2.7 Organic Chemistry: 1-hour Pack

AQA 7405 · Calculator allowed · about 60 minutes

Total Marks

Name: _____ Date: ____ / ____ / _____

Answer ALL questions. Show all your working.

1 Ethanoic acid reacts with ethanol in the presence of a small volume of concentrated sulfuric acid, under reflux, to form ethyl ethanoate.

(a) Write an equation for this esterification reaction, including state symbols. **(2)**

(b) State the role of concentrated sulfuric acid in this reaction. **(1)**

(c) In an experiment, 6.00 g of ethanoic acid (Mr = 60.0) was reacted with excess ethanol. The reaction produced 6.60 g of ethyl ethanoate (Mr = 88.0). Calculate the percentage yield of ethyl ethanoate. **(4)**

(d) Calculate the atom economy for the formation of ethyl ethanoate in this reaction, given Mr(ethanol) = 46.0. **(3)**

(e) Ethanoyl chloride, CH_3COCl, reacts much more readily with ethanol than ethanoic acid does, producing ethyl ethanoate without the need for a catalyst or heating. State one other observable difference between the reaction of ethanol with ethanoyl chloride and with ethanoic acid, and name the type of mechanism by which acyl chlorides react with alcohols. **(2)**

(Total for Question 1 is 12 marks)

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2 An alkene, Y, is a gas at room temperature. Y has a relative molecular mass (Mr) of 56 and contains only carbon and hydrogen. Complete combustion of 0.560 g of Y produced 1.76 g of carbon dioxide and 0.720 g of water.

(a) Calculate the molecular formula of Y. Show your working. **(5)**

(b) Y has several structural isomers. One isomer, but-2-ene, shows E/Z isomerism, but another isomer, but-1-ene, does not. State the structural requirement for E/Z isomerism, and explain, in terms of this requirement, why but-1-ene does not show E/Z isomerism. **(3)**

(c) Propene reacts with hydrogen bromide in an electrophilic addition reaction, forming a mixture of 1-bromopropane and 2-bromopropane, with 2-bromopropane as the major product. Outline the mechanism for the formation of 2-bromopropane, naming the type of intermediate formed. **(3)**

(d) Explain, in terms of the stability of the carbocation intermediates, why 2-bromopropane is the major product. **(2)**

(Total for Question 2 is 13 marks)

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3 Required practical: a student prepared a sample of 1-bromobutane from butan-1-ol using the following method. Butan-1-ol is heated under reflux with a mixture of sodium bromide and concentrated sulfuric acid; the crude product is then separated by distillation and purified.

(a) State the roles of sodium bromide and concentrated sulfuric acid in this preparation. **(2)**

(b) Write an equation for the reaction of butan-1-ol with hydrogen bromide to form 1-bromobutane. **(2)**

(c) Explain why the reaction mixture is heated under reflux, rather than in an open flask, during this stage of the preparation. **(2)**

(d) Describe how the crude 1-bromobutane product is purified after the reaction, explaining the purpose of each purification step. **(6)**

(e) A student reacted 7.40 g of butan-1-ol (Mr = 74.0) with excess sodium bromide and concentrated sulfuric acid, and obtained 9.13 g of pure 1-bromobutane (Mr = 137.0). Calculate the percentage yield of 1-bromobutane. **(4)**

(f) Suggest one reason, other than experimental or technique error, why the percentage yield of a preparation such as this is often less than 100%. **(2)**

(g) State how the student could show that the final 1-bromobutane product was pure. **(2)**

(h) State one safety precaution that should be taken when carrying out this preparation, giving a reason. **(2)**

(Total for Question 3 is 22 marks)

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Mark scheme · 2.7 Organic Chemistry: 1-hour Pack

Question 1

(a) correct formulae with a reversible arrow: $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$ **M1**

(a) all state symbols correct: (l), (l), (l), (l) cao **A1**

(a) Answer: $CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$

(b) acts as a catalyst cao **B1**

(b) Answer: Acts as a catalyst.

(c) moles ethanoic acid = 6.00/60.0 = 0.100 mol **M1**

(c) theoretical moles ester = 0.100 mol (1:1 ratio); theoretical mass = 0.100 x 88.0 = 8.80 g **M1**

(c) % yield = (6.60/8.80) x 100 **M1**

(c) 75.0% cao **A1**

(c) Answer: 75.0%

(d) sum of Mr of reactants = 60.0 + 46.0 = 106.0 **M1**

(d) atom economy = (Mr of desired product / sum of Mr of reactants) x 100 = (88.0/106.0) x 100 **M1**

(d) 83.0% (3 s.f.) cao **A1**

(d) Answer: 83.0%

(e) the reaction of ethanoyl chloride with ethanol produces steamy/misty white fumes of HCl gas (a vigorous, exothermic reaction), unlike the acid + alcohol reaction **B1**

(e) nucleophilic addition-elimination cao **B1**

(e) Answer: Misty white fumes of HCl are produced (vigorous reaction), unlike with ethanoic acid; mechanism is nucleophilic addition-elimination.

Question 2

(a) moles CO_2 = 1.76/44 = 0.0400 mol (= moles of C) **M1**

(a) moles H_2O = 0.720/18 = 0.0400 mol, so moles of H = 0.0800 mol **M1**

(a) mass of C + mass of H = (0.0400 x 12) + (0.0800 x 1) = 0.480 + 0.0800 = 0.560 g, equal to the sample mass, confirming no oxygen is present **M1**

(a) mole ratio C:H = 0.0400:0.0800 = 1:2, empirical formula CH_2 (empirical mass = 14) **M1**

(a) 56/14 = 4, so molecular formula = C_4H_8 cao **A1**

(a) Answer: C_4H_8

(b) there must be restricted rotation about the C=C double bond, and each carbon of the double bond must be attached to two different groups oe **B1**

(b) in but-1-ene, $CH_2=CHCH_2CH_3$, the C1 carbon of the double bond is attached to two hydrogen atoms (the same group twice) **B1**

(b) so but-1-ene cannot exist as two distinguishable geometric (E/Z) forms oe **B1**

(b) Answer: E/Z isomerism requires restricted rotation about C=C and two different groups on each double-bond carbon; in but-1-ene, C1 has two identical H atoms, so no E/Z isomerism is possible.

(c) H^+ (from HBr) adds to the terminal (CH_2=) carbon of propene, with the electron pair of the C=C π bond forming the new C-H bond **M1**

(c) this forms a secondary carbocation intermediate (positive charge on the central carbon), with Br^- released as a free ion **M1**

(c) Br^- then uses a lone pair to bond to the positively charged carbon, forming 2-bromopropane, $CH_3CHBrCH_3$ cao **A1**

(c) Answer: 2-bromopropane ($CH_3CHBrCH_3$) forms via a secondary carbocation intermediate.

(d) the secondary carbocation (leading to 2-bromopropane) is more stable than the primary carbocation (leading to 1-bromopropane) **B1**

(d) because alkyl groups are electron-donating (positive inductive effect), and there are more alkyl groups adjacent to the secondary carbocation, better stabilising/dispersing the positive charge oe **B1**

(d) Answer: The secondary carbocation is more stable than the primary one because more electron-donating alkyl groups disperse the positive charge, so it forms preferentially, giving 2-bromopropane as the major product.

Question 3

(a) NaBr and H_2SO_4 react together to generate hydrogen bromide, HBr, in situ: NaBr + H_2SO_4 -> $NaHSO_4$ + HBr **B1**

(a) the HBr formed then reacts with butan-1-ol, providing the Br^- nucleophile/substituting group oe **B1**

(a) Answer: NaBr + H_2SO_4 -> $NaHSO_4$ + HBr; the HBr generated reacts with the alcohol.

(b) correct formulae, C_4H_9OH and HBr as reactants, C_4H_9Br and H_2O as products **M1**

(b) C_4H_9OH + HBr -> C_4H_9Br + H_2O, correctly balanced cao **A1**

(b) Answer: C_4H_9OH + HBr -> C_4H_9Br + H_2O

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(c) reflux uses a vertical condenser that continuously condenses and returns evaporated volatile reactants and products (butan-1-ol, HBr, 1-bromobutane) to the flask **B1**

(c) this allows prolonged heating (to increase the rate/extent of reaction) without the loss of volatile substances oe **B1**

(c) Answer: Reflux returns evaporated volatile substances to the flask via the condenser, allowing prolonged heating without losing reactants or product.

(d) the crude product mixture is distilled, collecting the fraction with a boiling point close to that of 1-bromobutane (removes the least volatile/non-volatile impurities) **B1**

(d) the distillate is shaken with water in a separating funnel and the layers allowed to separate; the lower, organic (1-bromobutane) layer is run off and retained, as 1-bromobutane is denser than water **B1**

(d) the organic layer is then washed with sodium hydrogencarbonate solution to neutralise/remove acidic impurities (H_2SO_4/HBr), venting gas pressure (CO_2) regularly by inverting and opening the tap **B1**

(d) washed again with water to remove any remaining aqueous/hydrogencarbonate impurities **B1**

(d) dried using an anhydrous drying agent (e.g. anhydrous calcium chloride or magnesium sulfate) to remove residual traces of water, then decanted/filtered from the drying agent **B1**

(d) the dried liquid is redistilled, collecting only the fraction that boils at the correct literature temperature (close to 101°C), discarding the first and last fractions to ensure purity **B1**

(d) Answer: Distil crude product; separate organic layer in a separating funnel; wash with $NaHCO_3$(aq) then water; dry with anhydrous $CaCl_2$ or $MgSO_4$; redistil, collecting only the correct boiling-point fraction.

(e) moles butan-1-ol = 7.40/74.0 = 0.100 mol **M1**

(e) theoretical moles of 1-bromobutane = 0.100 mol (1:1 stoichiometry); theoretical mass = 0.100 x 137.0 = 13.7 g **M1**

(e) % yield = (9.13/13.7) x 100 **M1**

(e) 66.6% (3 s.f.) cao **A1**

(e) Answer: 66.6%

(f) a valid reason, e.g. some butan-1-ol undergoes a competing elimination side reaction with concentrated H_2SO_4 to form but-1-ene instead of substitution **B1**

(f) a further linked/alternative valid point, e.g. some product is inevitably lost during transfers between apparatus and during purification steps (distillation, separating funnel, drying) oe **B1**

(f) Answer: For example: some butan-1-ol undergoes elimination (side reaction) to form but-1-ene instead of substitution; and/or product is lost during transfers and purification steps.

(g) measure the boiling point of the product during (re)distillation using a thermometer **B1**

(g) compare to the known (data book) boiling point of 1-bromobutane (about 101°C); a pure sample boils over a narrow (1-2°C) range at the correct value, an impure sample boils over a wider range/at the wrong temperature oe **B1**

(g) Answer: Measure the boiling point during distillation and compare to the literature value (about 101°C); a pure sample boils over a narrow range at this temperature.

(h) a valid precaution, e.g. wear eye protection/gloves, and/or carry out the heating and distillation steps in a fume cupboard **B1**

(h) linked reason, e.g. concentrated H_2SO_4 is corrosive, and HBr/1-bromobutane vapours are toxic/irritant and should not be inhaled oe **B1**

(h) Answer: For example: work in a fume cupboard, because HBr and 1-bromobutane vapours are toxic/irritant, and wear eye protection because concentrated H_2SO_4 is corrosive.

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