H

NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME								
CLASS	1	9			TUTOR'S NAME			
CENTRE NUMBER	S					INDEX NUMBER		

CHEMISTRY

9729/02

Paper 2 Structured

31 August 2020

2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, index number, name and class on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	/25
2	/10
3	/14
4	/11
5	/15
Total	/75

This document consists of **23** printed pages and **1** blank page.

[Turn over

Answer **all** questions in the spaces provided.

1 Heavy metals can leach into water from taps inside older buildings due to the stagnation of water in tanks and water pipes inside the buildings.

A study of the tap water from a building showed that it contained small amounts of lead(II) ions, when consumed past a certain limit, have toxicological effects on human beings.

World Health Organisation (WHO) issues guidelines on the limits of various heavy metal ions in drinkable water. The WHO limit for lead(II) ions concentration is 5.0×10^{-8} mol dm^{-3}.

An environment agency wants to determine if the tap water from the building is within the WHO limits. Through a precipitation titration, the concentration of Pb^{2+} in the water sample can be determined.

You may find the following information useful:

- A titration was conducted where 1.00 dm^3 of sample water was titrated against aqueous sodium hydroxide.
- 1.00×10^{-5} mol of iron(II) nitrate was used as the indicator.
- At the end-point, the solid was filtered and the mass of lead(II) hydroxide precipitate was found to be 1.20×10^{-5} g.
- The water sample only contains lead ions as contaminants.

Precipitate	M_r	Colour of precipitate	value of K_{sp}	solubility / mol dm^{-3}
$Pb(OH)_2$	241.2	white	1.4×10^{-20}	**X**
$Fe(OH)_2$	89.8	green	4.9×10^{-17}	2.30×10^{-6}

(a) **(i)** Explain the term *solubility*.

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.....[1]

(ii) Determine the solubility of lead(II) hydroxide, **X** in mol dm^{-3}.

[1]

(iii) Using the data given, state what you would observe

at the beginning of the titration .....

at the end-point of the titration ..... [2]

(iv) Determine the amount of lead(II) hydroxide precipitated from the water sample.

[1]

(v) Determine the maximum concentration of Pb^{2+} left in the mixture at the end-point.

[2]

(vi) Hence, using your answers in **(iv)** and **(v)**, determine the initial concentration of Pb^{2+} in the water sample and deduce if the concentration is within the WHO limit.

[2]

(vii) To deduce whether Fe^{2+} is a good indicator in this titration, most of the lead(II) ions needs to be precipitated at the end-point.

Show that more than 90% of the lead(II) ions in the water sample has been precipitated when the end-point was reached.

[1]

(viii) Suggest another reason why Fe^{2+} ions are a good indicator for this titration.

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.....[1]

(ix) When excess sodium hydroxide was added after the end-point, it was observed that the white precipitate dissolved.
With the aid of relevant equations, explain the observations.

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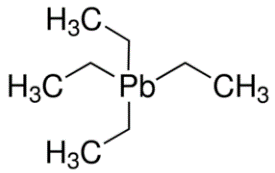
.....[2]

(b) Tetraethyl lead (TEL), an organometallic compound was the main anti-knock agent used in cars in the past. It is a dense, viscous (slow-flowing) liquid which is highly lipophilic - soluble in non-polar solvents such as petrol and hexane.



Tetraethyl lead (TEL)

(i) With reference to the structure and bonding of TEL, suggest a reason for its viscosity.

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.....[2]

(ii) TEL was synthesised industrially by heating a mixture of chloroethane on a powdered metal alloy of lead and sodium atoms according to the following equation.

$$4Na + Pb + 4CH_3CH_2Cl \rightarrow (CH_3CH_2)_4Pb + 4NaCl$$

The hypothetical 2-step mechanism involves:

Step 1: Homolytic cleavage of the carbon-chlorine bond in chloroethane to form an ethyl radical. Chlorine radical immediately reacts with sodium atom to form sodium chloride.

Step 2: Four ethyl radicals react with a lead atom from the alloy to form a TEL molecule.

Use the information given above to suggest a simple mechanism for the formation of a TEL molecule, showing clearly the movement of electrons by curly arrows.

[2]

(iii) Deduce the rate determining step.

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.....[1]

(c) Lead(II) ethanoate, $Pb(CH_3COO)_2$, also known as *sugar of lead* is a white crystalline solid which is soluble in water and has a sweet taste. Ancient Romans used sweeteners that contained lead(II) ethanoate to sweeten wine or preserve fruit. Lead(II) ethanoate is no longer used in the production of sweeteners because of its recognised toxicity.

Draw simple diagrams to show how a water molecule can be attached to a lead(II) cation, and to an ethanoate anion. Label each diagram to show the type of interaction involved.

Pb^{2+} cation	CH_3COO^- anion

[3]

[Turn Over

(d) Lead(II) carbonate thermally decomposes according to the equation.

$$PbCO_3(s) \rightarrow PbO(s) + CO_2(g) \qquad \Delta H_{decomp} < 0$$

Some enthalpy changes are listed below.

Enthalpy change of formation of $PbCO_3(s)$	=	–532 kJ mol^{-1}
Enthalpy change of atomisation of lead	=	+195 kJ mol^{-1}
Enthalpy change of combustion of carbon	=	–394 kJ mol^{-1}
Lattice energy of lead(II) oxide	=	–3520 kJ mol^{-1}
First electron affinity of oxygen	=	–141 kJ mol^{-1}
Second electron affinity of oxygen	=	+798 kJ mol^{-1}

By using data in this question and relevant data in the *Data Booklet*, construct a fully-labelled energy level diagram to determine the enthalpy change of decomposition of lead(II) carbonate.

Energy / kJ mol^{-1}

[4]

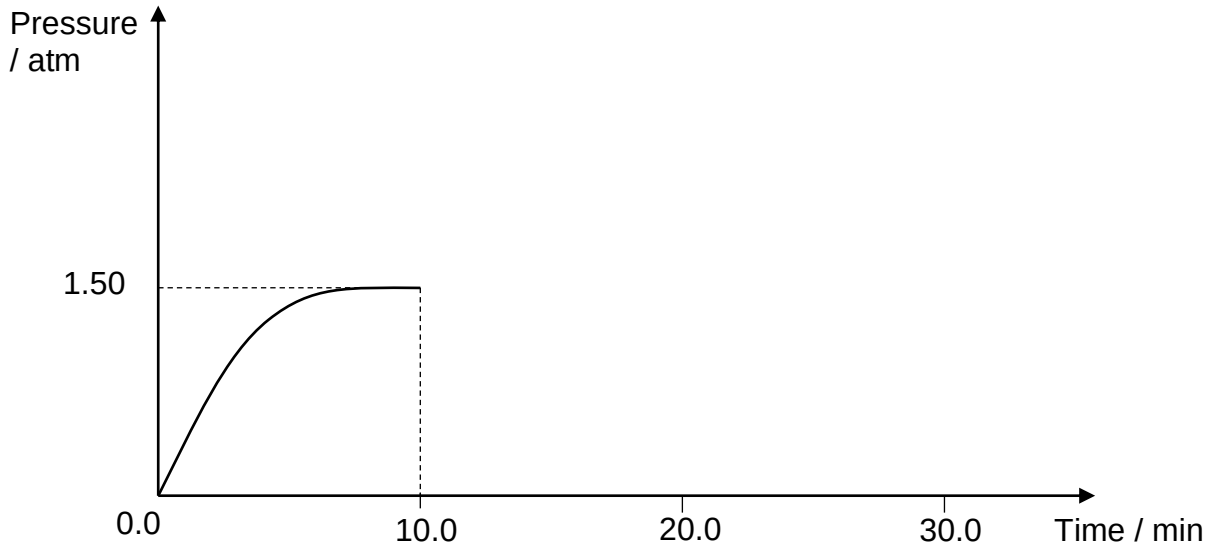
[Total: 25]

Question 2 starts on the next page.

2 When heated in a 5.0 dm^3 closed vessel at 450 °C, a 50.0 g sample of calcium carbonate decomposes according to the following equation:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g) \qquad \Delta H > 0$$

The pressure changes in the vessel are shown in the following graph:



(a) Calculate the K_c of the reaction at 450 °C.

[2]

(b) Calculate the percentage change in mass of solid at 10.0 min after equilibrium was reached.

[1]

(c) At time = 10.0 min, the pressure of CO_2 was increased to 2.00 atm. Equilibrium was achieved again at 20.0 min at the same temperature.

Sketch and label the pressure changes that occurred from 10.0 min to 20.0 min. [1]

(d) At time = 20.0 min, the temperature was decreased to 200 °C. A new equilibrium was achieved at 30.0 min.

Sketch the pressure changes that occurred from 20.0 min to 30 min. Explain your answer below.

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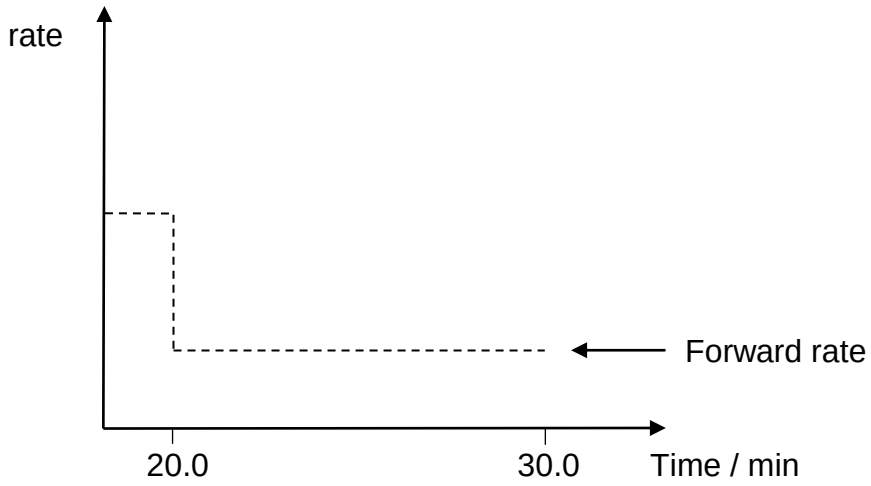
.....[3]

(e) When dynamic equilibrium is reached, the forward rate will be equal to the backward rate.

The graph below shows the change in **forward rate** (shown by dotted line - - - - -) of the decomposition reaction when temperature was decreased at 20.0 min.

Sketch the change in the backward rate of the reaction from 20.0 min to 30.0 min. Use a smooth line (——) to represent the backward rate on the graph.

Explain your answer below.



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[Total: 10]

3(a) There are three types of atomic radii listed in the *Data Booklet*: metallic, covalent and van der Waals.

(i) Explain what is meant by 'covalent radius of chlorine'.

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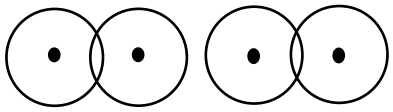
(ii) The diagram below represents two chlorine molecules. Label on the diagram the covalent radius **and** van der Waals radius of chlorine.



Legend:  represents a chlorine atom

d

[1]

(iii) The atomic radius of argon is described in the *Data Booklet* as the van der Waals radius. Suggest, with a reason, how the van der Waals radius of chlorine might compare with the van der Waals radius of argon.

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.....[1]

(iv) Suggest why argon does not have a covalent radius.

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.....[1]

(b) **X**, **Y** and **Z** are elements in Period 3. Data about the reactions of the oxides of **X**, **Y** and **Z** are given in the table below.

Reaction	Reagent added to oxide	Observation
1	HCl(aq)	Only oxide of **X** dissolves.
2	NaOH(aq)	Only oxides of **X** and **Z** dissolve.
3	$H_2O(l)$	Oxides **X** and **Y** do not dissolve. Green solution obtained when Universal Indicator is added.

(i) Based on the observation for each reaction, complete the following blanks by stating all the possible identities of the relevant element(s).

Reaction Deduction

1 **X** can be ……

2 **X** and **Z** can be ……

3 **X** and **Y** can be ……

[3]

(ii) Identify **X** and **Y**, and hence explain the observation for reaction 3.

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(c) The chlorides of the elements, sodium to phosphorus, dissolve or react with water.

(i) In the table below, state the variation in pH of the solutions obtained when one mole of each of these chlorides is separately added to 1 dm^3 of water.

	NaCl	$MgCl_2$	$AlCl_3$	PCl_5
pH of a 1 mol dm^{-3} solution				

[1]

(ii) Explain the pH of the resultant solutions when $MgCl_2$ and PCl_5 are added to excess water separately. Support your answer with relevant equations, showing state symbols.

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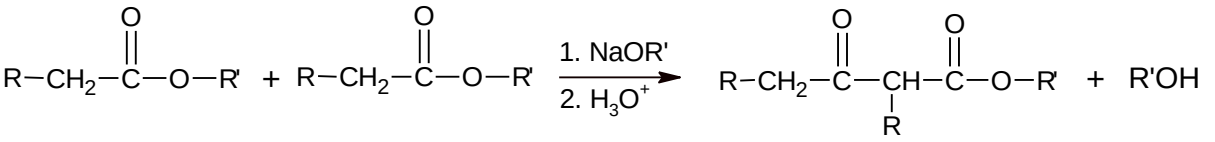
[Total: 14]

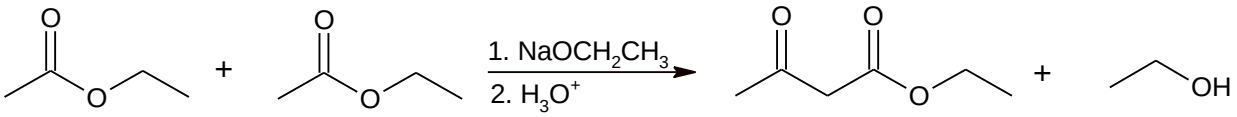
Question 4 starts on the next page.

4 The Claisen condensation occurs between two esters in the presence of a strong base to produce a keto ester and an alcohol.



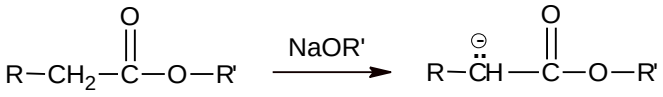
ester 1 ester 2 keto ester alcohol

An example of this reaction involving two ethyl ethanoate, with sodium ethoxide as the base, is shown below.



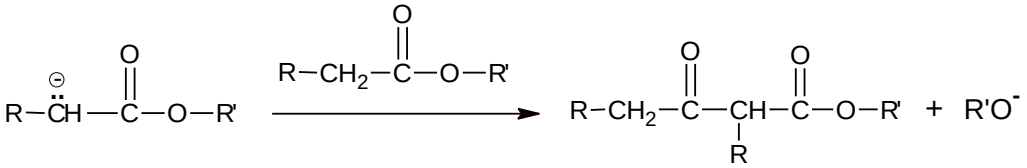
(a) For this reaction to occur, at least one of the reactants must have an α-hydrogen atom. The α-hydrogen atom is the hydrogen atom attached to the first carbon atom beside the carbonyl carbon atom. In the first step, this α-hydrogen atom is removed by a strong base, such as an alkoxide, resulting in the formation of an enolate anion.

step I



enolate anion

step II



enolate anion keto ester

(i) Suggest a reason why the α-hydrogen atom of the ester is acidic.

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[Turn Over

(ii) NaOH(aq) is not used as a strong base in step I to remove the α-hydrogen atom because it will react with the ester instead.

Explain how NaOH reacts with the ester.

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.....[1]

(iii) State the type of reaction between the ester and the enolate anion in the second step.

.....[1]

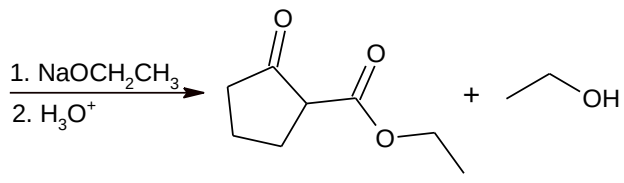
(iv) When two different esters are used as reactants in the Claisen condensation, a mixture of four different keto esters can be formed.

Suggest the structures of three possible keto esters produced when a mixture of ethyl ethanoate, $CH_3CO_2CH_2CH_3$, and ethyl propanoate, $CH_3CH_2CO_2CH_2CH_3$, is used.

[2]

(v) Suggest the structure of compound **A**.

A

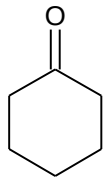


[1]

[Turn Over

(b) The Claisen condensation can also occur between a ketone and an ester. An α-hydrogen atom in the ketone is first removed by the strong base, and the subsequent reaction with the ester can then take place with the same mechanism described in part **(a)**.

Cyclohexanone reacts with one mole of compound **P** to produce compound **Q** and ethanol in the Claisen condensation.



cyclohexanone

$$+ \quad \mathbf{P} \xrightarrow[2.\ H_3O^+]{1.\ NaOCH_2CH_3} \mathbf{Q}\ (C_{10}H_{14}O_4) \quad + \ CH_3CH_2OH$$

Upon heating compound **Q** with dilute sulfuric acid, compound **R** ($C_8H_{10}O_4$) is obtained. Compound **R** gives an orange precipitate with 2,4-DNPH, but no silver mirror was observed with Tollen's reagent. When compound **R** is heated with acidified $K_2Cr_2O_7$, the orange solution remained. Effervescence was observed when solid Na_2CO_3 was added to compound **R**.

Suggest the structures of **P**, **Q** and **R** and explain the chemistry of the reactions occurred.

P

Q

R

[Turn Over

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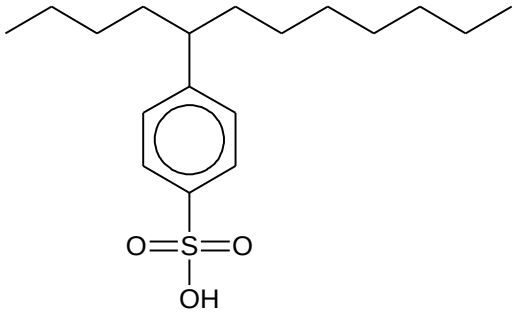
.....[5]

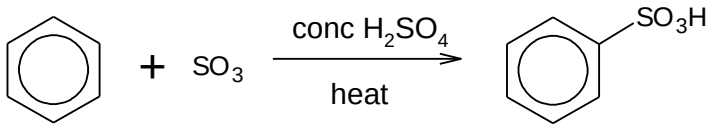
[Total: 11]

5 Alkyl benzenesulfonic acid is a class of organic compounds used in detergent formulations.



alkyl benzenesulfonic acid

(a) In the presence of sulfur trioxide, concentrated sulfuric acid and heat, benzene undergoes sulfonation to produce benzenesulfonic acid.



benzene benzenesulfonic acid

The mechanism of this reaction is similar to that of the nitration of benzene. Concentrated sulfuric acid is used in an initial step to generate the electrophile.

(i) State and explain the role of concentrated sulfuric acid in the initial step to generate the electrophile.

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.....[1]

(ii) Suggest a mechanism for the reaction between benzene and sulfur trioxide. Indicate clearly any intermediates that may be formed. Show all charges and relevant lone pairs and the movement of electron pairs by using curly arrows.

[3]

(iii) Describe how the structure and bonding of the six-membered ring intermediate of the mechanism in **(ii)** differ from those in benzene. In your answer refer to the hybridisation, the π bonding and the bond angles in the ring system.

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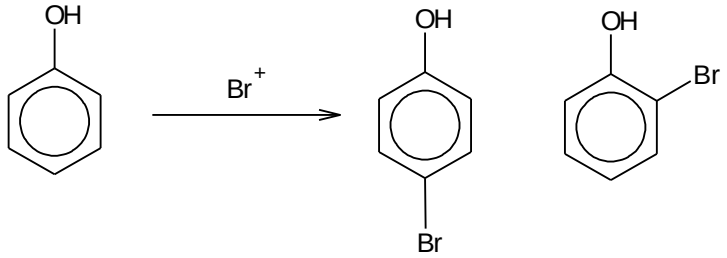
(b) In electrophilic substitution of *ortho*-, *para*-directors, a mixture of products slightly favouring *para* over *ortho* with a 60: 40 ratio is usually obtained.



para *ortho*

60 : 40

(i) Suggest why the *ortho*- products are less favoured over the *para*- products.

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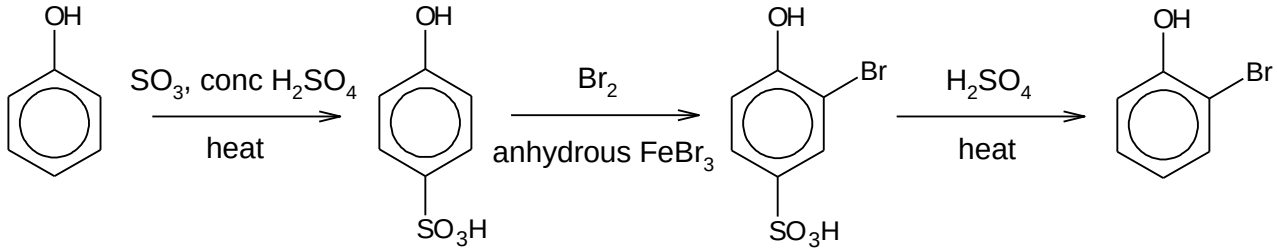
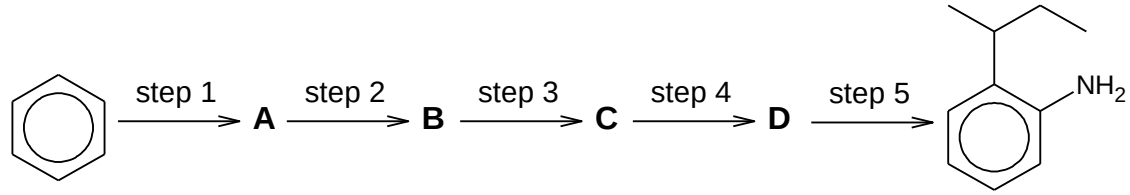
One way to get the *ortho*- products exclusively is to use the sulfonyl as a "blocking group". The *para*- position is first blocked with SO_3H, followed by performing the desired reaction at the *ortho*- position (e.g. bromination). As sulfonation is reversible, heating with strong acid will remove SO_3H, giving the *ortho*- substituted product.



(ii) 2-(butan-2-yl)aniline can be formed via a 5-step synthesis with benzene as the starting material. Draw the structures of the reaction intermediates and state the reagents and conditions for each step. One of your steps should include the use of sulfonyl as a "blocking group".



benzene 2-(butan-2-yl)aniline

A	**B**
C	**D**

Step 1 .....

Step 2 .....

Step 3 .....

Step 4 .....

Step 5 ..... [4]

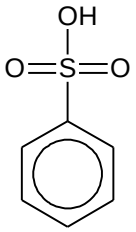
(iii) 2-(butan-2-yl)aniline exists as two stereoisomers.

Draw 3-dimensional diagrams to show the stereoisomers of 2-(butan-2-yl)aniline and state the type of stereoisomerism shown.

type of stereoisomerism.....

[1]

(c) Explain why benzenesulfonic acid is more acidic than ethanol.



benzenesulfonic acid

CH_3CH_2OH

ethanol

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[Total: 15]

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