# Topic 17: Organic Chemistry II

Edexcel A Level Chemistry • Paper 1 (9CH0/01)

17.1 Know that optical isomerism results from chirality in molecules with a single chiral centre.

Optical isomerism is a type of stereoisomerism. It occurs when a molecule contains a chiral centre — a carbon atom bonded to four different groups. This produces two non-superimposable mirror image molecules called enantiomers. The two enantiomers are related as object and mirror image (like left and right hands).

17.2 Understand that optical isomers are object and non-superimposable mirror images from asymmetric carbon atoms.

An asymmetric (chiral) carbon has four different substituents attached. The two enantiomers are mirror images that cannot be superimposed on each other, no matter how they are rotated. They have identical physical properties (m.p., b.p., solubility, density) and identical chemical properties with achiral reagents. The only difference: they rotate plane-polarised light in opposite directions by equal angles.

17.3 Know that optical activity is the ability of a single optical isomer to rotate plane-polarised monochromatic light.

A single enantiomer rotates the plane of plane-polarised monochromatic light either:

- Clockwise (+, dextrorotatory)
- Anticlockwise (–, laevorotatory)

The two enantiomers rotate by the same angle but in opposite directions. This is measured using a polarimeter.

17.4 Understand the nature of a racemic mixture.

A racemic mixture (racemate) contains equal amounts of both enantiomers. It shows no net optical activity because the rotations of the two enantiomers cancel exactly. Racemic mixtures are produced when a planar intermediate (e.g. a carbocation in SN1, or the planar C=O in nucleophilic addition with HCN) is attacked equally from both faces.

17.5 Be able to use data on optical activity as evidence for SN1 and SN2 mechanisms.

SN1 (tertiary halogenoalkanes): produces a racemic mixture — the planar carbocation intermediate is attacked from both sides with equal probability → no net optical activity.

SN2 (primary halogenoalkanes): produces a single enantiomer with inverted configuration (Walden inversion) — the nucleophile attacks from directly opposite the leaving group (backside attack). If a single enantiomer reacts via SN2, the product is a single enantiomer with the opposite configuration.

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17.6 Be able to identify the aldehyde and ketone functional groups.

Aldehyde: contains a –CHO group — the C=O carbon has one H and one carbon substituent (or H and H for methanal). Always at the end of the carbon chain. Named with suffix –al (e.g. ethanal, $CH_3CHO$).

Ketone: contains a C=O group where the carbonyl carbon is bonded to two carbon groups. Always in the middle of the chain. Named with suffix –one (e.g. propanone, $CH_3COCH_3$).

Both contain the carbonyl group (C=O) but can be distinguished by chemical tests.

17.7 Understand that: (i) aldehydes and ketones cannot form intermolecular H-bonds with each other, (ii) they can H-bond with water.

(i) Aldehydes and ketones have a C=O group (δ– on O, δ+ on C) but no O–H or N–H bond, so they cannot form hydrogen bonds with each other. Their boiling points are lower than alcohols of similar Mr.

(ii) The lone pairs on the C=O oxygen can accept H-bonds from water molecules (the δ+H of water bonds to the δ–O of C=O). This makes small aldehydes and ketones miscible with water.

17.8 Understand reactions of carbonyl compounds with: (i) Fehling's/Benedict's, Tollens', acidified dichromate, (ii) $LiAlH_4$, (iii) HCN/KCN, (iv) 2,4-DNPH, (v) $I_2$/NaOH.

(i) Distinguishing aldehydes from ketones:

- Fehling's/Benedict's (heat): aldehyde → brick-red precipitate of $Cu_2O$. Ketone: no change.
- Tollens' reagent (warm, ammoniacal $AgNO_3$): aldehyde → silver mirror (Ag deposited). Ketone: no change.
- Acidified $K_2Cr_2O_7$ (warm): aldehyde → orange turns green ($Cr^{3+}$). Ketone: no change.

(ii) Reduction with $LiAlH_4$ in dry ether:

Aldehyde → primary alcohol. Ketone → secondary alcohol.

[H] is used in equations to represent the hydride reducing agent.

(iii) Nucleophilic addition with HCN/KCN (room temperature):

C=O + HCN → hydroxynitrile. Mechanism: $CN^-$ (nucleophile) attacks the δ+C of C=O (curly arrow from lone pair on C of $CN^-$ to δ+C). The π-bond breaks, electrons go to O forming $O^-$. Then $H^+$ from HCN protonates the $O^-$. If a new chiral centre is created, a racemic mixture is produced (attack from either side of the planar C=O).

(iv) 2,4-DNPH (room temperature): orange/yellow precipitate forms with any carbonyl compound (aldehyde or ketone). Tests for the presence of C=O. Recrystallise the precipitate and measure the melting point to identify the specific carbonyl compound.

(v) Iodoform reaction ($I_2$/NaOH, warm): yellow precipitate of $CHI_3$ (triiodomethane) with a distinctive antiseptic smell. Positive result for: ethanal ($CH_3CHO$) and methyl ketones ($CH_3CO$– group).

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17.9 Be able to identify the carboxylic acid functional group.

Carboxylic acid: contains a –COOH group — the C=O and O–H are on the same carbon, always at the end of the chain. Named with suffix –oic acid (e.g. ethanoic acid, $CH_3COOH$). Weak acids: partially dissociate in water — $RCOOH \rightleftharpoons RCOO^- + H^+$.

17.10 Understand that hydrogen bonding affects physical properties of carboxylic acids.

Carboxylic acids can form hydrogen bonds via both the O–H and the C=O groups. In pure liquid or solid form they often exist as dimers — two molecules joined by two H-bonds (O–H···O=C and O=C···H–O). This gives them anomalously high boiling points compared to alcohols or aldehydes of similar Mr. Small carboxylic acids are soluble in water due to H-bonding with water molecules.

17.11 Understand that carboxylic acids can be prepared by: oxidation of alcohols/aldehydes, hydrolysis of nitriles.

From primary alcohols or aldehydes: reflux with excess acidified $K_2Cr_2O_7$ (orange → green). The alcohol is first oxidised to the aldehyde, then further to the carboxylic acid.

From nitriles (acid hydrolysis): $R–CN + 2H_2O + HCl \rightarrow R–COOH + NH_4Cl$. Reflux with dilute HCl. Produces a carboxylic acid with one more carbon atom than the original halogenoalkane used to make the nitrile (useful for chain extension).

17.12 Understand reactions of carboxylic acids with: (i) $LiAlH_4$, (ii) bases, (iii) $PCl_5$, (iv) alcohols/acid catalyst.

(i) Reduction with $LiAlH_4$ in dry ether: carboxylic acid → primary alcohol.

(ii) With bases (neutralisation): $RCOOH + NaOH \rightarrow RCOONa + H_2O$. Forms a carboxylate salt.

(iii) With $PCl_5$ (room temperature): $RCOOH + PCl_5 \rightarrow RCOCl + POCl_3 + HCl$. Steamy white fumes of HCl confirm the reaction. Produces an acyl chloride. ($PCl_5$ also tests for –OH groups.)

(iv) With alcohols (esterification, conc. $H_2SO_4$ catalyst, reflux): $RCOOH + R'OH \rightleftharpoons RCOOR' + H_2O$. Reversible reaction — equilibrium mixture. Esters have characteristic fruity smells.

17.13 Be able to identify acyl chloride and ester functional groups.

Acyl chloride: contains –COCl (a C=O bonded directly to Cl). Very reactive. Named with suffix –oyl chloride (e.g. ethanoyl chloride, $CH_3COCl$).

Ester: contains –COO– (a C=O bonded to O, which is bonded to another carbon). Named as alkyl alkanoate (e.g. ethyl ethanoate, $CH_3COOC_2H_5$). Esters are formed from a carboxylic acid and an alcohol.

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17.14 Understand reactions of acyl chlorides with: (i) water, (ii) alcohols, (iii) conc. ammonia, (iv) amines.

Acyl chlorides react vigorously at room temperature with no catalyst needed (much faster than carboxylic acids):

(i) + Water: RCOCl + $H_2O$ → RCOOH + HCl (steamy white fumes of HCl).

(ii) + Alcohol: RCOCl + R′OH → RCOOR′ + HCl. Ester formed — faster and goes to completion unlike acid/alcohol esterification.

(iii) + Conc. ammonia: RCOCl + $2NH_3$ → $RCONH_2$ + $NH_4Cl$. Primary amide formed.

(iv) + Amine ($RNH_2$): RCOCl + $R'NH_2$ → RCONHR′ + HCl. N-substituted (secondary) amide formed.

17.15 Understand the hydrolysis of esters in acidic and alkaline solution.

Acid hydrolysis: RCOOR′ + $H_2O$ ⇌ RCOOH + R′OH (reversible, reflux with dilute $H_2SO_4$). Produces carboxylic acid + alcohol. Equilibrium mixture — yield can be improved by excess water.

Alkaline hydrolysis (saponification): RCOOR′ + NaOH → RCOONa + R′OH (irreversible, reflux with NaOH). Produces the sodium salt of the carboxylic acid + alcohol. Irreversible because the carboxylate salt ($RCOO^-$) cannot react with the alcohol. This is the basis of soap-making.

17.16 Understand how polyesters are formed by condensation polymerisation.

Condensation polymerisation: monomers join together with the loss of a small molecule ($H_2O$) at each link.

Polyesters form from a dicarboxylic acid + a diol (two –OH groups). An ester bond (–COO–) forms at each link with loss of $H_2O$. Alternatively, a single monomer containing both –COOH and –OH can polymerise with itself (a hydroxy acid).

E.g. Terylene/PET: benzene-1,4-dicarboxylic acid + ethane-1,2-diol → polyester + $nH_2O$.

Unlike addition polymers, condensation polymers are biodegradable because the ester bonds can be hydrolysed.

ABOUT THESE NOTES

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