Mark scheme

Lesson 1b — from alkenes to benzene · 89 marks · OCR A H432

Notes

- Nothing on the paper needs teaching. It is Lesson 1 and Year 1, retrieved.
- Scaffolding cards go at the front; pupils fetch one when they are stuck and put it back. There are no answers on them.
- Do not answer chemistry questions while they work — point at the cards.
- Deliberately not on the paper: adding bromine to benzene. Bromine water appears only as the observation that benzene does NOT decolourise it — the evidence, not the reaction.
- The mechanism is the part to protect. If time is short, drop the naming questions rather than that.
- Hand out the mark scheme at the end and let them mark their own paper. One between two is plenty.
- Where the marks are for the mechanism is set out in full, with the figure, near the back.

Marking

Every (1) is one mark, awarded independently. Words in CAPITALS have to be there, or a clear equivalent. Tick the marks you have earned and circle the ones you have not — the circles are your revision list.

PART 1 **56 marks**

Revision from last year

Specification 4.1.1 nomenclature · 4.1.3 alkenes

Naming

1. Name these alkenes. **[5 marks]**

(a) $CH_3CH_2CH=CH_2$

(b) $CH_3CH=CHCH_2CH_3$

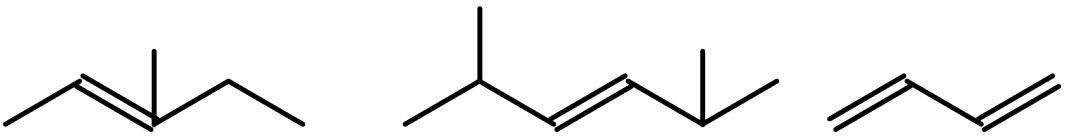
(c) $CH_2=C(CH_3)CH_2CH_3$

(d) $(CH_3)_2C=CHCH_3$

(e) $CH_2=CHCH=CH_2$

Answer: (a) but-1-ene (b) pent-2-ene (c) 2-methylbut-1-ene (d) 2-methylbut-2-ene (e) buta-1,3-diene. One mark each. The number goes immediately before the '-ene': but-1-ene, not 1-butene.

2. Name the three skeletal structures A, B and C. **[3 marks]**



A B C

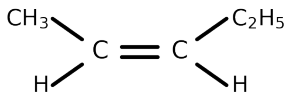
Answer: A 3-methylpent-2-ene (1). B 2,5-dimethylhex-3-ene (1). C buta-1,3-diene (1). C is the same compound as 1(e).

3. Only ONE of the alkenes in question 1 can show E/Z isomerism. **[3 marks]**

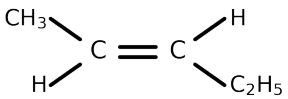
(a) Which one? Explain how you can tell.

(b) Draw and label its E and its Z isomer.

Answer: (a) (b) pent-2-ene (1). Each carbon of the C=C must carry two DIFFERENT groups. In (a), (c) and (e) one alkene carbon carries two hydrogens; in (d) one carries two CH_3 groups (1). (b) Z: the two carbon chains on the same side of the C=C. E: on opposite sides (1). cis/trans is the old name for the special case where each alkene carbon also carries an H.



Z-pent-2-ene
(the two carbon chains on the SAME side)



E-pent-2-ene
(the two carbon chains on OPPOSITE sides)

4. Name one compound from each family. **[7 marks]**

(a) $CH_3CH(CH_3)CH_2CH_3$

(b) $CH_3CH_2CH_2CH=CH_2$

(c) $CH_3CH(OH)CH_2CH_3$

(d) $CH_3CH_2CH_2CHO$

(e) $CH_3COCH_2CH_2CH_3$

(f) CH_3CH_2COOH

(g) $CH_3CHBrCH_2Cl$

Answer: (a) 2-methylbutane (b) pent-1-ene (c) butan-2-ol (d) butanal (e) pentan-2-one (f) propanoic acid (g) 2-bromo-1-chloropropane. One mark each.

(g) is the trap: numbering from the Cl end gives {1,2}, from the other end {2,3}, so {1,2} wins; prefixes then go in alphabetical order.

5. Draw the structure of each of these. **[3 marks]**

(a) 3-methylbutan-2-ol (b) 2-chloro-2-methylpropane (c) 2-methylpropanoic acid

Answer: (a) $CH_3CH(OH)CH(CH_3)CH_3$ (1). (b) $(CH_3)_3CCl$ (1). (c) $(CH_3)_2CHCOOH$ (1). Displayed, structural or skeletal all accepted.

6. Each of these names is wrong. Write the correct name and say what the mistake is. **[3 marks]**

(a) propan-1-al (b) 2-methylbutan-4-ol (c) 2-ethylpropane

Answer: (a) propanal — the CHO carbon is always carbon 1, so it takes no locant (1). (b) 3-methylbutan-1-ol — number from the end that gives the functional group the lowest locant (1). (c) 2-methylbutane — use the longest carbon chain, which is four carbons (1).

Reactions of alkenes

7. Complete the table for propene, $CH_3CH=CH_2$. Two marks per row: one for the reagents and conditions, one for the name of the product. **[10 marks]**

Answer: One mark for reagents and conditions, one for the product, in each row. Vague conditions score nothing: 'a catalyst' without naming it, or 'heat' without a temperature.

Reaction	Reagent(s) and conditions	Name of the organic product
Hydrogenation	**H_2, nickel catalyst, 150 °C**	**propane**
With bromine	**Br_2, room temperature, no catalyst**	**1,2-dibromopropane**
With hydrogen bromide	**HBr, room temperature**	**2-bromopropane (major product)**
Hydration	**steam ($H_2O(g)$), concentrated H_3PO_4 catalyst, ~300 °C, 60–70 atm**	**propan-2-ol (major)**
Addition polymerisation	**high pressure and a catalyst**	**poly(propene)**

8. Bromine water is added to propene and the tube is shaken. State what you would see, and what the observation tells you about the molecule. **[2 marks]**

Answer: The orange bromine water is decolourised — it goes colourless (1). This shows a C=C double bond is present (1). 'Goes clear' scores nothing: clear is not a colour.

9. When propene reacts with HBr, 2-bromopropane is the major product and 1-bromopropane the minor one. Explain why. **[3 marks]**

Answer: The $H\delta^+$ adds first, so two carbocations are possible: secondary $(CH_3)_2CH^+$ or primary $CH_3CH_2CH_2^+$ (1). The secondary carbocation is more stable, because two alkyl groups push electron density towards the positive carbon instead of one (1). More of the reaction goes through the more stable carbocation, so 2-bromopropane is the major product (1).

Electrophilic addition

10. Draw the full mechanism for the reaction of but-2-ene with bromine, Br_2. Show the dipole on the bromine molecule, every curly arrow, the intermediate with its charge, and the product. **[5 marks]**

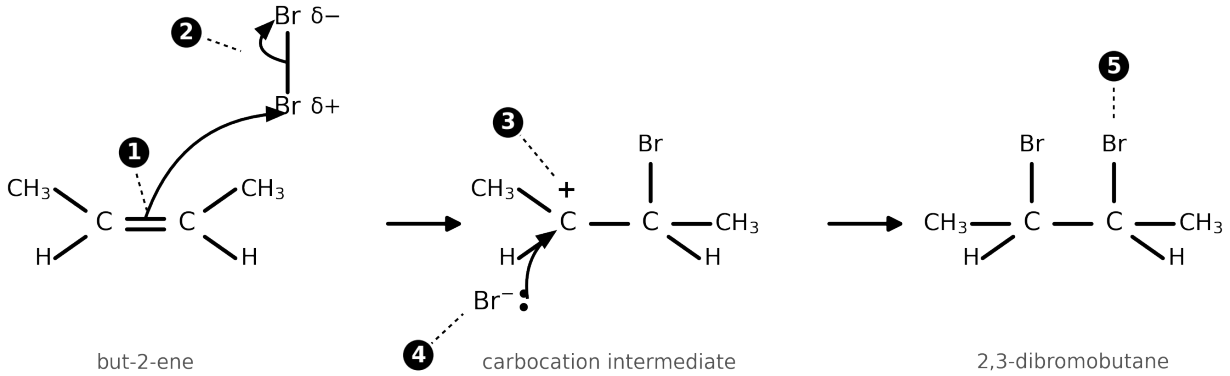
Answer: Mark 1 — δ+ and δ− on the Br_2 AND a curly arrow from the C=C to the δ+ Br. The tail must start ON the double bond, not on a carbon atom (1).

Mark 2 — a curly arrow from the MIDDLE of the Br–Br bond to the δ− Br (1).

Mark 3 — the carbocation: Br on one carbon, + on the OTHER carbon (1).

Mark 4 — a curly arrow from a LONE PAIR on Br^- to the positively charged carbon (1).

Mark 5 — the product, 2,3-dibromobutane (1).



11. Bromine, Br_2, is a non-polar molecule. Explain how it is able to react with an alkene at all. **[3 marks]**

Answer: The π bond has a high electron density, because its two electrons are localised between just two carbon atoms (1). This repels the electron pair in the Br–Br bond, INDUCING A DIPOLE, so the nearer bromine becomes δ+ (1). The δ+ bromine is an electrophile: it can accept a pair of electrons (1).

12. Name the type of mechanism you have drawn. **[1 mark]**

Answer: Electrophilic addition (1). Both words needed.

π bonding in ethene

13. Each carbon atom in ethene has four electrons in its outer shell. Describe how those four electrons are used, and explain how the π bond is formed. **[4 marks]**

Answer: THREE of the four are used in ordinary single bonds: two to hydrogen atoms and one to the other carbon (1). The FOURTH sits in a p-orbital at right angles to the plane of the molecule (1). The p-orbital on one carbon overlaps SIDEWAYS with the p-orbital on the other (1). This makes the π bond: electron density above and below the plane of the molecule (1).

one p-orbital on each carbon,
at right angles to the flat molecule

sideways overlap makes the π bond:
electron density above and below the molecule

14. State the shape around each carbon in ethene and the H–C–H bond angle. Then state what has happened to the π bond, and the new bond angle, when ethene reacts with bromine to give 1,2-dibromoethane. **[4 marks]**

Answer: Ethene: planar / trigonal planar (1), 120° (1). After the reaction the π bond has broken and its pair of electrons has been used to make a new single bond — the double bond has gone for good (1); the bond angle is now about 109.5° (1). Also creditworthy: rotation about the C–C bond is now possible.

PART 2 **11 marks**

Benzene: structure

Specification 6.1.1 (a)

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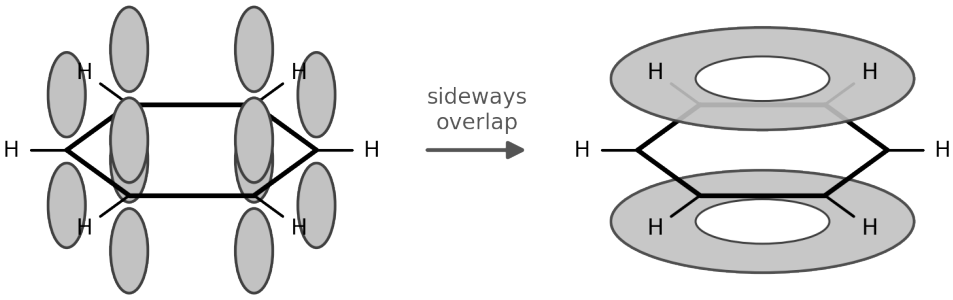
15. Each carbon atom in benzene also has four outer electrons. Describe how they are used, and explain how the delocalised π system is formed. **[4 marks]**

Answer: THREE of the four are used in ordinary single bonds: one to each neighbouring carbon and one to a hydrogen (1). The FOURTH sits in a p-orbital at right angles to the ring (1). Every p-orbital overlaps sideways with BOTH neighbours, all the way round the ring (1). This gives a ring of delocalised electron density above and below the ring — six delocalised electrons (1).



one p-orbital on each carbon, at right angles to the ring

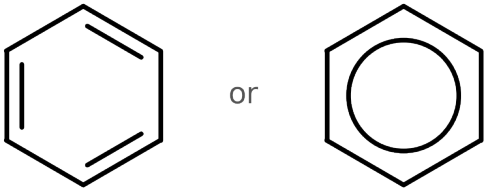
rings of electron density above and below the plane

16. State the shape of a benzene molecule, its bond angles, and the length of every C–C bond. **[2 marks]**

Answer: Planar regular hexagon (1). Bond angles 120°, and all six C–C bonds the same length, 0.139 nm (1).

17. Draw the Kekulé structure and the delocalised structure of benzene. **[2 marks]**

Answer: Kekulé: a hexagon with three alternating C=C and C–C bonds (1). Delocalised: a hexagon with a circle inside it (1).



Kekulé structure delocalised structure

18. Give the systematic name of the Kekulé structure. **[1 mark]**

Answer: Cyclohexa-1,3,5-triene (1).

19. State what each model predicts about the six C–C bonds in benzene. **[2 marks]**

Answer: Kekulé: two different bond lengths alternating round the ring — C=C 0.134 nm and C–C 0.153 nm (1). Delocalised: all six the same, 0.139 nm, between a single and a double bond (1).

PART 3 **16 marks**

Benzene: the evidence

Specification 6.1.1 (b) (f)

Evidence 1 — benzene resists reaction

20. Cyclohexene decolourises bromine water at room temperature. Benzene does not. Explain why, in terms of electron density. **[4 marks]**

Answer: In cyclohexene the π electrons are LOCALISED between two carbon atoms (1), so the electron density is high enough to polarise the Br_2 molecule / induce a dipole in it, and an electrophile forms (1). In benzene the π electrons are DELOCALISED over all six carbons (1), so the electron density between any two carbons is lower; it cannot polarise Br_2 and no reaction happens (1).

21. Explain why this observation was a problem for Kekulé's model. **[2 marks]**

Answer: Kekulé's structure contains three C=C double bonds, so benzene should undergo electrophilic addition and decolourise bromine water like an alkene (1). It does not, so those cannot be ordinary C=C bonds — the electrons must be delocalised (1).

Evidence 2 — bond lengths

22. X-ray diffraction was used to measure the carbon–carbon bonds in benzene. **[4 marks]**

(a) Give the length of a C–C single bond, a C=C double bond, and every bond in benzene.

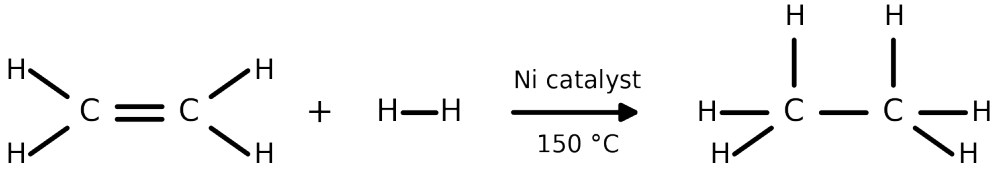
(b) Explain what the benzene value tells you.

Answer: (a) C–C 0.153 nm (1); C=C 0.134 nm (1); all six bonds in benzene 0.139 nm — all the same (1). (b) 0.139 nm lies between the single and the double bond length, so benzene has no alternating single and double bonds; every bond is identical and the electrons are delocalised (1).

Evidence 3 — enthalpy change of hydrogenation

23. Write the equation for the hydrogenation of ethene using DISPLAYED formulae, and state the conditions. **[3 marks]**

Answer: Displayed formulae on both sides — every atom and every bond drawn, including the H–H bond (1). Nickel catalyst (1). 150 °C (1). A skeletal or structural formula scores zero for the first mark.



ethene ethane

24. The enthalpy change of hydrogenation of cyclohexene, which has ONE C=C, is −120 kJ mol⁻¹. Predict the enthalpy change of hydrogenation of the Kekulé structure of benzene. Show your working. **[1 mark]**

Answer: 3 × (−120) = −360 kJ mol⁻¹ (1) — the Kekulé structure has three C=C bonds.

25. The measured enthalpy change of hydrogenation of benzene is −208 kJ mol⁻¹. Calculate the difference between the predicted and the measured value, and state what it tells you about benzene. **[2 marks]**

Answer: −208 − (−360) = 152 kJ mol⁻¹ less energy released (1). Benzene is therefore 152 kJ mol⁻¹ lower in energy / more stable than the Kekulé structure would be — the delocalisation energy (1).

Exam question

6 marks

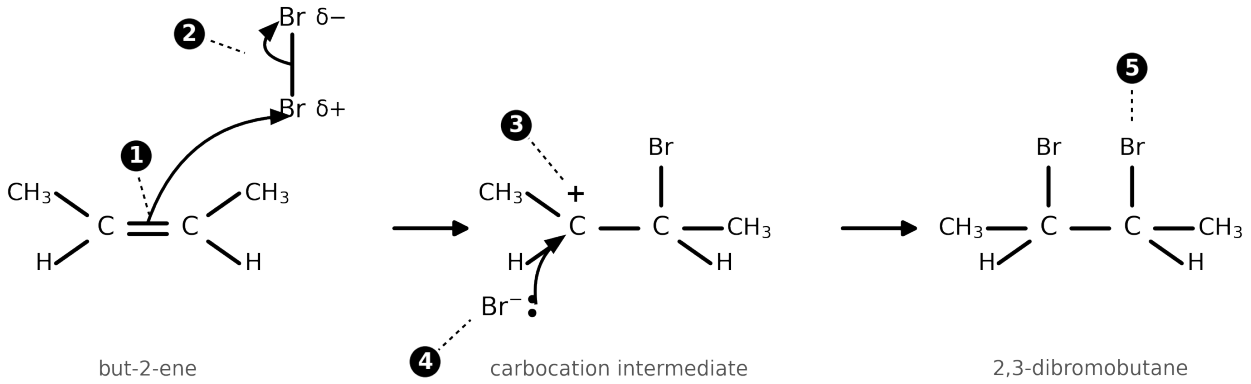
Specification 6.1.1 (a) (b)

E1. In 1865 Kekulé proposed a model for benzene with alternating single and double bonds. Describe and explain TWO pieces of experimental evidence that led scientists to replace this model with a delocalised model. In your answer, refer to bond lengths and to enthalpy changes. **[6 marks]**

Answer: Bond lengths: X-ray diffraction shows all six C–C bonds are the same length, 0.139 nm (1); this is between the single (0.153 nm) and double (0.134 nm) bond lengths, so there are no alternating single and double bonds (1). Enthalpy of hydrogenation: Kekulé predicts 3 × (−120) = −360 kJ mol⁻¹ but the measured value is −208 kJ mol⁻¹ (1); 152 kJ mol⁻¹ less energy is released, so benzene is more stable than the Kekulé structure (1). Explanation: the p-orbital on each carbon overlaps sideways with BOTH neighbours (1), so the π electrons are delocalised over all six carbons, which lowers the energy (1). Also creditworthy in place of one of the above: benzene does not decolourise bromine water, although Kekulé's three C=C bonds predict that it should.

Where the marks are: electrophilic addition

Five marks, and every one of them is a drawing decision.



1	Dipole shown (δ+ on the near bromine, δ− on the far one) AND a curly arrow from the C=C to the δ+ Br. The tail must sit on the double bond itself — an arrow starting at a carbon atom scores nothing.
2	A curly arrow from the MIDDLE of the Br–Br bond to the δ− bromine: the bond breaking heterolytically to give Br^-. An arrow drawn from the Br atom instead of the bond scores nothing.
3	The carbocation: bromine on one carbon and the + on the OTHER carbon. The + must be on a carbon, and not on the carbon that took the bromine.
4	A curly arrow from a LONE PAIR on the Br^- ion to the positively charged carbon. Starting it at the negative charge, or at the letters "Br", does not score.
5	The product: 2,3-dibromobutane, with both bromines on adjacent carbons.

The six ways this mark is thrown away

- ✗ The first arrow starts on a carbon atom instead of on the C=C bond.
- ✗ No dipole marked on the Br_2 — the δ+ and δ− are part of mark 1.
- ✗ The second arrow starts on the bromine atom rather than in the middle of the Br–Br bond.
- ✗ The + is put on the carbon that has just gained the bromine.
- ✗ The third arrow starts at the negative charge rather than at a lone pair.
- ✗ Arrowheads that stop short: an arrowhead has to touch the atom or bond that receives the electrons.

Extension — answers

48 marks.

1 Naming benzene rings

1. Name these: (a) C_6H_5Cl (b) $C_6H_5NO_2$ (c) 1,4-$C_6H_4(CH_3)_2$ (d) C_6H_5OH (e) C_6H_5COOH **[5 marks]**

Answer: (a) chlorobenzene (b) nitrobenzene (c) 1,4-dimethylbenzene (d) phenol (e) benzoic acid. One mark each.

2. Draw: (a) 1,2-dichlorobenzene (b) 4-nitromethylbenzene (c) 3-nitrophenol **[3 marks]**

Answer: (a) Cl on carbons 1 and 2 (1). (b) CH_3 on carbon 1 (methylbenzene is the parent, so it takes no locant) and NO_2 on carbon 4 (1). (c) OH on carbon 1 and NO_2 on carbon 3 (1).

3. Explain why 'hydroxybenzene' and '2,4,6-trinitrotoluene' are not acceptable systematic names. **[2 marks]**

Answer: Hydroxybenzene should be phenol — that compound has its own accepted name (1). 'Toluene' is a traditional name, not a systematic one: it must be 2,4,6-trinitromethylbenzene (1).

2 Nitration of benzene

1. State the reagents and conditions for the nitration of benzene, and explain why the temperature matters. **[3 marks]**

Answer: Concentrated HNO_3 (1) with concentrated H_2SO_4 as catalyst (1); 50 °C — above about 55 °C a second nitro group substitutes onto the ring, giving dinitrobenzene (1).

2. Write the equation that makes the electrophile, and the equation that regenerates the catalyst. **[2 marks]**

Answer: $HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$ (1). $H^+ + HSO_4^- \rightarrow H_2SO_4$ (1).

3. Benzene undergoes substitution, not addition. Use what you did in the main paper to explain why. **[3 marks]**

Answer: Addition would use up the delocalised π system permanently (1); benzene is 152 kJ mol^{-1} more stable than a molecule with three localised C=C bonds because of that delocalisation (1); substitution replaces a hydrogen atom and lets the delocalised ring re-form, so the stability is kept (1).

3 Alkanes and free-radical substitution

1. Methane reacts with chlorine in the presence of ultraviolet light. Write equations for the initiation step, both propagation steps, and one termination step. Label each one. **[5 marks]**

Answer: Initiation: $Cl_2 \rightarrow 2Cl\bullet$ (UV light causes homolytic fission) (1).

Propagation 1: $CH_4 + Cl\bullet \rightarrow \bullet CH_3 + HCl$ (1).

Propagation 2: $\bullet CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\bullet$ (1).

Termination: any two radicals joining, e.g. $\bullet CH_3 + Cl\bullet \rightarrow CH_3Cl$, $2Cl\bullet \rightarrow Cl_2$, or $2\bullet CH_3 \rightarrow C_2H_6$ (1).

All steps labelled and the UV condition stated (1).

2. Explain why this reaction gives a mixture of products, and why that makes it a poor way to make chloromethane in industry. **[2 marks]**

Answer: Further substitution happens: CH_3Cl reacts again to give CH_2Cl_2, $CHCl_3$ and CCl_4, and radicals can combine to give longer chains such as ethane (1). The yield of the compound you want is low and the mixture is expensive to separate (1).

4 Alcohols

1. Propan-1-ol is warmed with acidified potassium dichromate(VI). **[5 marks]**

(a) Name the reagent mixture in full.

(b) Give the product and the apparatus needed if you want the aldehyde.

(c) Give the product and the apparatus needed if you want the carboxylic acid.

Answer: (a) Potassium dichromate(VI), $K_2Cr_2O_7$, acidified with dilute sulfuric acid (1). (b) Propanal (1) — distil it off as it forms, so it cannot be oxidised further (1). (c) Propanoic acid (1) — heat under reflux with excess oxidising agent (1). The orange dichromate turns green in both cases.

2. Explain what happens when 2-methylpropan-2-ol is warmed with the same reagent, and why. **[2 marks]**

Answer: No reaction — it stays orange (1). It is a tertiary alcohol: the carbon carrying the OH has no hydrogen attached, and oxidation would require a C–C bond to break (1).

5 Haloalkanes

1. 1-bromobutane is warmed with aqueous sodium hydroxide. **[4 marks]**

(a) Name the type of reaction and the mechanism.

(b) Give the organic product.

(c) Name the nucleophile and say what makes it one.

Answer: (a) Hydrolysis; nucleophilic substitution (1). (b) Butan-1-ol (1). (c) The hydroxide ion, OH^- (1); it has a lone pair of electrons it can donate to the δ+ carbon (1).

2. 1-chlorobutane, 1-bromobutane and 1-iodobutane are warmed separately with aqueous silver nitrate in ethanol. Put them in order of how quickly a precipitate appears, and explain the order. **[3 marks]**

Answer: Fastest 1-iodobutane, then 1-bromobutane, then 1-chlorobutane (1). The rate depends on the carbon–halogen BOND ENTHALPY: C–I is weakest and breaks most easily, C–Cl is strongest (1). It does not follow bond polarity, which would predict the opposite order (1). Precipitates: AgCl white, AgBr cream, AgI yellow.

6 Isomers and a calculation

1. Draw and name the three alkenes with the molecular formula C_4H_8. There are also two cyclic isomers with the same formula — name them. **[5 marks]**

Answer: but-1-ene (1); but-2-ene (1); 2-methylpropene (1). Cyclic: cyclobutane (1) and methylcyclopropane (1). E- and Z-but-2-ene are stereoisomers of the same structural isomer, so they are not extra structural isomers.

2. Ethene reacts with steam to make ethanol: $C_2H_4 + H_2O \rightarrow C_2H_5OH$. **[4 marks]**

(a) Calculate the percentage atom economy for this reaction.

(b) 28.0 g of ethene gives 34.5 g of ethanol. Calculate the percentage yield.

(A_r: H 1.0, C 12.0, O 16.0)

Answer: (a) Only one product, so the atom economy is 100% (1) — (46.0/46.0) × 100 (1). (b) 28.0 g of C_2H_4 = 1.00 mol, so the theoretical yield is 1.00 mol of ethanol = 46.0 g (1). Percentage yield = 34.5/46.0 × 100 = 75.0% (1).