons** ⇒ aromatic. Benzene (6), naphthalene (10), cyclopentadienyl anion (6), tropylium cation (6).
- **Preparation:** cyclic polymerisation of ethyne; decarboxylation of sodium benzoate (soda lime); phenol + Zn dust.

08 Electrophilic substitution & directive influence

Reaction	Reagent	Electrophile
Nitration	conc. HNO_3 + conc. H_2SO_4	NO_2^+
Halogenation	Cl_2 + $FeCl_3$ (dark)	Cl^+
Sulphonation	fuming H_2SO_4	SO_3
Friedel-Crafts alkylation	RCl + anhyd. $AlCl_3$	R^+
Friedel-Crafts acylation	RCOCl + anhyd. $AlCl_3$	RCO^+

Mechanism: E^+ forms → attacks ring giving a σ-complex (arenium ion, loses aromaticity) → loses H^+ to restore the ring. Benzene + Cl_2 in UV light gives addition: BHC (gammaxene, $C_6H_6Cl_6$).

DIRECTIVE INFLUENCE OF SUBSTITUENTS

Ortho/para directing, activating: –OH, $–NH_2$, $–OCH_3$, $–CH_3$. **Ortho/para directing, deactivating:** halogens. **Meta directing, deactivating:** $–NO_2$, –CN, –CHO, –COOH, $–SO_3H$.

Carcinogenicity: polynuclear hydrocarbons with 4+ fused rings (from incomplete burning of tobacco, coal, petrol) are cancer-causing, e.g. 1,2-benzanthracene, 3-methylcholanthrene.

09 JEE Extra + Tricks

JEE LEVEL

- Markovnikov: H goes to carbon with more H. **Anti-Markovnikov** (Kharasch, peroxide effect) only with HBr.
- Ozonolysis gives position of double bond: each C=C becomes two C=O.
- Acidity of terminal alkynes: sp C–H acidic; reacts with Na, ammoniacal $AgNO_3$ (white ppt), Cu_2Cl_2 (red ppt). Acidity: $HC{\equiv}CH > CH_2{=}CH_2 > CH_3{-}CH_3$.
- Electrophilic aromatic substitution directing: -OH, $-NH_2$, $-CH_3$, halogens ⇒ o/p; $-NO_2$, -CHO, -COOH, -CN ⇒ m. Halogens are deactivating but o/p directing.
- Conformations: staggered ethane more stable than eclipsed (torsional strain ~12.5 kJ/mol); Newman projections.
- Wurtz reaction gives alkane with even number of C (R–R); Kolbe's electrolysis also gives R–R.

10 Solved questions

Q1. Product of propene + HBr with and without peroxide.

Without: 2-bromopropane (Markovnikov). With peroxide: 1-bromopropane.

Q2. An alkene on ozonolysis gives only propanone. Identify it.

$(CH_3)_2C{=}C(CH_3)_2$, 2,3-dimethylbut-2-ene.

Q3. Is cyclooctatetraene (8 π e^-, non-planar) aromatic?

No: 8 is not 4n + 2 and the ring is tub-shaped.

Q4. How to tell but-1-yne from but-2-yne?

But-1-yne (terminal) gives a white ppt with ammoniacal $AgNO_3$; but-2-yne doesn't.

11 Mistakes & practice

- Applying the peroxide effect to HCl or HI.
- Using Wurtz to make methane or odd-carbon alkanes cleanly.
- Calling halogens meta directing.
- Forgetting that Lindlar gives cis, Na/NH_3 gives trans.

1. Reagent to test unsaturation?
2. Hybridisation of carbons in benzene?
3. Most acidic: ethane, ethene, ethyne?
4. Product of CH_3COONa + soda lime?
5. Electrophile in nitration?

ANSWERS

1) Br_2 water / Baeyer's reagent · 2) sp^2 · 3) Ethyne · 4) CH_4 · 5) NO_2^+

12 Quick revision: 5 minutes before the exam

ALKANES

- Wurtz, soda lime, Kolbe.
- Free radical halogenation.
- Staggered more stable.

ALKENES

- Markovnikov; HBr + peroxide anti.
- Baeyer's: pink fades.
- Ozonolysis finds C=C.

ALKYNES

- Terminal H acidic.
- Lindlar cis, Na/NH_3 trans.
- 3 C_2H_2 → benzene.

BENZENE

- $(4n + 2)\ \pi\ e^-$.
- EAS: NO_2^+, Cl^+, SO_3, R^+, RCO^+.
- $-NO_2$ meta; $-OH$, $-X$ o/p.

Have a doubt? Ask the AI Doubt Solver at padhaiadda.netlify.app, or take the mock test on this chapter.