Arenes/Benzene Chemistry

Mark Scheme 2

Level	International A Level
Subject	Chemistry
Exam Board	Edexcel
Topic	Transition Metals & Organic Nitrogen Chemistry
Sub Topic	Arenes/Benzene Chemistry
Booklet	Mark Scheme 2

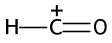
Time Allowed: **68 minutes**

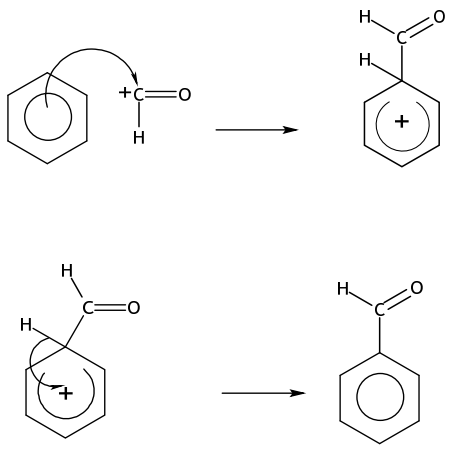
Score: **/56**

Percentage: **/100**

Grade Boundaries:

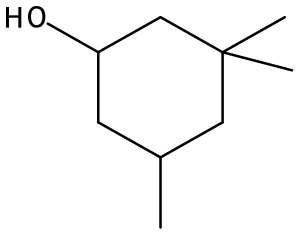
A*	A	B	C	D	E	U
>85%	'77.5%	70%	62.5%	57.5%	45%	<45%

Question Number	Acceptable Answer	Reject	Mark
1(a)(i)	 OR non-displayed structure (with atoms in any order) ALLOW Positive charge on any part of the structure OR Outside bracketed structure / formula	HCOCl / methanoyl chloride	1

Question Number	Acceptable Answer	Reject	Mark
1 (a)(ii)	 TE on incorrect electrophile in (a)(i) Positive charge on any part of the electrophile Curly arrow from on or within the circle to positively charged carbon ALLOW Curly arrow from anywhere within the hexagon Arrow to any part of the CHO^+ including to the + charge Non-displayed electrophile **(1)** Intermediate structure including charge with horseshoe covering at least 3 carbon atoms, **and** facing the tetrahedral carbon **and** some part of the positive charge must be within the horseshoe Ignore structure of side chain for this mark **(1)** Curly arrow from C—H bond to anywhere in the benzene ring reforming delocalized fully correct structure including correctly bonded substituent Substituent may be non-displayed **(1)** Correct Kekulé structures score full marks Ignore any involvement of AlX_4^- (or similar) in the formation of the final structure	Curly arrow on or outside the hexagon Dotted bonds to H and CHO **unless** clearly a dots & wedge 3-structure COH for CHO	3

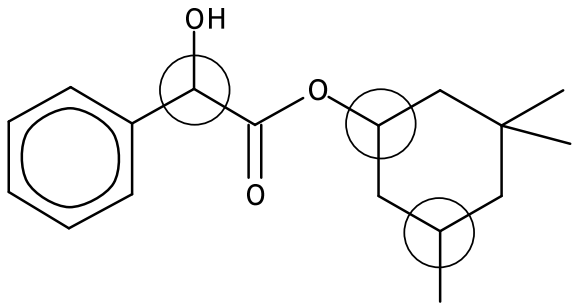
Question Number	Acceptable Answer	Reject	Mark
1(a)(iii)	hydrogen cyanide / HCN **(1)** potassium (or sodium) cyanide / KCN / NaCN ignore pH = 8 **(1)** OR KCN / NaCN **(1)** H_2SO_4 / HCl ignore concentrations and pH = 8 **(1)** OR HCN **(1)** NaOH / pH = 8 **(1)** ALLOW names or formula throughout	 NaOH NaOH	2

Question Number	Acceptable Answer	Reject	Mark
1(a)(iv)	Hydrochloric acid / HCl(aq) OR Sulfuric acid / H_2SO_4(aq) OR sodium hydroxide / NaOH / potassium hydroxide / KOH **and** followed by any **strong** acid / H^+ ALLOW HCl / H_2SO_4 / name or formula of any **strong** acid IGNORE Water / H_2O Concentrated Dilute		1

Question Number	Acceptable Answer	Reject	Mark
1(b)(i)	The first two marks are stand alone  **(1)** (Concentrated) sulfuric acid ALLOW Any named strong acid / correct formula with or without state symbol IGNORE Dilute / water **(1)** (Heat under) reflux **(1)** Condition mark dependent on the reagent mark being awarded or near miss.	OH bonded to ring the wrong way around Benzene ring H^+ / H_3O^+ Just 'heat'	3

Question Number	Acceptable Answer	Reject	Mark
1(b)(ii)	The esterification / reaction is reversible / an equilibrium (So yield is low) ALLOW Does not go to completion IGNORE References to cost/rate No TE on an incorrect reaction in (b)(i)		1

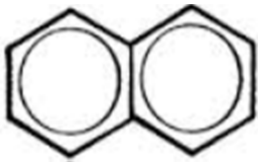
Question Number	Acceptable Answer	Reject	Mark
1(b)(iii)	PCl_5 reacts with both OH groups		1

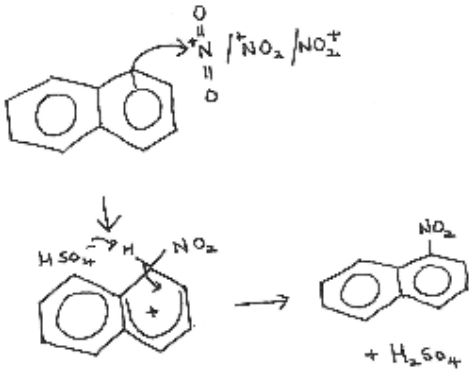
Question Number	Acceptable Answer	Reject	Mark
1(c)(i)	 All three correct scores 2 marks Two correct from three scores 1 mark More than three circled scores max 1 mark ALLOW Any clear labelling Any ring containing only one correct carbon		2

Question Number	Acceptable Answer	Reject	Mark
1(c)(ii)	**Any two from** Only one isomer may be (more) active One isomer (or more) may have a negative effect ALLOW Side effects Different isomers have different (biochemical) properties ALLOW higher dosage required to obtain sufficient amount of active isomer (so expensive) If no other mark is scored Separation of isomers needed OR Low yield can score 1 IGNORE References to **just** 'cost'	Geometric / structural isomers	2

Total for Question 1 = 16 marks

Question Number	Correct Answer	Reject	Mark
2(a)	X-ray diffraction/crystallography	X-rays alone X radiation IR/UV/nmr	1

Question Number	Correct Answer	Reject	Mark
2(b)	Mark independently **First mark:**  ALLOW Single ring and two double bonds Single ring around all atoms **(1)** **Second mark:** EITHER electrons delocalised (around the ring(s)) OR pi system around all (10) carbon atoms **(1)** **Third mark:** EITHER overlap of p-orbitals OR p/ pi-/π/ 10 (ALLOW pie) electrons **(1)** ALLOW six electrons if single ring and two double bonds shown Phthalic anhydride structure **2 max**	Single ring and three double bonds delocalised orbitals	3

Question Number	Correct Answer	Reject	Mark
2(c)	**First mark** Formation of nitronium ion (may combine equations) **(1)** $2H_2SO4 + HNO_3 \rightarrow$ $^+NO_2/NO_2^+ + H_3O^+ + 2HSO_4^-$ OR $H_2SO4 + HNO_3 \rightarrow$ $^+NO_2/NO_2^+ + H_2O + HSO4^-$ OR $H2SO4 + HNO3 \rightarrow H_2NO_3^+ + HSO_4^-$ **And** $H2NO_3^+ \rightarrow NO_2^+ + H_2O$ **Charges are needed for first mark**  TE on incorrect electrophile If benzene used instead of naphthalene **3 max** Do not penalise the use of Phthalic anhydride Correct Kekulé structures score full marks ALLOW multiple nitrations		4

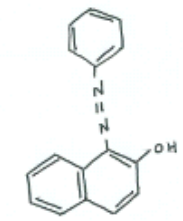
	Second mark Curly arrow from on or within the circle to (positive) N ALLOW Curly arrow from anywhere within the hexagon Arrow to **any** part of the electrophile including to the + charge (which can be anywhere on electrophile), OR Arrow to a point at least half the distance between ring and electrophile **(1)**	Curly arrow on or outside the hexagon	
	Third mark Intermediate structure including charge with horseshoe covering at least 3 carbon atoms, **and** facing the tetrahedral carbon **and** with some part of the positive charge within the horseshoe. ALLOW dotted horseshoe **(1)** IGNORE displayed nitro group even if incorrect A single lapse of omitting internal circle or double bonds in 3rd or 4th mark	Partial bonds to H or Subs group	
	Fourth mark If final product not 1, 4, 5 or 8 MP4 cannot be scored Curly arrow from C—H bond to anywhere in the ring reforming delocalised structure of a correct stable molecule. **(1)** IGNORE Absence of HSO_4^-/H_2SO_4/H^+	H_2 / H product	

Question Number	Correct Answer	Reject	Mark
2(d)	$C_{10}H_8$ This mark can be awarded if the molar mass of naphthalene has been used as 128 even if the skeletal formula in the equation has been used **(1)** $C_{10}H_8 + 12O_2 \rightarrow 10CO_2 + 4H_2O$ **(1)** ALLOW The balanced equation with skeletal formula of naphthalene scores both marks Ignore state symbols even if incorrect Number of moles of naphthalene = $\frac{1.28}{128}$ = 0.01(00) Volume of gas = 10 x 0.01 x 24.0 = 2.4(0) dm^3 /2400 cm^3 **(1)** ALLOW TE on incorrect formula of naphthalene for max 2		3

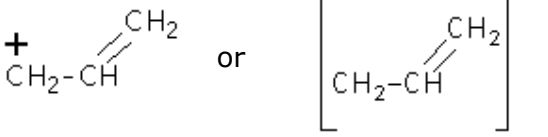
Question Number	Correct Answer	Reject	Mark
2(e)	Hydrogen /H_2 **(1)** **Second mark is consequential on Hydrogen** Heat/any specified temperature above 100^oC **And** nickel/ Ni /platinum/ Pt/ palladium / Pd catalyst **(1)**	H alone loses first mark but not second	2

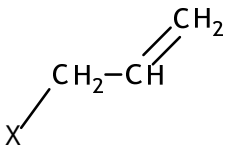
Question Number	Correct Answer	Reject	Mark
2(f)(i)	Water/H_2O		1

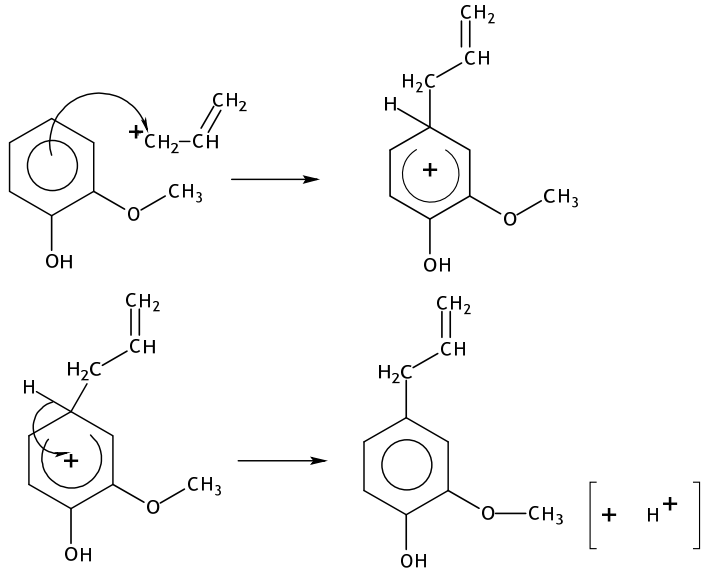
Question Number	Correct Answer	Reject	Mark
2(f)(ii)	(In strong acid) an oxygen (in the C–O/C=O/O–H bond) will protonate/gain H/H^+ **(1)** (In alkali) a proton is lost from each/both phenol group(s) ALLOW (In alkali) a proton/hydrogen/ H/H^+ is lost from phenol group(s) **(1)**		2

Question Number	Correct Answer	Reject	Mark
2(g)	Phenylamine is added to a mixture of sodium nitrite/ sodium nitrate(III)/ $NaNO_2$ **and** (dilute) hydrochloric acid/ HCl/ sulfuric acid/ H_2SO_4 ALLOW nitrous acid/ HNO_2 **(1)** at 5^oC/between 0 and 10^oC/ at 10^oC/ or less than $10\ ^oC$ ALLOW ice bath ALLOW any temperature or range of temperatures within that range **(1)** (A mixture of 2-naphthol and) aqueous sodium hydroxide/alkali is added to produce a dye **(1)**  OR rings in hexagons ALLOW $C_6H_5N_2$ group at any carbon except fused carbons **(1)**	Just sodium nitrate	4

(Total for Question 2 = 20 marks)

Question Number	Acceptable Answer	Reject	Mark
3(a)(i)	 or ALLOW Positive charge on any part of the carbocation Structural / fully displayed / skeletal formulae		1

Question Number	Acceptable Answer	Reject	Mark
3(a)(ii)	 X = Cl / Br / I OR structural / fully displayed / skeletal formulae OR 3- hloro/bromo/iodo prop(-1-)ene No TE on incorrect electrophile in (a)(i)	name without '3'	1

Question Number	Acceptable Answer	Reject	Mark
3 (a)(iii)	 TE on incorrect electrophile in (a)(i) If benzene used instead of substituted benzene OR If final product not 1,2,4 only MP1 & 2 scored Curly arrow from on / within the circle to positive C ALLOW Curly arrow from anywhere within the hexagon Arrow to **any** part of the electrophile including to the + charge (which can be anywhere on electrophile), OR Arrow to a point at least half the distance between ring and electrophile **(1)** Intermediate structure including charge with horseshoe covering at least 3 carbon atoms, **and** facing the tetrahedral carbon **and** with some part of the positive charge within the horseshoe. IGNORE substituent errors (incorrect position on ring or bond to substituent) at this marking point ALLOW dotted horseshoe **(1)** Curly arrow from C—H bond to anywhere in the benzene ring reforming delocalized structure of a correct stable molecule. Ignore any involvement of $AlCl_4^-$ in the final step **(1)** Correct Kekulé structures score full marks	Curly arrow on or outside the hexagon Partial bonds to H or CH_3 except for dot and wedge in 3-D structure	3

Question Number	Acceptable Answer	Reject	Mark
3(b)(i)	Stand alone marks Geometric / *E-Z* / cis-trans isomerism **(1)** Because isoeugenol has (two) different groups attached to each of the carbon atoms of the double bond ALLOW Because eugenol has two hydrogen atoms on one of the carbon atoms in the C=C **(1)** IGNORE References to the barrier to free rotation about the C=C	Optical isomerism	2

Question Number	Acceptable Answer	Reject	Mark
3(b)*(ii)	If no other mark is scored 'both eugenol and isoeugenol have eight peaks' scores 1 Candidates are only expected to interpret the spectra using knowledge of the (n+1) rule. **EITHER** The only (significant) difference is likely to be (in the peak areas / heights) due to the protons on the alkene chain **(1)** This mark may be awarded if the use of the alkene chain is indicated but not stated Both will have three sets of peaks due to the three sets of protons on the alkene chain **(1)** The alkene chain will give two doublets and a quintet in both isomers **(1)** In isoeugenol the doublets will have different peak areas / heights under the peaks / peak heights in ratio 1:3 whereas in eugenol the doublets will be the same height **(1)** **OR** Eugenol has areas / heights in the ratio 2:1:2:1:1:1:1:3 **(1)** and isoeugenol has peak areas / heights in the ratio 3:1:1:1:1:1:1:3 **(1)** The alkene chain will give two doublets and a quintet in both isomers **(1)** In isoeugenol the doublets will have different peak areas / heights under the peaks / peak heights in ratio 1:3 whereas in eugenol the doublets will be the same height **(1)** **OR** The only (significant) difference likely to be in the splitting pattern of the peaks due to the protons on the alkene chain **(1)** In eugenol the protons at the end of the alkene chain are in different environments so eugenol will have four sets of peaks whereas isoeugenol will have three sets of peaks **(1)**		4

3(b)*(ii) (cont)	In eugenol the alkene chain will give three doublets and a quintet **(1)** In isoeugenol the alkene chain will give two doublets and a quintet **(1)**		

Question Number	Acceptable Answer	Reject	Mark
3(b)(iii)	V_2O_5 oxidizes isoeugenol / alkene substituent (to the aldehyde & ketone) (and V(V) is reduced to a lower oxidation state) OR Explanation in terms of isoeugenol reducing V_2O_5 **(1)** H_2O_2 oxidizes vanadium back to the +5 oxidation state **(1)** Mechanism with H_2O_2 oxidizing V_2O_5 as the first step scores max 1 If no other mark is scored 'vanadium(V) is reduced then oxidized' scores 1 Ignore any reference to adsorption and desorption on the surface.	Just 'V_2O_5 oxidizes'	2

Question Number	Acceptable Answer	Reject	Mark
3(b)(iv)	Vanillin has an aldehyde group, suggesting a peak in the range 1740-1720 (cm^{-1}) whereas methyl vanillyl ketone has a ketone group suggesting a peak in the range 1700-1680 (cm^{-1}) (The peaks occur at different wavenumbers so the ketone peak could be seen) **(1)** These are general ranges and might overlap in the particular spectra OR Vanillin is an aromatic aldehyde OR Concentration of the ketone might be too small for the peak to be observed **(1)**		2

Question Number	Acceptable Answer	Reject	Mark
3(c)(i)	6 (moles of $S_2O_3^{2-}$ per mole CH_3O) **(1)** Stand alone mark In the sequence $ROCH_3 \equiv CH_3I \equiv IBr \equiv HIO_3 \equiv 3I_2 \equiv 6S_2O_3^{2-}$ **(1)**	Partial sequences	2

Question Number	Acceptable Answer	Reject	Mark
3(c)(ii)	Mr (vanillin) = 152 **(1)** **EITHER** % CH_3O in pure vanillin = 100 x 31/152 = 20.3947% **(1)** % purity of the vanillin = 100 x 20.09 / 20.3947 = 98.5058% **(1)** **OR** 20.09% weighs 31 So 100% weighs 100 x 31/20.09 = 154.31 So apparent molar mass = 154.31 **(1)** Therefore % purity is 152 x 100/154.31 = 98.5058% **(1)** **OR** Apparent mass CH_3O = 100 x 20.09/152 = 30.5368 **(1)** Therefore % purity is 100 x 30.5368 /31 = 98.5058% **(1)** Correct answer with no working scores 3 IGNORE SF except 1 SF		3

Total for Question 3 = 20 marks