AC7D Organic Chemistry: Depth and Exam Drill

AQA 7405 · Calculator allowed · about 170 minutes

Total Marks

Name: _____ Date: ____ / ____ / _____

Answer ALL questions. Show all your working.

1 This question tests core definitions and nomenclature for alkanes and halogenoalkanes.

(a) State the general formula for the homologous series of alkanes. **(1)**

(b) Define the term homologous series. **(1)**

(c) Give the IUPAC name of the following compound: BrCH2CH2CH(CH3)CH3. **(2)**

(Total for Question 1 is 4 marks)

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2 A hydrocarbon, Z, contains only carbon and hydrogen and has a relative molecular mass (Mr) of 84.0. Complete combustion of a 0.420 g sample of Z produced 1.32 g of carbon dioxide and 0.540 g of water.

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

(b) A chain isomer of Z, 2-methylpent-2-ene, CH3C(CH3)=CHCH2CH3, does not show E/Z isomerism, even though it is not a terminal alkene. Explain why, with reference to the groups attached to the carbon atoms of the double bond. **(2)**

(Total for Question 2 is 7 marks)

3 Ethane reacts with bromine in the presence of ultraviolet (UV) radiation via a free-radical substitution mechanism to form bromoethane and hydrogen bromide. Bond enthalpies: Br-Br = +193 kJ/mol; C-H (in ethane) = +413 kJ/mol; H-Br = +366 kJ/mol; H-Cl = +432 kJ/mol.

(a) Write an equation for the initiation step of this reaction, and state the type of bond fission involved. **(2)**

(b) Using the bond enthalpies given, calculate the enthalpy change for the first propagation step, C2H6 + Br* -> C2H5* + HBr. **(3)**

(c) Write an equation for the second propagation step that regenerates the bromine radical. **(2)**

(d) Give an equation for a termination step in this reaction, other than the reverse of the initiation step. **(1)**

(e) Initiation requires less energy for bromine than for chlorine, since the Br-Br bond (193 kJ/mol) is weaker than the Cl-Cl bond. Using the bond enthalpies given and your answer to part (b), explain why the overall reaction of ethane with bromine is nevertheless slower than the equivalent reaction with chlorine. **(2)**

(Total for Question 3 is 10 marks)

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4 2-methylbut-2-ene, CH3C(CH3)=CHCH3, reacts with hydrogen bromide, HBr, in an electrophilic addition reaction.

(a) Outline the mechanism for the formation of the major product, 2-bromo-2-methylbutane, naming the type of intermediate formed. **(3)**

(b) Explain, in terms of carbocation stability, why 2-bromo-2-methylbutane is the major product rather than 2-bromo-3-methylbutane. **(2)**

(c) A sample of 2-methylbut-2-ene of mass 7.00 g (Mr = 70.0) is reacted with excess HBr. The reaction produces 11.6 g of pure 2-bromo-2-methylbutane (Mr = 151.0) after purification, although other bromobutane isomers also form in small amounts. Calculate the percentage yield of 2-bromo-2-methylbutane. **(4)**

(Total for Question 4 is 9 marks)

5 A student investigates the hydrolysis of 2-bromo-2-methylpropane, (CH3)3CBr, in aqueous acetone by withdrawing samples at intervals and titrating each against standard sodium hydroxide solution to determine the concentration of (CH3)3CBr remaining. The results are shown below.

Time (s): 0, 300, 600, 900.

[(CH3)3CBr] remaining (mol dm-3): 0.0500, 0.0250, 0.0125, 0.00625.

(a) Show that these data are consistent with the reaction being first order with respect to (CH3)3CBr. **(2)**

(b) Calculate the rate constant, k, for this first-order reaction using k = ln2 / half-life. Give your answer to 3 significant figures, with units. **(3)**

(c) Using your value of k, calculate the initial rate of reaction at t = 0, when [(CH3)3CBr] = 0.0500 mol dm-3, using rate = k[(CH3)3CBr]. Give your answer to 3 significant figures. **(2)**

(Total for Question 5 is 7 marks)

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6 Pentan-3-ol, CH3CH2CH(OH)CH2CH3, and 2-methylhexan-2-ol, (CH3)2C(OH)CH2CH2CH2CH3, are two different classes of alcohol, used here to compare oxidation and dehydration behaviour.

(a) State whether pentan-3-ol is a primary, secondary or tertiary alcohol, and identify the type of carbonyl compound formed when it is oxidised with acidified potassium dichromate(VI) under reflux. **(2)**

(b) State whether 2-methylhexan-2-ol can be oxidised by acidified potassium dichromate(VI), and explain your answer. **(2)**

(c) When heated with concentrated sulfuric acid, 2-methylhexan-2-ol undergoes acid-catalysed dehydration (elimination) to form a mixture of two structural isomers: 2-methylhex-2-ene (the major product) and 2-methylhex-1-ene (a minor product). Give the structural formula of 2-methylhex-2-ene, name the mechanism, and explain, using Zaitsev's rule, why it is the major product. **(3)**

(d) Calculate the atom economy for the formation of 2-methylhex-2-ene (Mr = 98.0) from 2-methylhexan-2-ol (Mr = 116.0) in this dehydration reaction, given that water (Mr = 18.0) is the only by-product. **(3)**

(Total for Question 6 is 10 marks)

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7 1-bromobutane (a primary halogenoalkane) and 2-bromo-2-methylpropane, (CH3)3CBr (a tertiary halogenoalkane), both react with hydroxide ions in aqueous solution to form the corresponding alcohol, but by different mechanisms: a one-step mechanism for 1-bromobutane and a two-step mechanism, via a carbocation intermediate, for 2-bromo-2-methylpropane. Compare and explain these two mechanisms, including how the rate of each reaction depends on the concentrations of the halogenoalkane and hydroxide ion, the role of steric hindrance, and the role of carbocation stability, to explain why the two halogenoalkanes react by different routes.

(Total for Question 7 is 6 marks)

8 A student prepares a sample of the ester 3-methylbutyl ethanoate (isoamyl acetate) by heating 3-methylbutan-1-ol, (CH3)2CHCH2CH2OH, with an excess of glacial ethanoic acid and a few drops of concentrated sulfuric acid, under reflux. The crude ester is then purified by washing with sodium carbonate solution, separating the layers in a separating funnel, drying, and redistilling.

(a) Write an equation, including state symbols, for the esterification reaction between 3-methylbutan-1-ol and ethanoic acid to form 3-methylbutyl ethanoate. **(2)**

(b) State the role of concentrated sulfuric acid in this reaction, and explain why the reaction mixture is heated under reflux rather than in an open flask. **(2)**

(c) After washing the crude ester with aqueous sodium carbonate, the mixture separates into two layers in the separating funnel. State whether the ester forms the upper or lower layer, and explain your answer. **(2)**

(d) 4.40 g of 3-methylbutan-1-ol (Mr = 88.0) was reacted with excess ethanoic acid. After purification, 4.81 g of pure 3-methylbutyl ethanoate (Mr = 130.0) was obtained. Calculate the percentage yield. **(4)**

(e) The mass of 3-methylbutan-1-ol (4.40 g) was measured directly on a two-decimal-place balance with a reading uncertainty of ± 0.005 g. Calculate the percentage uncertainty in this mass measurement, to 3 significant figures. **(2)**

(Total for Question 8 is 12 marks)

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9 Benzene reacts with ethanoyl chloride, CH3COCl, in the presence of anhydrous aluminium chloride, forming phenylethanone (acetophenone) in a Friedel-Crafts acylation reaction.

(a) State the reagents and conditions needed for this reaction, other than benzene, and name the type of mechanism involved. **(2)**

(b) The electrophile is generated by reaction between ethanoyl chloride and aluminium chloride. Write an equation to show the formation of the electrophile, CH3CO+. **(2)**

(c) Outline the mechanism for the electrophilic substitution reaction between benzene and CH3CO+, including the role of AlCl4- in the final step. **(4)**

(d) Calculate the atom economy of this reaction for the formation of phenylethanone (Mr = 120.0), given Mr(benzene) = 78.0, Mr(ethanoyl chloride) = 78.5, and that HCl (Mr = 36.5) is the only by-product. **(3)**

(Total for Question 9 is 11 marks)

10 Two isomeric carbonyl compounds, P and Q, both have molecular formula C4H8O (Mr = 72.0). The proton (1H) NMR spectrum of P shows four signals: a 1H signal at 9.75 ppm, a 2H signal at 2.42 ppm, a 2H signal at 1.68 ppm, and a 3H signal at 0.97 ppm. The 1H NMR spectrum of Q shows three signals: a 3H signal at 1.05 ppm, a 2H signal at 2.45 ppm, and a 3H signal at 2.12 ppm, with no signal beyond 3.5 ppm.

(a) Identify compound P, explaining your reasoning using the chemical shift and integration of its NMR signals. **(3)**

(b) Identify compound Q, explaining your reasoning. **(1)**

(c) Compound Q, butan-2-one, is reduced using sodium borohydride, NaBH4, in aqueous solution to form butan-2-ol; one mole of NaBH4 can reduce up to four moles of carbonyl compound. 1.44 g of butan-2-one (Mr = 72.0) is reacted with 0.400 g of NaBH4 (Mr = 37.8). Show that NaBH4 is in excess, and calculate the maximum mass of butan-2-ol (Mr = 74.0) that could be formed. **(4)**

(Total for Question 10 is 8 marks)

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11 Glycine, H2NCH2COOH, is the simplest amino acid. Its carboxylic acid group has pKa1 = 2.34 and its protonated amine group (-NH3+) has pKa2 = 9.60. The Henderson-Hasselbalch equation is pH = pKa + log10([conjugate base]/[weak acid]).

(a) State the type of structure glycine adopts in aqueous solution at pH values between pKa1 and pKa2 (around neutral pH), and give its structural formula in this form. **(2)**

(b) Using the Henderson-Hasselbalch equation and pKa1 = 2.34, calculate the ratio of the concentration of the zwitterion (H3N+CH2COO-) to the fully protonated cation (H3N+CH2COOH) present in a glycine solution buffered at pH 3.34. **(3)**

(c) Predict, with a reason, whether glycine would migrate towards the positive or negative electrode during electrophoresis at pH 12.00 (a strongly alkaline solution, well above pKa2). **(2)**

(Total for Question 11 is 7 marks)

12 Ethanoic acid reacts with propan-1-ol in the presence of a strong acid catalyst to form propyl ethanoate in a reversible esterification reaction: $CH_3COOH + C_3H_7OH \leq> CH_3COOC_3H_7 + H_2O$. This reaction is very slightly exothermic in the forward direction. In an experiment at 373 K, 1.00 mol of ethanoic acid and 1.00 mol of propan-1-ol (with no ester or water initially present) were mixed in a sealed 1.00 dm^3 vessel and allowed to reach equilibrium. At equilibrium, the mixture was found to contain 0.667 mol of propyl ethanoate.

(a) Using the reaction stoichiometry, determine the equilibrium amounts, in mol, of ethanoic acid, propan-1-ol and water. **(3)**

(b) Write the expression for Kc for this reaction, and calculate its value at 373 K, stating its units. **(4)**

(c) State and explain the effect, if any, of increasing the temperature on the value of Kc, given that the esterification reaction is very slightly exothermic in the forward direction. **(2)**

(Total for Question 12 is 9 marks)

Mark scheme · AC7D Organic Chemistry: Depth and Exam Drill

Question 1

- (a) **B1** CnH(2n+2) cao
- **(a) Answer: CnH(2n+2)**
- (b) **B1** a series of compounds with the same general formula and similar chemical properties, in which successive members differ by CH2, and which show a gradual trend in physical properties oe
- **(b) Answer: A series of compounds with the same general formula and similar chemical properties, differing from one member to the next by CH2, showing a gradual trend in physical properties.**
- (c) **B1** longest chain containing the bromine correctly identified as a 4-carbon (butane) chain, numbered to give bromine the lowest locant (C1)
- (c) **B1** 1-bromo-3-methylbutane cao
- **(c) Answer: 1-bromo-3-methylbutane**

Question 2

- (a) **M1** moles CO2 = 1.32/44.0 = 0.0300 mol (= moles of C)
- (a) **M1** moles H2O = 0.540/18.0 = 0.0300 mol, so moles of H = 0.0600 mol
- (a) **M1** mass of C + mass of H = (0.0300 x 12.0) + (0.0600 x 1.0) = 0.360 + 0.0600 = 0.420 g, equal to the sample mass, confirming no oxygen is present
- (a) **M1** mole ratio C:H = 0.0300:0.0600 = 1:2, empirical formula CH2 (empirical mass = 14.0)
- (a) **A1** 84.0/14.0 = 6, so molecular formula = C6H12 cao
- **(a) Answer: C6H12**
- (b) **B1** E/Z isomerism requires restricted rotation about the C=C double bond and each carbon of the double bond must be attached to two different groups oe
- (b) **B1** in 2-methylpent-2-ene the left-hand double-bond carbon is attached to two identical CH3 groups (the chain methyl and the branch methyl), so this carbon does not have two different groups, and E/Z isomerism is not possible regardless of the groups on the other double-bond carbon oe
- **(b) Answer: The left-hand alkene carbon of 2-methylpent-2-ene carries two identical CH3 groups, so it fails the requirement for two different groups on each double-bond carbon, and no E/Z isomerism is possible.**

Question 3

- (a) **B1** Br2 -> 2Br* (or Br2 -> Br* + Br*)
- (a) **B1** homolytic fission, each bromine atom keeping one electron from the shared pair, initiated by UV light
- **(a) Answer: Br2 -> 2Br*, by homolytic fission initiated by UV light.**
- (b) **M1** identify bond broken = C-H (+413 kJ/mol) and bond formed = H-Br (+366 kJ/mol)
- (b) **M1** enthalpy change = bonds broken - bonds formed = 413 - 366
- (b) **A1** +47 kJ/mol (endothermic) cao
- **(b) Answer: +47 kJ/mol**
- (c) **M1** correct species: C2H5Br formed and Br* regenerated
- (c) **A1** C2H5* + Br2 -> C2H5Br + Br* cao
- **(c) Answer: C2H5* + Br2 -> C2H5Br + Br***
- (d) **B1** any valid radical-radical combination other than Br* + Br* -> Br2, e.g. C2H5* + Br* -> C2H5Br, or C2H5* + C2H5* -> C4H10 cao
- **(d) Answer: C2H5* + Br* -> C2H5Br (or C2H5* + C2H5* -> C4H10)**
- (e) **B1** the equivalent first propagation step for chlorine, C2H6 + Cl* -> C2H5* + HCl, breaks the same C-H bond (413) but forms the stronger H-Cl bond (432), so this step is exothermic for chlorine but endothermic for bromine (as calculated in part b)
- (e) **B1** the less favourable (more endothermic) propagation step for bromine has a higher activation energy, making this rate-determining step slower for bromine, so the overall chain reaction proceeds more slowly with bromine than with chlorine, even though bromine's initiation step is easier oe
- **(e) Answer: The rate-determining propagation step is exothermic for chlorine (bonds broken 413, bonds formed 432, so -19 kJ/mol) but endothermic for bromine (+47 kJ/mol), giving bromine's propagation step a higher activation energy and a slower overall reaction, despite its easier initiation step.**

Question 4

- (a) **M1** H+ (from HBr) adds to the CH carbon of the double bond (the carbon bonded to only one methyl group and one H), with the electron pair of the C=C π bond forming the new C-H bond
- (a) **M1** this forms a tertiary carbocation intermediate (positive charge on the carbon bonded to two methyl groups), with Br- released as a free ion
- (a) **A1** Br- then uses a lone pair to bond to the positively charged carbon, forming 2-bromo-2-methylbutane, CH3C(Br)(CH3)CH2CH3 cao
- **(a) Answer: 2-bromo-2-methylbutane forms via a tertiary carbocation intermediate.**
- (b) **B1** the tertiary carbocation (leading to 2-bromo-2-methylbutane) is more stable than the secondary carbocation that would lead to 2-bromo-3-methylbutane
- (b) **B1** because alkyl groups are electron-donating (positive inductive effect), and the tertiary carbocation has more alkyl groups adjacent to the positive carbon, better dispersing/stabilising the positive charge oe
- **(b) Answer: The tertiary carbocation is more stable than the secondary one, because more electron-donating alkyl groups disperse the positive charge, so it forms preferentially, giving 2-bromo-2-methylbutane as the major product.**
- (c) **M1** moles 2-methylbut-2-ene = 7.00/70.0 = 0.100 mol
- (c) **M1** theoretical moles of product = 0.100 mol (1:1 stoichiometry); theoretical mass = 0.100 x 151.0 = 15.1 g
- (c) **M1** % yield = (11.6/15.1) x 100
- (c) **A1** 76.8% (3 s.f.) cao
- **(c) Answer: 76.8%**

Question 5

- (a) **B1** the half-life (time for the concentration to halve) is constant at 300 s throughout the data: 0.0500 to 0.0250 in 300 s, 0.0250 to 0.0125 in the next 300 s, and 0.0125 to 0.00625 in the next 300 s
- (a) **B1** a constant half-life, independent of concentration, is characteristic of a first-order reaction, consistent with an SN1 mechanism in which only the halogenoalkane appears in the rate-determining step
- **(a) Answer: The half-life is constant at 300 s throughout, which is characteristic of a first-order reaction.**
- (b) **M1** k = ln2 / 300
- (b) **M1** ln2 = 0.6931
- (b) **A1** k = 2.31 x 10^{-3} s-1 cao
- **(b) Answer: 2.31 x 10^{-3} s-1**
- (c) **M1** rate = 2.31 x 10^{-3} x 0.0500
- (c) **A1** 1.16 x 10^{-4} mol dm-3 s-1 cao
- **(c) Answer: 1.16 x 10^{-4} mol dm-3 s-1**

Question 6

- (a) **B1** secondary alcohol
- (a) **B1** oxidised to pentan-3-one, a ketone (only one oxidation step is possible) cao
- **(a) Answer: Secondary alcohol; oxidised to pentan-3-one (a ketone).**
- (b) **B1** it cannot be oxidised (no colour change is observed)
- (b) **B1** because it is a tertiary alcohol: the carbon bonded to -OH has no hydrogen atom attached to it that could be removed in the oxidation step oe
- **(b) Answer: It cannot be oxidised, because it is a tertiary alcohol and the carbon bonded to -OH carries no hydrogen atom.**
- (c) **B1** structural formula (CH3)2C=CHCH2CH2CH3 cao
- (c) **B1** elimination (via a carbocation intermediate); Zaitsev's rule states that the more substituted (more stable) alkene is the major product of elimination
- (c) **A1** 2-methylhex-2-ene is trisubstituted (three alkyl groups on the two double-bond carbons) compared with the disubstituted 2-methylhex-1-ene, so it is more thermodynamically stable and forms as the major product oe
- **(c) Answer: (CH3)2C=CHCH2CH2CH3; elimination via a carbocation, favoured by Zaitsev's rule because it is the more substituted, more stable alkene.**
- (d) **M1** this is an intramolecular elimination (one reactant only), so total reactant Mr = Mr of the alcohol = 116.0
- (d) **M1** atom economy = (Mr of desired product / total reactant Mr) x 100 = (98.0/116.0) x 100
- (d) **A1** 84.5% (3 s.f.) cao
- **(d) Answer: 84.5%**

Question 7

- **Level 3** (5-6): A full and accurate comparison: correctly describes the one-step mechanism for 1-bromobutane (OH- attacks the delta+ carbon from the side opposite the leaving Br-, in a single step, with the rate depending on the concentrations of both the halogenoalkane and OH-), correctly describes the two-step mechanism for 2-bromo-2-methylpropane (slow ionisation to form a carbocation intermediate, then fast attack by OH-, with the rate depending only on the concentration of the halogenoalkane), and clearly explains, using both steric hindrance (from the three methyl groups on the tertiary carbon) and carbocation stability (tertiary more stable than primary), why each halogenoalkane reacts by its particular route.
- **Level 2** (3-4): A moderate comparison: describes the general difference between the two mechanisms (one-step versus two-step via an intermediate) with some correct detail, and refers to either steric hindrance or carbocation stability as a reason for the difference, but the explanation is incomplete, has minor errors, or omits how the rate depends on reactant concentrations for one or both halogenoalkanes.
- **Level 1** (1-2): Basic comments: states that the two halogenoalkanes react by different mechanisms or at different rates, with little or no correct mechanistic or kinetic detail, and no reference to steric hindrance or carbocation stability.
- **Indicative content:**
  - 1-bromobutane is a primary halogenoalkane; OH- is not sterically hindered from approaching the delta+ carbon, and attacks from the side opposite (backside relative) to the leaving Br- in a single, concerted step
  - this gives a rate equation of rate = k[1-bromobutane][OH-], i.e. the reaction is second order overall (first order in each reactant)
  - 2-bromo-2-methylpropane is a tertiary halogenoalkane; the three bulky methyl groups create steric hindrance that prevents OH- from approaching the carbon closely enough for a one-step attack
  - instead the C-Br bond breaks first, by heterolytic fission, in a slow step to form a tertiary carbocation intermediate and Br-
  - the tertiary carbocation is relatively stable because the three surrounding alkyl groups donate electron density (positive inductive effect), dispersing the positive charge enough for the carbocation to exist as a discrete intermediate
  - OH- then rapidly attacks the planar carbocation in a fast second step
  - this gives a rate equation of rate = k[2-bromo-2-methylpropane] only, independent of [OH-], so the reaction is first order overall
  - a primary carbocation, which would be needed for 1-bromobutane to react by the same two-step route, is too unstable (too little alkyl stabilisation) to form readily, so 1-bromobutane instead reacts by the single-step route
  - overall, the mechanism followed is governed by a balance of steric hindrance (favouring the one-step route for less hindered, primary substrates) and carbocation stability (favouring the two-step route for more substituted, tertiary substrates)

Question 8

- (a) **M1** correct formulae with a reversible arrow: CH3COOH + (CH3)2CHCH2CH2OH ≤> CH3COOCH2CH2CH(CH3)2 + H2O
- (a) **A1** all state symbols correct: (l), (l), (l), (l) cao
- **(a) Answer: CH3COOH(l) + (CH3)2CHCH2CH2OH(l) ≤> CH3COOCH2CH2CH(CH3)2(l) + H2O(l)**
- (b) **B1** acts as a catalyst
- (b) **B1** reflux uses a vertical condenser that continuously condenses and returns evaporated volatile substances to the flask, allowing prolonged heating (to increase the rate/extent of reaction) without loss of volatile reactants or product oe
- **(b) Answer: Catalyst; reflux returns evaporated volatile substances to the flask, allowing prolonged heating without losing reactants or product.**
- (c) **B1** upper layer
- (c) **B1** the ester is less dense than the aqueous layer, and the two liquids are immiscible (esters do not hydrogen-bond appreciably with water), so the ester floats on top oe
- **(c) Answer: Upper layer, because the ester is less dense than water and the two liquids are immiscible.**
- (d) **M1** moles 3-methylbutan-1-ol = 4.40/88.0 = 0.0500 mol
- (d) **M1** theoretical moles of ester = 0.0500 mol (1:1 ratio); theoretical mass = 0.0500 x 130.0 = 6.50 g
- (d) **M1** % yield = (4.81/6.50) x 100
- (d) **A1** 74.0% cao
- **(d) Answer: 74.0%**
- (e) **M1** % ... (0.005/4.40) x 100

Question 9

- (a) **B1** ethanoyl chloride with anhydrous aluminium chloride (AlCl3) catalyst, heated under reflux, in the absence of moisture
- (a) **B1** electrophilic substitution cao
- **(a) Answer: Ethanoyl chloride with anhydrous AlCl3 catalyst, reflux, anhydrous conditions; electrophilic substitution.**
- (b) **M1** correct species: AlCl4-
- (b) **A1** CH3COCl + AlCl3 -> CH3CO+ + AlCl4- cao
- **(b) Answer: CH3COCl + AlCl3 -> CH3CO+ + AlCl4-**
- (c) **M1** CH3CO+ (the electrophile) attacks the delocalised π electron ring system of benzene, forming a new bond to one ring carbon
- (c) **M1** this forms a positively charged intermediate (arenium ion/σ complex), in which delocalisation is disrupted and retained over only the other five carbons
- (c) **A1** AlCl4- acts as a base and removes an H+ from the carbon bonded to the COCH3 group
- (c) **A1** this restores full delocalisation (aromaticity) of the ring and regenerates the AlCl3 catalyst, forming phenylethanone cao
- **(c) Answer: CH3CO+ attacks the ring, forming a positively charged arenium ion intermediate; AlCl4- removes an H+ from this intermediate, restoring the aromatic ring, regenerating AlCl3 and forming phenylethanone.**
- (d) **M1** sum of Mr of reactants = 78.0 + 78.5 = 156.5
- (d) **M1** atom economy = (Mr of desired product / sum of Mr of reactants) x 100 = (120.0/156.5) x 100
- (d) **A1** 76.7% (3 s.f.) cao
- **(d) Answer: 76.7%**

Question 10

- (a) **B1** the 1H signal at 9.75 ppm (integration 1H) is characteristic of an aldehyde -CHO proton
- (a) **B1** the integration ratio 1:2:2:3 across four signals matches four different proton environments, consistent with a straight-chain -CH2CH2CH3 group attached to CHO
- (a) **A1** P is butanal, CH3CH2CH2CHO cao
- **(a) Answer: P is butanal, CH3CH2CH2CHO.**
- (b) **B1** no signal beyond 3.5 ppm rules out an aldehyde proton, so the carbonyl is a ketone; the integration ratio 3:2:3 (two CH3 environments plus one CH2) matches Q = butan-2-one, CH3COCH2CH3 cao
- **(b) Answer: Q is butan-2-one, CH3COCH2CH3.**
- (c) **M1** moles butan-2-one = 1.44/72.0 = 0.0200 mol
- (c) **M1** moles NaBH4 available = 0.400/37.8 = 0.0106 mol (3 s.f.); moles NaBH4 needed = 0.0200/4 = 0.00500 mol, which is less than 0.0106 mol available, confirming NaBH4 is in excess
- (c) **M1** moles butan-2-ol formed = 0.0200 mol (1:1 conversion, since butan-2-one is the limiting reagent)
- (c) **A1** mass = 0.0200 x 74.0 = 1.48 g cao
- **(c) Answer: 1.48 g**

Question 11

- (a) **B1** zwitterion
- (a) **B1** structural formula H3N+CH2COO- cao
- **(a) Answer: Zwitterion; H3N+CH2COO-.**
- (b) **M1** rearrange: log10(ratio) = pH - pKa1 = 3.34 - 2.34 = 1.00
- (b) **M1** ratio = $10^{1.00}$
- (b) **A1** 10.0 : 1 (zwitterion : cation) cao
- **(b) Answer: 10.0 : 1 (zwitterion to cation)**
- (c) **B1** at pH 12.00, well above pKa2 (9.60), the -NH3+ group has also lost a proton, so glycine exists mainly as the anion H2NCH2COO- (overall net negative charge)
- (c) **B1** a negatively charged species migrates towards the positive electrode (the anode) oe
- **(c) Answer: Towards the positive electrode (anode), because at pH 12.00 glycine exists mainly as the negatively charged anion H2NCH2COO-.**

Question 12

- (a) **M1** recognise the 1:1:1:1 stoichiometry, so the change in each reactant = -0.667 mol and the change in each product = +0.667 mol
- (a) **M1** equilibrium ethanoic acid = 1.00 - 0.667 = 0.333 mol; equilibrium propan-1-ol = 1.00 - 0.667 = 0.333 mol
- (a) **A1** equilibrium water = 0.667 mol cao
- **(a) Answer: Ethanoic acid = 0.333 mol; propan-1-ol = 0.333 mol; water = 0.667 mol.**
- (b) **M1** Kc = [CH3COOC3H7][H2O] / [CH3COOH][C3H7OH]
- (b) **M1** substitute concentrations (= moles, since the vessel volume is 1.00 dm3): (0.667 x 0.667) / (0.333 x 0.333)
- (b) **A1** Kc = 4.01 (3 s.f.) cao
- (b) **B1** no units, since the powers of concentration (mol dm-3) in the numerator and denominator are equal and cancel oe
- **(b) Answer: Kc = 4.01, no units**
- (c) **B1** Kc would decrease
- (c) **B1** by Le Chatelier's principle, increasing the temperature favours the endothermic (reverse) direction, shifting the equilibrium position back towards the reactants and reducing the proportion of products at equilibrium, so Kc decreases oe
- **(c) Answer: Kc would decrease, because increasing temperature favours the endothermic reverse reaction (Le Chatelier's principle), shifting the equilibrium position towards the reactants.**