

Organic chemistry (A Level introduction)

A-Level Chemistry 9701 · Topic 29 revision notes

Everything from the 4 lessons of this topic on a few pages: the key idea of each lesson, the diagram to remember, the points to learn and the traps examiners set. Read it, cover it, test yourself.

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| 1. <u>A Level functional groups and naming</u> | 3. <u>Structure of benzene</u> |
| 2. <u>A Level organic reactions</u> | 4. <u>Optical isomerism</u> |

1 A Level functional groups and naming

Syllabus 29.1

At A Level the organic toolkit grows. An **arene** contains a benzene ring (C_6H_5- is the **phenyl** group); a **halogenoarene** has a halogen joined directly to the ring; a **phenol** has $-OH$ joined directly to the ring. **Acyl chlorides** ($RCOCl$), **amides** ($RCONH_2$) and **nitriles** (RCN) are named from the parent acid or alkane, counting the functional carbon. **Amines** are classified by the number of carbon groups bonded to the nitrogen: one (**primary**, RNH_2), two (**secondary**, R_2NH) or three (**tertiary**, R_3N). An **amino acid** has both $-NH_2$ and $-COOH$, and 2-amino acids carry both on the same carbon. On a benzene ring, substituents get **locants** numbered to be as low as possible, as in 1,3-dinitrobenzene.

functional groups met at A Level

arene $C_6H_5CH_3$	phenol C_6H_5OH	acyl chloride CH_3COCl	amide CH_3CONH_2
amine $C_2H_5NH_2$	amino acid H_2NCH_2COOH	nitrile $CH_3C\equiv N$	halogenoarene C_6H_5Cl

amines: count the carbon groups on N

primary RNH_2 ethylamine	secondary R_2NH diethylamine	tertiary R_3N triethylamine
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Fig. 1: the A Level functional groups and the three classes of amine

Group, parent, locants.

- ✓ **Phenol:** OH directly on the ring; that carbon is C1.
- ✓ **Acyl chloride, amide, nitrile:** count the functional carbon in the stem.
- ✓ **Amines:** 1, 2 or 3 carbon groups on N.
- ✓ **Ring locants:** lowest set, alphabetical order.

Watch out!

Amines are classified by counting the **carbon groups on the nitrogen**, not by the type of carbon the nitrogen is on: $(\text{CH}_3)_3\text{CNH}_2$ is a **primary** amine even though it would be a tertiary alcohol if the NH_2 were OH. Phenol has **-OH directly on the ring**; $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ is an alcohol (phenylmethanol). Chlorobenzene is a halogenoarene; $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$, with Cl on a side chain, behaves like a halogenoalkane.

2 A Level organic reactions

Syllabus 29.2

In **electrophilic substitution** an electrophile such as NO_2^+ attacks the delocalised electrons of a benzene ring and replaces an H atom, so the ring survives. In **addition-elimination** a nucleophile adds to the $\text{C}=\text{O}$ carbon of an acyl chloride and then Cl^- is eliminated, leaving HCl . A **condensation** reaction joins two molecules with the loss of a small molecule such as H_2O or HCl . **Hydrolysis** breaks a bond by reaction with water, often catalysed by acid or alkali. **Reduction** adds hydrogen or removes oxygen (written $[\text{H}]$); **oxidation** adds oxygen or removes hydrogen (written $[\text{O}]$). **Diazotisation** turns phenylamine into a diazonium salt, which **couples** with phenol to make an azo dye.

A Level reaction types, one example each

electrophilic substitution	$\text{C}_6\text{H}_6 + \text{HNO}_3 \rightarrow \text{C}_6\text{H}_5\text{NO}_2 + \text{H}_2\text{O}$
addition-elimination	$\text{CH}_3\text{COCl} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{HCl}$
condensation	$\text{CH}_3\text{COCl} + \text{CH}_3\text{NH}_2 \rightarrow \text{CH}_3\text{CONHCH}_3 + \text{HCl}$
hydrolysis	$\text{CH}_3\text{CONH}_2 + \text{H}_2\text{O} + \text{H}^+ \rightarrow \text{CH}_3\text{COOH} + \text{NH}_4^+$
reduction	$\text{C}_6\text{H}_5\text{NO}_2 + 6[\text{H}] \rightarrow \text{C}_6\text{H}_5\text{NH}_2 + 2\text{H}_2\text{O}$
oxidation	$\text{C}_6\text{H}_5\text{CH}_3 + 3[\text{O}] \rightarrow \text{C}_6\text{H}_5\text{COOH} + \text{H}_2\text{O}$

Fig. 1: the six A Level reaction types, each with an example

What attacks, what is lost.

- ✓ **Arenes:** electrophilic substitution; the ring survives.
- ✓ **Acyl chlorides:** addition-elimination; HCl lost.
- ✓ **Condensation** loses a small molecule; **hydrolysis** uses water.
- ✓ **[H]** for reduction, **[O]** for oxidation; balance by atoms.

Watch out!

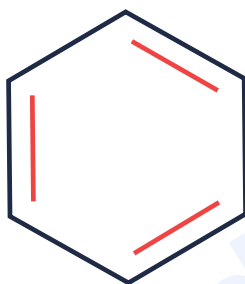
Benzene undergoes electrophilic **substitution**, not addition: an addition would destroy the stable delocalised ring. Addition-elimination happens at the **C=O carbon** of an acyl chloride, so it is not the same as nucleophilic substitution of a halogenoalkane. Hydrolysis and condensation are opposites: condensation **releases** a small molecule, hydrolysis **uses** water to split a bond.

3 Structure of benzene

Syllabus 29.3

Each carbon in benzene is **sp^2 hybridised**: it forms three sigma bonds (two to C, one to H) in a plane at **120°** , so the ring is **planar**. The remaining p orbital on each carbon overlaps sideways with both neighbours, forming a **delocalised pi system** of six electrons in rings **above and below** the plane. The evidence against the **Kekulé** structure is threefold: all six C-C bonds are **0.139 nm** , between C-C (0.154 nm) and C=C (0.134 nm); the **enthalpy of hydrogenation** is -208 kJ mol^{-1} , not the -360 kJ mol^{-1} predicted from three C=C bonds, so benzene is about **152 kJ mol^{-1} more stable**; and benzene **resists addition**, preferring substitution that keeps the delocalised ring.

Kekulé model



alternating C=C and C-C
 0.134 nm and 0.154 nm

delocalised model



six equal C-C bonds
all 0.139 nm

ΔH hydrogenation: predicted $3 \times (-120) = -360$, actual -208 kJ mol^{-1}
delocalisation makes benzene 152 kJ mol^{-1} more stable

Fig. 1: the Kekulé model against the delocalised model of benzene

sp^2 , planar, delocalised.

- ✓ **Bonding:** sp^2 , 120° , planar, p orbitals overlap sideways.
- ✓ **Lengths:** 0.154 nm (C-C), 0.139 (benzene), 0.134 nm (C=C).
- ✓ **Hydrogenation:** -360 predicted, -208 actual, 152 more stable.
- ✓ **Reactivity:** substitution, not addition.

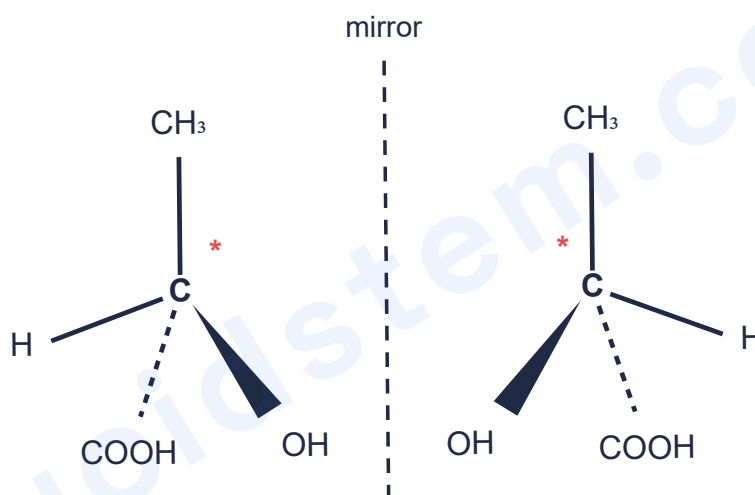
Watch out!

The circle does **not** mean benzene has no double bond character: every C-C bond has some. Stabilisation is 152 kJ mol^{-1} , the gap between -360 and -208 , not 208 . The pi electrons are **above and below** the plane of the ring, not in it; the sigma framework lies in the plane.

4 Optical isomerism

Syllabus 29.4

A **chiral centre** is a carbon atom bonded to **four different groups**. A molecule with one chiral centre exists as two **enantiomers**: **non-superimposable mirror images** of each other. Enantiomers have identical physical properties and identical reactions with non-chiral reagents, but they **rotate plane-polarised light** by equal amounts in **opposite directions**. A **racemic mixture** contains equal amounts of the two and has no net effect on plane-polarised light. Living systems are chiral, so enantiomers can act very differently as **drugs**: one enantiomer of thalidomide is a sedative, the other caused birth defects. A molecule with **n** chiral centres has at most **2^n** stereoisomers.



2-hydroxypropanoic acid (lactic acid): two enantiomers

* chiral centre: a carbon with four different groups

Fig. 1: the two enantiomers of 2-hydroxypropanoic acid, mirror images about a dashed mirror plane

Four different groups, two mirror images.

- ✓ **Chiral centre:** C with four different groups.
- ✓ **Enantiomers:** non-superimposable mirror images.
- ✓ **Racemic:** 50 : 50, no net rotation.
- ✓ **n centres:** up to **2^n** stereoisomers.

Watch out!

A chiral centre needs four **different groups**, not four different atoms: in butan-2-ol the CH_3 and C_2H_5 both join through carbon but are different groups. A carbon in a $\text{C}=\text{C}$ or $\text{C}=\text{O}$ is never a chiral centre. Enantiomers have the **same** boiling point, density and reactions with non-chiral reagents; only the direction of rotation of plane-polarised light (and their behaviour with other chiral molecules) differs. 2^n is a **maximum**: symmetrical molecules can have fewer.