

Alkanes and Alkenes

01 · ALKANES — STRUCTURE

C_nH_{2n+2} , all σ bonds, sp^3 carbon, tetrahedral at 109.5° . Free rotation about every C–C bond.

Non-polar, so only London forces: boiling point rises with chain length and falls with branching, and they are insoluble in water.

02 · WHY ALKANES ARE UNREACTIVE

C–C and C–H bonds are strong and almost non-polar, so there is no $\delta+$ carbon for a nucleophile to attack and no electron-rich site for an electrophile. Only radicals and combustion get past that.

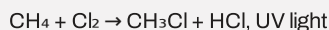
03 · COMBUSTION

Complete: $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$.

Incomplete: limited oxygen gives CO (toxic, binds haemoglobin) and carbon soot.

Other pollutants: NO_x from the high engine temperature, SO_2 from sulfur impurities, and unburnt hydrocarbons — all removed or reduced by a catalytic converter.

04 · FREE-RADICAL SUBSTITUTION



Initiation $Cl_2 \rightarrow 2Cl\cdot$ (homolysis by UV)

Propagation $Cl\cdot + CH_4 \rightarrow \cdot CH_3 + HCl$
 $\cdot CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\cdot$

Termination $Cl\cdot + \cdot CH_3 \rightarrow CH_3Cl$
 $2\cdot CH_3 \rightarrow C_2H_6$

Poor for synthesis: further substitution gives CH_2Cl_2 , $CHCl_3$ and CCl_4 , and termination gives a mixture.

05 · CRACKING

Long alkanes are broken into shorter, more useful ones plus an alkene.

Catalytic — zeolite, $\sim 450^\circ C$, moderate pressure; gives branched alkanes and arenes for fuels.

Thermal — higher temperature and pressure; gives more alkenes for polymers.

06 · ALKENES — STRUCTURE

C_nH_{2n} . The C=C is one σ plus one π bond; each carbon is sp^2 , trigonal planar at 120° .

The π electrons sit above and below the plane, exposed and easily attacked — so alkenes react with **electrophiles**. The π bond also blocks rotation, giving cis–trans isomerism.

07 · ADDITION REACTIONS OF ALKENES

Reagent	Conditions	Product
H_2	Ni, $150^\circ C$	alkane
Br_2	room temp	dibromoalkane
HBr	room temp	bromoalkane
steam	H_3PO_4 , $300^\circ C$, 60 atm	alcohol
cold dilute $KMnO_4$	—	diol

Test for a C=C: bromine water is decolourised from orange to colourless at room temperature.

08 · ELECTROPHILIC ADDITION MECHANISM

- The π electrons attack the $\delta+$ end of HBr (or induce a dipole in Br_2).
- The H–Br bond breaks heterolytically, giving Br^- and a **carbocation**.
- Br^- attacks the carbocation to give the product.

Curly arrow 1 from the C=C to the H; arrow 2 from the H–Br bond to Br; arrow 3 from the lone pair on Br^- to the positive carbon.

09 · MARKOVNIKOV'S RULE

The hydrogen adds to the carbon that already carries **more** hydrogens, because that route goes through the more stable carbocation.

Stability order **tertiary > secondary > primary**: alkyl groups are electron-releasing and spread the positive charge. So propene + HBr gives mainly 2-bromopropane.

10 · OXIDATION OF ALKENES

Cold dilute acidified $KMnO_4$ $\rightarrow$ diol; purple decolourises.

Hot concentrated acidified $KMnO_4$ $\rightarrow$ the C=C is cleaved. A terminal $=CH_2$ gives CO_2 ; $=CHR$ gives a carboxylic acid; $=CR_2$ gives a ketone — which lets you deduce where the double bond was.

11 · WORKED EXAMPLE — LOCATE THE C=C

An alkene C_5H_{10} gives propanone and ethanoic acid on vigorous oxidation. Identify it.

Propanone $\leftarrow (CH_3)_2C=$

Ethanoic acid $\leftarrow =CHCH_3$

Join the fragments: **$(CH_3)_2C=CHCH_3$** , 2-methylbut-2-ene.

12 · ADDITION POLYMERISATION

$n CH_2=CH_2 \rightarrow -(CH_2-CH_2)_n-$. Draw the repeat unit in brackets with bonds through them and n outside.

Poly(alkenes) are inert and non-biodegradable, so disposal means landfill, incineration with energy recovery, or recycling. PVC releases HCl on burning.

13 · WORKED EXAMPLE — MARKOVNIKOV

Predict the major product of but-1-ene + HBr.

H can add to C1 or C2.

Adding to C1 gives a **secondary** carbocation on C2.

Adding to C2 gives a primary carbocation on C1.

The secondary cation is the more stable, so the major product is **2-bromobutane**; 1-bromobutane forms in small amounts.

14 · ALKANES AGAINST ALKENES

	Alkane	Alkene
bonding	all σ	$\sigma + \pi$
attacked by	radicals	electrophiles
typical reaction	substitution	addition
$Br_2(aq)$	no change	decolourised
$KMnO_4$	no change	decolourised

MARKS LOST HERE

— Leaving out a termination step, or writing initiation without UV.

— Forgetting the induced dipole when Br_2 attacks a C=C.

— Predicting the minor product by ignoring carbocation stability.

— Drawing a polymer repeat unit still containing a double bond.

Arenes — Benzene Chemistry

15 · STRUCTURE OF BENZENE

C_6H_6 , planar, regular hexagon, all bond angles 120° , every carbon sp^2 . Each carbon's remaining p orbital overlaps sideways into a **delocalised π system** above and below the ring.

Evidence: all six C–C bonds are the same length, between a single and a double bond; and the enthalpy of hydrogenation is about 150 kJ mol^{-1} less exothermic than three times that of cyclohexene, so benzene is more stable than the Kekulé structure predicts.

16 · WHY SUBSTITUTION, NOT ADDITION

Addition would destroy the delocalised system and its extra stability. Substitution keeps the ring intact, so benzene undergoes **electrophilic substitution** — and it needs stronger conditions than an alkene because the π electrons are spread out and less available.

17 · THE FOUR SUBSTITUTIONS

Reaction	Reagents	Electrophile
nitration	conc. HNO_3 / conc. H_2SO_4 , $55^\circ C$	NO_2^+
halogenation	Cl_2 or Br_2 with $AlCl_3$ / $FeBr_3$	Cl^+ or Br^+
Friedel–Crafts alkylation	RCI / $AlCl_3$	R^+
Friedel–Crafts acylation	$RCOCl$ / $AlCl_3$	RCO^+

$AlCl_3$ is a **halogen carrier** — it polarises the reagent to generate the electrophile and is regenerated at the end.

18 · THE MECHANISM IN THREE STEPS

1 · Generate the electrophile



2 · Attack — two π electrons from the ring form a bond to the electrophile, giving an unstable intermediate with a broken delocalised system and a positive charge.

3 · Restore aromaticity — H^+ is lost from that carbon and the ring's delocalisation is re-formed.

19 · SIDE-CHAIN REACTIONS

UV light favours free-radical substitution in the side chain: methylbenzene + $Cl_2 \rightarrow$ chloromethylbenzene.

$AlCl_3$ and no light favours substitution in the ring instead. The condition decides the site.

Hot alkaline $KMnO_4$ oxidises any alkyl side chain all the way to $-COOH$: methylbenzene $\rightarrow$ benzoic acid.

20 · DIRECTING EFFECTS

Group	Effect	Directs to
$-OH$, $-NH_2$, $-CH_3$	activating	2- and 4-
$-NO_2$, $-COOH$, $-CHO$	deactivating	3-

Electron-releasing groups push charge into the ring, making it more reactive than benzene; electron-withdrawing groups do the reverse. Phenol reacts with bromine water alone, without a catalyst.

21 · WORKED EXAMPLE — PLAN A SYNTHESIS

Make 3-nitrobenzoic acid from methylbenzene.

Nitrate first and you get the 2- and 4- isomers, since $-CH_3$ directs there.

So **oxidise first**:

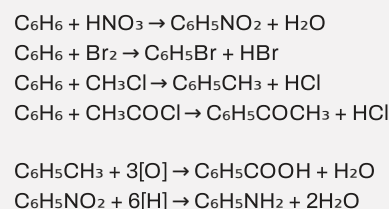
- 1 · hot alkaline $KMnO_4$, then $H^+ \rightarrow$ benzoic acid
- 2 · conc. HNO_3 / conc. H_2SO_4 , $55^\circ C \rightarrow$ the $-COOH$ group directs to the 3- position.

22 · COMPARING BENZENE WITH ALKENES

	Benzene	Alkene
π electrons	delocalised	localised
$Br_2(aq)$	no reaction	decolourised
typical reaction	substitution	addition

This test distinguishes them in seconds and is the standard exam question.

23 · EQUATIONS TO KNOW



24 · BENZENE, METHYLBENZENE, PHENOL

Reactivity to electrophiles rises in the order **benzene < methylbenzene < phenol**.

$-CH_3$ releases electrons inductively; $-OH$ donates a whole lone pair into the delocalised system. The more electron-rich the ring, the more readily it attracts an electrophile — which is why phenol needs only bromine water while benzene needs a halogen carrier.

25 · WORKED EXAMPLE — IDENTIFY THE PRODUCT

Methylbenzene is refluxed with Cl_2 in the presence of $AlCl_3$, then the product is treated with hot alkaline $KMnO_4$.

$AlCl_3$, no UV $\rightarrow$ ring substitution, and $-CH_3$ directs to 2- and 4- $\rightarrow$ 4-chloromethylbenzene
Hot alkaline $KMnO_4 \rightarrow$ the side chain is oxidised $\rightarrow$ **4-chlorobenzoic acid**

26 · WHY THE CONDITIONS MATTER

Nitration above about $60^\circ C$ gives dinitro products; below $50^\circ C$ the reaction is impractically slow. The quoted $55^\circ C$ is the working compromise.

Friedel–Crafts must be run in dry conditions, since $AlCl_3$ is hydrolysed by water and the catalyst is destroyed.

MARKS LOST HERE

- Drawing benzene with three localised double bonds when asked about delocalisation.
- Omitting the step that regenerates the aromatic ring by losing H^+ .
- Saying benzene decolourises bromine water.
- Nitrating before oxidising when the directing effects demand the reverse.