Chemistry Units 3 & 4

Chapter 9 — Reactions of organic compounds

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Chapter 9 Reactions of organic compounds — 9A Substitution, addition and oxidation

Theory

Whether an organic molecule reacts, and how, is largely decided by two features: whether its carbon skeleton is **saturated** (only single C–C and C–H bonds) or **unsaturated** (it contains a carbon–carbon double bond), and which **functional group** it carries. This subtopic examines three fundamental reaction types of the organic families met in Chapter 8: **substitution**, in which one atom or group replaces another on a *saturated* molecule; **addition**, in which a small molecule adds across the double bond of an *unsaturated* molecule; and **oxidation**, in which an alcohol is converted to an aldehyde, a carboxylic acid or a ketone by an oxidising agent.

Writing organic equations. The equations in this subtopic are written with **semi-structural (condensed) formulae**, so that the change to the functional group can be seen, and with any **reaction conditions or catalyst shown above the arrow** — for example UV light, a nickel catalyst, or an acid catalyst. Because the physical state of an organic compound depends on the exact conditions chosen, state symbols are not attached to the organic species; the focus is on which atoms are rearranged and what conditions are required.

Substitution — how saturated molecules react. In a saturated molecule every carbon atom already has four single bonds, so the molecule cannot take up any extra atoms. It can react only by **substitution**, in which one atom is **replaced** by another. An **alkane** undergoes substitution with a halogen (Cl_2 or Br_2) only in the presence of **ultraviolet (UV) light**, which supplies the energy to start the reaction; one hydrogen atom is replaced by a halogen atom and a molecule of hydrogen halide is released:

$$CH_4 + Cl_2 \xrightarrow{UV} CH_3Cl + HCl$$

The organic product is a **haloalkane**. Haloalkanes in turn react by substitution: warmed with **aqueous hydroxide ions**, the halogen atom is replaced by a **hydroxyl (–OH) group**, converting the haloalkane into an **alcohol**, and the halogen leaves as a halide ion:

$$CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$$

These two steps are the study-design routes to a primary haloalkane and to a primary alcohol by substitution.

Addition — how unsaturated molecules react. An **alkene** contains a **C=C double bond**, one component of which (the π bond) is relatively weak and reactive. The two carbon atoms of the double bond can each accept a new atom, so an alkene reacts by **addition**: a small molecule adds **across the double bond**, which becomes a single bond, and **nothing is released**. Four addition reactions are required.

- **Hydrogenation** — an alkene adds hydrogen over a **nickel catalyst**, forming the corresponding alkane:

$$CH_2{=}CH_2 + H_2 \xrightarrow{Ni} CH_3CH_3$$

- **Halogenation** — an alkene adds a halogen (no catalyst needed), forming a di-haloalkane. The rapid loss of the orange-brown colour of bromine is the standard test for a C=C double bond:

$$CH_2{=}CH_2 + Br_2 \rightarrow CH_2BrCH_2Br$$

- **Hydrohalogenation** — an alkene adds a hydrogen halide (HCl, HBr, …), forming a haloalkane:

$$CH_2{=}CH_2 + HCl \rightarrow CH_3CH_2Cl$$

- **Hydration** — an alkene adds water in the presence of an **acid catalyst**, forming an alcohol:

$$CH_2{=}CH_2 + H_2O \xrightarrow{H^+} CH_3CH_2OH$$

Because an alkene takes up the whole of the added molecule, addition is an efficient, atom-economical way of introducing a functional group into a hydrocarbon.

Oxidation of alcohols. A **primary or secondary alcohol** can be **oxidised** by warming it with an **acidified oxidising agent** — either acidified permanganate (MnO_4^- / H^+) or acidified dichromate ($Cr_2O_7^{2-} / H^+$). In the equation the oxidant is represented by $[O]$, standing for one oxygen atom supplied by the oxidising agent, and a molecule of water is formed. As it reacts, the oxidant **changes colour**, and this colour change is the observation that a reaction has taken place:

- acidified **permanganate**: **purple → colourless** (MnO_4^- reduced to Mn^{2+});
- acidified **dichromate**: **orange → green** ($Cr_2O_7^{2-}$ reduced to Cr^{3+}).

A **primary alcohol** is oxidised in two stages — first to an **aldehyde** (partial oxidation), then, with further oxidant, to a **carboxylic acid** (complete oxidation):

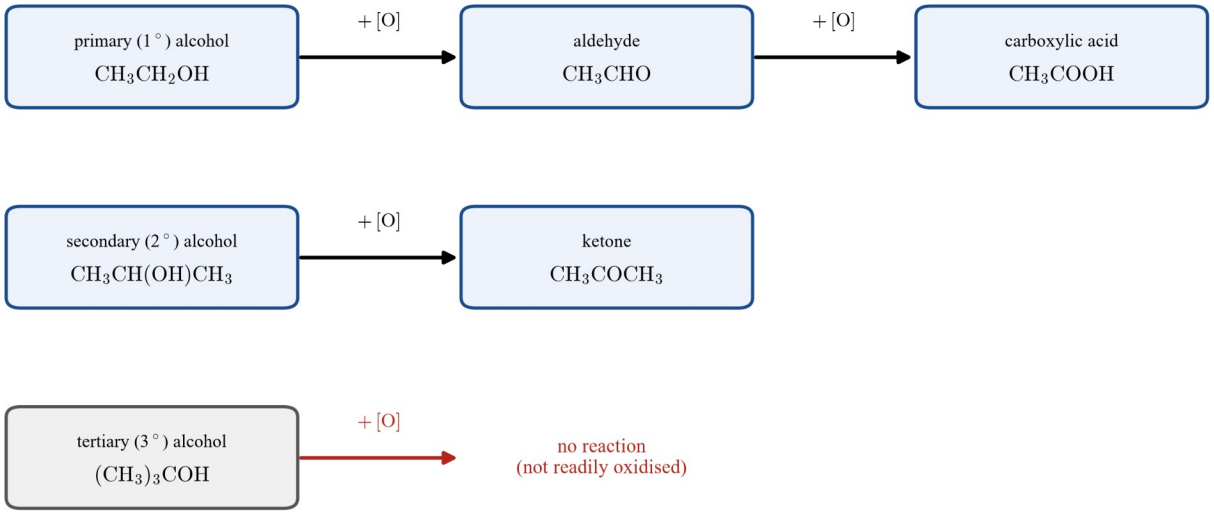
$$CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O$$

$$CH_3CH_2OH + 2[O] \rightarrow CH_3COOH + H_2O$$

A **secondary alcohol** is oxidised to a **ketone**, and no further:

$$CH_3CH(OH)CH_3 + [O] \rightarrow CH_3COCH_3 + H_2O$$

A **tertiary alcohol is not readily oxidised**: the carbon carrying the –OH is bonded to three other carbons and has no hydrogen atom to lose, so the oxidant is left unchanged and its colour **persists** (permanganate stays purple, dichromate stays orange). The loss or persistence of the oxidant's colour therefore distinguishes a tertiary alcohol from a primary or secondary one.



Recognising the reaction type. The type of reaction follows directly from the reactant. A **saturated** molecule — an alkane or a haloalkane — can react only by **substitution**; an **unsaturated** molecule — an alkene — reacts by **addition** across its C=C bond; and an **alcohol** warmed with an acidified oxidant undergoes **oxidation**. Reading the reactants therefore tells you both the reaction type and the class of product to expect.

Worked examples

Worked Example 1 — Ethane reacts with chlorine gas in the presence of UV light to give a monochlorinated product; that product is then warmed with aqueous sodium hydroxide. Write a balanced equation for each step, name the organic product, and state the reaction type.

Working	Comment
Step 1: $CH_3CH_3 + Cl_2 \xrightarrow{UV} CH_3CH_2Cl + HCl$	One H of ethane is replaced by Cl; UV light is essential to start the reaction.

Working	Comment
Organic product: **chloroethane**, CH_3CH_2Cl.	A haloalkane, general formula $C_nH_{2n+1}X$.
Type: **substitution** (ethane is saturated).	A saturated molecule cannot add atoms, so it substitutes.
Step 2: $CH_3CH_2Cl + OH^- \rightarrow CH_3CH_2OH + Cl^-$	The Cl atom is replaced by an $-OH$ group; the chlorine leaves as Cl^-.
Organic product: **ethanol**, CH_3CH_2OH; type **substitution**.	Charge balances: -1 on each side.

Worked Example 2 — Ethene undergoes addition with (i) hydrogen over a nickel catalyst, (ii) bromine, (iii) hydrogen chloride, and (iv) water with an acid catalyst. Write the equation for each, name the product, and classify the reactions.

Working	Comment
(i) $CH_2{=}CH_2 + H_2 \xrightarrow{Ni} CH_3CH_3$ → **ethane**	Hydrogenation: H adds across the C=C over a Ni catalyst.
(ii) $CH_2{=}CH_2 + Br_2 \rightarrow CH_2BrCH_2Br$ → **1,2-dibromoethane**	Halogenation: bromine's orange-brown colour is lost — the test for C=C.
(iii) $CH_2{=}CH_2 + HCl \rightarrow CH_3CH_2Cl$ → **chloroethane**	Hydrohalogenation: H and Cl add across the double bond.
(iv) $CH_2{=}CH_2 + H_2O \xrightarrow{H^+} CH_3CH_2OH$ → **ethanol**	Hydration: water adds across the C=C with an acid catalyst.
All four are **addition** reactions.	The double bond becomes a single bond and nothing is released.

Worked Example 3 — Propan-1-ol is warmed with acidified potassium permanganate. Write equations for its partial and its complete oxidation, name the organic product of each, and state the colour change of the oxidant.

Propan-1-ol is a **primary** alcohol, so it is oxidised first to an aldehyde and then, with more oxidant, to a carboxylic acid. Partial oxidation gives **propanal**:

$$CH_3CH_2CH_2OH + [O] \rightarrow CH_3CH_2CHO + H_2O$$

Continued oxidation gives **propanoic acid**:

$$CH_3CH_2CH_2OH + 2[O] \rightarrow CH_3CH_2COOH + H_2O$$

As it acts, the acidified permanganate is reduced from MnO_4^- to Mn^{2+}, so its colour changes from **purple to colourless**.

∴ propan-1-ol is oxidised to propanal and then to propanoic acid, and the purple permanganate is decolourised as the reaction proceeds.

Worked Example 4 — Samples of propan-2-ol and of 2-methylpropan-2-ol are each warmed with acidified potassium dichromate. Describe what happens to each, write an equation where a reaction occurs, and explain how the two alcohols can be told apart.

Propan-2-ol is a **secondary** alcohol, so it is oxidised to a **ketone**, propanone:

$$CH_3CH(OH)CH_3 + [O] \rightarrow CH_3COCH_3 + H_2O$$

The dichromate is reduced from $Cr_2O_7^{2-}$ to Cr^{3+}, so its colour changes from **orange to green**. 2-methylpropan-2-ol is a **tertiary** alcohol: its $-OH$ carbon carries no hydrogen atom, so it is **not readily oxidised** and there is **no reaction** — the dichromate stays orange.

∴ the secondary alcohol turns the dichromate from orange to green, whereas the tertiary alcohol leaves it orange; the colour change therefore distinguishes them.

Practice questions

Question 1 — Pentane reacts with chlorine under UV light to give the primary haloalkane 1-chloropentane, which is then warmed with aqueous hydroxide ions.

a. Write a balanced equation for the reaction of pentane with chlorine, showing the reaction condition.
b. Write a balanced equation for the reaction of 1-chloropentane with hydroxide ions and name the organic product.
c. State the reaction type for both steps and explain why a saturated molecule reacts in this way.

Question 2 — Hex-3-ene, $CH_3CH_2CH{=}CHCH_2CH_3$, undergoes three addition reactions.

a. Write the equation for the reaction of hex-3-ene with hydrogen over a nickel catalyst, showing the condition, and name the product.
b. Write the equation for the reaction of hex-3-ene with chlorine and name the product.
c. Write the equation for the reaction of hex-3-ene with water in the presence of an acid catalyst, showing the condition, and name the product.

Question 3 — But-2-ene, $CH_3CH{=}CHCH_3$, is an alkene.

a. Write the equation for its reaction with bromine and name the product.
b. Write the equation for its reaction with hydrogen bromide and name the product.
c. Classify both reactions and explain why an unsaturated molecule reacts in this way.

Question 4 — Pentan-1-ol, $CH_3CH_2CH_2CH_2CH_2OH$, is warmed with an acidified oxidising agent.

a. Write the equation for the partial oxidation of pentan-1-ol and name the organic product.
b. Write the equation for the complete oxidation of pentan-1-ol and name the organic product.
c. Name a suitable oxidising agent and state the colour change that would be observed.

Question 5 — Consider the oxidation of hexan-2-ol, $CH_3CH(OH)CH_2CH_2CH_2CH_3$, and of 2-methylpentan-2-ol, $CH_3CH_2CH_2C(CH_3)_2OH$.

a. Write the equation for the oxidation of hexan-2-ol, name the product and state its class of compound.
b. State and explain what is observed when 2-methylpentan-2-ol is warmed with acidified permanganate.
c. Explain how the colour change of the oxidant can be used to distinguish a secondary from a tertiary alcohol.

Question 6 — Reactions are classified by the reactant involved.

a. Classify each reaction as substitution, addition or oxidation: (i) $CH_3CH_3 + Cl_2$ under UV; (ii) $CH_2{=}CHCH_3 + H_2$ over Ni; (iii) $CH_3CH_2OH + [O]$.
b. A compound reacts with bromine to form 1,2-dibromohexane. Identify the compound and the reaction type.
c. Explain, in terms of bonding, why ethene reacts by addition whereas ethane reacts by substitution.

Question 7 — Butane, $CH_3CH_2CH_2CH_3$, reacts with chlorine under UV light to give a monochlorinated product in which the chlorine is on an end carbon. Write a balanced equation showing the condition, name the organic product, and state the reaction type.

Question 8 — Write a balanced equation, showing the condition, for the monobromination of propane under UV light to give 1-bromopropane, and explain why ultraviolet light is required.

Question 9 — 1-chlorobutane, $CH_3CH_2CH_2CH_2Cl$, is warmed with aqueous sodium hydroxide. Write a balanced equation using hydroxide ions, name the organic product, and state the reaction type.

Question 10 — Hexan-1-ol is to be prepared from hexane, $CH_3CH_2CH_2CH_2CH_2CH_3$, in two steps. Write a balanced equation for each step, showing any condition required, and name the intermediate haloalkane.

Question 11 — But-1-ene, $CH_2{=}CHCH_2CH_3$, is passed with hydrogen over a heated nickel catalyst. Write a balanced equation showing the condition, name the product, and classify the reaction.

Question 12 — Pent-1-ene, $CH_2{=}CHCH_2CH_2CH_3$, is bubbled through bromine water. Write a balanced equation, name the organic product, and state what would be observed.

Question 13 — Oct-4-ene, $CH_3CH_2CH_2CH{=}CHCH_2CH_2CH_3$, reacts with hydrogen chloride. Write a balanced equation, name the organic product, and explain why only one organic product is formed.

Question 14 — But-2-ene, $CH_3CH{=}CHCH_3$, reacts with steam in the presence of an acid catalyst. Write a balanced equation showing the condition, name the product, and classify the reaction.

Question 15 — Butan-1-ol, $CH_3CH_2CH_2CH_2OH$, is oxidised by an acidified oxidising agent. Write equations for (a) its partial oxidation to the aldehyde and (b) its complete oxidation to the carboxylic acid, naming each organic product.

Question 16 — Pentan-2-ol, $CH_3CH(OH)CH_2CH_2CH_3$, is warmed with acidified potassium dichromate. Write a balanced equation for its oxidation, name the organic product, and state the colour change of the oxidant.

Question 17 — An alcohol Z has the molecular formula $C_5H_{12}O$. When a sample of Z is warmed with acidified potassium permanganate, the purple colour persists. Name Z, give its semi-structural formula, and explain why it is not oxidised.

Question 18 — Classify each of the following reactions as substitution, addition or oxidation.

a. $CH_3OH + [O] \rightarrow HCHO + H_2O$

b. $CH_3CH_2CH_3 + Cl_2 \rightarrow CH_3CH_2CH_2Cl + HCl$

c. $CH_2{=}CHCH_2CH_3 + Br_2 \rightarrow CH_2BrCHBrCH_2CH_3$

Question 19 — Deduce the reactant in each case.

a. Compound X reacts with hydrogen over a nickel catalyst to give propane. Identify X, write the equation, and state the reaction type.

b. Compound W is oxidised by acidified dichromate to pentan-3-one, $CH_3CH_2COCH_2CH_3$. Name W, state its class of alcohol, and write the equation for the reaction.

Question 20 — Alkanes react with halogens only in the presence of ultraviolet light, whereas alkenes react with halogens readily in the dark at room temperature. Explain this difference in terms of the bonding in each molecule, and state how it allows bromine solution to be used as a test for a carbon–carbon double bond.

Question 21 — Three unlabelled bottles contain butan-1-ol, butan-2-ol and 2-methylpropan-2-ol. A few drops of acidified potassium dichromate are added to a separate sample of each, and the mixtures are warmed.

a. State what would be observed for each of the three alcohols.

b. Write a balanced equation for the oxidation of butan-2-ol and name the organic product.

c. Explain why this test identifies the tertiary alcohol but cannot by itself distinguish the primary alcohol from the secondary alcohol.

Answers

1 a $CH_3CH_2CH_2CH_2CH_3 + Cl_2 \xrightarrow{UV} CH_3CH_2CH_2CH_2CH_2Cl + HCl$; b $CH_3CH_2CH_2CH_2CH_2Cl + OH^- \rightarrow CH_3CH_2CH_2CH_2CH_2OH + Cl^-$, pentan-1-ol; c both substitution — a saturated molecule has no C=C to add across, so an atom can only be replaced. **2** a $CH_3CH_2CH{=}CHCH_2CH_3 + H_2 \xrightarrow{Ni} CH_3CH_2CH_2CH_2CH_2CH_3$, hexane; b $CH_3CH_2CH{=}CHCH_2CH_3 + Cl_2 \rightarrow CH_3CH_2CHClCHClCH_2CH_3$, 3,4-dichlorohexane; c $CH_3CH_2CH{=}CHCH_2CH_3 + H_2O \xrightarrow{H^+} CH_3CH_2CH(OH)CH_2CH_2CH_3$, hexan-3-ol. **3** a $CH_3CH{=}CHCH_3 + Br_2 \rightarrow CH_3CHBrCHBrCH_3$, 2,3-dibromobutane; b $CH_3CH{=}CHCH_3 + HBr \rightarrow CH_3CHBrCH_2CH_3$, 2-bromobutane; c both addition — the C=C provides two carbons that each take up an added atom. **4** a $CH_3CH_2CH_2CH_2CH_2OH + [O] \rightarrow CH_3CH_2CH_2CH_2CHO + H_2O$, pentanal; b $CH_3CH_2CH_2CH_2CH_2OH + 2[O] \rightarrow CH_3CH_2CH_2CH_2COOH + H_2O$, pentanoic acid; c acidified permanganate, purple → colourless (or acidified dichromate, orange → green). **5** a $CH_3CH(OH)CH_2CH_2CH_2CH_3 + [O] \rightarrow CH_3COCH_2CH_2CH_2CH_3 + H_2O$, hexan-2-one, a ketone; b no reaction — a tertiary alcohol is not readily oxidised, so the permanganate stays purple; c a primary/secondary alcohol reacts and decolourises the oxidant (colour change), a tertiary alcohol does not (colour persists). **6** a (i) substitution, (ii) addition, (iii) oxidation; b hex-1-ene, $CH_2{=}CHCH_2CH_2CH_2CH_3$, addition; c ethene has a reactive C=C double bond across which atoms can add, whereas ethane is saturated and can only have a hydrogen replaced by substitution. **7** $CH_3CH_2CH_2CH_3 + Cl_2 \xrightarrow{UV} CH_3CH_2CH_2CH_2Cl + HCl$; 1-chlorobutane; substitution. **8** $CH_3CH_2CH_3 + Br_2 \xrightarrow{UV} CH_3CH_2CH_2Br + HBr$; UV light supplies the energy needed to start the reaction, without which the alkane's strong single bonds are not broken. **9** $CH_3CH_2CH_2CH_2Cl + OH^- \rightarrow CH_3CH_2CH_2CH_2OH + Cl^-$; butan-1-ol; substitution. **10** $CH_3CH_2CH_2CH_2CH_2CH_3 + Cl_2 \xrightarrow{UV} CH_3CH_2CH_2CH_2CH_2CH_2Cl + HCl$, then $CH_3CH_2CH_2CH_2CH_2CH_2Cl + OH^- \rightarrow CH_3CH_2CH_2CH_2CH_2CH_2OH + Cl^-$; intermediate 1-chlorohexane. **11** $CH_2{=}CHCH_2CH_3 + H_2 \xrightarrow{Ni} CH_3CH_2CH_2CH_3$; butane; addition (hydrogenation). **12** $CH_2{=}CHCH_2CH_2CH_3 + Br_2 \rightarrow CH_2BrCHBrCH_2CH_2CH_3$; 1,2-dibromopentane; the orange-brown bromine water is decolourised. **13** $CH_3CH_2CH_2CH{=}CHCH_2CH_2CH_3 + HCl \rightarrow CH_3CH_2CH_2CHClCH_2CH_2CH_2CH_3$; 4-chlorooctane; oct-4-ene is symmetrical, so either double-bond carbon taking the Cl gives the same molecule. **14** $CH_3CH{=}CHCH_3 + H_2O \xrightarrow{H^+} CH_3CH(OH)CH_2CH_3$; butan-2-ol; addition (hydration). **15** a $CH_3CH_2CH_2CH_2OH + [O] \rightarrow CH_3CH_2CH_2CHO + H_2O$, butanal; b $CH_3CH_2CH_2CH_2OH + 2[O] \rightarrow CH_3CH_2CH_2COOH + H_2O$, butanoic acid. **16** $CH_3CH(OH)CH_2CH_2CH_3 + [O] \rightarrow CH_3COCH_2CH_2CH_3 + H_2O$; pentan-2-one; orange → green. **17** Z = 2-methylbutan-2-ol, $CH_3CH_2C(CH_3)_2OH$ — the only tertiary alcohol of formula $C_5H_{12}O$; its –OH carbon has no H to lose, so it is not readily oxidised. **18** a oxidation; b substitution; c addition. **19** a X = propene, $CH_2{=}CHCH_3 + H_2 \xrightarrow{Ni} CH_3CH_2CH_3$, addition; b W = pentan-3-ol, a secondary alcohol, $CH_3CH_2CH(OH)CH_2CH_3 + [O] \rightarrow CH_3CH_2COCH_2CH_3 + H_2O$. **20** an alkane has only strong single bonds, so energy from UV light is needed before a hydrogen can be substituted; an alkene's C=C contains a weaker, reactive π bond across which a halogen adds without UV, so a compound that rapidly decolourises bromine solution in the dark contains a C=C (reasoning in the solution). **21** a butan-1-ol and butan-2-ol both turn the dichromate from orange to green; 2-methylpropan-2-ol gives no reaction (stays orange); b $CH_3CH(OH)CH_2CH_3 + [O] \rightarrow CH_3COCH_2CH_3 + H_2O$, butanone; c only the tertiary alcohol leaves the dichromate orange, but the primary and secondary alcohols are both oxidised and both give the same orange → green change.

Fully-worked solutions

Question 1 a. Pentane is an alkane, so it reacts with chlorine by substitution, but only when UV light supplies the energy to begin the reaction. One H on an end carbon is replaced by Cl and a molecule of HCl is released: $CH_3CH_2CH_2CH_2CH_3 + Cl_2 \xrightarrow{UV} CH_3CH_2CH_2CH_2CH_2Cl + HCl$. b. 1-chloropentane reacts with hydroxide ions: the Cl atom is replaced by an $-OH$ group and leaves as a chloride ion, giving the primary alcohol **pentan-1-ol**: $CH_3CH_2CH_2CH_2CH_2Cl + OH^- \rightarrow CH_3CH_2CH_2CH_2CH_2OH + Cl^-$. Both atoms and charge (-1 each side) balance. c. Both steps are **substitution**. Pentane and 1-chloropentane are saturated — every carbon already has four single bonds — so no atom can be added; a reaction is only possible by replacing an existing atom with another.

Question 2 a. Hydrogen adds across the double bond over a nickel catalyst (hydrogenation): $CH_3CH_2CH{=}CHCH_2CH_3 + H_2 \xrightarrow{Ni} CH_3CH_2CH_2CH_2CH_2CH_3$, giving **hexane**. b. Chlorine adds across the double bond, one Cl atom going to each of the two double-bond carbons (halogenation): $CH_3CH_2CH{=}CHCH_2CH_3 + Cl_2 \rightarrow CH_3CH_2CHClCHClCH_2CH_3$, giving **3,4-dichlorohexane**. c. Water adds across the double bond with an acid catalyst (hydration): $CH_3CH_2CH{=}CHCH_2CH_3 + H_2O \xrightarrow{H^+} CH_3CH_2CH(OH)CH_2CH_2CH_3$, giving **hexan-3-ol**. Hex-3-ene is symmetrical about its double bond, so the $-OH$ group can join either double-bond carbon and the same alcohol results.

Question 3 a. Bromine adds across the C=C of but-2-ene, one Br on each of the two double-bond carbons: $CH_3CH{=}CHCH_3 + Br_2 \rightarrow CH_3CHBrCHBrCH_3$, **2,3-dibromobutane**. b. Hydrogen bromide adds across the C=C; because but-2-ene is symmetrical, both double-bond carbons are equivalent and only one product forms: $CH_3CH{=}CHCH_3 + HBr \rightarrow CH_3CHBrCH_2CH_3$, **2-bromobutane**. c. Both are **addition** reactions. But-2-ene is unsaturated: its C=C double bond has a reactive π component, and the two carbons of the double bond can each take up an added atom, so the added molecule adds across the double bond, which becomes a single bond, without anything being released.

Question 4 a. Pentan-1-ol is a primary alcohol; partial oxidation replaces two H atoms (one from the $-OH$, one from the same carbon) to form the aldehyde **pentanal** and a molecule of water: $CH_3CH_2CH_2CH_2CH_2OH + [O] \rightarrow CH_3CH_2CH_2CH_2CHO + H_2O$. b. Further oxidation converts the aldehyde group to a carboxyl group, giving **pentanoic acid**: $CH_3CH_2CH_2CH_2CH_2OH + 2[O] \rightarrow CH_3CH_2CH_2CH_2COOH + H_2O$. c. A suitable oxidant is **acidified potassium permanganate**, which changes from **purple to colourless** as MnO_4^- is reduced to Mn^{2+} (acidified dichromate, changing from orange to green, is equally acceptable).

Question 5 a. Hexan-2-ol is a secondary alcohol; its $-OH$ carbon (carbon 2) is bonded to two other carbons and carries one H, so oxidation removes that H and the $-OH$ hydrogen to form a **ketone**, hexan-2-one: $CH_3CH(OH)CH_2CH_2CH_2CH_3 + [O] \rightarrow CH_3COCH_2CH_2CH_2CH_3 + H_2O$. b. **No reaction** occurs. 2-methylpentan-2-ol is a tertiary alcohol: its $-OH$ carbon is bonded to three other carbons and has no hydrogen atom to lose, so it cannot be oxidised in this way and the permanganate remains **purple**. c. A primary or secondary alcohol is oxidised by the acidified oxidant, so the oxidant is reduced and its colour changes (permanganate purple → colourless, or dichromate orange → green). A tertiary alcohol is not oxidised, so the oxidant's colour does not change. Observing whether the colour changes or persists therefore distinguishes a secondary alcohol from a tertiary one.

Question 6 a. (i) An alkane (CH_3CH_3) with a halogen under UV is **substitution**; (ii) an alkene ($CH_2{=}CHCH_3$) with hydrogen is **addition**; (iii) an alcohol with an oxidant $[O]$ is **oxidation**. b. 1,2-dibromohexane, $CH_2BrCHBrCH_2CH_2CH_2CH_3$, has a bromine atom on each of carbons 1 and 2, so it is formed by adding Br_2 across a C=C between those two carbons. The compound is **hex-1-ene**, $CH_2{=}CHCH_2CH_2CH_2CH_3$, and the reaction type is **addition**. c. Ethene contains a **C=C double bond** whose π component is weak and reactive; the two double-bond carbons can each accept a new atom, so ethene reacts by **addition** across the double bond. Ethane is **saturated** — every carbon already has four single bonds — so it cannot take up extra atoms and can react only by **substituting** a hydrogen atom (and only with UV light).

Question 7 Butane is saturated, so it reacts with chlorine by substitution under UV light, one H on an end carbon being replaced by Cl and HCl released: $\mathrm{CH_3CH_2CH_2CH_3 + Cl_2 \xrightarrow{UV} CH_3CH_2CH_2CH_2Cl + HCl}$. The organic product is **1-chlorobutane** and the reaction type is **substitution**.

Question 8 Propane is an alkane, so under UV light one H on an end carbon is replaced by Br to give 1-bromopropane, with HBr released: $\mathrm{CH_3CH_2CH_3 + Br_2 \xrightarrow{UV} CH_3CH_2CH_2Br + HBr}$. Ultraviolet light is required because propane is saturated and contains only strong single bonds; substitution can begin only when enough energy is supplied to break bonds in the reactants, and the UV light provides it. In the dark, propane and bromine do not react.

Question 9 The hydroxide ion replaces the chlorine atom of 1-chlorobutane, which leaves as a chloride ion, giving the primary alcohol **butan-1-ol**: $\mathrm{CH_3CH_2CH_2CH_2Cl + OH^- \rightarrow CH_3CH_2CH_2CH_2OH + Cl^-}$. The reaction type is **substitution**; atoms and charge (-1 each side) balance.

Question 10 An alkane cannot be converted to an alcohol in one step, so the halogen is introduced first and then replaced. Step 1 — under UV light, chlorine replaces one H on an end carbon of hexane, giving the primary haloalkane **1-chlorohexane**: $\mathrm{CH_3CH_2CH_2CH_2CH_2CH_3 + Cl_2 \xrightarrow{UV} CH_3CH_2CH_2CH_2CH_2CH_2Cl + HCl}$. (Bromine under UV light, giving 1-bromohexane, works equally well.) Step 2 — warmed with aqueous hydroxide ions, the Cl atom is replaced by an $\mathrm{-OH}$ group and leaves as a chloride ion, giving the primary alcohol **hexan-1-ol**: $\mathrm{CH_3CH_2CH_2CH_2CH_2CH_2Cl + OH^- \rightarrow CH_3CH_2CH_2CH_2CH_2CH_2OH + Cl^-}$. Both steps are **substitution** reactions.

Question 11 Hydrogen adds across the double bond of but-1-ene over a heated nickel catalyst, converting the alkene to the alkane **butane**: $\mathrm{CH_2{=}CHCH_2CH_3 + H_2 \xrightarrow{Ni} CH_3CH_2CH_2CH_3}$. This is an **addition** (hydrogenation) reaction.

Question 12 Bromine adds across the C=C of pent-1-ene, placing one Br on each of the two double-bond carbons: $\mathrm{CH_2{=}CHCH_2CH_2CH_3 + Br_2 \rightarrow CH_2BrCHBrCH_2CH_2CH_3}$, giving **1,2-dibromopentane**. The observation is that the **orange-brown bromine water is decolourised**, confirming a C=C double bond.

Question 13 Hydrogen chloride adds across the double bond of oct-4-ene, the H going to one double-bond carbon and the Cl to the other: $\mathrm{CH_3CH_2CH_2CH{=}CHCH_2CH_2CH_3 + HCl \rightarrow CH_3CH_2CH_2CHClCH_2CH_2CH_2CH_3}$, giving **4-chlorooctane**. Only one organic product forms because oct-4-ene is **symmetrical** about its double bond: carbons 4 and 5 each carry a propyl group and a hydrogen atom, so the two are equivalent. Whichever of them takes the chlorine atom, numbering the eight-carbon chain from the nearer end places the Cl on carbon 4, so the same molecule results either way.

Question 14 Water (as steam) adds across the double bond of but-2-ene in the presence of an acid catalyst, giving the alcohol **butan-2-ol**: $\mathrm{CH_3CH{=}CHCH_3 + H_2O \xrightarrow{H^+} CH_3CH(OH)CH_2CH_3}$. This is an **addition** (hydration) reaction. But-2-ene is symmetrical, so the $\mathrm{-OH}$ group can join either double-bond carbon and only one alcohol is possible.

Question 15 Butan-1-ol is a primary alcohol, oxidised in two stages. a. Partial oxidation to the aldehyde **butanal**: $\mathrm{CH_3CH_2CH_2CH_2OH + [O] \rightarrow CH_3CH_2CH_2CHO + H_2O}$. b. Complete oxidation to the carboxylic acid **butanoic acid**: $\mathrm{CH_3CH_2CH_2CH_2OH + 2[O] \rightarrow CH_3CH_2CH_2COOH + H_2O}$.

Question 16 Pentan-2-ol is a secondary alcohol; its $\mathrm{-OH}$ carbon (carbon 2) is bonded to two other carbons and carries one hydrogen, so oxidation gives the **ketone** pentan-2-one: $\mathrm{CH_3CH(OH)CH_2CH_2CH_3 + [O] \rightarrow CH_3COCH_2CH_2CH_3 + H_2O}$. The acidified dichromate is reduced from $\mathrm{Cr_2O_7^{2-}}$ to $\mathrm{Cr^{3+}}$, so its colour changes from **orange to green**.

Question 17 The permanganate keeps its purple colour, so no oxidation has occurred; Z must therefore be a **tertiary** alcohol, in which the carbon bearing the $\mathrm{-OH}$ group is bonded to three other carbon atoms. Building a five-carbon alcohol of that kind gives only one possibility: a three-carbon chain with the $\mathrm{-OH}$ carbon also carrying two methyl groups. Z is **2-methylbutan-2-ol**, $\mathrm{CH_3CH_2C(CH_3)_2OH}$ — the only tertiary alcohol with the formula $\mathrm{C_5H_{12}O}$.

Because its –OH carbon carries no hydrogen atom, there is no hydrogen for the oxidant to remove, so Z is not readily oxidised, the permanganate is not reduced and its purple colour persists.

Question 18 a. An alcohol (methanol) is converted to an aldehyde by an oxidising agent $[\mathrm{O}]$, with water formed — **oxidation**. b. One hydrogen of the saturated alkane propane is replaced by chlorine, releasing HCl — **substitution**. c. A bromine molecule adds across the C=C double bond of but-1-ene, which becomes a single bond, and nothing is released — **addition**.

Question 19 a. Hydrogenation of an alkene gives the corresponding alkane; propane has three carbons, so X is the three-carbon alkene **propene**: $\mathrm{CH_2{=}CHCH_3 + H_2 \xrightarrow{Ni} CH_3CH_2CH_3}$. The reaction type is **addition**. b. A ketone is produced by oxidising a **secondary** alcohol, and oxidation converts the –OH carbon into the C=O carbon without changing the carbon skeleton. Pentan-3-one has its C=O on carbon 3 of a five-carbon chain, so W is the alcohol with –OH on carbon 3, **pentan-3-ol**: $\mathrm{CH_3CH_2CH(OH)CH_2CH_3 + [O] \rightarrow CH_3CH_2COCH_2CH_3 + H_2O}$.

Question 20 An **alkane is saturated**: every carbon atom is joined by four strong single (σ) bonds, and the molecule can react only by having one of those bonds broken so that a hydrogen atom is **replaced** by a halogen atom. Breaking a strong single bond needs a substantial input of energy, which **ultraviolet light supplies**; in the dark an alkane and a halogen do not react. An **alkene is unsaturated**: its **C=C double bond** is made up of a strong σ bond and a second, weaker and more reactive ***π* bond**. The π bond breaks readily, so the two double-bond carbons each take up one atom of the halogen molecule and the halogen **adds across the double bond** at room temperature without any UV light. This difference is what makes bromine solution a test for unsaturation: when bromine solution is added in the dark, a compound containing a **C=C double bond decolourises the orange-brown colour rapidly**, whereas a saturated compound leaves the colour unchanged, so rapid decolourisation shows that a carbon–carbon double bond is present.

Question 21 a. **Butan-1-ol** (a primary alcohol) and **butan-2-ol** (a secondary alcohol) are both oxidised by the acidified dichromate, so in each of those two bottles the dichromate changes from **orange to green** as $\mathrm{Cr_2O_7^{2-}}$ is reduced to $\mathrm{Cr^{3+}}$. **2-methylpropan-2-ol** is a tertiary alcohol and is not readily oxidised, so its dichromate **stays orange** (no reaction). b. Butan-2-ol is a secondary alcohol, so it is oxidised to the ketone **butanone**: $\mathrm{CH_3CH(OH)CH_2CH_3 + [O] \rightarrow CH_3COCH_2CH_3 + H_2O}$. c. The tertiary alcohol is the only one of the three whose –OH carbon carries no hydrogen atom, so it is the only one that cannot be oxidised; it is identified as the sample in which the dichromate **remains orange**. The primary and secondary alcohols are both oxidised, and in both cases the dichromate is reduced from $\mathrm{Cr_2O_7^{2-}}$ to $\mathrm{Cr^{3+}}$, so both give an identical **orange → green** change. The test therefore cannot tell butan-1-ol from butan-2-ol; separating those two would require identifying their oxidation products (a carboxylic acid from the primary alcohol, a ketone from the secondary).

Chapter 9 Reactions of organic compounds — 9B Condensation and hydrolysis

Theory

Two of the most important reactions of the oxygen- and nitrogen-containing organic families are **condensation** and **hydrolysis** — a forward-and-reverse pair. In a **condensation reaction** two molecules join together to form a single larger molecule, with the elimination of a small molecule; throughout this subtopic that small molecule is **water**. In a **hydrolysis reaction** the reverse happens: a larger molecule is split into two smaller ones by the addition of the elements of water ("hydro-" = water, "-lysis" = splitting). Recognising which of the two is occurring is a matter of asking a single question — is a molecule of water being *removed* (condensation) or *added* (hydrolysis)?

Esterification — a condensation. When a **carboxylic acid** and an **alcohol** are warmed together with a little concentrated sulfuric acid, they join to form an **ester**, releasing water. The reaction is called **esterification**:

$$\mathrm{R{-}COOH(l) + R'{-}OH(l) \rightleftharpoons R{-}COO{-}R'(l) + H_2O(l)}$$

The $-\mathrm{OH}$ of the acid and the $-\mathrm{H}$ of the alcohol's hydroxyl are eliminated together as one molecule of water, and the two fragments join through the $-\mathrm{COO}-$ **ester linkage**. The concentrated $\mathrm{H_2SO_4}$ is an **acid catalyst**: it is not consumed and does not appear in the balanced equation. Esterification is a **reversible** reaction, so a double arrow ($\rightleftharpoons$) is used and the mixture reaches **equilibrium** with all four species present (this is why the yield of ester is always less than 100% — see below). The naming of the ester follows the rule met in 8D: the acid supplies the *…anoate* second word (from the acyl group $\mathrm{R{-}CO-}$) and the alcohol supplies the alkyl first word, so ethanoic acid and propan-1-ol give **propyl ethanoate**.

Amide formation — a condensation. A **carboxylic acid** also condenses with **ammonia** or an **amine**, again losing water, to form an **amide**. With ammonia the product is a **primary amide** (the $-\mathrm{CONH_2}$ group met in 8D):

$$\mathrm{R{-}COOH(l) + NH_3(g) \rightarrow R{-}CONH_2(s) + H_2O(l)}$$

With a primary amine $\mathrm{R'{-}NH_2}$, one of the $-\mathrm{H}$ atoms on the nitrogen is eliminated with the acid's $-\mathrm{OH}$ as water, leaving the **amide linkage** $-\mathrm{CO{-}NH}-$ joining the two fragments:

$$\mathrm{R{-}COOH(l) + R'{-}NH_2(g) \rightarrow R{-}CO{-}NH{-}R'(l) + H_2O(l)}$$

This $-\mathrm{CO{-}NH}-$ linkage is the same bond that joins amino-acid units together in proteins, so amide condensation underlies the building of these large biological molecules. Amide formation is written with a single arrow ($\rightarrow$) at this level. An amide is identified in this course from its **structure** — the $-\mathrm{CONH_2}$ group of a primary amide, or the wider $-\mathrm{CO{-}NH}-$ linkage of an *N*-substituted amide such as $\mathrm{CH_3CONHCH_3}$ — and is described by naming the **carboxylic acid** and the **ammonia or amine** from which it forms.

Extension — the *-amide* suffix. *Systematic amide names are not on the study design's IUPAC-naming list and are not assessed in this course. They are set out here only so that you can read them when you meet them; every amide name used in this subtopic is supplied to you, and no graded item asks you to produce one.* Primary amides are named by replacing the *-oic acid* ending of the parent carboxylic acid with *-amide*, so $\mathrm{CH_3CONH_2}$ is ethanamide and $\mathrm{CH_3CH_2CONH_2}$ is propanamide. The study design's naming list runs only to non-cyclic hydrocarbons, haloalkanes, primary amines, alcohols, aldehydes, ketones, carboxylic acids and non-branched esters, and the current Data Book nomenclature table carries no amide row. What *is* required is the structure — recognising the $-\mathrm{CONH_2}$ group and the $-\mathrm{CO{-}NH}-$ linkage, and identifying the carboxylic acid and the ammonia or amine that form them.

The ester and amide linkages. Both condensations forge a new linkage on the carbonyl carbon by eliminating water: the **ester linkage** $-\mathrm{CO{-}O}-$ (from an acid and an alcohol) and the **amide linkage** $-\mathrm{CO{-}NH}-$ (from an acid and ammonia or an amine). In each the carbonyl ($\mathrm{C{=}O}$) always lies on the **acid-derived side** of the linking atom — a fact that lets the two parent molecules be recovered by "cutting" the linkage.

Hydrolysis of esters. Hydrolysis reverses these condensations by adding water back across the linkage. An ester is hydrolysed under either acidic or basic conditions. **Acid-catalysed hydrolysis** is the exact reverse of esterification and so is an equilibrium; using a large excess of water drives it toward the acid and alcohol:

$$\text{R–COO–R}'(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{R–COOH}(\text{l}) + \text{R}'\text{–OH}(\text{l})$$

Base hydrolysis (with hot sodium hydroxide solution) instead gives the **carboxylate salt** and the alcohol, and goes essentially to **completion**:

$$\text{R–COO–R}'(\text{l}) + \text{NaOH}(\text{aq}) \rightarrow \text{R–COONa}(\text{aq}) + \text{R}'\text{–OH}(\text{l})$$

Because the acid is removed as its unreactive carboxylate salt, the reverse (esterification) cannot occur, so a single arrow (→) is used. Base hydrolysis of an ester is called **saponification** — the reaction by which fats and oils are turned into soaps.

Hydrolysis of amides. An amide is likewise hydrolysed by adding water across the $-\text{CO–NH}-$ linkage, regenerating the carboxylic acid and the ammonia or amine from which it was built:

$$\text{R–CONH}_2(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{R–COOH}(\text{l}) + \text{NH}_3(\text{g})$$

$$\text{R–CO–NH–R}'(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{R–COOH}(\text{l}) + \text{R}'\text{–NH}_2(\text{g})$$

(Under acidic conditions the base leaves as its protonated salt and under basic conditions the acid leaves as its carboxylate; the neutral-form products shown are the standard summary.) The hydrolysis of amide linkages is how proteins in food are broken back down into their amino-acid units during digestion.

Retrosynthesis — cutting the linkage. To find the two molecules that formed a given ester or amide, locate the linkage and cut it, then complete each fragment with the elements of water. For an **ester** $\text{R–CO–O–R}'$, cut the single C–O bond: the carbonyl side gains $-\text{OH}$ to become the **carboxylic acid** R–COOH, and the other side gains $-\text{H}$ to become the **alcohol** $\text{R}'\text{–OH}$. For an **amide** $\text{R–CO–NH–R}'$, cut the C–N bond: the carbonyl side becomes the **acid** R–COOH and the nitrogen side becomes the **amine** $\text{R}'\text{–NH}_2$ (or **ammonia** for a primary amide). Because the carbonyl always sits on the acid-derived side, there is only ever one correct way to split the linkage.

Why esterification is an equilibrium, and how to raise the yield. Because both esterification and its reverse (acid hydrolysis) proceed under the same acidic conditions, the reaction is reversible and settles at an equilibrium in which unreacted acid and alcohol remain — the yield of ester is therefore incomplete. Applying Le Châtelier's principle (Chapter 6), the position of equilibrium can be shifted toward the ester by **using an excess** of the cheaper reactant (acid or alcohol), by **removing water** as it forms (concentrated H_2SO_4 also acts as a dehydrating agent), or by **removing the ester** by distillation as it is produced. The acid catalyst speeds the approach to equilibrium equally in both directions and does **not** by itself change the position of equilibrium or the yield.

Condensation and hydrolysis in biological molecules. The same forward-and-reverse pair builds and breaks down the large molecules of living things. A **biomacromolecule** is a very large molecule assembled from many small repeating units (**monomers**) joined by repeated **condensation** — each linkage formed eliminates one molecule of water. **Hydrolysis** reverses this, adding the elements of water across each linkage to release the monomers again; this is what happens when the large biomolecules in food are broken down during **digestion**. Three families matter here, and each is joined by one of the linkages already met in this subtopic.

Proteins — the amide (peptide) linkage. Proteins are built from **2-amino acids**: molecules carrying both an amino group $-\text{NH}_2$ and a carboxyl group $-\text{COOH}$ on the same carbon, the second carbon counting from the $-\text{COOH}$ end, so that the general structure is $\text{H}_2\text{NCH(R)COOH}$. The **side chain** R is what distinguishes one amino acid from another — R = $-\text{H}$ in **glycine**, $-\text{CH}_3$ in **alanine**, $-\text{CH}_2\text{OH}$ in **serine** — and a table of these structures is supplied in the Data Book. The $-\text{COOH}$ of one amino acid condenses with the $-\text{NH}_2$ of the next through the **amide linkage** $-\text{CO–NH}-$; in this biological context that same $-\text{CO–NH}-$ bond is called the **peptide linkage**. Two amino acids condense, eliminating one molecule of water, to give a **dipeptide**, and a long chain of amino acids makes a protein. Using the simplest amino acid (glycine, $\text{H}_2\text{NCH}_2\text{COOH}$) as an illustration:

$$2\,\text{H}_2\text{NCH}_2\text{COOH}(\text{s}) \rightarrow \text{H}_2\text{NCH}_2\text{CONHCH}_2\text{COOH}(\text{s}) + \text{H}_2\text{O}(\text{l})$$

A chain of n amino acids is held together by $n-1$ peptide linkages, so building it eliminates $n-1$ molecules of water. Hydrolysis of those peptide linkages during digestion returns the free amino acids — exactly the amide hydrolysis met

above, applied many times over. To identify the amino acids released from a given peptide, **cut every** $-\mathrm{CO–NH}-$ **linkage** and complete each fragment with the elements of water: every fragment then carries both an $-\mathrm{NH_2}$ and a $-\mathrm{COOH}$ group, and its side chain R tells you which amino acid it is.

Lipids (fats and oils) — three ester linkages. A fat or oil is a **triglyceride**: a **triester** of one **glycerol** molecule (propane-1,2,3-triol, $\mathrm{C_3H_5(OH)_3}$, which carries three $-\mathrm{OH}$ groups) with **three fatty-acid** molecules (long-chain carboxylic acids, R–COOH). Each glycerol $-\mathrm{OH}$ condenses with the $-\mathrm{COOH}$ of one fatty acid to form an **ester linkage** $-\mathrm{COO}-$ — the very reaction of esterification — so assembling one triglyceride eliminates **three** molecules of water:

$$\mathrm{C_3H_5(OH)_3(l) + 3\,R–COOH(l) \rightarrow C_3H_5(OOCR)_3(l) + 3\,H_2O(l)}$$

Hydrolysis of a triglyceride (the reverse) regenerates the glycerol and three fatty-acid molecules; base hydrolysis of these same ester linkages is the **saponification** that makes soap (met above).

Carbohydrates — the glycosidic linkage. Carbohydrates are built from **monosaccharides** such as **glucose**, $\mathrm{C_6H_{12}O_6}$. Two monosaccharides condense — an $-\mathrm{OH}$ on one joining an $-\mathrm{OH}$ on the other and eliminating water — to give a **disaccharide** joined by a **glycosidic linkage**, a $-\mathrm{C–O–C}-$ bridge:

$$\mathrm{2\,C_6H_{12}O_6(s) \rightarrow C_{12}H_{22}O_{11}(s) + H_2O(l)}$$

Repeating this condensation thousands of times links glucose units into the energy-storage polysaccharides **starch** (in plants) and **glycogen** (in animals), $(\mathrm{C_6H_{10}O_5})_n$:

$$n\,\mathrm{C_6H_{12}O_6(s) \rightarrow (C_6H_{10}O_5)_n(s) + n\,H_2O(l)}$$

Note how this equation is arrived at: the polymer is written as n repeats of the unit $\mathrm{C_6H_{10}O_5}$, which is one glucose molecule *minus* one water, so n molecules of water are eliminated. Counting linkages instead would give $n-1$, because n units in a chain are joined by $n-1$ linkages; with n running into the thousands the two counts are indistinguishable, and the repeat-unit equation above is the standard form. Hydrolysis breaks the glycosidic linkages back to glucose for energy.

The common pattern. In all three families the logic is identical: **condensation** joins many monomers into one large storage molecule, losing **one water per linkage**, and **hydrolysis** reverses it, adding one water per linkage to release the monomers. So proteins ↔ amino acids (peptide linkage), triglycerides ↔ glycerol + fatty acids (ester linkage), and starch/glycogen ↔ glucose (glycosidic linkage). At this level the glycosidic and triglyceride structures are represented generically — you are not required to draw the full stereochemistry of a sugar or to specify which glycerol $-\mathrm{OH}$ reacts.

Worked examples

Worked Example 1 — Propan-1-ol is warmed with ethanoic acid and a few drops of concentrated sulfuric acid. Predict the organic product, name it, and write a balanced equation for its formation.

Working	Comment
Reactants are a carboxylic acid (ethanoic acid) and an alcohol (propan-1-ol).	An acid-plus-alcohol pair undergoes **esterification**, a condensation.
The acid's $-\mathrm{OH}$ and the alcohol's $-\mathrm{H}$ leave together as $\mathrm{H_2O}$; the fragments join through a $-\mathrm{COO}-$ ester linkage.	Exactly one molecule of water is eliminated per ester linkage formed.
Acyl group from the acid: $\mathrm{CH_3CO}-$ → *ethanoate* (second word).	The acid names the *…anoate* part.
Alkyl group from the alcohol: $\mathrm{CH_3CH_2CH_2}-$ → *propyl* (first word).	The alcohol names the alkyl part.
Ester: **propyl ethanoate**, $\mathrm{CH_3COOCH_2CH_2CH_3}$.	Carbonyl sits on the acid-derived side of the bridging O.

Working	Comment
$CH_3COOH(l) + CH_3CH_2CH_2OH(l) \rightleftharpoons CH_3COOCH$	Reversible ($\rightleftharpoons$); the concentrated H_2SO_4 is the catalyst, not a reactant.

Worked Example 2 — Methyl propanoate is hydrolysed. Write balanced equations for (i) its acid-catalysed hydrolysis and (ii) its hydrolysis by hot sodium hydroxide solution, and name the organic products of each.

Working	Comment
Methyl propanoate $= CH_3CH_2COOCH_3$; the $-COO-$ linkage joins a propanoyl group to a methyl group.	Hydrolysis "cuts" the linkage by inserting the elements of water.
Cut the C–O bond: the carbonyl side regains $-OH \rightarrow CH_3CH_2COOH$; the methyl side regains $-H \rightarrow CH_3OH$.	Acyl side → **acid**; alkyl side → **alcohol**.
(i) $CH_3CH_2COOCH_3(l) + H_2O(l) \rightleftharpoons CH_3CH_2COOH(l$	Acid hydrolysis is the **reverse** of esterification, so $\rightleftharpoons$; excess water drives it forward. Products: **propanoic acid + methanol**.
(ii) $CH_3CH_2COOCH_3(l) + NaOH(aq) \rightarrow CH_3CH_2COO$	Base removes the acid as its **carboxylate salt**, so the reaction goes to completion (→). Products: **sodium propanoate + methanol**.

Worked Example 3 — (i) Propanoic acid reacts with ammonia to form a primary amide and water. Write the balanced equation and give the semi-structural and molecular formulas of the amide. (ii) The amide $CH_3CH_2CONHCH_3$ can be regarded as forming by a condensation between a carboxylic acid and an amine. Identify the two parent molecules and write the equation, marking the amide linkage.

(i) A carboxylic acid and ammonia eliminate water to form the $-CONH_2$ group of a primary amide. The acyl group CH_3CH_2CO- keeps its three carbons, so the amide is $CH_3CH_2CONH_2$, molecular formula C_3H_7NO:

$$CH_3CH_2COOH(l) + NH_3(g) \rightarrow CH_3CH_2CONH_2(s) + H_2O(l)$$

(ii) The amide linkage in $CH_3CH_2CONHCH_3$ is $-CO–NH-$. Cutting the C–N bond, the carbonyl side regains $-OH$ to give the acid CH_3CH_2COOH (**propanoic acid**), and the nitrogen side regains $-H$ to give the amine CH_3NH_2 (**methylamine**):

$$CH_3CH_2COOH(l) + CH_3NH_2(g) \rightarrow CH_3CH_2CONHCH_3(l) + H_2O(l)$$

∴ propanoic acid with ammonia gives the primary amide $CH_3CH_2CONH_2$; the same acid with methylamine gives the *N*-substituted amide $CH_3CH_2CONHCH_3$, whose $-CO–NH-$ linkage is the same linkage that joins amino-acid units in proteins.

Worked Example 4 — (i) The primary amide $CH_3CH_2CH_2CONH_2$ is hydrolysed. Write the equation and name the products. (ii) During digestion the peptide linkages of a protein are hydrolysed. The dipeptide $H_2NCH_2CONHCH(CH_3)COOH$ is a two-unit fragment of such a chain; write the equation for its hydrolysis and identify the two amino acids released, given that glycine is H_2NCH_2COOH and alanine is $H_2NCH(CH_3)COOH$.

(i) Hydrolysis inserts water across the $-CONH_2$ group, regenerating the parent acid and ammonia:

$$CH_3CH_2CH_2CONH_2(s) + H_2O(l) \rightarrow CH_3CH_2CH_2COOH(l) + NH_3(g)$$

The products are **butanoic acid** and **ammonia**.

(ii) Locate the peptide linkage $-\mathrm{CO–NH}-$ and add the elements of water across it: the carbonyl side regains $-\mathrm{OH}$ and the nitrogen side regains $-\mathrm{H}$. Each fragment released therefore carries both an $-\mathrm{NH_2}$ and a $-\mathrm{COOH}$ group on its second carbon — each is a 2-amino acid.

$$\mathrm{H_2NCH_2CONHCH(CH_3)COOH(s)+H_2O(l)\rightarrow H_2NCH_2COOH(s)+H_2NCH(CH_3)COOH(s)}$$

(each side C 5, H 12, N 2, O 4). The carbonyl side gives the fragment with R = $-\mathrm{H}$, **glycine**; the nitrogen side gives the fragment with R = $-\mathrm{CH_3}$, **alanine**.

∴ amide hydrolysis reverses amide formation, splitting the $-\mathrm{CO–NH}-$ linkage into a carboxylic acid and an amine (or ammonia, for a primary amide); when that linkage lies inside a protein the fragments released are its amino acids — exactly how proteins are broken down during digestion.

Worked Example 5 — Glycerol, $\mathrm{C_3H_5(OH)_3}$, reacts with three molecules of butanoic acid, $\mathrm{CH_3CH_2CH_2COOH}$ (a short-chain fatty acid), to form a triglyceride. Write a balanced equation for the reaction, name the linkage formed, and state how many molecules of water are eliminated.

Working	Comment
Glycerol carries three $-\mathrm{OH}$ groups; each butanoic acid carries one $-\mathrm{COOH}$.	A triglyceride is a **triester** of glycerol with three fatty-acid molecules.
Each $-\mathrm{OH}$ condenses with one $-\mathrm{COOH}$, eliminating one $\mathrm{H_2O}$ and forming one **ester linkage** $-\mathrm{COO}-$.	This is esterification, repeated three times.
Three ester linkages form, so **three** molecules of water are eliminated.	One water per linkage — the hallmark of condensation.
$\mathrm{C_3H_5(OH)_3(l)+3CH_3CH_2CH_2COOH(l)\rightarrow C_3H_5(}$	Product = glyceryl tributanoate, $\mathrm{C_{15}H_{26}O_6}$. Atoms balance (each side C 15, H 32, O 9).

Worked Example 6 — (i) Two molecules of glucose, $\mathrm{C_6H_{12}O_6}$, condense to form the disaccharide maltose. Write a balanced equation, name the linkage formed, and state the number of water molecules eliminated. (ii) Write the equation for the hydrolysis of maltose and relate the reaction to digestion.

(i) An $-\mathrm{OH}$ group on one glucose molecule condenses with an $-\mathrm{OH}$ group on the other, eliminating one molecule of water and joining the two units through a **glycosidic linkage** (a $-\mathrm{C–O–C}-$ bridge). Two monosaccharides give one disaccharide, so exactly **one** molecule of water is eliminated:

$$\mathrm{2C_6H_{12}O_6(s)\rightarrow C_{12}H_{22}O_{11}(s)+H_2O(l)}$$

(each side C 12, H 24, O 12).

(ii) Hydrolysis adds the elements of water back across the glycosidic linkage, splitting maltose into its two glucose units:

$$\mathrm{C_{12}H_{22}O_{11}(s)+H_2O(l)\rightarrow 2C_6H_{12}O_6(s)}$$

This is what happens when a carbohydrate is digested: the glycosidic linkages of starch and glycogen are hydrolysed to release glucose, which the body oxidises for energy.

∴ two glucose molecules condense (losing one water) into a disaccharide through a glycosidic linkage, and hydrolysis (adding one water) reverses it — the same condensation/hydrolysis pattern that governs esters, amides, triglycerides and proteins.

Practice questions

Question 1 — Methanol is warmed with butanoic acid and a few drops of concentrated sulfuric acid.

a. Name the ester formed.
b. Write a balanced equation for its formation.

c. State why the equation is written with a ⇌ arrow rather than a → arrow.

Question 2 — Ethyl ethanoate, $CH_3COOCH_2CH_3$, is hydrolysed.

a. Write the equation for its acid-catalysed hydrolysis and name the organic products.
b. Write the equation for its hydrolysis by hot sodium hydroxide solution and name the organic products.
c. Explain why the base hydrolysis proceeds essentially to completion whereas the acid hydrolysis reaches equilibrium.

Question 3 — Ethanoic acid reacts with ammonia.

a. Give the semi-structural and molecular formulas of the amide formed.
b. Write a balanced equation for the reaction.
c. Name the linkage formed and the small molecule eliminated.

Question 4 — Consider the ester propyl methanoate, $HCOOCH_2CH_2CH_3$.

a. Identify the carboxylic acid and the alcohol from which it is formed.
b. Write the esterification equation that forms it.
c. Write the equation for its acid-catalysed hydrolysis.

Question 5 — Propanamide, $CH_3CH_2CONH_2$, is hydrolysed.

a. Write the equation for its hydrolysis and name the products.
b. State the functional group produced on the carbon-containing product.
c. Explain the relationship between this reaction and the formation of propanamide from propanoic acid and ammonia.

Question 6 — For each reaction below, state whether it is a **condensation** or a **hydrolysis** reaction and identify the small molecule involved.

a. $CH_3COOH + CH_3CH_2OH \rightleftharpoons CH_3COOCH_2CH_3 + H_2O$
b. $CH_3CH_2COOCH_3 + H_2O \rightleftharpoons CH_3CH_2COOH + CH_3OH$
c. $CH_3CH_2COOH + NH_3 \rightarrow CH_3CH_2CONH_2 + H_2O$

Question 7 — Write a balanced equation for the esterification of propanoic acid with ethanol, and name the ester formed.

Question 8 — Name the ester formed from pentanoic acid and methanol, and write a balanced equation for its formation.

Question 9 — Methyl butanoate undergoes acid-catalysed hydrolysis. Write the equation and name the organic products.

Question 10 — Propyl ethanoate is heated with sodium hydroxide solution. Write the equation and name the organic products.

Question 11 — Consider the ester ethyl butanoate, $CH_3CH_2CH_2COOCH_2CH_3$. Identify the parent carboxylic acid and alcohol, and write the equation for its acid-catalysed hydrolysis.

Question 12 — Butanoic acid reacts with ammonia. Write a balanced equation, and give the molecular formula of the amide formed.

Question 13 — Ethanamide, CH_3CONH_2, is hydrolysed. Write the equation and name the products.

Question 14 — The amide $CH_3CONHCH_2CH_3$ is hydrolysed. Write a balanced equation, name the two organic products, and name the linkage that is broken.

Question 15 — An ester has the semi-structural formula $CH_3CH_2COOCH_2CH_2CH_2CH_3$. Name it and identify the two compounds that react to form it.

Question 16 — Methyl hexanoate, $CH_3CH_2CH_2CH_2CH_2COOCH_3$, is heated with sodium hydroxide solution. Write the equation, name the organic products, and give the general term for the base hydrolysis of an ester.

Question 17 — Classify each reaction as condensation or hydrolysis, and give the small molecule involved.

(i) $CH_3CONH_2 + H_2O \rightarrow CH_3COOH + NH_3$

(ii) $CH_3CH_2COOH + CH_3OH \rightleftharpoons CH_3CH_2COOCH_3 + H_2O$

(iii) $CH_3CH_2CH_2COOH + NH_3 \rightarrow CH_3CH_2CH_2CONH_2 + H_2O$

Question 18 — Explain why esterification is described as an equilibrium reaction, and describe two ways in which the yield of ester can be increased. Refer to Le Châtelier's principle.

Question 19 — A student mixes ethanoic acid and ethanol with concentrated sulfuric acid to make ethyl ethanoate. Explain **two** distinct roles played by the concentrated sulfuric acid in this preparation, stating for each whether it increases the **rate** at which equilibrium is reached, the **yield** of ester, or both.

Question 20 — Ethyl propanoate is hydrolysed under acidic conditions using a large excess of water. The carboxylic acid produced is separated from the equilibrium mixture and is then reacted with ammonia. Write a balanced equation for each step, and give the semi-structural formula of the final organic product.

Question 21 — An unknown compound X, containing only carbon, hydrogen and oxygen, is hydrolysed under acidic conditions to give propanoic acid and propan-1-ol as the only organic products.

a. Identify X, giving its name and semi-structural formula.
b. Write the equation for the hydrolysis of X.
c. Explain how the hydrolysis products show that X is an ester rather than an amide.

Question 22 — Glycerol, $C_3H_5(OH)_3$, reacts with three molecules of hexanoic acid, $CH_3CH_2CH_2CH_2CH_2COOH$, to form a triglyceride. Write a balanced equation for the reaction, name the type of linkage formed, and state how many molecules of water are eliminated.

Question 23 — Alanine, $H_2NCH(CH_3)COOH$, and serine, $H_2NCH(CH_2OH)COOH$, are two of the 2-amino acids from which proteins are built.

a. Write a balanced equation for the condensation in which the $-COOH$ group of one alanine molecule reacts with the $-NH_2$ group of one serine molecule, giving the semi-structural formula of the dipeptide, and name the linkage formed.
b. Write a balanced equation for the hydrolysis of this dipeptide and name the two products.
c. A short protein chain is assembled from five amino-acid molecules. State how many peptide linkages it contains and how many molecules of water are eliminated as it forms, and explain your reasoning.

Question 24 — A triglyceride, glyceryl trioctanoate $C_3H_5(OOCC_7H_{15})_3$, is completely hydrolysed (octanoic acid $= CH_3(CH_2)_6COOH$). Write a balanced equation for the reaction, name the two products, and state how many molecules of water are added.

Question 25 — Plants store energy as **starch**, a polymer of glucose, $C_6H_{12}O_6$, whose formula may be written $(C_6H_{10}O_5)_n$.

a. Write a balanced equation for the condensation of n molecules of glucose into starch.
b. Write a balanced equation for the complete hydrolysis of starch into glucose.
c. Explain, in terms of condensation and hydrolysis, how starch serves as an energy store in a plant and how it is broken down when eaten.

Question 26 — Proteins, triglycerides and carbohydrates are all assembled by condensation and broken down by hydrolysis.

a. For each of the three families, name the monomer(s) it is built from, the linkage that joins them, and the small molecule eliminated when a linkage forms.
b. State the number of water molecules eliminated when a single triglyceride is assembled from its building blocks, and explain why.
c. Explain why hydrolysis is described as the reverse of condensation.

Answers

1 a methyl butanoate; b $CH_3CH_2CH_2COOH(l) + CH_3OH(l) \rightleftharpoons CH_3CH_2CH_2COOCH_3(l) + H_2O(l)$; c the reaction is reversible and reaches equilibrium (the reverse, acid hydrolysis, occurs under the same conditions). **2** a $CH_3COOCH_2CH_3(l) + H_2O(l) \rightleftharpoons CH_3COOH(l) + CH_3CH_2OH(l)$ — ethanoic acid + ethanol; b $CH_3COOCH_2CH_3(l) + NaOH(aq) \rightarrow CH_3COONa(aq) + CH_3CH_2OH(l)$ — sodium ethanoate + ethanol; c base removes the acid as its carboxylate salt, preventing the reverse reaction, so it goes to completion; acid hydrolysis is the reverse of esterification and reaches equilibrium. **3** a CH_3CONH_2, C_2H_5NO; b $CH_3COOH(l) + NH_3(g) \rightarrow CH_3CONH_2(s) + H_2O(l)$; c amide linkage $-CO–NH-$; water. **4** a methanoic acid and propan-1-ol; b $HCOOH(l) + CH_3CH_2CH_2OH(l) \rightleftharpoons HCOOCH_2CH_2CH_3(l) + H_2O(l)$; c $HCOOCH_2CH_2CH_3(l) + H_2O(l) \rightleftharpoons HCOOH(l) + CH_3CH_2CH_2OH(l)$. **5** a $CH_3CH_2CONH_2(s) + H_2O(l) \rightarrow CH_3CH_2COOH(l) + NH_3(g)$ — propanoic acid + ammonia; b carboxyl group ($-COOH$); c hydrolysis is the exact reverse of the condensation (amide formation). **6** a condensation (esterification), water eliminated; b hydrolysis (of an ester), water added; c condensation (amide formation), water eliminated. **7** ethyl propanoate; $CH_3CH_2COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3CH_2COOCH_2CH_3(l) + H_2O(l)$. **8** methyl pentanoate; $CH_3CH_2CH_2CH_2COOH(l) + CH_3OH(l) \rightleftharpoons CH_3CH_2CH_2CH_2COOCH_3(l) + H_2O(l)$. **9** $CH_3CH_2CH_2COOCH_3(l) + H_2O(l) \rightleftharpoons CH_3CH_2CH_2COOH(l) + CH_3OH(l)$ — butanoic acid + methanol. **10** $CH_3COOCH_2CH_2CH_3(l) + NaOH(aq) \rightarrow CH_3COONa(aq) + CH_3CH_2CH_2OH(l)$ — sodium ethanoate + propan-1-ol. **11** butanoic acid and ethanol; $CH_3CH_2CH_2COOCH_2CH_3(l) + H_2O(l) \rightleftharpoons CH_3CH_2CH_2COOH(l) + CH_3CH_2OH(l)$. **12** $CH_3CH_2CH_2COOH(l) + NH_3(g) \rightarrow CH_3CH_2CH_2CONH_2(s) + H_2O(l)$; amide $= C_4H_9NO$. **13** $CH_3CONH_2(s) + H_2O(l) \rightarrow CH_3COOH(l) + NH_3(g)$ — ethanoic acid + ammonia. **14** $CH_3CONHCH_2CH_3(l) + H_2O(l) \rightarrow CH_3COOH(l) + CH_3CH_2NH_2(g)$ — ethanoic acid + ethylamine; amide linkage $-CO–NH-$. **15** butyl propanoate; from propanoic acid and butan-1-ol. **16** $CH_3CH_2CH_2CH_2CH_2COOCH_3(l) + NaOH(aq) \rightarrow CH_3CH_2CH_2CH_2CH_2COONa(aq) + CH_3OH(l)$ — sodium hexanoate + methanol; saponification. **17** (i) hydrolysis (of an amide), water added; (ii) condensation (esterification), water eliminated; (iii) condensation (amide formation), water eliminated. **18** esterification is reversible (the reverse, acid hydrolysis, occurs under the same acidic conditions), so it reaches equilibrium with acid and alcohol remaining; yield is raised by using an excess of one reactant and/or by removing water (or removing the ester by distillation), each of which shifts the equilibrium toward the ester (Le Châtelier). **19** (1) **acid catalyst** — it lowers the activation energy, so equilibrium is reached more quickly: this increases the **rate** only (a catalyst does not shift the position of equilibrium, so it does not change the yield); (2) **dehydrating agent** — it absorbs the water produced, and removing a product shifts the equilibrium toward the ester (Le Châtelier): this increases the **yield**. **20** step 1 $CH_3CH_2COOCH_2CH_3(l) + H_2O(l) \rightleftharpoons CH_3CH_2COOH(l) + CH_3CH_2OH(l)$; step 2 $CH_3CH_2COOH(l) + NH_3(g) \rightarrow CH_3CH_2CONH_2(s) + H_2O(l)$; final organic product $CH_3CH_2CONH_2$ (propanamide). **21** a propyl propanoate, $CH_3CH_2COOCH_2CH_2CH_3$; b $CH_3CH_2COOCH_2CH_2CH_3(l) + H_2O(l) \rightleftharpoons CH_3CH_2COOH(l) + CH_3CH_2CH_2OH(l)$; c the products are a carboxylic acid and an alcohol (both contain only C, H and O, no nitrogen); an amide would hydrolyse to a carboxylic acid and an amine (or ammonia), which contains nitrogen — since neither product contains nitrogen, X must be an ester. **22** glyceryl trihexanoate; $C_3H_5(OH)_3(l) + 3CH_3CH_2CH_2CH_2CH_2COOH(l) \rightarrow C_3H_5(OOCCH_2CH_2CH_2CH_2CH_3)_3(l) + 3H_2O(l)$; **ester linkage** $-COO-$; **3** molecules of water. **23** a $H_2NCH(CH_3)COOH(s) + H_2NCH(CH_2OH)COOH(s) \rightarrow H_2NCH(CH_3)CONHCH(CH_2OH)COOH(s) + H_2O(l$ — dipeptide $H_2NCH(CH_3)CONHCH(CH_2OH)COOH$; **amide (peptide) linkage** $-CO–NH-$; b $H_2NCH(CH_3)CONHCH(CH_2OH)COOH(s) + H_2O(l) \rightarrow H_2NCH(CH_3)COOH(s) + H_2NCH(CH_2OH)COOH(s$ — alanine and serine; c **4** peptide linkages and **4** molecules of water — n units in a chain are joined by $n-1$ linkages, and one water is eliminated per linkage formed. **24** $C_3H_5(OOCC_7H_{15})_3(l) + 3H_2O(l) \rightarrow C_3H_5(OH)_3(l) + 3CH_3(CH_2)_6COOH(l)$ — glycerol and octanoic acid; **3** molecules of water added. **25** a $nC_6H_{12}O_6(s) \rightarrow (C_6H_{10}O_5)_n(s) + nH_2O(l)$; b $(C_6H_{10}O_5)_n(s) + nH_2O(l) \rightarrow nC_6H_{12}O_6(s)$; c condensation stores energy by joining many glucose units

(eliminating water); hydrolysis (adding water) breaks the glycosidic linkages back to glucose during digestion. **26** a proteins — amino acids, amide/peptide linkage $-\text{CO–NH}-$, water; triglycerides — one glycerol + three fatty acids, ester linkage $-\text{COO}-$, water; carbohydrates — monosaccharides (glucose), glycosidic linkage $-\text{C–O–C}-$, water; b **3** (three ester linkages form, one water eliminated per linkage); c hydrolysis adds water across a linkage to split a molecule, exactly reversing condensation, which eliminates water to form the linkage.

Fully-worked solutions

Question 1 a. Carboxylic acid + alcohol → ester (esterification). The acid (butanoic acid) gives the *butanoate* second word; the alcohol (methanol) gives the *methyl* first word → **methyl butanoate**, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_3$. b. $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}(\text{l}) + \text{CH}_3\text{OH}(\text{l}) \rightleftharpoons \text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_3(\text{l}) + \text{H}_2\text{O}(\text{l})$. Atoms balance (each side C 5, H 12, O 3), and one H_2O is eliminated. c. Esterification is reversible: under the acidic conditions the reverse reaction (acid hydrolysis of the ester) also occurs, so the mixture reaches equilibrium rather than going to completion — hence $\rightleftharpoons$.

Question 2 a. $\text{CH}_3\text{COOCH}_2\text{CH}_3(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CH}_3\text{COOH}(\text{l}) + \text{CH}_3\text{CH}_2\text{OH}(\text{l})$. Cutting the $-\text{COO}-$ linkage, the acyl side becomes **ethanoic acid** and the alkyl side becomes **ethanol**. This is the exact reverse of esterification, so $\rightleftharpoons$. b. $\text{CH}_3\text{COOCH}_2\text{CH}_3(\text{l}) + \text{NaOH}(\text{aq}) \rightarrow \text{CH}_3\text{COONa}(\text{aq}) + \text{CH}_3\text{CH}_2\text{OH}(\text{l})$. Products are **sodium ethanoate** and **ethanol** (each side C 4, H 9, O 3, Na 1). c. In base hydrolysis the carboxylic acid is neutralised and removed as its carboxylate salt (CH_3COO^-), so the reverse esterification cannot occur and the reaction goes to completion. Acid hydrolysis produces the free carboxylic acid and alcohol, both of which can recombine (esterify) under the same acidic conditions, so an equilibrium is set up.

Question 3 a. A carboxylic acid with ammonia gives a primary amide, $-\text{CONH}_2$. The acyl group $\text{CH}_3\text{CO}-$ of ethanoic acid keeps its two carbons, so the semi-structural formula is CH_3CONH_2 and the molecular formula is $\text{C}_2\text{H}_5\text{NO}$ (C 2, H 5, N 1, O 1). b. $\text{CH}_3\text{COOH}(\text{l}) + \text{NH}_3(\text{g}) \rightarrow \text{CH}_3\text{CONH}_2(\text{s}) + \text{H}_2\text{O}(\text{l})$ (each side C 2, H 7, N 1, O 2). c. The new linkage is the amide linkage $-\text{CO–NH}-$ (here as the terminal $-\text{CONH}_2$); the small molecule eliminated is **water**.

Question 4 a. Split $\text{HCOOCH}_2\text{CH}_2\text{CH}_3$ at the $-\text{COO}-$ linkage: the acyl side $\text{HCO}-$ → methanoate → **methanoic acid** (HCOOH); the alkyl side $-\text{CH}_2\text{CH}_2\text{CH}_3$ → propyl → **propan-1-ol** ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$). b. $\text{HCOOH}(\text{l}) + \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}(\text{l}) \rightleftharpoons \text{HCOOCH}_2\text{CH}_2\text{CH}_3(\text{l}) + \text{H}_2\text{O}(\text{l})$ (each side C 4, H 10, O 3). c. Acid hydrolysis is the reverse: $\text{HCOOCH}_2\text{CH}_2\text{CH}_3(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HCOOH}(\text{l}) + \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}(\text{l})$.

Question 5 a. Water is added across the $-\text{CONH}_2$ group:
$\text{CH}_3\text{CH}_2\text{CONH}_2(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{CH}_3\text{CH}_2\text{COOH}(\text{l}) + \text{NH}_3(\text{g})$. The products are **propanoic acid** and **ammonia** (each side C 3, H 9, N 1, O 2). b. The carbon-containing product, propanoic acid, carries a **carboxyl group** ($-\text{COOH}$). c. This hydrolysis is the exact reverse of the condensation by which propanamide is made from propanoic acid and ammonia: condensation removes water to form the amide, hydrolysis adds water to reform the acid and ammonia.

Question 6 a. **Condensation** (esterification): an acid and an alcohol join and **eliminate** a molecule of **water**. b. **Hydrolysis** (of an ester): a molecule of **water** is **added** across the ester linkage, splitting it into an acid and an alcohol. c. **Condensation** (amide formation): an acid and ammonia join and **eliminate** a molecule of **water**.

Question 7 Propanoic acid supplies the *propanoate* second word and ethanol the *ethyl* first word → **ethyl propanoate**. $\text{CH}_3\text{CH}_2\text{COOH}(\text{l}) + \text{CH}_3\text{CH}_2\text{OH}(\text{l}) \rightleftharpoons \text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3(\text{l}) + \text{H}_2\text{O}(\text{l})$ (each side C 5, H 12, O 3).

Question 8 Pentanoic acid gives *pentanoate*; methanol gives *methyl* → **methyl pentanoate**.
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}(\text{l}) + \text{CH}_3\text{OH}(\text{l}) \rightleftharpoons \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOCH}_3(\text{l}) + \text{H}_2\text{O}(\text{l})$ (each side C 6, H 14, O 3).

Question 9 Methyl butanoate is $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_3$. Acid hydrolysis reverses esterification:
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_3(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}(\text{l}) + \text{CH}_3\text{OH}(\text{l})$. Products: **butanoic acid** and **methanol** (each side C 5, H 12, O 3).

Question 10 Propyl ethanoate is $CH_3COOCH_2CH_2CH_3$. With hot NaOH the ester is saponified: $CH_3COOCH_2CH_2CH_3(l) + NaOH(aq) \rightarrow CH_3COONa(aq) + CH_3CH_2CH_2OH(l)$. Products: **sodium ethanoate** and **propan-1-ol** (each side C 5, H 11, O 3, Na 1).

Question 11 Split $CH_3CH_2CH_2COOCH_2CH_3$ at the linkage: acyl side $CH_3CH_2CH_2CO-$ → **butanoic acid**; alkyl side $-CH_2CH_3$ → **ethanol**. Acid hydrolysis: $CH_3CH_2CH_2COOCH_2CH_3(l) + H_2O(l) \rightleftharpoons CH_3CH_2CH_2COOH(l) + CH_3CH_2OH(l)$ (each side C 6, H 14, O 3).

Question 12 Butanoic acid + ammonia → primary amide + water; the four-carbon acyl group $CH_3CH_2CH_2CO-$ keeps its four carbons, giving the primary amide $CH_3CH_2CH_2CONH_2$. $CH_3CH_2CH_2COOH(l) + NH_3(g) \rightarrow CH_3CH_2CH_2CONH_2(s) + H_2O(l)$ (each side C 4, H 11, N 1, O 2). The molecular formula of the amide is C_4H_9NO (C 4, H 9, N 1, O 1).

Question 13 Ethanamide hydrolyses by adding water across $-CONH_2$: $CH_3CONH_2(s) + H_2O(l) \rightarrow CH_3COOH(l) + NH_3(g)$. Products: **ethanoic acid** and **ammonia** (each side C 2, H 7, N 1, O 2).

Question 14 Hydrolysis adds the elements of water across the amide linkage: cut the C–N bond of $CH_3CONHCH_2CH_3$, giving the carbonyl side $-OH$ and the nitrogen side $-H$. The carbonyl side CH_3CO- becomes CH_3COOH and the nitrogen side $-NHCH_2CH_3$ becomes $CH_3CH_2NH_2$:

$$CH_3CONHCH_2CH_3(l) + H_2O(l) \rightarrow CH_3COOH(l) + CH_3CH_2NH_2(g)$$

(each side C 4, H 11, N 1, O 2). The organic products are **ethanoic acid** and **ethylamine**, and the linkage broken is the **amide linkage** $-CO–NH-$.

Question 15 Split $CH_3CH_2COOCH_2CH_2CH_2CH_3$ at the $-COO-$ linkage: the acyl side CH_3CH_2CO- has three carbons → *propanoate* (second word); the alkyl side $-CH_2CH_2CH_2CH_3$ has four carbons → *butyl* (first word). The ester is **butyl propanoate**. Completing each fragment with the elements of water — $-OH$ to the carbonyl side, $-H$ to the other — gives **propanoic acid** (CH_3CH_2COOH) and **butan-1-ol** ($CH_3CH_2CH_2CH_2OH$).

Question 16 Base hydrolysis (saponification) of methyl hexanoate: $CH_3CH_2CH_2CH_2CH_2COOCH_3(l) + NaOH(aq) \rightarrow CH_3CH_2CH_2CH_2CH_2COONa(aq) + CH_3OH(l)$. Products: **sodium hexanoate** and **methanol** (each side C 7, H 15, O 3, Na 1). The base hydrolysis of an ester is called **saponification**.

Question 17 (i) A molecule of water is **added** across the $-CONH_2$ group, splitting the amide → **hydrolysis** (of an amide); small molecule = **water**. (ii) An acid and an alcohol join and **eliminate** water → **condensation** (esterification); small molecule = **water**. (iii) An acid and ammonia join and **eliminate** water → **condensation** (amide formation); small molecule = **water**.

Question 18 Esterification is reversible because the forward reaction (acid + alcohol → ester + water) and the reverse reaction (acid hydrolysis of the ester) both proceed under the same acidic conditions; the system therefore reaches a dynamic equilibrium in which unreacted acid and alcohol remain, so the yield of ester is incomplete. By Le Châtelier's principle the equilibrium can be shifted toward the ester (raising the yield) by, for example: (1) adding an **excess** of one reactant (the acid or the alcohol), which drives the system to consume the other; and (2) **removing water** as it forms — concentrated sulfuric acid acts as a dehydrating agent — or removing the ester by distillation, so the system responds by producing more ester.

Question 19 (1) The concentrated sulfuric acid is an **acid catalyst**: it provides an alternative reaction pathway of lower activation energy, speeding the forward and reverse reactions equally so that equilibrium is reached more quickly. Because it speeds both directions equally it cannot shift the position of equilibrium, so this role increases the **rate** only — not the yield. (2) It also acts as a **dehydrating agent**, absorbing the water as it is produced. Removing a product shifts the position of equilibrium to the right (Le Châtelier), so this role increases the **yield** of ethyl ethanoate. ∴ role (1) raises the rate alone and role (2) raises the yield; together they give a faster reaction *and* a higher yield, but

for different reasons. (Note that a genuinely dehydrating quantity of H_2SO_4 is needed for role (2) — a few catalytic drops would serve role (1) only.)

Question 20 Step 1 (acid hydrolysis of ethyl propanoate): $CH_3CH_2COOCH_2CH_3(l) + H_2O(l) \rightleftharpoons CH_3CH_2COOH(l) + CH_3CH_2OH(l)$, giving propanoic acid (and ethanol). Step 2 (condensation of propanoic acid with ammonia): $CH_3CH_2COOH(l) + NH_3(g) \rightarrow CH_3CH_2CONH_2(s) + H_2O(l)$. ∴ the final organic product has the semi-structural formula $CH_3CH_2CONH_2$ (the primary amide propanamide).

Question 21 a. Acid hydrolysis of an ester gives a carboxylic acid and an alcohol; recombining the fragments through a $-COO-$ linkage (acid on the carbonyl side, alcohol on the other) gives **propyl propanoate**, $CH_3CH_2COOCH_2CH_2CH_3$ (from propanoic acid and propan-1-ol). b. $CH_3CH_2COOCH_2CH_2CH_3(l) + H_2O(l) \rightleftharpoons CH_3CH_2COOH(l) + CH_3CH_2CH_2OH(l)$ (each side C 6, H 14, O 3). c. The hydrolysis products are a carboxylic acid and an alcohol, both of which contain only carbon, hydrogen and oxygen. Hydrolysis of an **amide** would instead give a carboxylic acid together with **ammonia or an amine**, which contains **nitrogen**. Since X contains only C, H and O and neither product contains nitrogen, X cannot be an amide; it must be an **ester**.

Question 22 Glycerol has three $-OH$ groups and each hexanoic acid one $-COOH$; the three condense to a triester (triglyceride), each linkage eliminating one water. The product is **glyceryl trihexanoate**, $C_{21}H_{38}O_6$.

$$C_3H_5(OH)_3(l) + 3CH_3CH_2CH_2CH_2CH_2COOH(l) \rightarrow C_3H_5(OOCCH_2CH_2CH_2CH_2CH_3)_3(l) + 3H_2O(l)$$

Each side has C 21, H 44, O 9. The linkage formed is the **ester linkage** $-COO-$, and **3** molecules of water are eliminated (one per ester linkage).

Question 23 a. The $-COOH$ of alanine condenses with the $-NH_2$ of serine: the acid's $-OH$ and one $-H$ from the nitrogen leave together as H_2O, and the two units join through the new $-CO–NH-$ bond. Alanine keeps its $-NH_2$ end free and serine keeps its $-COOH$ end free, so the dipeptide is $H_2NCH(CH_3)CONHCH(CH_2OH)COOH$:

$$H_2NCH(CH_3)COOH(s) + H_2NCH(CH_2OH)COOH(s) \rightarrow H_2NCH(CH_3)CONHCH(CH_2OH)COOH(s) + H_2O(l$$

Atoms balance: alanine is $C_3H_7NO_2$ and serine is $C_3H_7NO_3$, so each side has C 6, H 14, N 2, O 5 (the dipeptide is $C_6H_{12}N_2O_4$). The linkage formed is the **amide linkage** $-CO–NH-$, called the **peptide linkage** in a protein. b. Hydrolysis adds the elements of water back across the peptide linkage, giving $-OH$ to the carbonyl side and $-H$ to the nitrogen side, so each fragment again carries both an $-NH_2$ and a $-COOH$ group:

$$H_2NCH(CH_3)CONHCH(CH_2OH)COOH(s) + H_2O(l) \rightarrow H_2NCH(CH_3)COOH(s) + H_2NCH(CH_2OH)COOH(s$$

(each side C 6, H 14, N 2, O 5). The products are the two original amino acids, **alanine** (side chain R = $-CH_3$) and **serine** (R = $-CH_2OH$). c. Five amino-acid units joined end to end in a single chain are held together by **4** peptide linkages — n units in a chain are joined by $n-1$ linkages, because the first unit needs no linkage and every unit added after it contributes exactly one. Each linkage forms by eliminating one molecule of water, so **4** molecules of water are eliminated.

Question 24 Hydrolysis adds the elements of water across each of the three ester linkages, releasing glycerol and three molecules of the fatty acid (octanoic acid):

$$C_3H_5(OOCC_7H_{15})_3(l) + 3H_2O(l) \rightarrow C_3H_5(OH)_3(l) + 3CH_3(CH_2)_6COOH(l)$$

Each side has C 27, H 56, O 9. The products are **glycerol** and **octanoic acid**, and **3** molecules of water are added (one per ester linkage broken).

Question 25 a. The count of water molecules follows from the **repeat-unit formula** given in the stem. The repeat unit $C_6H_{10}O_5$ is one glucose molecule *minus* one water ($C_6H_{12}O_6 - H_2O = C_6H_{10}O_5$), so writing the polymer as n such units means n molecules of water must appear on the product side for the equation to balance:

$$n\,C_6H_{12}O_6(s) \rightarrow (C_6H_{10}O_5)_n(s) + n\,H_2O(l)$$

(each side C $6n$, H $12n$, O $6n$). Counting linkages instead gives $n-1$ waters, because n units in a chain are joined by $n-1$ glycosidic linkages; for starch n runs into the thousands, so the two counts are indistinguishable in practice and the repeat-unit equation above is the standard form. b. Complete hydrolysis reverses this, adding n molecules of water to release n glucose molecules:

$$(C_6H_{10}O_5)_n(s) + n\,H_2O(l) \rightarrow n\,C_6H_{12}O_6(s)$$

c. When glucose is plentiful, the plant stores the energy by **condensing** many glucose molecules into insoluble starch, eliminating water at each glycosidic linkage; the compact, insoluble polymer is an efficient energy store. When the starch is eaten, **hydrolysis** of those glycosidic linkages (adding water) breaks it back into glucose, which is absorbed and oxidised to release the stored energy. Storage is condensation; digestion is hydrolysis.

Question 26 a. **Proteins** are built from **amino acids** joined by the **amide (peptide) linkage** $-CO–NH-$, eliminating **water** as each linkage forms. **Triglycerides** are built from **one glycerol and three fatty acids** joined by **ester linkages** $-COO-$, eliminating **water**. **Carbohydrates** are built from **monosaccharides** (e.g. glucose) joined by **glycosidic linkages** $-C–O–C-$, eliminating **water**. b. **Three** molecules of water. A triglyceride contains three ester linkages (one for each of the glycerol's three $-OH$ groups reacting with a fatty-acid $-COOH$), and condensation eliminates exactly one water per linkage formed, so $3 \times 1 = 3$ molecules of water are eliminated. c. Condensation joins two molecules into a larger one by **eliminating** the elements of water at the new linkage; hydrolysis does the exact opposite — it **adds** the elements of water across that linkage to split the larger molecule back into the smaller ones. Because one reaction removes the water that the other puts back, hydrolysis is the reverse of condensation.

Chapter 9 Reactions of organic compounds — 9C Reaction pathways and sustainable production

Theory

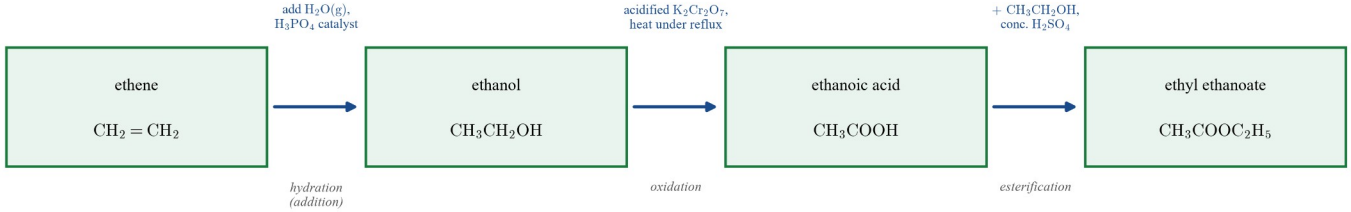
A single organic reaction rarely takes a raw starting material all the way to a useful target molecule. Instead, chemists join several of the reactions met in 9A (substitution, addition and oxidation) and 9B (condensation and hydrolysis) end-to-end, so that the **product of one step becomes the reactant of the next**. This planned sequence of conversions is a **reaction pathway**, and designing one — then judging how efficient and how sustainable it is — is the central skill of this subtopic.

The reaction toolkit. Every pathway is assembled from a small set of functional-group conversions, each with its own reagents and conditions. These are the reactions to combine:

Conversion	Reagents and conditions	Reaction type
alkene → alcohol	steam $H_2O(g)$, H_3PO_4 catalyst	addition (hydration)
alkene → alkane	H_2, Ni catalyst	addition (hydrogenation)
alkene → haloalkane	HX (e.g. HBr)	addition
alkene → dihaloalkane	X_2 (e.g. Br_2)	addition (halogenation)
haloalkane → alcohol	$NaOH(aq)$, warm	substitution
haloalkane → primary amine	NH_3 (excess)	substitution
primary alcohol → aldehyde	acidified $K_2Cr_2O_7$, gentle heat, distil off	oxidation (partial)
primary alcohol → carboxylic acid	acidified $K_2Cr_2O_7$, heat under reflux	oxidation (full)
secondary alcohol → ketone	acidified $K_2Cr_2O_7$, heat	oxidation
carboxylic acid + alcohol → ester	conc. H_2SO_4 catalyst, heat	condensation (esterification)
carboxylic acid + ammonia or amine → amide	heat	condensation
ester + water → acid + alcohol	dilute acid or base, heat	hydrolysis

As in 9A, the oxidation of an alcohol is written with the shorthand $[O]$, standing for **one oxygen atom supplied by the oxidising agent** — here the acidified dichromate, which is itself reduced as it accepts electrons from the alcohol. A **partial** oxidation to the aldehyde uses one $[O]$, and the **full** oxidation to the carboxylic acid uses two.

Designing a multi-step synthesis. To convert a given starting material into a target molecule, work out which functional group must change at each stage, then pick the toolkit reaction that makes that change. For example, ethene can be converted into ethyl ethanoate in three steps — hydrate the alkene to an alcohol, oxidise the alcohol to the carboxylic acid, then esterify the acid with more of the alcohol:



The boxes are the molecules and the arrows carry the reagents and conditions; reading such a **reaction pathway map** from left to right gives the whole synthesis, while reading a single arrow tells you the reagents for one step. When a

map is only partly given, each blank is deduced by asking *what reactant and conditions turn this functional group into the next one?* The three steps of the map above are:

$$CH_2{=}CH_2(g) + H_2O(g) \rightarrow CH_3CH_2OH(l)$$

$$CH_3CH_2OH(l) + 2[O] \rightarrow CH_3COOH(l) + H_2O(l)$$

$$CH_3COOH(l) + CH_3CH_2OH(l) \rightarrow CH_3COOC_2H_5(l) + H_2O(l)$$

Percentage yield. No real reaction converts every reactant molecule into product: reactions may not reach completion, side reactions occur, an equilibrium may lie short of products, and some product is always lost on transfer and purification. The **percentage yield** compares the mass (or amount) actually obtained with the maximum that the balanced equation predicts:

$$\text{percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\,\%$$

The theoretical yield is found by ordinary stoichiometry — convert the limiting reactant to an amount in mole, apply the mole ratio, then convert to a mass. Because each step of a pathway has a yield below 100%, the losses **compound**: the **overall percentage yield** of a multi-step pathway is the *product* of the individual step yields (written as decimals),

$$\text{overall yield} = (\text{yield}_1) \times (\text{yield}_2) \times \ldots \times 100\,\%$$

so a three-step route with steps of 90%, 80% and 75% delivers only $0.90 \times 0.80 \times 0.75 = 0.54$, or 54%, of the theoretical amount. This is a strong reason to prefer shorter pathways.

Atom economy. Percentage yield measures how well a *particular batch* was run; **atom economy** measures something more fundamental — what fraction of the *reactant atoms* end up in the desired product, according to the balanced equation, even if the reaction goes perfectly:

$$\text{atom economy} = \frac{n(\text{desired product}) \times M(\text{desired product})}{\sum n(\text{reactant}) \times M(\text{reactant})} \times 100\,\%$$

where each n is the **coefficient** of that species in the balanced equation. Most of the equations met here have every coefficient equal to 1, so the expression reduces to $M(\text{desired product})$ divided by the sum of the reactant molar masses; but a coefficient greater than 1 must always be carried into the calculation — if two mole of the desired product form per mole of a reactant, the numerator is $2 \times M(\text{desired product})$.

A reaction in which the reactants combine into a **single product** — every **addition** reaction of an alkene, for instance — has an atom economy of 100%, because no atoms are left over. **Substitution**, **condensation** and **hydrolysis** reactions always fall below 100%, because they release a small by-product (a salt such as $NaBr$, or a molecule of H_2O or HCl) whose atoms are "wasted" from the point of view of the target. A high atom economy is an advantage for industry and for society: it means less reactant mass is bought and then thrown away, less waste must be treated or disposed of, and the process is cheaper and less polluting per tonne of product.

Atom economy and percentage yield are independent. A reaction can have 100% atom economy yet a poor yield if it does not go to completion; and a reaction can run in high yield yet have a low atom economy if half of its reactant mass is designed to leave as a by-product.

Green chemistry and the sustainability of production. *Green chemistry* is the design of chemical processes that reduce or eliminate hazardous substances and waste. When the manufacture of an organic compound is evaluated for **sustainability**, several green chemistry principles are weighed together:

- **use of renewable feedstocks** — sourcing carbon from crops, plant oils or biomass, which are replenished on a human timescale, rather than from finite crude oil and natural gas (e.g. bioethanol from fermented sugar, or biodiesel from plant triglycerides);
- **catalysis** — using a catalyst, which provides an alternative reaction pathway of *lower activation energy*, so the reaction runs faster and at a lower temperature. A catalyst is not consumed and lets a process operate with greater energy efficiency;

- **designing safer chemicals and reducing waste and hazard** — choosing reactions of **high atom economy** that generate little by-product, avoiding toxic reagents and solvents, and making products that are less hazardous.

Evaluating a route means comparing it against these principles with **evidence** — quoting the feedstock, the atom economy, whether a catalyst is used, the energy demand, and the nature of any waste — and then reaching a **conclusion** about which route is more sustainable. This is exactly the shape of the extended-response question that commonly closes the examination: choose at least two green chemistry principles, support each with specific evidence for the routes being compared, and finish with a clear recommending statement.

Worked examples

Worked Example 1 — Design a three-step pathway to convert ethene into ethyl ethanoate. For each step, state the reagent(s) and conditions, name the organic product, and write a balanced equation with states.

Working	Comment
Step 1 — hydration (addition). Reagents: steam $H_2O(g)$, H_3PO_4 catalyst. Product: **ethanol**.	Add water across the C=C double bond; the single product means 100% atom economy.
$CH_2{=}CH_2(g) + H_2O(g) \rightarrow CH_3CH_2OH(l)$	
Step 2 — oxidation (full). Reagents: acidified $K_2Cr_2O_7$, heat under reflux. Product: **ethanoic acid**.	Refluxing with excess oxidant drives the primary alcohol all the way to the carboxylic acid.
$CH_3CH_2OH(l) + 2[O] \rightarrow CH_3COOH(l) + H_2O(l)$	$[O]$ is one oxygen atom supplied by the oxidising agent.
Step 3 — esterification (condensation). Reagents: ethanol, conc. H_2SO_4 catalyst, heat. Product: **ethyl ethanoate**.	The acid from step 2 is esterified with more of the ethanol from step 1.
$CH_3COOH(l) + CH_3CH_2OH(l) \rightarrow CH_3COOC_2H_5(l$	Water is the condensation by-product.

Worked Example 2 — In the pathway ethene → ethanol → ethanoic acid, the hydration step proceeds in 92.0% yield and the oxidation step in 85.0% yield. Starting from 5.60 g of ethene ($M = 28.0\ \text{g mol}^{-1}$), calculate (a) the mass of ethanol obtained, (b) the mass of ethanoic acid obtained, and (c) the overall percentage yield of ethanoic acid from ethene.

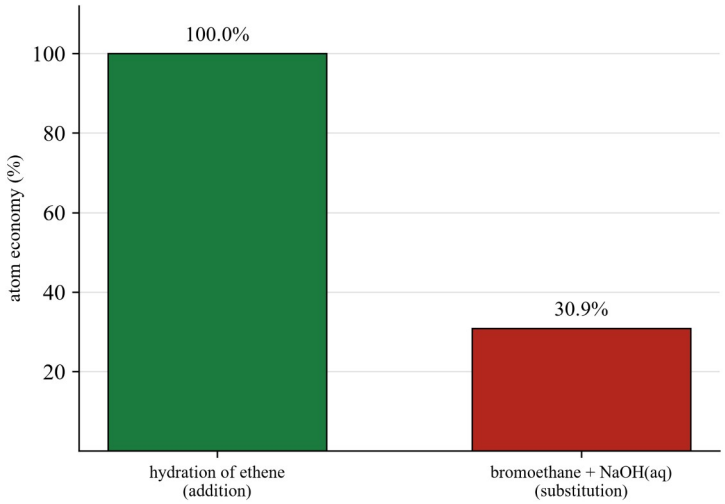
Working	Comment
$n(\text{ethene}) = \dfrac{5.60}{28.0} = 0.200\ \text{mol}$	Amount of starting material.
$n(\text{ethanol}) = 0.200 \times 0.920 = 0.184\ \text{mol}$	Mole ratio is 1:1; apply the 92.0% step yield.
$m(\text{ethanol}) = 0.184 \times 46.0 = 8.46\ \text{g}$	(a) Mass of ethanol ($M = 46.0\ \text{g mol}^{-1}$), 3 sig figs.
$n(\text{ethanoic acid}) = 0.184 \times 0.850 = 0.1564\ \text{mol}$	Oxidation is 1:1; apply the 85.0% step yield.
$m(\text{ethanoic acid}) = 0.1564 \times 60.0 = 9.38\ \text{g}$	(b) Mass of ethanoic acid ($M = 60.0\ \text{g mol}^{-1}$).
$\text{overall yield} = 0.920 \times 0.850 \times 100 = 78.2\,\%$	(c) The step yields multiply, since the losses compound.

Worked Example 3 — Ethanol can be manufactured either by the direct hydration of ethene, $CH_2{=}CH_2 + H_2O \rightarrow CH_3CH_2OH$ (Route 1), or by the substitution reaction of bromoethane with aqueous sodium hydroxide, $C_2H_5Br + NaOH \rightarrow C_2H_5OH + NaBr$ (Route 2). Calculate the atom economy of each route for ethanol and comment on which is greener.

Using $M(C_2H_5OH) = 46.0$, $M(CH_2{=}CH_2) = 28.0$, $M(H_2O) = 18.0$, $M(C_2H_5Br) = 108.9$ and $M(NaOH) = 40.0\ \text{g mol}^{-1}$:

$$\text{Route 1: atom economy} = \frac{46.0}{28.0 + 18.0} \times 100 = \frac{46.0}{46.0} \times 100 = 100\,\%$$

$$\text{Route 2: atom economy} = \frac{46.0}{108.9 + 40.0} \times 100 = \frac{46.0}{148.9} \times 100 = 30.9\,\%$$



∴ Route 1 is an addition reaction whose only product is ethanol, so it has a **100% atom economy** — no reactant atoms are wasted. Route 2 is a substitution reaction in which the sodium and bromine atoms leave as the by-product NaBr, so only 30.9% of the reactant mass ends up in the ethanol. Route 1 is far greener: it generates no waste salt, uses fewer reactant atoms per gram of product, and needs no separate step to make the haloalkane first.

Worked Example 4 — A factory produces ethyl ethanoate by esterification, $CH_3COOH + CH_3CH_2OH \rightarrow CH_3COOC_2H_5 + H_2O$, using a conc. H_2SO_4 catalyst. In one batch, 0.500 mol of ethanoic acid is reacted with excess ethanol and 39.6 g of ethyl ethanoate ($M = 88.0\ \text{g mol}^{-1}$) is collected. Calculate (a) the percentage yield and (b) the atom economy, and (c) comment, with reference to one green chemistry principle, on the use of the catalyst.

Theoretical yield: the acid and ester are in a 1:1 ratio, so

$$m(\text{theoretical}) = 0.500 \times 88.0 = 44.0\,\text{g}, \text{percentage yield} = \frac{39.6}{44.0} \times 100 = 90.0\,\%$$

Atom economy (using $M(\text{acid}) = 60.0$ and $M(\text{ethanol}) = 46.0\ \text{g mol}^{-1}$):

$$\text{atom economy} = \frac{88.0}{60.0 + 46.0} \times 100 = \frac{88.0}{106.0} \times 100 = 83.0\,\%$$

∴ the batch yield is 90.0% and the atom economy is 83.0% (the remaining 17% of reactant mass leaves as the water by-product). Against the green chemistry principle of **catalysis**, the conc. H_2SO_4 provides an alternative reaction pathway of lower activation energy, so the esterification reaches equilibrium faster and at a lower temperature; because the catalyst is not consumed, the process is more energy-efficient than the same reaction run without it.

Practice questions

Question 1 — Consider the two-step conversion of propan-1-ol into propyl propanoate.

a. Name the reagent and conditions that oxidise propan-1-ol to propanoic acid, and write a balanced equation for the step (use $[O]$), with states.
b. Propyl propanoate is made by esterifying propanoic acid with an alcohol. Name the alcohol and the catalyst, and write a balanced equation for the step, with states.
c. Explain why this counts as a two-step "reaction pathway" rather than two unrelated reactions.

Question 2 — A reaction pathway map runs: ethene → **X** → ethanoic acid → **Y**, where the three arrows are steps 1, 2 and 3 in turn.

a. Identify compound **X** and give the reagent and conditions for step 1.

b. Give the reagent and conditions for step 2 and write a balanced equation (use $[\mathrm{O}]$), with states.
c. If **Y** is ethyl ethanoate, identify the other reactant needed in step 3 and name the catalyst.

Question 3 — For the hydration of ethene, $\mathrm{CH_2{=}CH_2 + H_2O \rightarrow CH_3CH_2OH}$:

a. Calculate the theoretical mass of ethanol obtainable from 14.0 g of ethene.
b. If 18.4 g of ethanol is actually obtained, calculate the percentage yield of this step.
c. The ethanol is then oxidised to ethanoic acid in 80.0% yield. Calculate the overall percentage yield of ethanoic acid from ethene.

Question 4 — Chloroethane is converted to ethanol by warm aqueous sodium hydroxide:
$\mathrm{C_2H_5Cl + NaOH \rightarrow C_2H_5OH + NaCl}$.

a. Calculate the atom economy of this route for ethanol. (Use $M(\mathrm{C_2H_5Cl}) = 64.5\ \mathrm{g\ mol^{-1}}$.)
b. The same ethanol can be made by the hydration of ethene, which has a 100% atom economy. State which route produces less waste.
c. Explain what happens to the "lost" atoms in the chloroethane route.

Question 5 — Biodiesel is manufactured by the transesterification of plant triglycerides with methanol, using a small amount of NaOH as a catalyst. Petrodiesel is refined from crude oil.

a. State the feedstock for each fuel and identify which is renewable.
b. Name the green chemistry principle illustrated by using only a small amount of NaOH.
c. Give one further green chemistry advantage of biodiesel over petrodiesel.

Question 6 — Propan-1-ol is oxidised to propanoic acid, $\mathrm{CH_3CH_2CH_2OH + 2[O] \rightarrow CH_3CH_2COOH + H_2O}$, which is then esterified with ethanol to ethyl propanoate,
$\mathrm{CH_3CH_2COOH + CH_3CH_2OH \rightarrow CH_3CH_2COOC_2H_5 + H_2O}$.

a. Calculate the atom economy of the esterification step. (Use M: propanoic acid 74.0, ethanol 46.0, ethyl propanoate $102.0\ \mathrm{g\ mol^{-1}}$.)
b. Starting from 0.300 mol of propan-1-ol, the oxidation gives 85.0% yield and the esterification 90.0% yield. Calculate the mass of ethyl propanoate obtained.
c. Calculate the overall percentage yield of ethyl propanoate from propan-1-ol.

Question 7 — Write a balanced equation, with states, and state the reagent and conditions, for the single step that converts ethene into bromoethane. Name the reaction type and state the atom economy of the step.

Question 8 — Design a two-step pathway to convert 1-bromobutane into butanoic acid. For each step give the reagent and conditions, name the intermediate or product, and write a balanced equation with states (use $[\mathrm{O}]$ for the oxidation).

Question 9 — The oxidation of butan-1-ol can be stopped at the aldehyde, butanal, instead of proceeding to the acid. State the difference in reagent or conditions that achieves this, and write a balanced equation (use $[\mathrm{O}]$), with states, for the formation of butanal.

Question 10 — In the esterification $\mathrm{CH_3COOH + CH_3CH_2OH \rightarrow CH_3COOC_2H_5 + H_2O}$, 0.250 mol of ethanoic acid is reacted with excess ethanol and 16.5 g of ethyl ethanoate ($M = 88.0\ \mathrm{g\ mol^{-1}}$) is obtained. Calculate the percentage yield.

Question 11 — A synthesis is carried out in three steps with individual yields of 72.0%, 94.0% and 86.0%. Calculate the overall percentage yield of the synthesis.

Question 12 — Chloroethane can be made by the substitution reaction $\mathrm{C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl}$ (in ultraviolet light). Calculate the atom economy of this reaction for chloroethane. (Use M: ethane 30.0, $\mathrm{Cl_2}$ 71.0, chloroethane $64.5\ \mathrm{g\ mol^{-1}}$.)

Question 13 — Ethene reacts with bromine: $CH_2{=}CH_2 + Br_2 \rightarrow CH_2BrCH_2Br$.

a. Calculate the atom economy of this reaction for 1,2-dibromoethane. (Use M: ethene 28.0, Br_2 159.8, 1,2-dibromoethane $187.8\,\text{g mol}^{-1}$.)
b. Explain why every addition reaction of an alkene has this same atom economy.

Question 14 — Explain the difference between percentage yield and atom economy, and hence explain how a reaction can have a 100% atom economy while its percentage yield is well below 100%.

Question 15 — Ethene (7.00 g) is converted to ethanol (hydration, 95.0% yield) and then to ethanoic acid (oxidation, 88.0% yield).

a. Calculate the mass of ethanoic acid obtained.
b. Calculate the overall percentage yield of ethanoic acid from ethene.

Question 16 — Methyl ethanoate is made by esterifying ethanoic acid with methanol: $CH_3COOH + CH_3OH \rightarrow CH_3COOCH_3 + H_2O$. Calculate the atom economy for methyl ethanoate. (Use M: ethanoic acid 60.0, methanol 32.0, methyl ethanoate $74.0\,\text{g mol}^{-1}$.)

Question 17 — Propan-1-ol can be made from 1-bromopropane by substitution with warm $NaOH(aq)$: $C_3H_7Br + NaOH \rightarrow C_3H_7OH + NaBr$. Calculate the atom economy of this route for propan-1-ol (use $M(C_3H_7Br) = 122.9\,\text{g mol}^{-1}$), and state the main sustainability drawback that this figure reveals.

Question 18 — Design a pathway to convert bromoethane into ethanamide, CH_3CONH_2. Give the reagent and conditions for each step, name each intermediate, and write a balanced equation with states for each of the three steps.

Question 19 — Complete this reaction pathway map: 1-chloropropane → propan-1-ol → propanal, in which the first arrow is step **A** and the second is step **B**. Identify the reagents and conditions **A** and **B**, and name the type of reaction occurring at each step.

Question 20 — A sustainability audit compares two routes to ethanol: Route 1, the fermentation of glucose, $C_6H_{12}O_6 \rightarrow 2\,C_2H_5OH + 2\,CO_2$; and Route 2, the hydration of ethene obtained from crude oil.

a. Calculate the atom economy of Route 1 for ethanol. (Use M: glucose 180.0, ethanol $46.0\,\text{g mol}^{-1}$.)
b. State which route uses a renewable feedstock.
c. Give one reason Route 1 might still be judged less sustainable despite its renewable feedstock.

Question 21 — A company can manufacture ethyl ethanoate by either of two routes.

- **Route P** — esterification of ethanoic acid with ethanol using a conc. H_2SO_4 catalyst (atom economy 83%); the ethanol is produced by the fermentation of sugar cane.
- **Route Q** — reaction of bromoethane with sodium ethanoate, $CH_3COONa + C_2H_5Br \rightarrow CH_3COOC_2H_5 + NaBr$ (atom economy 46%); the bromoethane is derived from crude-oil ethene.

Evaluate the two routes with respect to green chemistry principles. In your response, refer to at least two green chemistry principles with supporting evidence, and give a concluding statement recommending one route. *(6 marks)*

Answers

1 a acidified $K_2Cr_2O_7$, heat under reflux; $CH_3CH_2CH_2OH(l)+2[O] \rightarrow CH_3CH_2COOH(l)+H_2O(l)$; b propan-1-ol, conc. H_2SO_4; $CH_3CH_2COOH(l)+CH_3CH_2CH_2OH(l) \rightarrow CH_3CH_2COOC_3H_7(l)+H_2O(l)$; c the product of step 1 (propanoic acid) is the reactant of step 2. **2** a **X** = ethanol; steam $H_2O(g)$, H_3PO_4 catalyst; b acidified $K_2Cr_2O_7$, heat under reflux; $CH_3CH_2OH(l)+2[O] \rightarrow CH_3COOH(l)+H_2O(l)$; c ethanol; conc. H_2SO_4. **3** a $23.0\,g$; b $80.0\,\%$; c $64.0\,\%$. **4** a $44.0\,\%$; b the hydration of ethene; c the Na and Cl atoms leave in the by-product NaCl (waste salt), not in the ethanol. **5** a biodiesel — plant triglycerides (renewable); petrodiesel — crude oil (non-renewable); b catalysis; c e.g. renewable feedstock / near carbon-neutral combustion / biodegradable. **6** a $85.0\,\%$; b $23.4\,g$; c $76.5\,\%$. **7** $CH_2{=}CH_2(g)+HBr(g) \rightarrow CH_3CH_2Br(l)$; hydrogen bromide, room temperature, no catalyst needed; addition (hydrohalogenation); atom economy $100\,\%$. **8** Step 1 $NaOH(aq)$, warm: $C_4H_9Br(l)+NaOH(aq) \rightarrow C_4H_9OH(aq)+NaBr(aq)$ (butan-1-ol); Step 2 acidified $K_2Cr_2O_7$, reflux: $C_4H_9OH(l)+2[O] \rightarrow C_3H_7COOH(l)+H_2O(l)$ (butanoic acid). **9** Use a limited amount of oxidant and warm gently, distilling the butanal off as it forms (rather than heating under reflux with excess oxidant); $C_4H_9OH(l)+[O] \rightarrow C_3H_7CHO(l)+H_2O(l)$. **10** $75.0\,\%$. **11** $58.2\,\%$. **12** $63.9\,\%$. **13** a $100\,\%$; b the two reactants add together to form a single product with no by-product, so all reactant atoms are in the product. **14** See solution — atom economy is set by the balanced equation; yield is set by how the reaction actually runs. **15** a $12.5\,g$; b $83.6\,\%$. **16** $80.4\,\%$. **17** $36.8\,\%$; most of the reactant mass leaves as the waste salt NaBr, so the route is wasteful (low atom economy). **18** $C_2H_5Br(l)+NaOH(aq) \rightarrow C_2H_5OH(aq)+NaBr(aq)$ [$NaOH(aq)$, warm]; $CH_3CH_2OH(l)+2[O] \rightarrow CH_3COOH(l)+H_2O(l)$ [acidified $K_2Cr_2O_7$, reflux]; $CH_3COOH(l)+NH_3(g) \rightarrow CH_3CONH_2(s)+H_2O(l)$ [ammonia, heat] (ethanol, ethanoic acid, ethanamide). **19 A** = $NaOH(aq)$, warm (substitution); **B** = acidified $K_2Cr_2O_7$, gentle heat with distillation (partial oxidation). **20** a $51.1\,\%$; b Route 1 (glucose from crops); c e.g. large land/water use, the energy needed to distil the dilute ethanol, or competition with food production. **21** Evaluation (see solution): renewable feedstock and higher atom economy favour Route P; recommend Route P.

Fully-worked solutions

Question 1 a. Full oxidation of the primary alcohol needs acidified $K_2Cr_2O_7$ with heating under reflux (excess oxidant), which uses two $[O]$:

$$CH_3CH_2CH_2OH(l)+2[O] \rightarrow CH_3CH_2COOH(l)+H_2O(l)$$

b. Propyl propanoate is the ester of propanoic acid with **propan-1-ol**; the catalyst is conc. H_2SO_4:

$$CH_3CH_2COOH(l)+CH_3CH_2CH_2OH(l) \rightarrow CH_3CH_2COOC_3H_7(l)+H_2O(l)$$

c. It is a pathway because the steps are linked: the propanoic acid made in step 1 is the reactant that is esterified in step 2, so the two reactions run in sequence to convert one starting material into the final target.

Question 2 a. **X** = ethanol. Step 1 is the hydration of ethene: steam $H_2O(g)$ with an H_3PO_4 catalyst. b. Step 2 is the full oxidation of ethanol with acidified $K_2Cr_2O_7$, heated under reflux:

$$CH_3CH_2OH(l)+2[O] \rightarrow CH_3COOH(l)+H_2O(l)$$

c. To make ethyl ethanoate, the ethanoic acid must be esterified with **ethanol**, catalysed by conc. H_2SO_4.

Question 3 a. $n(\text{ethene}) = \dfrac{14.0}{28.0} = 0.500\,\text{mol}$. The mole ratio ethene : ethanol is 1:1, so the theoretical amount of ethanol is 0.500 mol and $m = 0.500 \times 46.0 = 23.0\,g$. b. $\text{percentage yield} = \dfrac{18.4}{23.0} \times 100 = 80.0\,\%$. c. The losses compound, so the overall yield is the product of the two step yields: $0.800 \times 0.800 \times 100 = 64.0\,\%$.

Question 4 a. $\text{atom economy} = \dfrac{M(\text{C}_2\text{H}_5\text{OH})}{M(\text{C}_2\text{H}_5\text{Cl}) + M(\text{NaOH})} \times 100 = \dfrac{46.0}{64.5 + 40.0} \times 100 = \dfrac{46.0}{104.5} \times 100 = 44.0\,\%$. b. The hydration of ethene (100% atom economy) produces less waste. c. In the chloroethane route the sodium and chlorine atoms end up in the by-product NaCl; that mass (and the mass of the NaOH used) is "lost" from the target ethanol and becomes waste.

Question 5 a. Biodiesel's feedstock is **plant triglycerides** (vegetable oils), which are **renewable** because crops regrow within a season; petrodiesel's feedstock is **crude oil**, which is finite and non-renewable. b. Using only a small, unconsumed quantity of NaOH illustrates the principle of **catalysis**. c. Any one of: biodiesel is derived from a renewable feedstock; the CO_2 released when it burns was recently absorbed from the atmosphere by the crop, so its net emissions are lower (near carbon-neutral); it is biodegradable and less toxic if spilled.

Question 6 a. $\text{atom economy} = \dfrac{102.0}{74.0 + 46.0} \times 100 = \dfrac{102.0}{120.0} \times 100 = 85.0\,\%$. b. Both steps are 1:1, so $n(\text{ester}) = 0.300 \times 0.850 \times 0.900 = 0.2295\,\text{mol}$, and $m = 0.2295 \times 102.0 = 23.4\,\text{g}$.
c. $\text{overall yield} = 0.850 \times 0.900 \times 100 = 76.5\,\%$.

Question 7

$$\text{CH}_2{=}\text{CH}_2(\text{g}) + \text{HBr}(\text{g}) \rightarrow \text{CH}_3\text{CH}_2\text{Br}(\text{l})$$

The reagent is **hydrogen bromide** gas at room temperature; no catalyst is needed. The H and the Br add across the C=C double bond, which becomes a single bond, so the step is an **addition** (hydrohalogenation). Both reactants are taken up entirely into the single product, so the atom economy is $\dfrac{108.9}{28.0 + 80.9} \times 100 = 100\,\%$.

Question 8 Step 1 — substitution of the haloalkane with warm aqueous hydroxide gives the primary alcohol **butan-1-ol**:

$$\text{C}_4\text{H}_9\text{Br}(\text{l}) + \text{NaOH}(\text{aq}) \rightarrow \text{C}_4\text{H}_9\text{OH}(\text{aq}) + \text{NaBr}(\text{aq})$$

Step 2 — full oxidation of the primary alcohol with acidified $\text{K}_2\text{Cr}_2\text{O}_7$, heated under reflux, gives **butanoic acid**:

$$\text{C}_4\text{H}_9\text{OH}(\text{l}) + 2[\text{O}] \rightarrow \text{C}_3\text{H}_7\text{COOH}(\text{l}) + \text{H}_2\text{O}(\text{l})$$

Question 9 To stop at the aldehyde, use a limited amount of oxidant and warm gently, **distilling the butanal off as it forms** so it cannot be oxidised further; this contrasts with heating under reflux with excess oxidant, which would carry the reaction on to butanoic acid. Partial oxidation uses a single $[\text{O}]$:

$$\text{C}_4\text{H}_9\text{OH}(\text{l}) + [\text{O}] \rightarrow \text{C}_3\text{H}_7\text{CHO}(\text{l}) + \text{H}_2\text{O}(\text{l})$$

Question 10 The acid and ester are in a 1:1 ratio, so the theoretical mass of ethyl ethanoate is $0.250 \times 88.0 = 22.0\,\text{g}$.

$$\text{percentage yield} = \frac{16.5}{22.0} \times 100 = 75.0\,\%$$

Question 11 The step yields multiply: $\text{overall yield} = 0.720 \times 0.940 \times 0.860 \times 100 = 58.2\,\%$.

Question 12

$$\text{atom economy} = \frac{M(\text{C}_2\text{H}_5\text{Cl})}{M(\text{C}_2\text{H}_6) + M(\text{Cl}_2)} \times 100 = \frac{64.5}{30.0 + 71.0} \times 100 = \frac{64.5}{101.0} \times 100 = 63.9\,\%$$

The remaining atoms leave as the by-product HCl, which is why this substitution falls short of 100%.

Question 13 a. $\text{atom economy} = \dfrac{187.8}{28.0 + 159.8} \times 100 = \dfrac{187.8}{187.8} \times 100 = 100\,\%$. b. In an addition reaction the two reactant molecules combine into a **single product** with no by-product, so every atom of both reactants is incorporated into the product; the numerator and denominator of the atom-economy expression are therefore equal, giving 100%.

Question 14 **Atom economy** is a property of the *balanced equation*: it is the fraction of the reactant mass that appears in the desired product, assuming the reaction goes perfectly to completion. **Percentage yield** is a property of the *actual run*: it is the actual amount obtained divided by the theoretical maximum. They are independent. A reaction such as an alkene addition can have a 100% atom economy (no by-product in its equation) yet still give a low percentage yield, because in practice the reaction may not reach completion, side reactions may occur, or product may be lost during transfer and purification — none of which is captured by the atom economy.

Question 15 a. $n(\text{ethene}) = \dfrac{7.00}{28.0} = 0.250\,\text{mol}$. Both steps are 1:1, so $n(\text{ethanoic acid}) = 0.250 \times 0.950 \times 0.880 = 0.2090\,\text{mol}$, and $m = 0.2090 \times 60.0 = 12.5\,\text{g}$. b. overall yield $= 0.950 \times 0.880 \times 100 = 83.6\,\%$.

Question 16

$$\text{atom economy} = \frac{M(\text{CH}_3\text{COOCH}_3)}{M(\text{CH}_3\text{COOH}) + M(\text{CH}_3\text{OH})} \times 100 = \frac{74.0}{60.0 + 32.0} \times 100 = \frac{74.0}{92.0} \times 100 = 80.4\,\%$$

The lost mass is the water by-product of the condensation.

Question 17

$$\text{atom economy} = \frac{M(\text{C}_3\text{H}_7\text{OH})}{M(\text{C}_3\text{H}_7\text{Br}) + M(\text{NaOH})} \times 100 = \frac{60.0}{122.9 + 40.0} \times 100 = \frac{60.0}{162.9} \times 100 = 36.8\,\%$$

The figure is low because most of the reactant mass (the sodium and, especially, the heavy bromine atom) leaves as the waste salt NaBr rather than entering the product; the route is therefore wasteful and generates a salt stream that must be treated.

Question 18 The target carries an amide group, which is built by condensing a carboxylic acid with ammonia; the carboxylic acid must in turn come from a primary alcohol, and the alcohol from the haloalkane. Working backwards therefore fixes the order bromoethane → ethanol → ethanoic acid → ethanamide.

Step 1 — substitution of the haloalkane with warm NaOH(aq) gives the primary alcohol **ethanol**:

$$\text{C}_2\text{H}_5\text{Br(l)} + \text{NaOH(aq)} \rightarrow \text{C}_2\text{H}_5\text{OH(aq)} + \text{NaBr(aq)}$$

Step 2 — full oxidation with acidified $\text{K}_2\text{Cr}_2\text{O}_7$, heated under reflux, gives **ethanoic acid**:

$$\text{CH}_3\text{CH}_2\text{OH(l)} + 2[\text{O}] \rightarrow \text{CH}_3\text{COOH(l)} + \text{H}_2\text{O(l)}$$

Step 3 — condensation of the acid with ammonia on heating gives the primary amide **ethanamide**:

$$\text{CH}_3\text{COOH(l)} + \text{NH}_3\text{(g)} \rightarrow \text{CH}_3\text{CONH}_2\text{(s)} + \text{H}_2\text{O(l)}$$

The intermediates are ethanol and ethanoic acid; the target is ethanamide. Note that only the first step is a substitution — the pathway ends with a condensation, which is why water and a waste salt are both produced along the way and the overall atom economy is well below 100%.

Question 19 **A** converts a haloalkane into an alcohol: warm aqueous NaOH(aq) — a **substitution** reaction, $\text{C}_3\text{H}_7\text{Cl(l)} + \text{NaOH(aq)} \rightarrow \text{C}_3\text{H}_7\text{OH(aq)} + \text{NaCl(aq)}$. **B** converts the primary alcohol into an aldehyde: acidified $\text{K}_2\text{Cr}_2\text{O}_7$ with gentle heating, distilling the propanal off as it forms — a **partial oxidation**, $\text{C}_3\text{H}_7\text{OH(l)} + [\text{O}] \rightarrow \text{C}_2\text{H}_5\text{CHO(l)} + \text{H}_2\text{O(l)}$.

Question 20 a. Only the ethanol is the desired product; two moles of ethanol form per mole of glucose:

$$\text{atom economy} = \frac{2 \times 46.0}{180.0} \times 100 = \frac{92.0}{180.0} \times 100 = 51.1\,\%$$

b. Route 1, because the glucose comes from crops, is the renewable feedstock (Route 2 uses ethene from finite crude oil). c. Despite the renewable feedstock, Route 1 may be judged less sustainable because of the large area of land and volume of water needed to grow the crop, the energy required to distil the dilute fermentation mixture, the competition with food production, and the CO_2 released as a by-product of fermentation.

Question 21 This is an evaluation against green chemistry principles; a full-mark response compares **both** routes for at least two principles, cites evidence, and concludes.

- **Renewable feedstocks:** Route P obtains its ethanol from the fermentation of sugar cane, a renewable crop that regrows each season, whereas Route Q ultimately draws its carbon from crude-oil ethene, a finite fossil resource. On this principle Route P is superior.
- **Atom economy / waste reduction:** Route P (esterification, atom economy 83%) loses only a small water molecule as by-product, while Route Q (substitution, atom economy 46%) discards more than half of its reactant mass as the waste salt $NaBr$, which must then be treated or disposed of. Route P generates far less waste per tonne of ester.
- **Catalysis / energy efficiency:** Route P uses a conc. H_2SO_4 catalyst, which lowers the activation energy and lets the reaction proceed faster at a lower temperature without being consumed; Route Q requires a stoichiometric salt reagent that is used up.

Conclusion: Route P is the more sustainable process and is the one to recommend — it uses a renewable feedstock, has a substantially higher atom economy with much less waste, and is catalysed for energy efficiency. The main trade-off to acknowledge is the land and water needed to grow the sugar-cane feedstock.

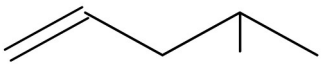
Topic 3 Test A — Organic synthesis (multiple choice)

Time allowed: 30 minutes · 25 marks · One scientific calculator permitted · The Chemistry Data Sheet (back of the Practice Examinations booklet) may be used.

Choose the response that is correct or that best answers the question. A correct answer scores 1 mark; an incorrect answer scores 0. Marks are not deducted for incorrect answers. No marks are given if more than one answer is completed for any question. Where required, use these relative atomic masses: H 1.0, C 12.0, N 14.0, O 16.0, Na 23.0, Cl 35.5, Br 79.9.

Question 1

The skeletal formula of a hydrocarbon is shown below.



Which one of the following is its molecular formula?

A. C_6H_{12}

B. C_6H_{14}

C. C_5H_{10}

D. C_6H_{10}

Question 2

Each of the following molecular formulae represents a compound containing **only one** functional group. Which one could represent **either** an aldehyde or a ketone?

A. $C_3H_6O_2$

B. $C_4H_{10}O$

C. C_3H_8O

D. C_4H_8O

Question 3

How many structural isomers have the molecular formula C_4H_9Br?

A. 2

B. 3

C. 4

D. 5

Question 4

Which one of the following is the correct IUPAC name of $CH_3CH_2CH(CH_3)CH_2CH_2CH_3$?

A. 3-methylhexane

B. 4-methylhexane

C. 2-methylhexane

D. 3-methylpentane

Question 5

Which one of the following is the correct IUPAC name of $CH_3CH_2CH=CHCH_2CH_3$?

A. hex-2-ene

B. hexane

C. hex-3-ene

D. hex-4-ene

Question 6

Which one of the following is the correct IUPAC name of $CH_3CHBrCH_2CH_2CH_3$?

A. 1-bromopentane

B. 2-bromopentane

C. 4-bromopentane

D. 3-bromopentane

Question 7

The compound $CH_3CH_2CH(OH)CH_2CH_2CH_3$ is best described as

A. hexan-3-ol, a secondary alcohol.

B. hexan-4-ol, a secondary alcohol.

C. hexan-3-ol, a primary alcohol.

D. hexan-3-ol, a tertiary alcohol.

Question 8

Which one of the following is the correct IUPAC name of $CH_3CH_2COCH_2CH_2CH_3$?

A. hexan-2-one

B. hexanal

C. hexan-3-one

D. hexan-4-one

Question 9

Which one of the following is the correct IUPAC name of $(CH_3)_2CHCH_2CH_2COOH$?

A. 2-methylpentanoic acid

B. hexanoic acid

C. 4-methylpentanal

D. 4-methylpentanoic acid

Question 10

Which one of the following is the correct IUPAC name of the ester $CH_3CH_2CH_2COOCH_2CH_2CH_3$?

A. butyl propanoate

B. propyl butanoate

C. propyl propanoate

D. ethyl butanoate

Question 11

The compound $CH_3CH_2CH_2CH_2NH_2$ is correctly named and classified as

A. butan-1-amine, a primary amine.

B. butan-2-amine, a primary amine.

C. butan-1-amine, a secondary amine.

D. butanamide, a primary amide.

Question 12

Which one of the following is the correct IUPAC name of $(CH_3)_2CHCH_2CHO$?

A. 2-methylbutanal

B. 3-methylbutan-1-ol

C. 3-methylbutanal

D. 3-methylbutanoic acid

Question 13

The compound $HOCH_2CH_2CH_2CHO$ contains which two functional groups?

A. carboxyl and hydroxyl

B. hydroxyl and ketone

C. hydroxyl and ester

D. hydroxyl and aldehyde

Question 14

For which one of the following compounds is **hydrogen bonding** the strongest type of intermolecular force between its molecules?

A. butanal, $CH_3CH_2CH_2CHO$

B. 1-chlorobutane, $CH_3CH_2CH_2CH_2Cl$

C. butan-1-amine, $CH_3CH_2CH_2CH_2NH_2$

D. pentane, $CH_3CH_2CH_2CH_2CH_3$

Question 15

Four compounds each contain six carbon atoms. Which one has the **highest** boiling point?

A. hexane

B. hexan-1-ol

C. hexanal

D. 1-chlorohexane

Question 16

1-bromopentane is heated with an excess of ammonia. The organic product is

A. pentan-1-ol.

B. pentanamide.

C. pentane.

D. pentan-1-amine.

Question 17

Ethene reacts with bromine, and ethane reacts with chlorine in the presence of ultraviolet light. These two reactions are, respectively,

A. addition and substitution.

B. substitution and addition.

C. addition and addition.

D. substitution and substitution.

Question 18

When propene reacts with bromine, the organic product is

A. 1-bromopropane.

B. 2-bromopropane.

C. 1,3-dibromopropane.

D. 1,2-dibromopropane.

Question 19

Separate samples of butan-1-ol, butan-2-ol and 2-methylpropan-2-ol are each warmed with acidified potassium dichromate. In which sample(s) does the orange colour of the dichromate persist (no reaction)?

A. butan-1-ol only

B. 2-methylpropan-2-ol only

C. butan-2-ol and 2-methylpropan-2-ol

D. all three samples

Question 20

Propan-1-ol is warmed with butanoic acid and a few drops of concentrated sulfuric acid. The organic product is

A. butyl propanoate.

B. propyl butanamide.

C. propyl butanoate.

D. propyl propanoate.

Question 21

Methyl pentanoate is heated with aqueous sodium hydroxide solution. The organic products are

A. pentanoic acid and methanol.

B. sodium methanoate and pentan-1-ol.

C. methanoic acid and pentan-1-ol.

D. sodium pentanoate and methanol.

Question 22

Pentan-1-ol is treated with acidified potassium dichromate. Which one of the following procedures gives **pentanoic acid** as the main organic product?

A. Heat the mixture under reflux with an excess of the oxidant.

B. Warm the mixture gently and distil the organic product off as it forms.

C. Warm the mixture gently with a limited amount of the oxidant, then add aqueous NaOH.

D. Pass the vapour with $\mathrm{H_2}$ over a heated nickel catalyst.

Question 23

In the esterification of pentanoic acid with ethanol, $0.400\,\mathrm{mol}$ of pentanoic acid is reacted with excess ethanol and $41.6\,\mathrm{g}$ of ethyl pentanoate ($M = 130.0\,\mathrm{g\ mol^{-1}}$) is obtained. Which one of the following is closest to the percentage yield?

A. $40.0\,\%$

B. $80.0\,\%$

C. $125\,\%$

D. $20.0\,\%$

Question 24

1-bromobutane is hydrolysed to butan-1-ol: $C_4H_9Br + NaOH \rightarrow C_4H_9OH + NaBr$. Using $M(C_4H_9Br) = 136.9$, $M(NaOH) = 40.0$ and $M(C_4H_9OH) = 74.0\,g\,mol^{-1}$, which one of the following is closest to the atom economy of this route for butan-1-ol?

A. 41.8%

B. 58.2%

C. 100%

D. 54.0%

Question 25

A synthesis is carried out in three steps with individual percentage yields of 90.0%, 90.0% and 80.0%. Which one of the following is closest to the overall percentage yield of the synthesis?

A. 86.7%

B. 64.8%

C. 72.0%

D. 260%

End of Topic 3 Test A

Topic 3 Test A — solutions

Question	Answer	Question	Answer
1	A	14	C
2	D	15	B
3	C	16	D
4	A	17	A
5	C	18	D
6	B	19	B
7	A	20	C
8	C	21	D
9	D	22	A
10	B	23	B
11	A	24	A
12	C	25	B
13	D		

Question 1 — A. Each vertex and free line-end is a carbon, so the chain has five carbons with one methyl branch (six carbons in all) and one carbon–carbon double bond; adding hydrogens to complete four bonds at each carbon gives C_6H_{12} (an alkene, C_nH_{2n}). **B** treats the molecule as a saturated alkane (C_6H_{14}), ignoring the double bond; **C** counts only the five chain carbons and misses the branch; **D** removes two hydrogens too many (as if there were two degrees of unsaturation).

Question 2 — D. Aldehydes and ketones share the general formula $C_nH_{2n}O$, and C_4H_8O fits it ($n=4$): butanal and butan-2-one are both single-functional-group compounds of that formula. **A** is $C_nH_{2n}O_2$, which with a single functional group must be a carboxylic acid or an ester; **B** and **C** are $C_nH_{2n+2}O$, the saturated alcohols, which have no degree of unsaturation and so cannot contain a carbonyl group.

Question 3 — C. The four isomers of C_4H_9Br are 1-bromobutane, 2-bromobutane, 1-bromo-2-methylpropane and 2-bromo-2-methylpropane. **A** counts only the two straight-chain positions; **B** misses one of the branched isomers; **D** overcounts by treating a duplicate as distinct.

Question 4 — A. The longest continuous chain is six carbons (hexane) with a methyl branch; numbering from the end that gives the lowest locant places the branch on C3, giving **3-methylhexane**. **B** numbers from the wrong end (4 instead of 3); **C** places the branch at the wrong carbon; **D** miscounts the parent chain as five carbons.

Question 5 — C. The parent is a six-carbon chain (hex-) with the double bond between C3 and C4; numbering from either end gives the lower locant 3, so the name is **hex-3-ene**. **A** and **D** quote the wrong locant; **B** ignores the carbon–carbon double bond altogether.

Question 6 — B. The parent chain is pentane and the bromine is on C2 (numbering from the nearer end); a halogen is always a prefix, giving **2-bromopentane**. **C** numbers from the wrong end (4 instead of 2); **A** and **D** place the halogen on the wrong carbon.

Question 7 — A. The longest chain is six carbons and the hydroxyl is on C3, giving **hexan-3-ol**; that carbon is bonded to two other carbons, so the alcohol is **secondary**. **B** quotes the wrong locant (C3 is lower than C4); **C** and **D** misclassify the alcohol — the –OH carbon is bonded to two carbons, not one (primary) or three (tertiary).

Question 8 — C. The carbonyl is internal (a ketone) in a six-carbon chain; numbering from the nearer end places it at C3, giving **hexan-3-one**. **A** quotes the wrong locant; **D** numbers from the wrong end; **B** wrongly names it as the aldehyde hexanal (an aldehyde carbonyl must be terminal).

Question 9 — D. The terminal –COOH makes this a carboxylic acid; the longest chain including the carboxyl carbon (C1) is five carbons with a methyl branch on C4, giving **4-methylpentanoic acid**. **A** numbers the chain from the

wrong end; **B** ignores the branch and miscounts a straight six-carbon chain; **C** names it as an aldehyde, the wrong functional group.

Question 10 — B. Splitting at the –COO– linkage, the acyl (acid-derived) side $CH_3CH_2CH_2CO–$ gives *butanoate* (the second word) and the alkyl (alcohol-derived) side $–CH_2CH_2CH_3$ gives *propyl* (the first word): **propyl butanoate**. **A** names the ester backwards (acid and alcohol parts swapped); **C** miscounts the acyl group; **D** miscounts the alkyl group.

Question 11 — A. The nitrogen is bonded to a three-carbon-plus-one chain end (C1 of butane) and to only one carbon, so it is a **primary amine**, named **butan-1-amine**. **B** quotes the wrong locant; **C** confuses "primary" (nitrogen bonded to one carbon) with the count used for alcohols; **D** names it as an amide, but there is no carbonyl group.

Question 12 — C. The terminal –CHO is an aldehyde group, and its carbon is always C1 of the parent chain; the longest chain containing it is four carbons (butanal) with a methyl branch on C3, giving **3-methylbutanal**. **A** numbers the chain from the wrong end (the aldehyde carbon cannot be C4, and its locant is never quoted); **B** names it as an alcohol, but there is no –OH group; **D** misreads the terminal –CHO as a carboxyl –COOH.

Question 13 — D. The molecule has an –OH group (hydroxyl) on one end and a terminal –CHO group (aldehyde) on the other. **A** misreads the aldehyde as a carboxyl (–COOH); **B** misreads the terminal –CHO as an internal ketone; **C** reads the two oxygen atoms together as an ester linkage –COO–, but they sit at opposite ends of the molecule and are not bonded to the same carbon.

Question 14 — C. butan-1-amine has an N–H bond, so it can form **hydrogen bonds**. **A** butanal (polar C=O, no N–H or O–H) and **B** 1-chlorobutane (polar C–Cl) have only dipole–dipole forces as their strongest attraction; **D** pentane is non-polar and has only dispersion forces.

Question 15 — B. hexan-1-ol has an O–H group and so forms hydrogen bonds, the strongest of the intermolecular forces, giving it the highest boiling point of the four. **C** hexanal and **D** 1-chlorohexane are polar (dipole–dipole) but cannot hydrogen-bond; **A** hexane has only dispersion forces.

Question 16 — D. Ammonia substitutes for the halogen on the saturated carbon, so the –Br is replaced by $–NH_2$ to give the primary amine **pentan-1-amine** (an excess of ammonia is used so that the amine formed is not itself substituted). **A** is the product of substitution by hydroxide ions, not by ammonia; **B** is the primary amide $–CONH_2$, which needs a carboxylic acid and ammonia, not a haloalkane; **C** assumes the bromine is simply lost, which no reagent here achieves.

Question 17 — A. Ethene is unsaturated: bromine adds across its C=C double bond (**addition**). Ethane is saturated: under UV light one hydrogen is replaced by chlorine, releasing HCl (**substitution**). **B** reverses the two; **C** and **D** wrongly assign the same reaction type to both.

Question 18 — D. Bromine adds across the C=C double bond of propene, one Br on each of the two double-bond carbons, giving **1,2-dibromopropane**. **A** and **B** are the products of adding a hydrogen halide (only one halogen added), not Br_2; **D**'s isomer **C** (1,3-dibromopropane) cannot form by addition across the double bond.

Question 19 — B. Only 2-methylpropan-2-ol is a **tertiary** alcohol: its –OH carbon carries no hydrogen atom, so it is not readily oxidised and the dichromate stays orange. butan-1-ol (primary) and butan-2-ol (secondary) are both oxidised, turning the dichromate green. **A**, **C** and **D** each wrongly include an alcohol that does react.

Question 20 — C. A carboxylic acid and an alcohol undergo esterification (a condensation) with a concentrated H_2SO_4 catalyst; butanoic acid supplies *butanoate* and propan-1-ol supplies *propyl*, giving **propyl butanoate**. **A** names the ester backwards; **B** is an amide (which forms from an amine, not an alcohol); **D** uses the wrong acid.

Question 21 — D. Base hydrolysis (with hot NaOH solution) removes the acid as its carboxylate salt, giving **sodium pentanoate and methanol**. **A** gives the acid-hydrolysis products (the free acid, not its salt); **B** and **C** split the ester on the wrong side of the linkage.

Question 22 — A. Pentan-1-ol is a primary alcohol, so it oxidises first to pentanal and then on to pentanoic acid; reaching the acid requires the aldehyde to stay in the flask, which is what **heating under reflux with an excess of oxidant** achieves. **B** distils the aldehyde away before it can be oxidised further, so it stops at pentanal; **C** also stops at

the aldehyde (limited oxidant, gentle warming), and the NaOH added afterwards does not oxidise it; **D** is hydrogenation, a reduction, which is the opposite of the change required.

Question 23 — B. The acid and ester are in a 1:1 ratio, so the theoretical mass is $0.400 \times 130.0 = 52.0\,\mathrm{g}$ and the percentage yield is $\dfrac{41.6}{52.0} \times 100 = 80.0\,\%$. **A** uses a 1:2 acid-to-ester ratio, doubling the theoretical mass to $104\,\mathrm{g}$ and halving the yield; **C** inverts the ratio ($52.0 / 41.6 = 125\,\%$); **D** quotes the fraction lost ($100 - 80$).

Question 24 — A. $\text{atom economy} = \dfrac{M(\mathrm{C_4H_9OH})}{M(\mathrm{C_4H_9Br}) + M(\mathrm{NaOH})} \times 100 = \dfrac{74.0}{136.9 + 40.0} \times 100 = 41.8\,\%$. **B** is the complementary $100 - 41.8$; **C** wrongly assumes an addition reaction (no by-product); **D** is an unrelated value.

Question 25 — B. The losses compound, so the overall yield is the product of the step yields: $0.900 \times 0.900 \times 0.800 \times 100 = 64.8\,\%$. **A** averages the three yields; **C** multiplies only two of them (0.900×0.800); **D** adds them.

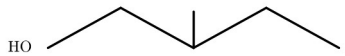
Topic 3 Test B — Organic synthesis (short and extended response)

Time allowed: 50 minutes · 40 marks · One scientific calculator permitted · The Chemistry Data Sheet (back of the Practice Examinations booklet) may be used.

Answer all questions in the spaces provided. Give simplified answers to all numerical questions, with an appropriate number of significant figures. Show all working; no marks are given for an incorrect answer unless accompanied by working. Ensure chemical equations are balanced and that formulas include states, e.g. $\mathrm{H_2(g)}$, $\mathrm{NaCl(s)}$. *In organic equations, show any catalyst or condition above the arrow and use* $[\mathrm{O}]$ *for the oxygen supplied by an oxidising agent. Where required, use these relative atomic masses:* $\mathrm{H}\,1.0$, $\mathrm{C}\,12.0$, $\mathrm{N}\,14.0$, $\mathrm{O}\,16.0$, $\mathrm{Na}\,23.0$, $\mathrm{Br}\,79.9$.

Question 1 (6 marks)

The skeletal formula of compound X is shown below.



a. Deduce the molecular formula of X. 1 mark

b. Give the IUPAC name of X, and classify it as a primary, secondary or tertiary alcohol, justifying your classification. 2 marks

c. Draw a semi-structural or skeletal formula for a structural isomer of X that is a **tertiary** alcohol, and give its IUPAC name. 2 marks

d. X is a structural isomer of the straight-chain alcohol hexan-1-ol. Hexan-1-ol boils at $157\,°\mathrm{C}$ and X at $152\,°\mathrm{C}$. Explain, in terms of intermolecular forces, why the two boiling points are close and why X has the lower of the two. 1 mark

Question 2 (5 marks)

Four organic compounds are P, Q, R and S:

- P: $\mathrm{CH_3CH_2COOCH_3}$
- Q: $\mathrm{CH_3CH_2CH_2NH_2}$
- R: $\mathrm{CH_3CH_2CONH_2}$
- S: $\mathrm{CH_3COCH_3}$

a. State the functional-group family (ester, amine, amide, aldehyde, ketone, …) to which each of P, Q, R and S belongs. 2 marks

b. State which two of P, Q, R and S are able to form hydrogen bonds **between their own molecules**, and identify the feature that allows them to do so. 1 mark

c. R ($M = 73\,\mathrm{g\,mol^{-1}}$) boils at $213\,°\mathrm{C}$, whereas P ($M = 88\,\mathrm{g\,mol^{-1}}$) boils at $80\,°\mathrm{C}$. Explain this difference in terms of intermolecular forces. 2 marks

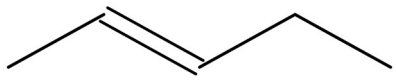
Question 3 (6 marks)

This question concerns three separate reactions.

a. 3-methylbutan-2-ol, $\mathrm{(CH_3)_2CHCH(OH)CH_3}$, is warmed with acidified potassium dichromate. Write a balanced equation for its oxidation (use $[\mathrm{O}]$), name the organic product, and state the colour change of the oxidant. 2 marks

b. 1-chlorobutane is warmed with aqueous sodium hydroxide. Write a balanced equation using hydroxide ions, name the organic product, and state the reaction type. 2 marks

c. Pent-2-ene (shown below) is reacted with hydrogen over a heated nickel catalyst. Write a balanced equation showing the condition above the arrow, name the organic product, and state the reaction type.



2 marks

Question 4 (6 marks)

The large molecules in food are assembled in living cells by **condensation** reactions and are broken down during digestion by **hydrolysis**.

a. Sucrose, $C_{12}H_{22}O_{11}$, is a disaccharide. Write a balanced equation, with states, for its complete hydrolysis into two monosaccharide molecules, each of molecular formula $C_6H_{12}O_6$, and name the linkage that is broken. 2 marks

b. A fat forms when one molecule of glycerol, $C_3H_5(OH)_3$, condenses with three molecules of stearic acid, $C_{17}H_{35}COOH$. Write a balanced equation, with states, for this reaction, and name the linkage formed. 2 marks

c. The dipeptide $H_2NCH_2CONHCH(CH_2OH)COOH$ is hydrolysed during digestion. Write a balanced equation, with states, for the reaction, name the linkage that is broken, and identify the two 2-amino acids released, given that glycine is H_2NCH_2COOH and serine is $H_2NCH(CH_2OH)COOH$. 2 marks

Question 5 (6 marks)

Ethyl butanoate is manufactured in two steps: in step 1, butan-1-ol is oxidised to butanoic acid; in step 2, the butanoic acid is esterified with ethanol using a concentrated sulfuric acid catalyst. Use the molar masses $M(\text{butan-1-ol}) = 74.0$, $M(\text{butanoic acid}) = 88.0$, $M(\text{ethanol}) = 46.0$ and $M(\text{ethyl butanoate}) = 116.0\ \text{g mol}^{-1}$.

a. Write a balanced equation, with states, for the esterification (step 2), and calculate its atom economy for ethyl butanoate.

2 marks

b. Step 1 proceeds in $80.0\,\%$ yield and step 2 in $75.0\,\%$ yield. Calculate the mass of butan-1-ol that must be supplied to this two-step route to obtain $34.8\,\text{g}$ of ethyl butanoate. Give your answer in g. 2 marks

c. Calculate the overall percentage yield of ethyl butanoate from butan-1-ol, and explain why it is lower than either individual step yield. 2 marks

Question 6 (5 marks)

To measure the yield of the ethyl butanoate preparation, a student repeats it five times, each time starting from the same quantities of reactants, for which the theoretical yield of ester is $5.80\,\text{g}$. The mass of purified ester collected in each trial is measured on an electronic balance reading to $0.01\,\text{g}$:

Trial	1	2	3	4	5
Mass of ester (g)	4.62	4.71	4.58	3.85	4.65

a. Identify the outlier in the data, and suggest one reason it might have occurred. 1 mark

b. Using the four consistent results, calculate the mean mass of ester and hence the mean percentage yield. 2 marks

c. The four consistent results are close to one another. State the term that describes this quality of the data, and explain, in terms of the reaction, why even a carefully performed preparation cannot give a $100\,\%$ yield. 1 mark

d. State the resolution of the balance and the reading uncertainty in a single mass measurement, and write the trial 1 result in the form (mass ± uncertainty). 1 mark

Question 7 (6 marks)

Ethyl butanoate (a flavouring compound) can be manufactured by either of two routes.

- **Route 1** — esterification of butanoic acid with ethanol using a concentrated H_2SO_4 catalyst (atom economy $86.6\,\%$); both the acid and the ethanol are obtained by the fermentation of plant sugars.
- **Route 2** — reaction of sodium butanoate with bromoethane, $CH_3CH_2CH_2COONa(aq) + C_2H_5Br(l) \rightarrow CH_3CH_2CH_2COOC_2H_5(l) + NaBr(aq)$; the bromoethane is derived from crude-oil ethene.

Use the molar masses $M(\text{sodium butanoate}) = 110.0$, $M(\text{bromoethane}) = 108.9$ and $M(\text{ethyl butanoate}) = 116.0\,\text{g mol}^{-1}$.

a. Calculate the atom economy of Route 2 for ethyl butanoate. 2 marks

b. Identify the by-product of each route, and state which route generates less waste per mole of ester. 1 mark

c. Evaluate the two routes with respect to sustainability. In your response, refer to at least two green chemistry principles with supporting evidence, and give a concluding statement recommending one route.

3 marks

End of Topic 3 Test B

Topic 3 Test B — solutions

Question 1 X is drawn as a five-carbon chain carrying a methyl branch on C3, with a hydroxyl group on the terminal carbon C1.

(a) Counting the atoms: 6 C (5 chain + 1 branch), 14 H and 1 O, so the molecular formula is $C_6H_{14}O$. **(1 mark: $C_6H_{14}O$.)**

(b) The parent chain (five carbons) carries the –OH on C1 and a methyl branch on C3, so X is **3-methylpentan-1-ol**. The –OH carbon (C1) is bonded to only one other carbon, so X is a **primary (1°)** alcohol. **(1 mark** name 3-methylpentan-1-ol; **1 mark** primary, justified by the –OH carbon being bonded to one other carbon.)

(c) Any tertiary alcohol of formula $C_6H_{14}O$ is accepted — its –OH carbon must be bonded to three other carbons. For example **2-methylpentan-2-ol**, $CH_3CH_2CH_2C(CH_3)_2OH$, whose C2 carries the –OH plus two methyl groups and the propyl chain. (**3-methylpentan-3-ol**, $CH_3CH_2C(CH_3)(OH)CH_2CH_3$, and **2,3-dimethylbutan-2-ol**, $(CH_3)_2C(OH)CH(CH_3)_2$, are equally correct.) **(1 mark** a correct tertiary structure of formula $C_6H_{14}O$; **1 mark** its matching IUPAC name.)

(d) The two compounds are isomers, so they have the same molar mass and the same number of electrons, and both are primary alcohols carrying one O–H group; both therefore form **hydrogen bonds** of the same strength, which is why their boiling points are close. The remaining difference is one of **shape**: hexan-1-ol is an unbranched chain whose molecules can lie alongside one another over their whole length, whereas the methyl branch on X makes its molecules more compact, giving a smaller surface of contact and so slightly **weaker dispersion forces** — hence X boils $5\,°C$ lower. **(1 mark: same hydrogen bonding (isomers, both primary alcohols) so similar boiling points, but the branched isomer has the smaller contact area and weaker dispersion forces, so it boils lower.)**

Question 2

(a) P is an **ester** (–COO– linkage); Q is a (primary) **amine** ($-NH_2$ on a carbon); R is a (primary) **amide** ($-CONH_2$); S is a **ketone** (internal C=O). **(2 marks: all four correct for 2 marks; two or three correct for 1 mark.)**

(b) **Q (the amine) and R (the amide)** can form hydrogen bonds between their own molecules, because each contains an **N–H bond** (hydrogen bonded to a small, highly electronegative nitrogen atom). P (ester) and S (ketone) have a polar C=O but no N–H or O–H, so they cannot hydrogen-bond to themselves. **(1 mark: Q and R, because of their N–H bonds.)**

(c) R (propanamide) carries two N–H bonds, so its molecules attract one another by **hydrogen bonding**. P (methyl propanoate) has a polar C=O group but no N–H or O–H bond, so the strongest attraction between its molecules is only **dipole–dipole**. Hydrogen bonding is much stronger than dipole–dipole attraction, so far more energy is needed to separate the amide molecules. Note that R boils $133\,°C$ higher even though it is the **lighter** of the two (73 against $88\,g\,mol^{-1}$) and so has the weaker dispersion forces: the difference cannot be explained by molecular size and must come from the hydrogen bonding. **(1 mark** R hydrogen-bonds (N–H) while P has only dipole–dipole; **1 mark** hydrogen bonding is the stronger force and outweighs R's smaller molar mass / weaker dispersion forces.)

Question 3

(a) 3-methylbutan-2-ol is a secondary alcohol, so it is oxidised to a **ketone**, 3-methylbutan-2-one:

$$(CH_3)_2CHCH(OH)CH_3(l) + [O] \rightarrow (CH_3)_2CHCOCH_3(l) + H_2O(l)$$

The acidified dichromate is reduced from $Cr_2O_7^{2-}$ to Cr^{3+}, so its colour changes from **orange to green**. (Atoms balance: each side C 5, H 12, O 2.) **(1 mark** balanced equation with the correct ketone product; **1 mark** orange → green.)

(b) The hydroxide ion replaces the chlorine atom, which leaves as a chloride ion, giving **butan-1-ol**; the reaction type is **substitution**:

$$CH_3CH_2CH_2CH_2Cl(l) + OH^-(aq) \rightarrow CH_3CH_2CH_2CH_2OH(aq) + Cl^-(aq)$$

(Atoms and charge balance: -1 on each side.) **(1 mark** balanced equation with OH^-/Cl^-; **1 mark** product butan-1-ol and reaction type substitution.)

(c) Hydrogen adds across the C=C double bond over the nickel catalyst (an **addition**, specifically hydrogenation), converting the alkene to the alkane **pentane**:

$$CH_3CH=CHCH_2CH_3(l) + H_2(g) \xrightarrow{Ni} CH_3CH_2CH_2CH_2CH_3(l)$$

(Atoms balance: each side C 5, H 12.) **(1 mark** balanced equation with the Ni condition above the arrow; **1 mark** product pentane and reaction type addition/hydrogenation.)

Question 4

(a) Hydrolysis adds the elements of water across the –C–O–C– bridge joining the two sugar units, releasing one monosaccharide molecule from each side:

$$C_{12}H_{22}O_{11}(aq) + H_2O(l) \rightarrow 2C_6H_{12}O_6(aq)$$

(Atoms balance: each side C 12, H 24, O 12.) The linkage broken is the **glycosidic linkage**. **(1 mark** balanced equation with states; **1 mark** glycosidic linkage.)

(b) Each of the three –OH groups of glycerol condenses with the –COOH of one fatty-acid molecule, eliminating one water molecule per linkage — three in all:

$$C_3H_5(OH)_3(l) + 3C_{17}H_{35}COOH(s) \rightarrow C_3H_5(OOCC_{17}H_{35})_3(s) + 3H_2O(l)$$

(Atoms balance: each side C 57, H 116, O 9.) The linkage formed is the **ester linkage,** –COO– (the product is a triglyceride, a triester). **(1 mark** balanced equation with states, including the coefficients 3 and 3; **1 mark** ester linkage.)

(c) Adding the elements of water across the –CO–NH– bridge gives back the two amino acids — the carbonyl side regains –OH and the nitrogen side regains –H:

$$H_2NCH_2CONHCH(CH_2OH)COOH(s) + H_2O(l) \rightarrow H_2NCH_2COOH(s) + H_2NCH(CH_2OH)COOH(s)$$

(Atoms balance: each side C 5, H 12, N 2, O 5.) The linkage broken is the **amide linkage,** –CO–NH–, called the **peptide linkage** in a protein, and the amino acids released are **glycine** and **serine**. **(1 mark** balanced equation with states; **1 mark** peptide (amide) linkage AND both amino acids named.)

Question 5

(a) The esterification joins the acid and alcohol through a –COO– linkage, eliminating water:

$$CH_3CH_2CH_2COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3CH_2CH_2COOC_2H_5(l) + H_2O(l)$$

(Atoms balance: each side C 6, H 14, O 3.) The atom economy for ethyl butanoate is

$$\text{atom economy} = \frac{M(\text{ester})}{M(\text{acid}) + M(\text{alcohol})} \times 100 = \frac{116.0}{88.0 + 46.0} \times 100 = \frac{116.0}{134.0} \times 100 = 86.6\,\%.$$

(1 mark balanced esterification equation ($\rightleftharpoons$); **1 mark** atom economy $86.6\,\%$.)

(b) Work backwards from the ester. Both steps are in a 1:1 mole ratio, so

$$n(\text{ester}) = \frac{34.8}{116.0} = 0.300\,\text{mol}, n(\text{butan-1-ol}) = \frac{0.300}{0.800 \times 0.750} = \frac{0.300}{0.600} = 0.500\,\text{mol},$$

$$m(\text{butan-1-ol}) = 0.500 \times 74.0 = 37.0\,\text{g}.$$

$\therefore$ 37.0 g of butan-1-ol must be supplied. **(1 mark** divides (rather than multiplies) by both step yields to reach 0.500 mol; **1 mark** 37.0 g, 3 sig figs.)

(c) The overall yield is the product of the two step yields:

$$\text{overall yield} = 0.800 \times 0.750 \times 100 = 60.0\,\%.$$

It is lower than either individual step (80.0% or 75.0%) because the losses **compound**: only 80.0% of the butan-1-ol survives step 1, and only 75.0% of *that* survives step 2, so the fractions multiply rather than add. **(1 mark** overall yield 60.0 %; **1 mark** the step losses multiply/compound.)

Question 6

(a) The **outlier is trial 4 (**3.85 g**)**, which is well below the other four (all 4.5–4.7 g). A plausible cause is loss of product during transfer or purification (for example spillage, or incomplete collection of the ester). **(1 mark: trial 4 identified as the outlier with a valid reason.)**

(b) Mean of the four consistent results:

$$\acute{m} = \frac{4.62 + 4.71 + 4.58 + 4.65}{4} = \frac{18.56}{4} = 4.64\,\text{g}.$$

Mean percentage yield:

$$\frac{4.64}{5.80} \times 100 = 80.0\,\%.$$

(1 mark mean mass 4.64 g (outlier excluded); **1 mark** mean yield 80.0 %.)

(c) The results are **precise** (repeatable — they lie close together, showing good agreement between trials). Even a careful preparation cannot reach 100% because esterification is a **reversible reaction that reaches equilibrium**, so unreacted acid and alcohol always remain, and some ester is inevitably lost during transfer and purification. **(1 mark: precision/repeatability named AND the reason — reversible reaction reaching equilibrium (plus transfer losses) — so yield is below 100%.)**

(d) The balance is a **digital** instrument, so its resolution is the **last displayed digit**, 0.01 g, and a single reading is quoted to ± that last digit: the reading uncertainty is ± 0.01 g, so trial 1 is (4.62 ± 0.01) g. (The half-a-division rule applies to an *analogue* graduated scale such as a burette, not to a digital display.) **(1 mark: resolution** 0.01 g **with uncertainty** ± 0.01 g**, i.e.** (4.62 ± 0.01) g**.)**

Question 7

$$\text{atom economy (Route 2)} = \frac{M(\text{ethyl butanoate})}{M(\text{sodium butanoate}) + M(\text{bromoethane})} \times 100 = \frac{116.0}{110.0 + 108.9} \times 100 = \frac{116.0}{218.9} \times 100 = 53.$$

(1 mark correct expression with the two reactant masses summed; **1 mark** 53.0 %.)

(a) Route 1 releases **water** as its by-product; Route 2 releases the salt **sodium bromide,** NaBr. Route 1 generates **less waste** per mole of ester (a small water molecule rather than a whole salt formula unit — consistent with its far higher atom economy, 86.6% versus 53.0%). **(1 mark: water vs** NaBr**, and Route 1 generates less waste.)**

(b) *Model answer (rubric).* A full-mark response compares **both** routes against at least two green chemistry principles with evidence, then concludes.

- **Renewable feedstocks:** Route 1 obtains both its butanoic acid and its ethanol from the fermentation of plant sugars, a renewable feedstock that regrows each season, whereas Route 2 draws its carbon (the bromoethane) from finite crude oil. Route 1 is superior on this principle.

- **Atom economy / waste minimisation:** Route 1 (atom economy 86.6%) loses only a small water molecule, while Route 2 (atom economy 53.0%) discards almost half of its reactant mass as the waste salt $NaBr$, which must then be treated or disposed of. Route 1 generates far less waste per tonne of ester.
- **Catalysis / energy efficiency (either principle earns credit):** Route 1 uses a concentrated H_2SO_4 catalyst, which provides an alternative reaction pathway of lower activation energy and is not consumed, so the process runs faster and at a lower temperature; Route 2 consumes its reagents stoichiometrically.

Conclusion: Route 1 is the more sustainable process and is the one to recommend — it uses a renewable feedstock, has a much higher atom economy with far less waste, and is catalysed for energy efficiency. The trade-off to acknowledge is the land and water needed to grow the fermentation feedstock. **(1 mark** two green chemistry principles applied to both routes with specific evidence; **1 mark** correct use of the atom-economy/feedstock evidence; **1 mark** a clear concluding recommendation of Route 1.)