2.11 Chemistry: Aromatic Chemistry, Carbonyls and Amines: 30-minute Pack

AQA 7405 · Calculator allowed · about 30 minutes

Total Marks

Name: _____ Date: ____ / ____ / _____

Answer ALL questions. Show all your working.

1 Propanal, CH_3CH_2CHO, and propanone, CH_3COCH_3, are both reduced by aqueous sodium tetrahydridoborate(III), $NaBH_4$, to alcohols.

(a) Describe the mechanism for the reduction of propanal by $NaBH_4$, including the role of the hydride ion. **(4)**

(b) State a reagent, and the conditions needed, that would distinguish propanal from propanone using a simple test-tube test, and state what would be observed with propanal. **(3)**

(c) 2,4-dinitrophenylhydrazine (Brady's reagent) reacts with propanal (and with propanone) to give an orange precipitate, confirming the presence of a carbonyl group but not distinguishing between the two compounds. Explain how this orange precipitate could then be used to identify which specific carbonyl compound (e.g. propanal or propanone) was originally present. **(2)**

(d) Calculate the atom economy for the conversion of propanone, C_3H_6O (Mr = 58), into propan-2-ol, C_3H_8O (Mr = 60), by reduction, treating the overall reaction as simple addition of H_2 (Mr = 2) across the C=O bond, with propan-2-ol as the only product. **(2)**

(Total for Question 1 is 11 marks)

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2 Glycine (aminoethanoic acid), H_2NCH_2COOH, is the simplest naturally occurring amino acid.

(a) Define the term 'zwitterion' and state the type of ion glycine forms at its isoelectric point. **(2)**

(b) Explain why glycine exists mainly as a cation in strongly acidic solution, but mainly as an anion in strongly alkaline solution. **(3)**

(c) Glycine and alanine can react together to form a dipeptide. State the type of reaction that occurs and name the type of linkage formed between the two amino acid residues. **(2)**

(Total for Question 2 is 7 marks)

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3 Compound Q is an amine used as a precursor in a pharmaceutical synthesis route. Compound Q contains only carbon, hydrogen and nitrogen. Complete combustion of 12.1 g of Q produces 35.2 g of carbon dioxide and 9.9 g of water. On combustion analysis, all of the nitrogen in Q is converted to gaseous nitrogen, N_2, and 1.40 g of N_2 is also collected.

(a) Calculate the empirical formula of compound Q. **(4)**

(b) Given that the relative molecular mass, Mr, of compound Q is 121, determine its molecular formula. **(1)**

(c) Compound Q reacts with dilute hydrochloric acid to form a soluble salt. Suggest the class of organic compound to which Q belongs. **(1)**

(Total for Question 3 is 6 marks)

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Mark scheme · 2.11 Chemistry: Aromatic Chemistry, Carbonyls and Amines: 30-minute Pack

Question 1

(a) $NaBH_4$ provides a hydride ion, H-, which acts as a nucleophile **B1**

(a) the carbon atom of the C=O group is delta-positive (polarised, due to oxygen being more electronegative), so it is attacked by the hydride ion **B1**

(a) a new C-H bond forms as the hydride ion's electron pair moves to carbon, while the electron pair in the C=O π bond moves onto the oxygen, forming an alkoxide ion intermediate **B1**

(a) the alkoxide ion is then protonated (by water or on addition of dilute acid) to give the alcohol product, propan-1-ol **B1**

(a) Answer: H- (nucleophile) attacks the delta+ carbonyl carbon; the C=O π electrons move onto O forming an alkoxide intermediate, which is then protonated to give propan-1-ol.

(b) Tollens' reagent (ammoniacal silver nitrate) **B1**

(b) warmed (in a water bath) **B1**

(b) propanal gives a silver mirror (Ag^+ reduced to Ag), while propanone gives no visible change/no silver mirror **B1**

(b) Answer: Tollens' reagent, warmed: propanal (an aldehyde) forms a silver mirror; propanone (a ketone) gives no reaction.

(c) the orange precipitate (2,4-dinitrophenylhydrazone derivative) is recrystallised to purify it, and its melting point is measured **B1**

(c) the measured melting point is compared with data book (literature) values of melting points of known 2,4-dinitrophenylhydrazone derivatives, to identify which specific aldehyde/ketone was present **B1**

(c) Answer: Purify (recrystallise) the derivative, measure its melting point, and match this against data book values for known derivatives to identify the specific carbonyl compound.

(d) atom economy = (Mr of desired product / sum of Mr of all reactants) x 100 = 60 / (58 + 2) x 100 **M1**

(d) = 100% **A1**

(d) Answer: Atom economy = 100%

Question 2

(a) a zwitterion is a species (molecule) that carries both a positive and a negative charge (on different atoms within the same species), with an overall net charge of zero **B1**

(a) at its isoelectric point, glycine exists predominantly as the zwitterion, $+H_3NCH_2COO-$ **B1**

(a) Answer: A zwitterion carries both a positive and a negative charge but has zero overall net charge; at its isoelectric point glycine exists mainly as the zwitterion $+H_3NCH_2COO-$.

(b) in strongly acidic solution, there is a high concentration of H^+ ions, which protonates the $-NH_2$ (or -COO-) group, giving the fully protonated cation, $+H_3NCH_2COOH$ **B1**

(b) in strongly alkaline solution, there is a high concentration of OH^- ions, which removes/accepts a proton from the -COOH (or $-NH_3^+$) group, giving the fully deprotonated anion, H_2NCH_2COO- **B1**

(b) the position of these acid-base equilibria shifts depending on the pH (H^+ concentration) of the solution, so the dominant species present changes with pH **B1**

(b) Answer: In strongly acidic solution, excess H^+ protonates the amine/carboxylate group to give the cation $+H_3NCH_2COOH$; in strongly alkaline solution, OH^- removes a proton from the ammonium/acid group to give the anion H_2NCH_2COO-.

(c) condensation reaction (with loss of a molecule of water) **B1**

(c) peptide bond (amide linkage) **B1**

(c) Answer: Condensation reaction (loss of H_2O); a peptide (amide) bond is formed.

Question 3

(a) moles CO_2 = 35.2 / 44 = 0.800 mol, so moles C = 0.800 mol **M1**

(a) moles H_2O = 9.9 / 18 = 0.550 mol, so moles H = 2 x 0.550 = 1.10 mol **M1**

(a) moles N_2 = 1.40 / 28 = 0.0500 mol, so moles N = 2 x 0.0500 = 0.100 mol **M1**

(a) ratio C : H : N = 0.800 : 1.10 : 0.100 = 8 : 11 : 1, so empirical formula = $C_8H_{11}N$ **A1**

(a) Answer: Empirical formula = $C_8H_{11}N$

(b) empirical formula mass of $C_8H_{11}N$ = (8x12)+(11x1)+14 = 121, which equals the given Mr, so the molecular formula is the same as the empirical formula, $C_8H_{11}N$; ft their empirical formula from (a) if the mass matches **B1**

(b) Answer: Molecular formula = $C_8H_{11}N$

(c) an amine (the nitrogen lone pair accepts a proton from HCl to form an ammonium/aminium salt, characteristic of amines) **B1**

(c) Answer: Q is an amine.

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