2.11 Chemistry: Aromatic Chemistry, Carbonyls and Amines: Test Pack

AQA 7405 · Calculator allowed · about 40 minutes

Total Marks

Name: _____ Date: ____ / ____ / _____

Answer ALL questions. Show all your working.

1 Benzene, C_6H_6, can be represented either by a Kekule model, with alternating single and double carbon-carbon bonds, or by a delocalised model, in which all six ring carbon-carbon bonds are identical and a ring of delocalised π electron density lies above and below the plane of the ring.

(a) State two pieces of experimental evidence that support the delocalised model of benzene over the Kekule model. **(2)**

(b) Describe the delocalised model of bonding in benzene. **(3)**

(c) The standard enthalpy of hydrogenation of cyclohexene (one C=C double bond) is -120 kJ/mol. (i) Calculate the enthalpy of hydrogenation that would be predicted for a hypothetical molecule 'cyclohexa-1,3,5-triene', containing three isolated, non-interacting C=C double bonds. (ii) The actual enthalpy of hydrogenation of benzene is -208 kJ/mol. Calculate the extra stabilisation (delocalisation/resonance energy) of benzene compared with this hypothetical molecule. **(4)**

(Total for Question 1 is 9 marks)

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2 Required practical: a student is asked to prepare a solid ester, compound S, by reacting 3-methylphenol with an excess of benzoyl chloride, C_6H_5COCl, in the presence of a small amount of pyridine (which acts as a base to remove the HCl by-product), with the reaction mixture cooled in ice. The crude solid product is filtered, washed with cold water, and then purified by recrystallisation. A sample of the purified compound S is then used to determine its melting point.

(a) Describe how the crude solid compound S, once isolated by filtration, would be purified by recrystallisation. **(4)**

(b) Explain why the solvent chosen for the recrystallisation of compound S must dissolve it well when hot but only sparingly when cold. **(2)**

(c) The purified compound S is found to have a melting point range of 62-64°C. The data book (literature) melting point of pure compound S is 65°C. Evaluate the purity of the sample, and state what you would expect to observe about the melting point range of an impure sample compared with a pure one. **(3)**

(d) The student reacts 2.16 g of 3-methylphenol (Mr = 108.14) with an excess of benzoyl chloride. After purification, 3.18 g of pure compound S (Mr = 212.24) is obtained. Calculate the percentage yield of compound S. **(4)**

(e) Suggest one reason, other than an incomplete reaction, why the actual yield of compound S obtained is less than the theoretical yield. **(1)**

(f) Name the type of reaction occurring between 3-methylphenol and benzoyl chloride, and identify the other product formed alongside compound S. **(2)**

(g) State one hazard associated with using benzoyl chloride in this preparation, and one precaution the student should take because of it. **(1)**

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(h) The melting point range obtained (62-64°C) suggests the sample is not yet fully pure. Suggest one modification to the purification procedure that could improve the purity of compound S further, and explain why it would help. **(2)**

(Total for Question 2 is 19 marks)

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Mark scheme · 2.11 Chemistry: Aromatic Chemistry, Carbonyls and Amines: Test Pack

Question 1

(a) X-ray diffraction shows all six C-C bond lengths in benzene are equal (about 0.139-0.140 nm), a value between a C-C single bond (0.154 nm) and a C=C double bond (0.134 nm) oe **B1**

(a) the enthalpy of hydrogenation of benzene is much less exothermic than the value predicted for a Kekule structure with three localised double bonds oe; accept: benzene does not readily decolourise bromine water/undergo the addition reactions typical of alkenes **B1**

(a) Answer: Equal C-C bond lengths (X-ray data) and a less exothermic enthalpy of hydrogenation than predicted for three localised double bonds.

(b) each carbon atom is sp2 hybridised and forms σ bonds to two other carbon atoms and one hydrogen atom, all in the same plane oe **B1**

(b) each carbon atom has one electron in a p-orbital, perpendicular to the plane of the ring **B1**

(b) the p-orbitals overlap sideways (above and below the plane) to form a ring of delocalised π electron density spread over all six carbon atoms **B1**

(b) Answer: sp2 carbons each contribute one p-electron; sideways overlap of the six p-orbitals forms a delocalised π system of electron density above and below the ring plane.

(c) predicted enthalpy = 3 x (-120) = -360 kJ/mol **M1**

(c) -360 kJ/mol for the hypothetical triene **A1**

(c) stabilisation = predicted - actual = (-360) - (-208), ft their predicted value from (i) **dM1**

(c) 152 kJ/mol (allow awrt 150-152); benzene is 152 kJ/mol more stable (less exothermic hydrogenation) than the hypothetical Kekule triene **A1**

(c) Answer: Predicted enthalpy of hydrogenation = -360 kJ/mol; delocalisation (resonance) stabilisation = 152 kJ/mol

Question 2

(a) dissolve the crude solid in a minimum volume of a hot, suitable solvent (one in which the solid is soluble hot but only sparingly soluble cold) **B1**

(a) filter the hot solution (e.g. through a fluted/hot filter funnel, or add a little decolourising charcoal and filter) to remove any insoluble impurities **B1**

(a) allow the filtrate to cool slowly (e.g. to room temperature, then in ice) so that crystals of compound S form, leaving soluble impurities in solution **B1**

(a) filter the crystals under reduced pressure (Buchner filtration), wash with a small volume of ice-cold solvent, and allow the crystals to dry **B1**

(a) Answer: Dissolve in minimum hot solvent, hot-filter, cool slowly to crystallise, then filter (Buchner) under reduced pressure, wash with cold solvent, and dry.

(b) dissolving well when hot allows a small (minimum) volume of solvent to be used, and allows the solid to be hot-filtered to remove insoluble impurities **B1**

(b) being only sparingly soluble when cold means the compound crystallises out (while soluble impurities, present in low concentration, remain dissolved in the solvent) on cooling, giving a purer, higher-yield crop of crystals **B1**

(b) Answer: Good hot solubility allows use of a small volume and hot filtration; poor cold solubility forces the pure compound to crystallise out while soluble impurities stay in solution, improving purity and recovery.

(c) the sample is not completely pure, since its melting point (62-64°C) is lower than, and does not match, the literature value (65°C) **B1**

(c) impurities lower the melting point (freezing point depression) and broaden the melting point range **B1**

(c) a pure sample would be expected to melt sharply over a narrow range (typically within about 1-2°C) at (or very close to) the literature value **B1**

(c) Answer: The sample is impure (melts below and over a wider range than the pure literature value); impurities depress and broaden the melting point range, whereas a pure sample melts sharply, close to 65°C.

(d) moles of 3-methylphenol = 2.16 / 108.14 = 0.01997 mol (0.0200 mol to 3 sf) **M1**

(d) since 3-methylphenol : compound S is a 1:1 ratio, theoretical (maximum) mass of S = 0.01997 x 212.24 = 4.24 g **M1**

(d) percentage yield = (actual mass / theoretical mass) x 100 = (3.18 / 4.24) x 100, ft their theoretical mass **dM1**

(d) 75.0% (accept 74.9-75.1%; awrt 75%) **A1**

(d) Answer: Percentage yield = 75.0%

(e) any one: product lost during transfers between apparatus / some product remains dissolved in the mother liquor (recrystallisation solvent) and is not recovered / product lost during filtration or washing / a competing side reaction occurs oe, any sensible practical loss **B1**

(e) Answer: For example, some of the product is lost in solution in the recrystallisation mother liquor (or lost during transfers/filtration).

(f) nucleophilic addition-elimination (condensation) **B1**

(f) hydrogen chloride, HCl (removed as it forms by reaction with the pyridine present) **B1**

(f) Answer: Nucleophilic addition-elimination (condensation); HCl is the other product (mopped up by the pyridine).

(g) hazard: corrosive/lachrymator (irritant, causes eyes to water) and reacts with moisture to release HCl fumes; precaution: carry out the reaction in a fume cupboard and wear eye protection/gloves (either a matching hazard/precaution pair for the mark) **B1**

(g) Answer: Benzoyl chloride is corrosive/a lachrymator (irritant); the reaction should be carried out in a fume cupboard, wearing eye protection.

(h) modification: e.g. repeat (a second) recrystallisation of the crystals obtained / use a smaller volume of solvent / add decolourising charcoal during the hot filtration stage, any one sensible suggestion **B1**

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(h) explanation: a further recrystallisation removes more of the remaining soluble impurities (which stay in solution) at each stage, giving a narrower melting point range closer to the literature value oe, matched to the suggestion given **B1**

(h) Answer: For example, carry out a second recrystallisation: each recrystallisation leaves more impurities behind in solution, so repeating it removes more impurity and gives a sharper, higher melting point range closer to 65°C.

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