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ANSWER BOOK

Electrophilic substitution: nitration and Friedel–Crafts acylation

Aromatic chemistry and amines · Unit C21

AQA 3.3.10.2 · OCR A 6.1.1 (d), 6.1.1 (e), 6.1.1 (g), 6.1.1 (i) to (l), 6.2.4 (d)

18 questions · 63 marks

NAVY EDITION

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SECTION A · Short, 1 to 2 marks

A1 ESN-Q22

B1 the product is 1-bromo-3-nitrobenzene. **B1** the nitro group withdraws electron density from the ring and directs the incoming electrophile to position 3. [2]

SECTION B · Standard, 3 to 5 marks

B1 ESN-Q2

B1 $HNO_3 + H_2SO_4 \rightarrow H_2NO_3^+ + HSO_4^-$, sulfuric acid protonating nitric acid. **B1** $H_2NO_3^+ \rightarrow NO_2^+ + H_2O$; accept the single equation $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$ for both marks. **B1** the H^+ lost from the ring at the end of the mechanism combines with HSO_4^-. **B1** $H^+ + HSO_4^- \rightarrow H_2SO_4$, so the sulfuric acid is regenerated and not used up overall. [4]

B2 ESN-Q7

B1 the electrophile is the acylium ion, CH_3CO^+, with the positive charge on the carbonyl carbon. **B1** aluminium chloride is a catalyst acting as a halogen carrier, accepting a lone pair from chlorine. **B1** $CH_3COCl + AlCl_3 \rightarrow CH_3CO^+ + AlCl_4^-$. **B1** $H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$, re-forming the catalyst and giving off hydrogen chloride. [4]

B3 ESN-Q9

B1 $CH_3COCl + AlCl_3 \rightarrow CH_3CO^+ + AlCl_4^-$. **B1** a curly arrow from within the hexagon to the carbonyl carbon of CH_3CO^+, the carbon carrying +. **B1** the intermediate with H and $COCH_3$ on the same carbon and a horseshoe with + inside it across the other five carbons. **B1** a curly arrow from the C–H bond into the ring, with H^+ lost. [4]

B4 ESN-Q24

B1 $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$; accept $HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$, with the regeneration then written as one step. **B1** $C_6H_6 + NO_2^+ \rightarrow C_6H_5NO_2 + H^+$, the substitution step summarised from the mechanism. **B1** $H^+ + HSO_4^- \rightarrow H_2SO_4$ and $H_3O^+ + HSO_4^- \rightarrow H_2SO_4 + H_2O$, the two hydrogensulfate ions taking back the two protons. **B1** adding the equations cancels NO_2^+, H^+, H_3O^+, $2HSO_4^-$ and $2H_2SO_4$, leaving $C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$; the sulfuric acid is regenerated unchanged, so it is a catalyst. [4]

B5 ESN-Q15

B1 ethene is attacked by a neutral polar molecule, HBr, whereas benzene needs a positive ion, NO_2^+, made with a catalyst. **B1** both form a positively charged intermediate after the electrophile accepts a pair of π electrons. **B1** ethene's carbocation is attacked by Br^-, giving electrophilic addition. **B1** benzene's intermediate loses H^+ and regains its delocalised ring, giving electrophilic substitution. [4]

B6 ESN-Q17

B1 step 1: concentrated nitric acid and concentrated sulfuric acid at 50 °C. **B1** the intermediate is nitrobenzene, $C_6H_5NO_2$. **B1** step 2: tin and concentrated hydrochloric acid, heated under reflux, reduce the nitro group; allow iron for tin. **B1** sodium hydroxide is then added to release phenylamine from the phenylammonium salt. [4]

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B7 ESN-Q19 **B1** $Br_2 + FeBr_3 \rightarrow Br^+ + FeBr_4^-$, the carrier accepting a lone pair from bromine; accept the polarised Br–Br–$FeBr_3$ complex. **B1** a curly arrow from within the hexagon to Br^+, or to the δ+ bromine of the complex. **B1** the intermediate with H and Br on one carbon and a horseshoe with + over the other five, then an arrow from the C–H bond into the ring. **B1** $H^+ + FeBr_4^- \rightarrow FeBr_3 + HBr$, re-forming iron(III) bromide. [4]

B8 ESN-Q1 **B1** concentrated nitric acid; reject dilute nitric acid. **B1** concentrated sulfuric acid, which acts as a catalyst. **B1** a temperature of about 50 °C, kept below about 55 °C to prevent further nitration; 'heat' alone is not enough. [3]

B9 ESN-Q4 **B1** the delocalised ring gives benzene extra stability, about 152 kJ mol^{-1}. **B1** addition would leave a product with no delocalised ring, so that stability would be lost. **B1** in substitution H^+ is lost and the delocalised ring is restored, giving a more stable product. [3]

B10 ESN-Q12 **M1** total Mr of the reactants = 78.0 + 78.5 = 156.5. **M1** atom economy = 120.0 ÷ 156.5 × 100. **A1** atom economy = 76.7%, to three significant figures. [3]

B11 ESN-Q13 **B1** water from the air hydrolyses aluminium chloride, giving steamy fumes of hydrogen chloride. **B1** the hydrated aluminium compound can no longer accept a lone pair from the chlorine of the acyl chloride. **B1** so little acylium ion forms, there is little electrophile, and the catalyst is lost. [3]

B12 ESN-Q14 **B1** the electrophile is the acylium ion $C_6H_5CO^+$. **B1** $C_6H_5COCl + AlCl_3 \rightarrow C_6H_5CO^+ + AlCl_4^-$. **B1** the product is the ketone $C_6H_5COC_6H_5$, diphenylmethanone, with HCl as the other product. [3]

B13 ESN-Q16 **B1** the π electrons in benzene are delocalised over six carbons, so the electron density at any one bond is lower than in a C=C bond. **B1** benzene's electron density is too low to polarise a neutral molecule such as Br_2. **B1** a positive ion is attracted strongly enough to the ring to accept a pair of the delocalised electrons. [3]

B14 ESN-Q20 **B1** a lone pair on the oxygen of phenol overlaps with the ring and is partly delocalised into it. **B1** this increases the electron density of the ring above benzene's. **B1** phenol's ring can therefore polarise a bromine molecule and attack it directly, whereas benzene needs a halogen carrier to make Br^+. [3]

B15 ESN-Q21 **B1** an alkyl group releases electron density into the ring, so the alkylbenzene reacts faster than benzene and is alkylated again. **B1** an acyl group withdraws electron density from the ring through its C=O group, so the ketone is less reactive than benzene and is not acylated again. **B1** benzene is used in large excess, so the electrophile is far more likely to meet benzene than the alkylbenzene. [3]

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B16 ESN-Q23 **B1** in ultraviolet light the methyl group is substituted by free radicals, giving (chloromethyl)benzene, $C_6H_5CH_2Cl$. **B1** with aluminium chloride the ring is substituted at positions 2 and 4, giving 1-chloro-2-methylbenzene and 1-chloro-4-methylbenzene. **B1** with alkaline manganate(VII) and then acid the side chain is oxidised to COOH, giving benzoic acid, C_6H_5COOH. [3]

SECTION C · Long, 6 marks or more

C1 ESN-Q3 **Indicative content** [6]

B1 an equation forming NO_2^+: $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$; accept $HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$ or the two steps. **B1** a curly arrow that starts inside the hexagon, on the delocalised electrons, and ends on the nitrogen atom of NO_2^+; reject an arrow to an oxygen. **B1** the intermediate drawn with H and NO_2 on the same carbon, and a horseshoe with + inside it over the other five carbons only. **B1** a curly arrow from the middle of the C–H bond on that carbon back into the ring, with H^+ shown leaving and nitrobenzene formed. **B1** $H^+ + HSO_4^- \rightarrow H_2SO_4$, showing that the sulfuric acid is regenerated and acts as a catalyst. **B1** losing H^+ restores the delocalised ring and keeps its stability, which an addition product with no delocalised ring would lose.

Levels

Level 3 (5–6 marks) the equation for NO_2^+ formation, every curly arrow and the intermediate with its horseshoe and charge are correct, the sulfuric acid is shown to be regenerated, and the loss of H^+ is explained as restoring the delocalised ring's stability.

Level 2 (3–4 marks) the electrophile is formed correctly, with the arrow into the ring and the intermediate drawn; the arrow from the C–H bond back into the ring, the regenerated catalyst, or the stability argument for substitution is absent.

Level 1 (1–2 marks) NO_2^+ is named or one arrow drawn; the intermediate commonly keeps a full circle, or nitric acid itself is shown attacking the ring.

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