Questions

Q1.

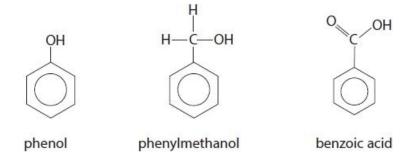
This is a question about the analysis of three aromatic substances with —OH groups.

Write the equation for the **complete** combustion of phenol. State symbols are not required.

(2)

Q2.

This is a question about the analysis of three aromatic substances with —OH groups.



When burned in air, these aromatic compounds undergo incomplete combustion.

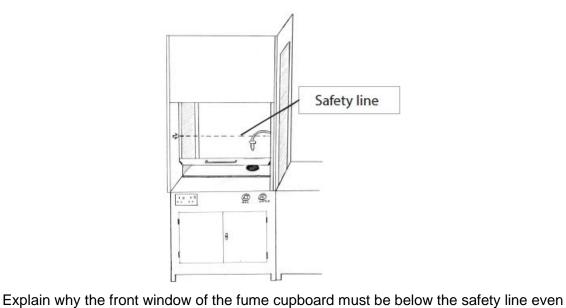
(i) Calculate the percentage composition by mass of carbon in both phenylmethanol and benzoic acid.

(3)

(ii) Give the expected observation when these aromatic compounds undergo incomplete combustion.	
	(1)
	i
(iii) Identify another type of organic compound which will also produce the same observation as in (ii).	
	(1)

(Total for question = 7 marks)

(iv) These combustion experiments must be carried out in a fume cupboard.



with the exhaust fan switched on.	(2)

Q3.

Antifebrin was the trade name for N-phenylethanamide which was used as a painkiller until paracetamol was discovered.

Paracetamol is structurally similar to Antifebrin, but has a hydroxy group attached directly to the benzene ring.

The bromination of the benzene ring in paracetamol occurs much more readily compared to the bromination of benzene.

Explain this increased reactivity.	
	(2)

This question is about aluminium chloride.

At high temperatures, aluminium chloride exists as AlCl₃ molecules.

(i) Draw a dot-and-cross diagram of an aluminium chloride molecule, AlCl₃. Show the outer shell electrons only.

(1)

(ii) Predict the shape of an AlCl₃ molecule and the Cl-Al-Cl bond angle.

Shape of AlCl₃
Cl−Al−Cl bond angle

(2)

(iii) Aluminium chloride is used as a catalyst in the alkylation of benzene.

Draw the mechanism for the reaction between benzene and chloromethane using aluminium chloride as the catalyst.

Include an equation for the formation of the electrophile, and any relevant curly arrows.

(4)

Q5.

This question is about the arenes, ethylbenzene, xylene, and phenol, which can be identified in wine samples using gas chromatography.



Ethylbenzene can be formed by the reaction of a chloroalkane with benzene, catalysed by aluminium chloride, AICI₃.

(i) Draw the **displayed** formula of the chloroalkane required for this reaction.

(1)

(ii) Draw the mechanism for this reaction.

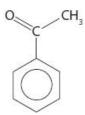
Include equations showing the role of the catalyst and how it is regenerated.

(5)

iii) Explain whether phenol is likely to be less or more reactive than benzene with the chloroalkane from (i).	3)

Q6.

Phenylethanone is an ingredient in many types of chewing gum.



One method for the production of phenylethanone involves the reaction of benzene with ethanoyl chloride, CH₃COCI.

(i) Write the equation for the formation of the electrophile, CH₃CO⁺, from ethanoyl chloride using the catalyst aluminium chloride.

(1)

(ii) Complete the diagram, including curly arrows, to show the mechanism for the reaction between this electrophile and benzene to produce phenylethanone. Include the regeneration of the catalyst.

(4)





Q7.

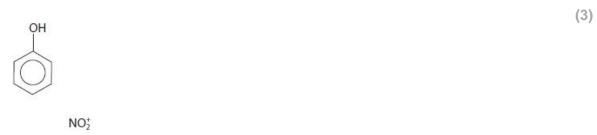
Phenol is a feedstock in the production of many organic molecules.



Phenol can be nitrated to produce 4-nitrophenol.



(i) The mechanisms of the nitration of phenol and of benzene are similar. Complete the diagram, using curly arrows, to show a possible mechanism for the reaction between the electrophile, NO_2^+ , and phenol to produce 4-nitrophenol.



(ii) What is the mass, in grams, of 4-nitrophenol produced from 0.94 g of phenol if the yield of this isomer is 15%?

		(1)
Α	0.14	
D	1.39	
	B C	A 0.14 B 0.21 C 0.68 D 1.39

(iii) Draw two structural isomers of 4-nitrophenol which have a benzene ring.

(1)

Q8.

Phenol is a feedstock in the production of many organic molecules.



Phenol reacts with bromine water.

(i) Complete the equation for the reaction of phenol with excess bromine water, using the **skeletal** formula of the organic product.



ii) Compare and contrast the bromination of phenol with the bromination of benzene.	
	(3)
	•

Q9.

This question is about the preparation and analysis of paracetamol.

$$HO \longrightarrow N-C-CH_3$$

Paracetamol may be prepared from phenol in three stages.

In Stage 1, phenol is nitrated using dilute nitric acid.

The nitration of benzene requires concentrated nitric acid at 55°C with a catalyst of concentrated sulfuric acid.

Both these reactions are electrophilic substitution.

(i)	Explain why phenol can be nitrated using milder conditions than benzene.	
		(2)
••••		

(ii) A mixture of 2-nitrophenol and 4-nitrophenol is produced in Stage 1. They are separated by steam distillation.

The boiling temperature of 2-nitrophenol is 215°C and that of 4-nitrophenol is 279°C. Explain, in terms of intermolecular forces, why 4-nitrophenol has a higher boiling temperature than 2-nitrophenol.

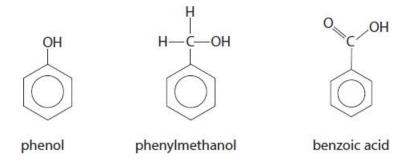
You may include a diagram in your answer.

(2)

 	•••••	 •••••

Q10.

This is a question about the analysis of three aromatic substances with —OH groups.



Spectroscopy is an effective means of distinguishing between molecules.

(i) Compare and contrast the infrared spectra of phenol, phenylmethanol and benzoic acid. Include relevant bonds and their wavenumber ranges using the Data Booklet.
(5

(ii) Predict the number of peaks present, and their chemical shifts, in the ¹³ C nuclear magnetic resonance (NMR) spectrum of phenylmethanol. Use the information in the Data Booklet to help you.	
	<i>(-)</i>
	(3)
H	
II C OII	
н—с—он	
$H \subset C \subset H$	
н	
phenylmethanol	
(iii) Give the formula of a fragment ion, with its <i>m/z</i> value, that you would expect to be present in the mass spectrum of benzoic acid but not in the mass spectrum of phenol or the mass spectrum of phenylmethanol.	
•	(6)
	(2)

Q11.

Explain the difference in the reactivity of bromine with benzene and with phenol.

Include the type of reaction, the products that form, and any conditions required. Mechanisms for the reactions are **not** required.

(6)

Q12.

Phenylethene, commonly known as styrene, is an important substance in the production of polystyrene which is used for some types of plastic packaging. Phenylethene can be made from benzene in a three-step synthesis.



Some of the following compounds can be used to make phenylethene from benzene.

Aluminium chloride	Chloroethane	Ethanal	Ethanol
Ethanoic acid	Ethanoyl chloride	Ethene	Ether
Hydrochloric acid, concentrated	Lithium tetrahydridoaluminate(III)	Phosphoric acid, concentrated	Sulfuric acid, concentrated

Selecting **only** from these compounds, devise a synthetic pathway for converting benzene into phenylethene, clearly identifying compounds **A** and **B** and stating the appropriate conditions for each step.

(5)

Mark Scheme

Q1.

Question Number	Answer	Additional Guidance	Mark
	 correct formula (phenol) (1) 	Example of equation $C_6H_5OH + 7O_2 \rightarrow 6CO_2 + 3H_2O$ Allow C_6H_6O	(2)
	 balanced equation (1) 	Do not award [O] Ignore state symbols even if incorrect	

Q2.

Question Number	Answer	Additional Guidance	Mark
(i)	 mass of carbon in both substances (1) molar masses of both substances (1) calculation of percentages by mass of carbon (1) 	Example of calculation (12 x 7 =) 84 Phenylmethanol 108 and Benzoic acid 122 Phenylmethanol (84 ÷ 108) x100 = 78%/ 77.8%/ 77.78% / 77.7% Benzoic acid (84 ÷ 122) x 100 = 68.85%/ 68.9%/69% Ignore sf except 1 Allow TE on incorrect Mr values Allow (2) for 11.1% and 9.8% calculated using 12 not 84 Allow 'rescue' (1) for one substance completely correct	(3)

Question Number	Answer	Additional Guidance	Mark
(ii)	A description that makes reference to:		(1)
	black smoke	Allow Black fumes/soot/(yellow) smoky flame / grey smoke	
		Ignore carbon particulates	
		Do not award carbon monoxide/yellow flame	

Question Number	Answer	Additional Guidance	Mark
(iii)	An answer that makes reference to • Alkenes	Allow Cycloalkenes/cycloalkanes/alkynes/ carbon-carbon double bonds Ignore Ethene/named alkenes/named alkynes Do not award benzene/arenes	(1)

Question Number	Answer	Additional Guidance	Mark
(iv)	An explanation that makes reference to (window) above the safety line means the exhaust system is not strong enough to draw in the fumes (1) so the toxic fumes will escape (into the laboratory) (1)	Allow reverse argument Allow reference to exhaust/fan not able to prevent gas escaping Allow poisonous/harmful/irritant/ carbon monoxide/soot for 'toxic fumes' Ignore reference to protection from	(2)

Q3.

Question Number	Answer	Additional Guidance	Mark
	An explanation that makes reference to the following points: • lone pair (of electrons) from the oxygen and will interact with the delocalised ring of electrons / increase the (pi/n) electron density of the benzene ring (1)	Allow reference to the lone pair (of electrons) from the nitrogen Ignore activation of ring Do not award charge density	(2)
	which increases the reactivity toward electrophiles (such as bromine)/ which means that the bromine is more easily polarised (1)	Allow Br ⁺ /Br ⁵⁺ for electrophile Allow reference to benzene as being a stronger nucleophile	
		Do not award references to electrophilic addition	50

Q4.

Question Number	Answer	Additional Guidance	Mark
(i)	dot-and-cross diagram	Example of diagram Allow electrons in overlapping circles Allow all dots / all crosses Ignore inner shell electrons, even if incorrect Ignore lines as bonds e.g. Do not award diagram with lone pair on Al	(1)

Question Number	Answer		Additional Guidance	Mark
(ii)	An answer that makes reference to the following points:	-	Mark independently	(2)
		(1)	Both words needed	
	shape – trigonal planar		Allow triangular for trigonal – but not just tri	
	• bond angle - 120°	(1)	Allow marks for labelled diagram	
			Note	
			If shape is pyramidal, no mark for M1 but allow (1) for 107°	
			No TE for any other shape	

Question Number	Answer	8	Additional Guidance	Mark
(iii)]	Example of mechanism	(4)
			$CH_3Cl + AlCl_3 \rightarrow CH_3^+ + [AlCl_4]^-$	
			CH₃	
			СH ₃ (+ H ¹)	
	equation for the	(1)	Allow AlCl ₄ ⁻ / ⁵⁺ CH ₃ -AlCl ₄ ⁵⁻	
	formation of the electrophile	(1)	Allow curly arrow from anywhere within the hexagon	
	curly arrow from on or within the circle to CH ₃ ⁺	1	Allow curly arrow to any part of CH ₃ +, including the + charge Do not award curly arrow from outside the hexagon	
		1	Allow dotted / dashed lines for horseshoe Do not award dotted bonds to H and CH3 unless clearly part of a 3D structure	
	structure of intermediate including charge with some part of the charge within the horseshoe and horseshoe covering at least 3 carbon atoms and facing the tetrahedral carbon	(1)	Ignore any involvement of AlCl ₄ ⁻ in the final step /HCl Note Correct Kekulé structures score full marks	
	curly arrow from C- H bond to anywhere in the hexagon reforming the delocalised structure			

Q5.

Question Number	Answer	Additional Guidance	Mark
(i)	H—C—C—H H—CI	Do not award skeletal or structural formulae	(1)

Question Number	Answer	Additional Guidance	Mark
(ii)	M1 equation to show formation of electrophile	Example of mechanism Penalise incorrect halogenoalkane in (a)(i) only $CH_3CH_2CI + AICI_3 \rightarrow CH_3CH_2^+ + AICI_4^-$ Ignore any curly arrows given in the equation	(5)
	• M2 curly arrow from anywhere on the central ring to positive carbon (1)	Allow curly arrow from anywhere within the hexagon Do not award if curly arrow to CH_3 carbon in $CH_3CH_2^+$ Do not award if curly arrow to $C_2H_5^+$ Horseshoe facing the tetrahedral carbon and covering at least three carbon atoms Some part of the positive charge in the horseshoe	
	M3 structure of intermediate (1)	Do not award dotted lines unless clearly part of a 3D structure	
	M4 curly arrow from C-H bond to reform the ring (1)	AlCl ₄ − + H ₊ → AlCl ₃ + HCl Ignore regeneration step if part of the mechanism Mechanism CH ₃ CH ₂ + CH ₂ CH ₃ (+H')	
	M5 equation showing regeneration of catalyst (1)	Allow TE from (a)(i)	

Question Number	Answer	Additional Guidance	Mark
(iii)	An explanation that makes reference to the following points:		(3)
	Phenol is likely to be more reactive because		
	M1 lone pair on oxygen (atom of –OH group) delocalises / is incorporated into the (benzene) ring / donated to the ring (1)		
	M2 which increases the electron density (of the ring) (1)	Do not award M2 if mention of "charge density" / "electronegativity" Ignore references to "the ring becomes more negative"	
	M3 making the ring / phenol more susceptible to electrophilic attack (1)	Award "making the ring more nucleophilic" / "making the ring more susceptible to attack by a positive ion"	
		Ignore references to "activation of the ring"	

Q6.

Question Number	Answer	Additional Guidance	Mark
(i)	CH₃COCI + AlCI₃ → CH₃CO+ + AlCI₄-	Accept use of FeCl ₃ /Fe +Cl ₂	(1)
		Allow displayed formulae Do not award C₂H₃OCl	
		Ignore state symbols even if incorrect	

Question Number	Answer	Additional Guidance	Mark
(ii)	 electron pair movement from ring to electrophile (1) formula of intermediate ion (1) 	CH ₃ H ⁺ + AICI ₊ → AICI ₃ + HCI Do not award curly arrow that ends at the CH ₃ Allow arrow starting anywhere within the hexagon 'Horseshoe' to cover at least three carbon atoms and face the tetrahedral carbon and with some part of the plus sign inside 'horseshoe' Allow Kekulé diagrams Do not award dotted bonds unless part of a 3D structure	(4)
	curly arrow from C-H bond to reform delocalised ring (1)		
	correct product and equation to show regeneration of catalyst and HCl (1)	Could be shown in reaction mechanism Ignore curly arrows	

Q7.

Question	Acceptable Answer	Additional Guidance	Mark
(i)	An answer that makes reference to • Electron pair movement from ring to electrophile (1)	Allow arrow that starts from anywhere within the hexagon but it must go to the nitrogen of the ion	(3)
	Formula of intermediate ion (1)	'Horseshoe' to cover at least three carbon atoms, facing the tetrahedral carbon and part of the + sign to be inside the 'horseshoe' Do not award '+' charge on the tetrahedral carbon Do not award dotted bonds unless part of a 3D structure	
	Curly arrow from C-H bond to reform delocalised ring and correct final structure with H ⁺ also formed (1)	Curly arrow to go from the bond to anywhere inside the ring Accept the drawing of HSO ₄ ⁻ to remove the H from the ring as long as H ₂ SO ₄ is given as the product instead of H ⁺ Exemplar mechanism	
		Do not penalise attachment of OH/NO ₂ to benzene ring Penalise incorrect product: 1 mark	

Question Number	Acceptable Answer	Mark
(ii)	The only correct answer is B	(1)
	A is incorrect because this is 15% of the mass of the starting material	
	${m c}$ is incorrect because this is the percentage of the starting mass over the max mass of product	
	D is incorrect because this is 100% yield and not 15%	

Question Number			Additional Guidance	Mark
(iii)	OH NO ₂ and	OH NO ₂	Ignore connectivity of OH/NO ₂	(1)

Q8.

Question Number		Additional Guidance	Mark
(i)	OH → Br → Br → SHBr	Ignore state symbols even if incorrect	(2)
	 Structure of 2,4,6-tribromophenol (1) 	Do not award C ₆ H ₃ OBr ₃	
	 Balanced equation (1) 	M2 dependent on M1	

Question Number	Acceptable Answer	Additional Guidance	Mark
(ii)	An answer that makes reference to the following:	Ignore comments of ease of reaction	(3)
	Similarity • Both electrophilic substitution (1)	Should be stated clearly as a similarity	
	Any two from: Contrast No need of a halogen carrier with phenol (1)	Accept reverse argument Allow Fe/FeBr ₃ /AlBr ₃ with benzene Do not award just 'catalyst'	
	oxygen's lone pair of electrons interacts with the benzene ring of delocalised electrons so electrophilic attack more likely (1)	Allow reference to OH group Allow 'bromine' for 'electrophilic' Do not award for nucleophilic attack	
	Tri-substitution of phenol compared to mono for benzene (1)	Allow "multiple-" for "tri-"	
	Bromination of phenol requires bromine in aqueous solution but benzene requires liquid bromine (1)		
	Bromination of phenol requires room temperature but benzene requires heating (under reflux) / reflux (1)		

Q9.

Question Number	Answer	Additional Guidance	Mark
(i)	An explanation that makes reference to the following points: the electron density of the (benzene) ring is greater in phenol (than in benzene) because the lone pair (of electrons) on oxygen and overlaps with the pi cloud / delocalised electrons / delocalised system	(1) Allow lone pair (of electrons) on oxygen feeds into / donates into / interacts with the delocalised electrons / system Ignore electron pushing effect of OH	(2)

Question Number	Answer		Additional Guidance	Mark
(ii)	An explanation that makes reference to the following points:			(2)
	they both form hydrogen bonds	(1)	Allow M1 and M2 shown in diagrams Ignore reference to other specific types of intermolecular forces	
	in 4-nitrophenol the hydrogen bonds join molecules in a straight chain / at both ends / at opposite ends (of the molecule so are stronger) or	(1)	Allow 4-nitrophenol forms stronger intermolecular hydrogen bonds / forces / interactions	
	2-nitrophenol forms intramolecular hydrogen bonds / forces / interactions (so fewer intermolecular hydrogen bonds)	(2)	Allow in 2-nitrophenol the hydrogen bonds join 2 molecules together / form a dimer (so there are fewer / weaker hydrogen bonds)	
			Allow in 2-nitrophenol the hydrogen bonds are on the same side (of the molecule)	

Q10.

Question Number	Answer	Additional Guidance	Mark
Number (i)	An answer that makes reference to • (M1) (similarity) all have arene C-H absorptions Either 3030 (cm ⁻¹) or 750 and/or 700 (cm ⁻¹) (1) • (M2) only phenol and phenylmethanol have O-H 3750 - 3200 (cm ⁻¹) (1) • (M3) only benzoic acid has O-H 3300 - 2500 (cm ⁻¹) (1) • (M4) only benzoic acid has C=O 1700	Bond and wavenumber ranges necessary for each mark Do not award 880/830/780 (cm ⁻¹) Do not award –OH / C–OH by penalising once only in M2 and M3	(5)
	- 1680 (cm ⁻¹) (1) • (M5) only phenylmethanol has alkane C–H absorptions either 2962 - 2853 (cm ⁻¹) or 1485 - 1365 (cm ⁻¹) (1)	All 5 correct bonds with no wavenumber ranges scores (3) 4 correct etc scores (2) and 3 correct etc scores (1) All 5 correct wavenumber ranges with no bonds or incorrect bonds scores (3) 4 correct etc scores (2) and 3 correct etc scores (1) Penalise any additional peaks once only Ignore references to different fingerprint regions	

Question Number	Answer	Additional Guidance	Mark
(ii)	An answer that makes reference to	Allow any range within the stated ranges Penalise single values as opposed to ranges once only	(3)
	• five peaks (in the ¹³ C NMR spectrum) (1)	Accept annotations on diagram	
	(four) aromatic peaks within the chemical shift range of 165 - 105 (ppm) (1)		
	(one) peak (for the C-OH) within the chemical shift range of 75 - 55 (ppm) (1)	Penalise additional peaks once only when three or more types of peak are stated	

Question Number	Answer	Additional Guidance	Mark
(iii)	An answer that makes reference to	Example of a suitable formula	(2)
	suitable formula of fragment ion (1)	C ₆ H ₅ COO+ or C ₆ H ₅ CO+ Do not award C ₇ H ₅ O ₂ + or C ₇ H ₅ O+	
	• matching <i>m/z</i> value (1)	m/z = 121 or 105 Allow COOH* (1) Do not award bond to the fragment, e.g. —COOH* m/z = 45 (1) No TE on incorrect fragment ions such as CH3*	

Q11.

Question Number	Acceptable Answers			Additional Guidance	Mark
*	This question assesses a student's ability to show a coherent and logically structured answer with linkages and fully-sustained reasoning. Marks are awarded for indicative content and for how the answer is structured and shows lines of reasoning. The following table shows how the marks should be awarded for indicative content.			Guidance on how the mark scheme should be applied: The mark for indicative content should be added to the mark for lines of reasoning. For example, an answer with five indicative marking points that	(6)
	Number of indicative marking points seen in answer 6 5-4 3-2 1 0 The following tab structure and lines		ks should be awarded for	is partially structured with some linkages and lines of reasoning scores 5 marks (3 marks for indicative content and 2 marks for partial structure and some linkages and lines of reasoning). If there are no linkages between points, the same five indicative	
				marking points would yield an overall score of 3 marks (3 marks for indicative content and no marks for linkages).	

Answer shows a coherent and logical structure with linkages and fully sustained lines of reasoning demonstrated throughout.	Number of marks awarded for structure of answer and sustained line of reasoning	In general it would be expected that 5 or 6 indicative points would get 2 reasoning marks, and 3 or 4 indicative points would get 1 mark for reasoning, and 0, 1 or 2 indicative points would score zero marks for reasoning.
Answer is partially structured with some linkages and lines of reasoning.	1	General points to note If there is any incorrect chemistry, deduct mark(s) from the reasoning. If
Answer has no linkages between points and is unstructured.	0	no reasoning mark(s) awarded do not deduct mark(s).

Comment: Look for the indicative marking points first, then consider the mark for structure of answer and sustained line of reasoning

Indicative content

IP1 Type of reaction

Both reactions are (examples of) electrophilic substitution

· IP2 Products

Benzene forms bromobenzene and phenol forms 2,4,6-tribromophenol

IP3 Comparison of reactivity

Benzene is less reactive (than phenol) / phenol is more reactive (than benzene)

IP4 Conditions

Benzene requires (a catalyst of) FeBr3 and phenol does not require a catalyst / can react with just bromine water

IP5 Lone pair

(Phenol is more susceptible to electrophilic attack) because the lone pair on the oxygen (atom in phenol) delocalises into the ring / π system

IP6 Electron density

Increasing the electron density of the ring / π system

If names and formulae are given, both must be correct

Do not award addition-elimination for substitution

Allow these products shown as structures in equations, even if equations are not fully correct Allow any feasible dibromophenol / tribromophenol Ignore dibromobenzene / tribromobenzene

Allow Fe / FeCl₃ / AlBr₃ / AlCl₃ / Lewis Acid catalyst Allow Friedel-Crafts catalyst / halogen carrier Can be shown in equation Allow phenol reacts at room temperature Ignore reference to heat / mechani

Ignore reference to heat / mechanism Allow IP4 if stated that only benzene requires a catalyst

Allow lone pair on oxygen is donated into the ring Allow OH for oxygen

Allow activates the ring Do not award increases the electronegativity / charge density of the ring Penalise omission of 'the ring / π system' once only in IP5 and 6

Q12.

Question Number	Acceptable Answer	Additional Guidance	Mark
	An answer that makes reference to the following: synthetic pathway that consists of: (Step 1) • (acylation of benzene) using ethanoyl chloride (1)	The compounds used can be stated or given within equations.	(5)
	use of aluminium chloride (and heat) (1)	Only award if part of a Friedel-Crafts reaction	
	(Step 2) • (reduction of) A with LiAlH ₄ in ether (dry) (1)	Only award if given to reduce an aromatic carbonyl or carboxylic acid	
	(Step 3) • (dehydration of) B with (conc.) phosphoric acid/H ₃ PO ₄ (1) (Intermediates) • identification of	Allow (conc.) sulfuric acid/ H ₂ SO ₄ Only award if given to dehydrate an aromatic alcohol	
	• Identification of A as phenylethanone and B as (1-)phenylethanol	Accept formulae for names, but if both given, then both must be correct This also applies to reagents	