JEE MAIN · PAPER 1 · CHEMISTRY

15 Hydrocarbons

Formula & concept sheet

Alkanes, alkenes, alkynes and benzene: every NCERT method of preparation and reaction as drawn schemes, with the mechanisms (free radical, electrophilic addition, electrophilic substitution), the rules (Markovnikov, peroxide effect, Saytzeff, directing effects), conformations, tests and counting formulas. Each idea is explained first, then the reactions and the traps.

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READ ALONGSIDE NCERT XI · Hydrocarbons

HOW TO USE THIS SHEET

1. **Skim** — Read the Key ideas, then the formula cards.
2. **Memorise** — Learn the formulas and check every Trap box.
3. **Test** — Do the worked examples, then this chapter's PYQs.
4. **Revise** — Use the last-minute checklist before the exam.

Formula memorise · **Key idea** why it works · **Trap** marks lost here · **PYQ** how it is asked

Practise this chapter with real past-paper questions on Prep Vault. Written for revision, not as a first read.

CHAPTER 15

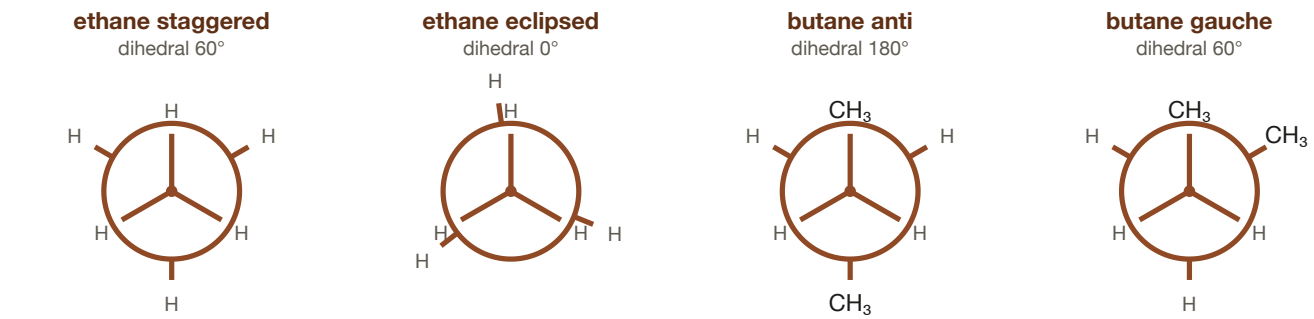
Hydrocarbons

NCERT XI · Hydrocarbons

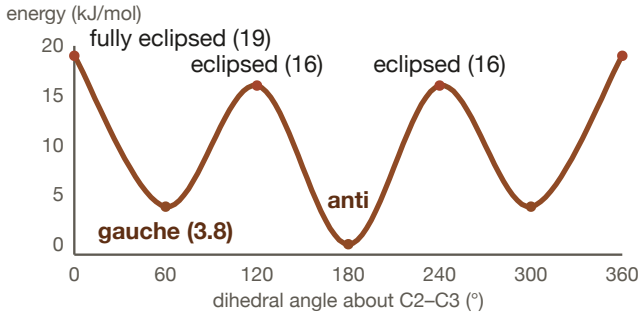
Covers: classification, conformations of ethane and butane · alkanes: preparation, halogenation, combustion, isomerisation, aromatisation · alkenes: geometrical isomerism, preparation, addition, oxidation, ozonolysis, polymerisation · alkynes: acidity, addition, hydration, polymerisation · benzene: structure, aromaticity, electrophilic substitution, directing effects, addition.

1 Alkanes: conformations, preparation and reactions

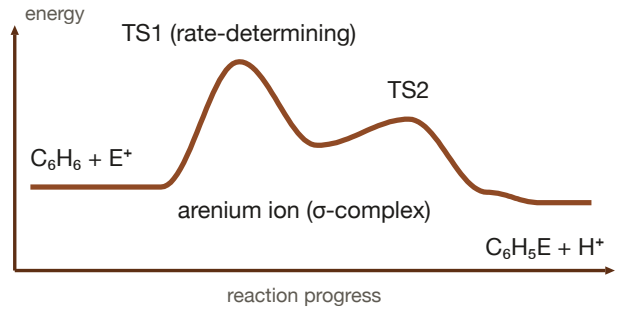
- Alkanes (C_nH_{2n+2}) have only σ bonds and sp^3 carbon; they are non-polar, insoluble in water, and unreactive except in **combustion** and **free-radical substitution** (and cracking/isomerisation). Boiling points rise with chain length and fall with branching.
- **Conformations** arise by rotation about the $C-C$ bond. Ethane: **staggered** (dihedral $60°$) is the most stable, **eclipsed** ($0°$) the least, torsional strain about 12 kJ mol^{-1} (NCERT 12.5); rotation is still fast at room temperature. n-Butane about C_2-C_3: anti $>$ gauche $>$ eclipsed (CH_3/H) $>$ fully eclipsed (CH_3/CH_3).



Newman projections looking along the C–C bond; the back carbon is drawn behind the circle



anti is the most stable conformer of butane, then gauche, then the eclipsed forms



the first step loses aromaticity (slow); the second restores it (fast)

PREPARATION OF ALKANES

METHOD	EQUATION	NOTE
hydrogenation of alkenes, alkynes	$CH_2{=}CH_2 + H_2 \xrightarrow{\text{Ni, } 523{-}573\ \text{K}} CH_3CH_3$ (Sabatier-Senderens); Pt or Pd work at room temperature	same carbon skeleton
reduction of RX	$RX + 2\,[H] \xrightarrow{\text{Zn, } H^+} RH + HX$ (also $LiAlH_4$, $Zn{-}Cu$ couple)	same carbon number
Wurtz	$2\,RX + 2\,Na \xrightarrow{\text{dry ether}} R{-}R + 2\,NaX$	even-carbon symmetric alkanes; CH_4 cannot be made; a mixture of two RX gives 3 alkanes
decarboxylation	$RCOONa + NaOH \xrightarrow{\text{CaO, heat}} RH + Na_2CO_3$	one carbon fewer: sodium ethanoate gives methane
Kolbe electrolysis	$2\,RCOONa + 2\,H_2O \longrightarrow R{-}R + 2\,CO_2 + H_2 + 2\,NaOH$	anode: $R{-}R$ and CO_2; cathode: H_2; acetate gives ethane (not methane); a mixture of two salts gives 3 alkanes
Grignard	$RMgX + H_2O \longrightarrow RH + Mg(OH)X$	CH_3MgBr gives methane
from carbides	$Al_4C_3 + 12\,H_2O \longrightarrow 4\,Al(OH)_3 + 3\,CH_4$	methane

REACTIONS OF ALKANES

REACTION	EQUATION AND CONDITIONS
halogenation (free radical)	$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$ and further to CH_2Cl_2, $CHCl_3$, CCl_4. Initiation $Cl_2 \longrightarrow 2\,Cl\cdot$; propagation $Cl\cdot + RH \longrightarrow R\cdot + HCl$, $R\cdot + Cl_2 \longrightarrow RCl + Cl\cdot$; termination: radicals pair (traces of ethane). Reactivity $F_2 > Cl_2 > Br_2 > I_2$ (I_2 is reversible: HI is removed by HIO_3)
combustion	$C_nH_{2n+2} + \frac{3n+1}{2}O_2 \rightarrow nCO_2 + (n+1)H_2O$ (e.g. pentane needs 8 mol O_2); incomplete combustion gives CO or carbon black
controlled oxidation	$2\,CH_4 + O_2 \xrightarrow{\text{Cu, } 523\ \text{K, } 100\ \text{atm}} 2\,CH_3OH$; $CH_4 + O_2 \xrightarrow{Mo_2O_3} HCHO + H_2O$; $(CH_3)_3CH \xrightarrow{KMnO_4} (CH_3)_3COH$
isomerisation	n-alkane $\xrightarrow{\text{anhyd. } AlCl_3/HCl}$ branched alkane (higher octane number)
aromatisation	n-hexane $\xrightarrow{Cr_2O_3/V_2O_5/Mo_2O_3,\ 773\ \text{K, } 10\text{-}20\ \text{atm}}$ benzene; n-heptane gives toluene
pyrolysis (cracking)	high temperature: higher alkane gives smaller alkanes and alkenes; $C_{12}H_{26} \longrightarrow C_7H_{16} + C_5H_{10}$

PRODUCT RATIO, RADICAL HALOGENATION

$$\%\ \text{product} \propto (\text{number of equivalent H}) \times (\text{relative reactivity})$$

Cl_2 at 298 K: $3^\circ : 2^\circ : 1^\circ \approx 5 : 3.8 : 1$; Br_2 far more selective ($1600 : 82 : 1$)

COMBUSTION OF C_xH_y

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$$

eudiometry: after cooling, the volume contraction per volume of gas is $1 + \frac{y}{4}$

WHY IT WORKS

Bromine is more selective than chlorine because $Br\cdot$ abstracts H in an endothermic step with a late, product-like transition state, so the stability of the radical ($3^\circ > 2^\circ > 1^\circ$) matters far more. A molecule with only one kind of H (methane, ethane, neopentane, cyclohexane) gives a single monochloro product.

QUICK CHECK

Percent of 2-chloropropane and 1-chloropropane from chlorination of propane ($2^\circ : 1^\circ = 3.8 : 1$)?

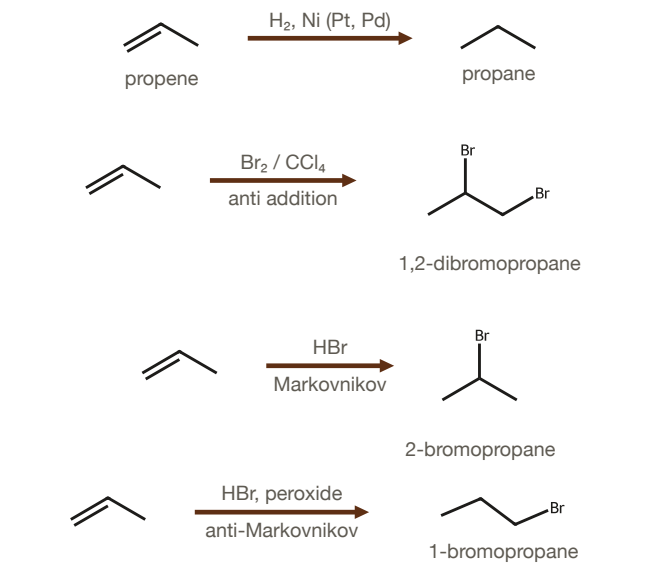
Answer: 2°: $2 \times 3.8 = 7.6$; 1°: $6 \times 1 = 6$; $\frac{7.6}{13.6} = 55.9\%$ 2-chloro, 44.1% 1-chloro.

2 Alkenes

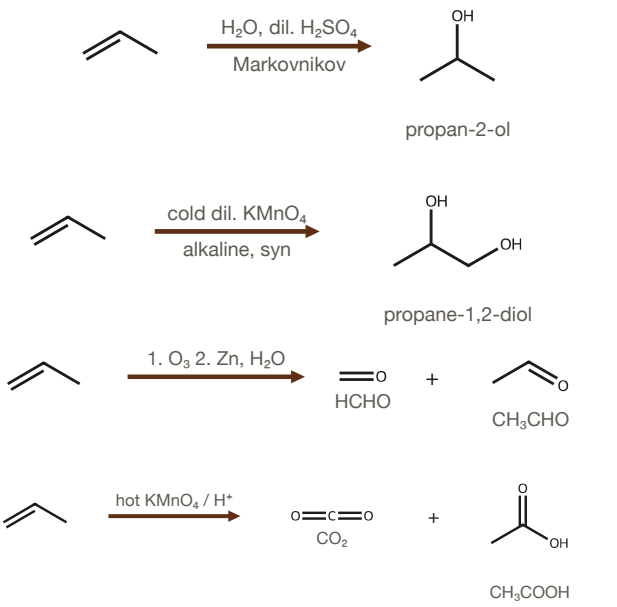
- Alkenes (C_nH_{2n}) have a $C{=}C$ made of one σ and one π bond (sp^2, planar, 120°). The π bond is weaker and more exposed, so alkenes undergo **electrophilic addition**. Restricted rotation gives **cis-trans (E-Z)** isomers when each carbon has two different groups.
- Stability: more alkyl groups on the double bond (hyperconjugation) means a more stable alkene, lower heat of hydrogenation: tetra- $>$ tri- $>$ di- $>$ mono-substituted; trans $>$ cis (cis has the higher dipole moment and boiling point, trans the higher melting point).

PREPARATION OF ALKENES

METHOD	EQUATION OR RULE
partial reduction of alkynes	$RC{\equiv}CR + H_2 \xrightarrow{\text{Lindlar: } Pd/CaCO_3 \text{ poisoned with quinoline}} cis{-}alkene$; $Na/liq\cdot NH_3$ gives the **trans**-alkene
dehydrohalogenation	$R{-}CH_2{-}CHX{-}R' + alc\cdot KOH \xrightarrow{heat} alkene + KX + H_2O$; Saytzeff: the more substituted alkene is major; reactivity $3^\circ > 2^\circ > 1^\circ$, $I > Br > Cl$
dehalogenation	$BrCH_2CH_2Br + Zn \longrightarrow CH_2{=}CH_2 + ZnBr_2$ (vicinal dihalide)
dehydration of alcohols	$C_2H_5OH \xrightarrow{conc\cdot H_2SO_4,\ 443\,K} CH_2{=}CH_2 + H_2O$; 2° and 3° go through a carbocation (E1) and can rearrange; ease $3^\circ > 2^\circ > 1^\circ$; at 413 K the ether forms instead



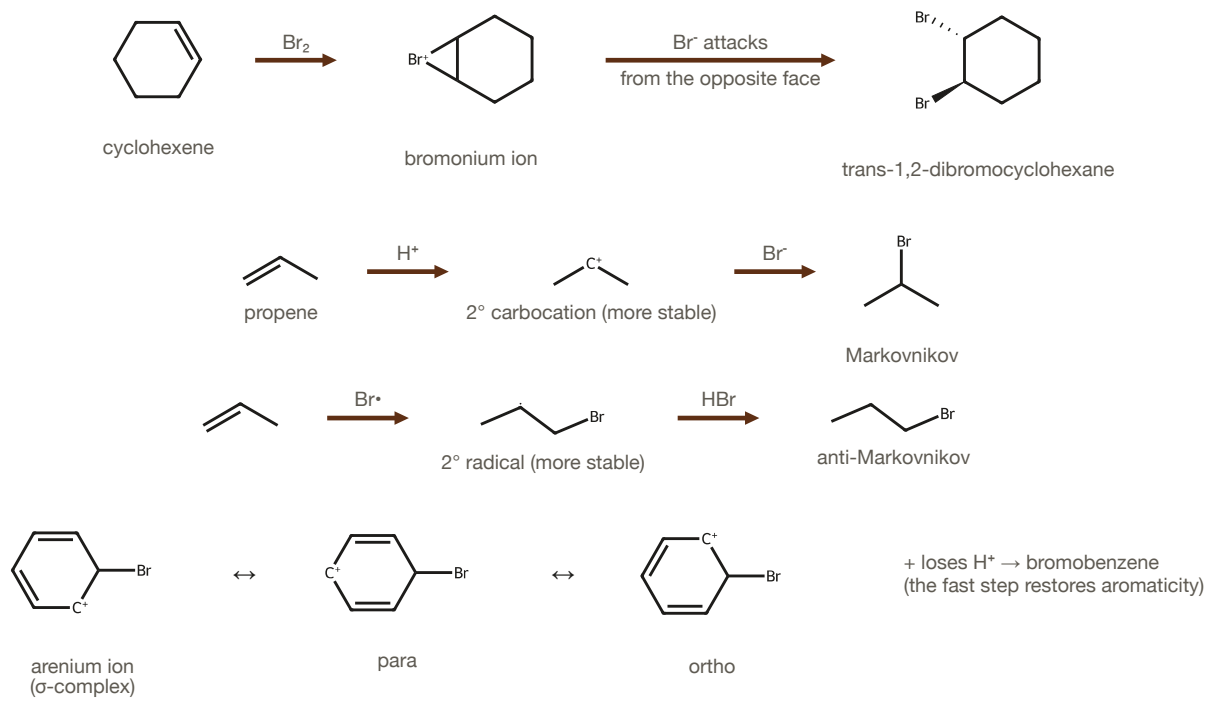
reactions of propene (1): addition of H_2, Br_2, HBr (Markovnikov) and HBr with peroxide (anti-Markovnikov)



reactions of propene (2): hydration, Baeyer test, ozonolysis and oxidative cleavage

REACTIONS OF ALKENES: RULES AND MECHANISMS

REAGENT	PRODUCT AND RULE
H_2 / Ni, Pt, Pd	alkane; syn addition on the metal surface
Br_2 in CCl_4	vicinal dibromide; **anti** addition through a cyclic bromonium ion; the red-brown colour disappears: the test for unsaturation
HX	**Markovnikov**: H goes to the carbon with more H (the more stable carbocation forms); rearrangements possible; reactivity $HI > HBr > HCl$
HBr + peroxide	**anti-Markovnikov** (Kharasch, peroxide effect): a free-radical chain through the more stable radical; only HBr (HCl: bond too strong; HI: $I\cdot$ adds back)
H_2O / dil. H_2SO_4	alcohol, Markovnikov (hydration through a carbocation)
cold dilute alkaline $KMnO_4$ (Baeyer)	vicinal **diol** (syn); purple colour lost, brown MnO_2; test for unsaturation
hot $KMnO_4$ / H^+ (or $K_2Cr_2O_7$)	cleavage: $=CH_2 \rightarrow CO_2 + H_2O$; $=CHR \rightarrow RCOOH$; $=CR_2 \rightarrow R_2C{=}O$
O_3 then Zn/H_2O	ozonolysis: $C{=}C$ cut to two $C{=}O$ (aldehydes/ketones); Zn removes H_2O_2 so aldehydes are not oxidised; 2-methylbut-2-ene gives propanone + ethanal
polymerisation	high T, p, initiator: ethene $\rightarrow$ polythene; propene $\rightarrow$ polypropylene



mechanisms: bromonium ion gives anti addition (trans product); Markovnikov goes through the more stable carbocation, HBr/peroxide through the more stable radical; arenium ion (three resonance forms) is the intermediate of electrophilic substitution

KEY IDEA

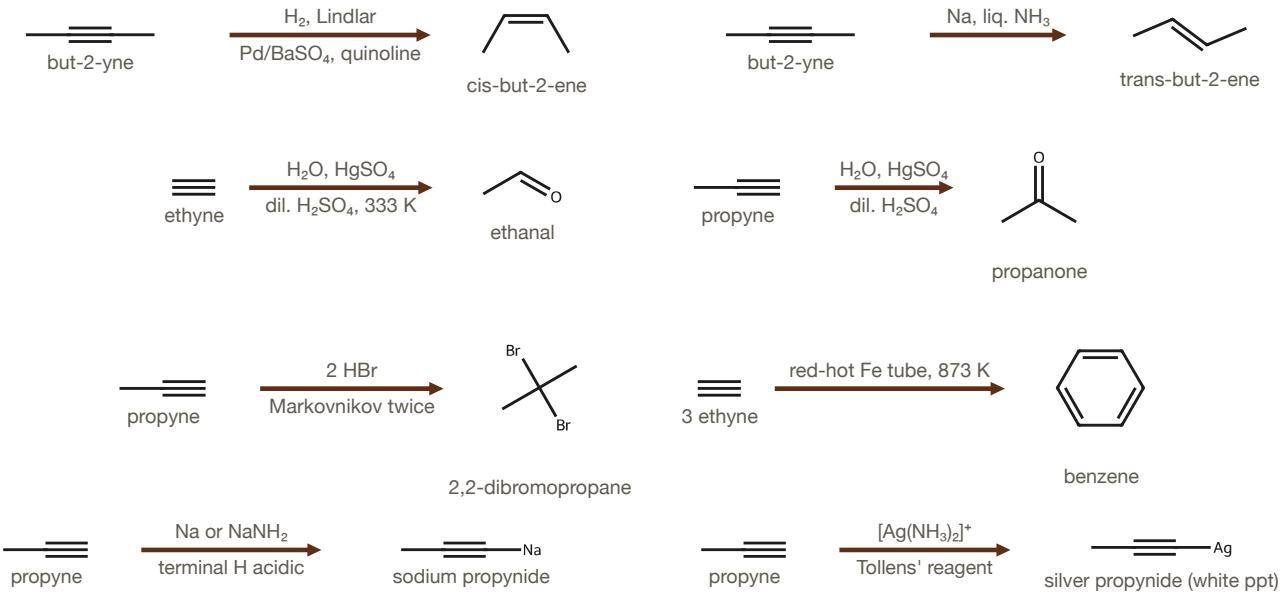
To predict an addition product, find the more stable intermediate: carbocation ($3^\circ > 2^\circ$) for HX and H_2O (Markovnikov), radical for HBr/peroxide (anti-Markovnikov), cyclic ion for Br_2 (anti). Read an ozonolysis answer backwards by joining the two carbonyl carbons with $C{=}C$.

QUICK CHECK

Ozonolysis (O_3, Zn/H_2O) gives only ethanal. Identify the alkene; and the product of hot $KMnO_4$ on but-2-ene.

Answer: But-2-ene ($CH_3CH{=}CHCH_3$); hot $KMnO_4$ gives $2\ CH_3COOH$.

3 Alkynes



reactions of alkynes: partial reduction (Lindlar cis, Na/liq. NH_3 trans), hydration (Markovnikov, enol then ketone), double addition of HBr, acidic hydrogen and cyclic trimerisation

PREPARATION AND TESTS

ITEM	EQUATION OR FACT
from calcium carbide	$CaC_2 + 2\,H_2O \longrightarrow HC{\equiv}CH + Ca(OH)_2$
from dihalides	vicinal or geminal dihalide $+$ 2 alc. KOH (then $NaNH_2$ for the vinyl halide step): double dehydrohalogenation
acidic hydrogen	$HC{\equiv}CH + Na \longrightarrow HC{\equiv}C{-}Na^+ + \frac{1}{2}\,H_2$ (*sp* carbon, 50% *s* character); acidity $HC{\equiv}CH > CH_2{=}CH_2 > CH_3CH_3$; internal alkynes (but-2-yne) have none
test for terminal alkynes	ammoniacal $AgNO_3$: white silver acetylide; ammoniacal Cu_2Cl_2: red copper(I) acetylide
hydration	$HC{\equiv}CH + H_2O \xrightarrow{HgSO_4,\ dil\cdot H_2SO_4,\ 333\,K} [CH_2{=}CHOH] \longrightarrow CH_3CHO$ (enol tautomerises); propyne gives propanone; only ethyne gives an aldehyde
addition of HX, X2	two molecules add, Markovnikov each time: propyne $+$ $2HBr$ gives 2,2-dibromopropane (geminal); Br_2 gives the tetrabromide
trimerisation	$3\,HC{\equiv}CH \xrightarrow{red-hot\ Fe\ tube,\ 873\,K} C_6H_6$; propyne gives mesitylene (1,3,5-trimethylbenzene)
combustion	$C_nH_{2n-2} + \frac{3n-1}{2}O_2 \rightarrow nCO_2 + (n-1)H_2O$; oxy-acetylene flame

REMEMBER

- **Lindlar** = cis; **Na/liq.** NH_3 = trans; both stop at the alkene.
- Only **terminal** alkynes react with Na and give the Ag/Cu precipitates.
- Alkynes are less reactive than alkenes towards electrophiles (the vinyl cation is less stable) but add HX twice.

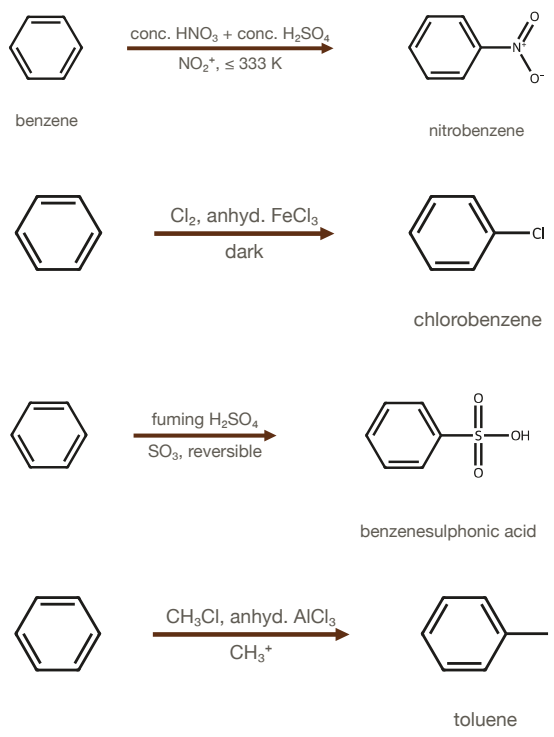
QUICK CHECK

Road map: a vicinal dibromide with $NaNH_2$, then $HgSO_4/H_2SO_4$ gives a ketone that gives a yellow precipitate with $I_2/NaOH$. What is the ketone?

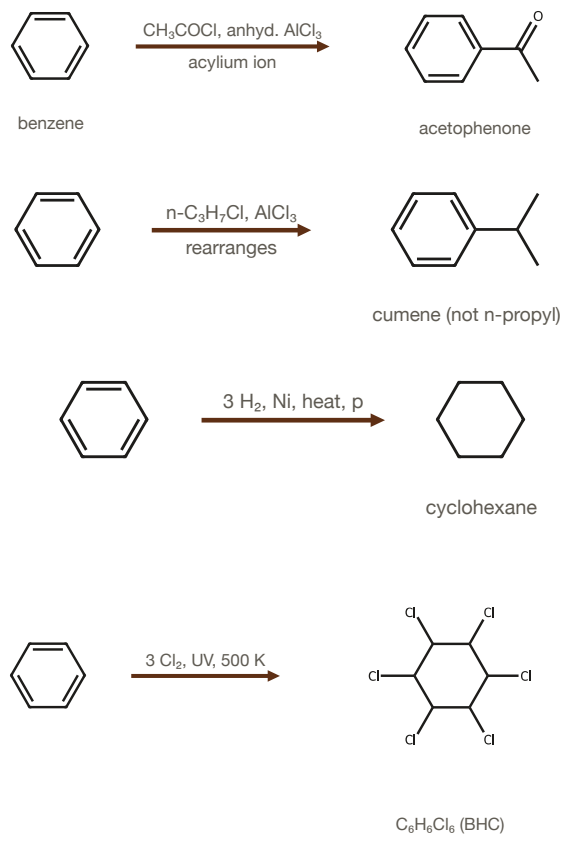
Answer: The dibromide gives a terminal alkyne (propyne); Markovnikov hydration gives propanone, a methyl ketone: positive iodoform test.

4 Benzene and aromatic substitution

- Benzene is planar, all carbons sp^2, $\mathrm{C-C}$ 139 pm (between single 154 and double 134), six delocalised π electrons: aromatic $(4n+2)$. The resonance energy makes it prefer **substitution** (keeps the ring) to addition.
- **Preparation**: trimerisation of ethyne; decarboxylation of sodium benzoate with soda lime; $\mathrm{C_6H_5OH + Zn \longrightarrow C_6H_6 + ZnO}$.
- **Mechanism** of electrophilic substitution: (1) the reagent generates $\mathrm{E^+}$; (2) $\mathrm{E^+}$ attacks the ring (slow, rate-determining) to give the **arenium ion** (σ complex, one sp^3 carbon, aromaticity lost, three resonance forms); (3) loss of $\mathrm{H^+}$ (fast) restores the ring.



electrophilic substitution of benzene (1): nitration, halogenation, sulphonation, Friedel-Crafts alkylation



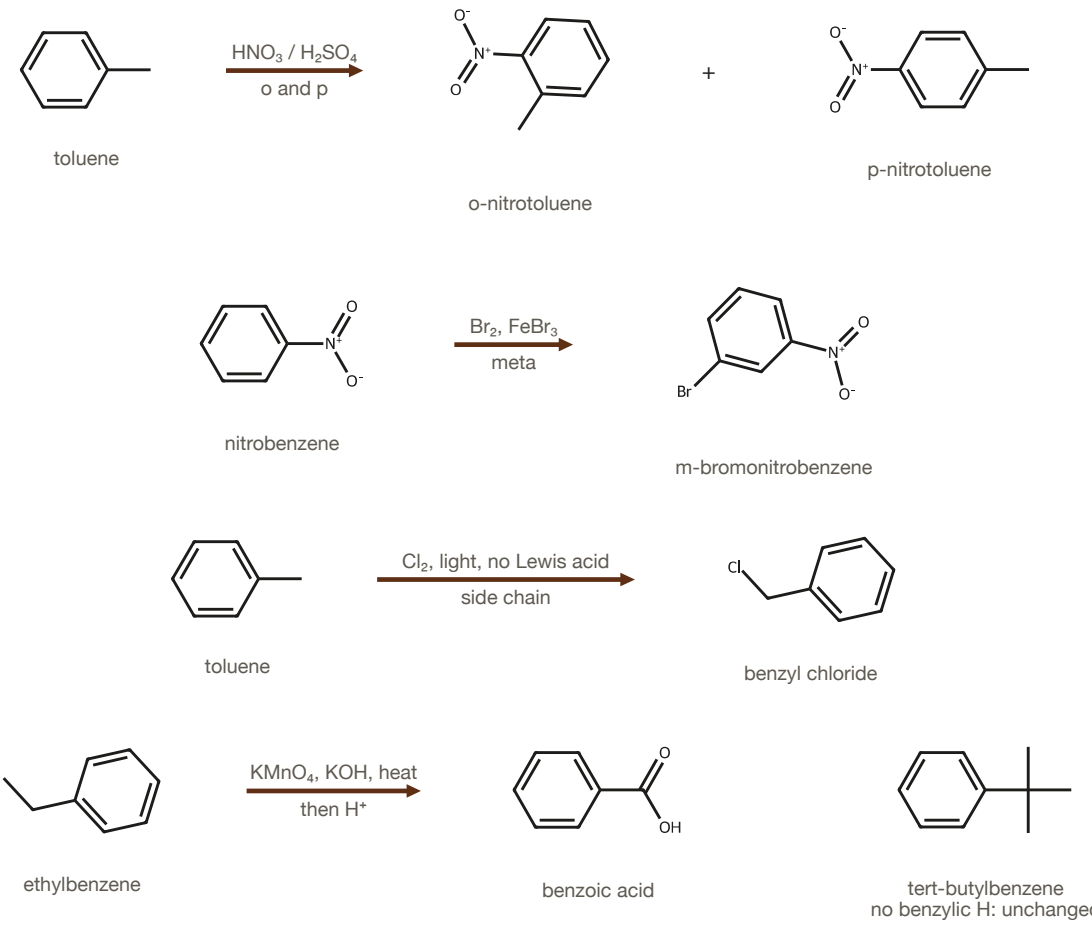
electrophilic substitution of benzene (2): Friedel-Crafts acylation, rearrangement in alkylation, and addition reactions

ELECTROPHILIC SUBSTITUTION REAGENTS

REACTION	REAGENT AND ELECTROPHILE	REMARKS
nitration	conc. $\mathrm{HNO_3}$ + conc. $\mathrm{H_2SO_4}$; $\mathrm{HNO_3 + 2\,H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2\,HSO_4^-}$	$\mathrm{NO_2^+}$ nitronium; keep T low
halogenation	$\mathrm{Cl_2}$ or $\mathrm{Br_2}$ with anhyd. $\mathrm{FeCl_3}$, $\mathrm{FeBr_3}$ or $\mathrm{AlCl_3}$, in the dark	polarised halogen; iodination needs an oxidant
sulphonation	fuming $\mathrm{H_2SO_4}$ (oleum), electrophile $\mathrm{SO_3}$	reversible: dilute acid or steam removes $-\mathrm{SO_3H}$ (a blocking group)
Friedel-Crafts alkylation	RCl + anhyd. $\mathrm{AlCl_3}$, $\mathrm{R^+}$	polyalkylation; rearrangement: n-propyl chloride gives cumene
Friedel-Crafts acylation	RCOCl or $\mathrm{(RCO)_2O}$ + anhyd. $\mathrm{AlCl_3}$, acylium $\mathrm{RCO^+}$	no rearrangement, no polysubstitution; then Clemmensen gives the n-alkylbenzene
addition reactions	$\mathrm{C_6H_6 + 3\,H_2 \xrightarrow{Ni,\ heat,\ p} C_6H_{12}}$; $\mathrm{C_6H_6 + 3\,Cl_2 \xrightarrow{h\nu,\ 500\,K} C_6H_6Cl_6}$ (BHC)	only under forcing conditions
combustion	$\mathrm{2\,C_6H_6 + 15\,O_2 \longrightarrow 12\,CO_2 + 6\,H_2O}$	sooty flame (high C : H)

DIRECTING AND ACTIVATING EFFECTS

CLASS	GROUPS	EFFECT
o/p directing, activating (strong to weak)	$-\mathrm{O}-$, $-\mathrm{NH_2}$, $-\mathrm{NHR}$, $-\mathrm{NR_2}$, $-\mathrm{OH}$, $-\mathrm{OR}$, $-\mathrm{NHCOCH_3}$, $-\mathrm{OCOR}$, $-\mathrm{R}$, $-\mathrm{C_6H_5}$	push electrons ($+M$ or $+I$ /hyperconjugation): ring more reactive
o/p directing, deactivating	$-\mathrm{F}$, $-\mathrm{Cl}$, $-\mathrm{Br}$, $-\mathrm{I}$	$-I > +M$: slower than benzene, but $+M$ directs o/p
meta directing, deactivating	$-\mathrm{NO_2}$, $-\mathrm{NR_3}^+$, $-\mathrm{CN}$, $-\mathrm{SO_3H}$, $-\mathrm{CHO}$, $-\mathrm{COR}$, $-\mathrm{COOH}$, $-\mathrm{COOR}$, $-\mathrm{CONH_2}$, $-\mathrm{CCl_3}$, $-\mathrm{CF_3}$	withdraw electrons ($-M/-I$): ring less reactive



directing effects and the side chain: activating o/p directors (–CH_3), meta directors (–NO_2); light or heat halogenates the side chain, a Lewis acid the ring; $KMnO_4$ turns any alkyl side chain into –COOH

USING THE TABLE

- Reactivity towards electrophiles: phenol > anisole > toluene > benzene > chlorobenzene > benzoic acid > nitrobenzene.
- Disubstituted ring: the stronger activator controls; avoid the crowded position between two meta groups. The para product usually dominates for bulky groups.
- $-\mathrm{OH}$ is o/p; $-\mathrm{CN}$ is meta. Halogenation in the ring needs a Lewis acid and the dark; in the side chain it needs light or heat and no Lewis acid.

TRAP

Friedel-Crafts fails on strongly deactivated rings (nitrobenzene) and on aniline (the N lone pair binds $\mathrm{AlCl_3}$); aryl and vinyl halides cannot be the alkylating agent. Side-chain oxidation needs at least one benzylic H: $\mathrm{C_6H_5CH_2R} \rightarrow \mathrm{C_6H_5COOH}$, tert-butylbenzene is untouched.

5 Worked examples

COMBUSTION

An alkane needs 8 mol of O_2 per mol for complete combustion. Its formula? How many monochloro products if it is the one with a single product?

$\frac{3n+1}{2} = 8 \Rightarrow n = 5$, pentane (isomers); neopentane $C(CH_3)_4$ gives one monochloro product (all 12 H equivalent)

EUDIOMETRY

10 mL of a hydrocarbon burns completely in excess O_2; contraction on cooling is 20 mL. C_xH_y with $x = 2$?

contraction per mL $= 1 + \frac{y}{4} = 2 \Rightarrow y = 4$: C_2H_4, ethene

KOLBE AND WURTZ

Alkanes obtained on electrolysing a mixture of sodium acetate and sodium propanoate?

ethane (CH_3-CH_3), propane ($CH_3-C_2H_5$), butane ($C_2H_5-C_2H_5$): 3

PERCENT BR

Percent of bromine in the product of cyclohexene with Br_2.

$C_6H_{10}Br_2$, $M = 242$: $\frac{160}{242} = 66.1\%$

MARKOVNIKOV AND ANTI

Products of $CH_3CH{=}CH_2$ with HBr and with HBr /peroxide; and of 3-methylbut-1-ene with HCl.

2-bromopropane; 1-bromopropane. 3-methylbut-1-ene: the 2° cation rearranges by a 1, 2-hydride shift to the 3° cation: 2-chloro-2-methylbutane is the major product

DIRECTING

Major mononitration products of toluene and of benzoic acid.

toluene ($-CH_3$, o/p): *o*- and *p*-nitrotoluene; benzoic acid ($-COOH$, meta): *m*-nitrobenzoic acid

CONVERSION

Ethyne to benzene to nitrobenzene to *m*-dinitrobenzene.

$$3\,C_2H_2 \xrightarrow{873\,K} C_6H_6 \xrightarrow{HNO_3/H_2SO_4} C_6H_5NO_2 \xrightarrow{HNO_3\ (fuming),\ H_2SO_4,\ heat} m\text{-}C_6H_4(NO_2)_2$$

REAGENT CHOICE

cis-But-2-ene from but-2-yne; trans from but-2-yne; ethanal from ethyne.

H_2, Lindlar; Na, liq. NH_3; H_2O, $HgSO_4$, dil. H_2SO_4

6 Last-minute checklist

BEFORE YOU ANSWER

Alkane: free radical. Alkene or alkyne: electrophilic addition (Markovnikov unless peroxide). Benzene: electrophilic substitution; check the directing group and the conditions (Lewis acid, dark; or light for the side chain).

- Alkane prep: hydrogenation, Wurtz (even C), decarboxylation (one C less), Kolbe (R−R at anode; acetate gives ethane), Grignard + water; reactions: radical halogenation, combustion $(3n+1)/2$, isomerisation, aromatisation.
- Alkene prep: Lindlar (cis), Na/NH_3 (trans), alc. KOH (Saytzeff), Zn dehalogenation, dehydration (443 K); reactions: H_2, Br_2 (anti), HX (Markovnikov), HBr/peroxide only, hydration, Baeyer diol, hot $KMnO_4$ cleavage, ozonolysis.
- Alkyne: acidic *sp* C−H (Na, $NaNH_2$, Ag^+, Cu^+ acetylides, terminal only); hydration gives ketone (ethyne: ethanal); double HX; trimerisation to benzene.
- Benzene: nitration NO_2^+, halogenation (Lewis acid, dark), sulphonation (reversible), FC alkylation (rearranges), FC acylation (clean); meta: NO_2, CN, COOH, CHO, SO_3H; o/p: OH, NH_2, R, halogens (deactivating).
- Counts: Wurtz or Kolbe on a mixture gives 3 alkanes; one monochloro product means all H equivalent; ethane torsion about 12 kJ mol^{-1}; anti is the most stable butane conformer.

Now test it. Practise this chapter with past-paper and bank questions on Prep Vault. **Practice this chapter →**