HWA CHONG INSTITUTION
C2 Preliminary Examinations
Higher 2

CANDIDATE NAME		**CT GROUP**	**14S**
CENTRE NUMBER		**INDEX NUMBER**	

CHEMISTRY

9647/03

Paper 3 Free Response

17 September 2015

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet

INSTRUCTIONS TO CANDIDATES

Write your name and class on all the work you hand in.

Write in dark blue or black pen.

You may use a soft pencil for any diagrams, graphs or rough working.

Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.

Begin each question on a **new** piece of paper.

A Data Booklet is provided.

You are reminded of the need for good English and clear presentation in your answers.

The number of marks is given in brackets [ ] at the end of each question or part question.

At the end of the examination, fasten all your work securely together.

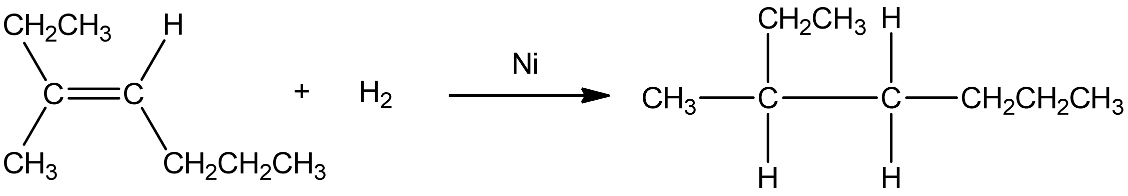
Circle the **question numbers** for the questions that you have attempted on the **cover page** provided.

This document consists of **11** printed pages.

Answer any **four** questions.

1 Margarine was first created in 1869 as a response to a challenge from the French emperor Louis Napoleon III to make a cheap substitute for butter for the army and lower classes. Today, margarine is made by passing hydrogen gas over unsaturated vegetable oils in the presence of a nickel catalyst.

A representative reaction may be written as given below:

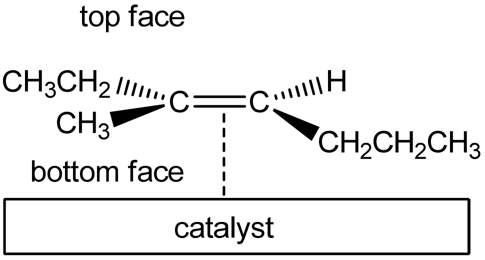


(a) **(i)** State the type of catalysis that this hydrogenation reaction undergoes. [1]

(ii) State the type of isomerism that the product displays and draw diagrams to illustrate the isomerism. [2]

(iii) In this type of catalysis, one side (bottom face) of the planar alkene molecule is adsorbed to the surface of the catalyst. Both the hydrogen atoms will be added to the same side of the alkene which is adsorbed to the catalyst and not the other side (top face).

The diagram below illustrates how the alkene molecule may be adsorbed to the surface of the catalyst.



In the light of this information and your answer to **(a)(ii)**, explain why the product mixture does not rotate plane-polarised light. The use of a diagram may aid in the clarity of your explanation. [3]

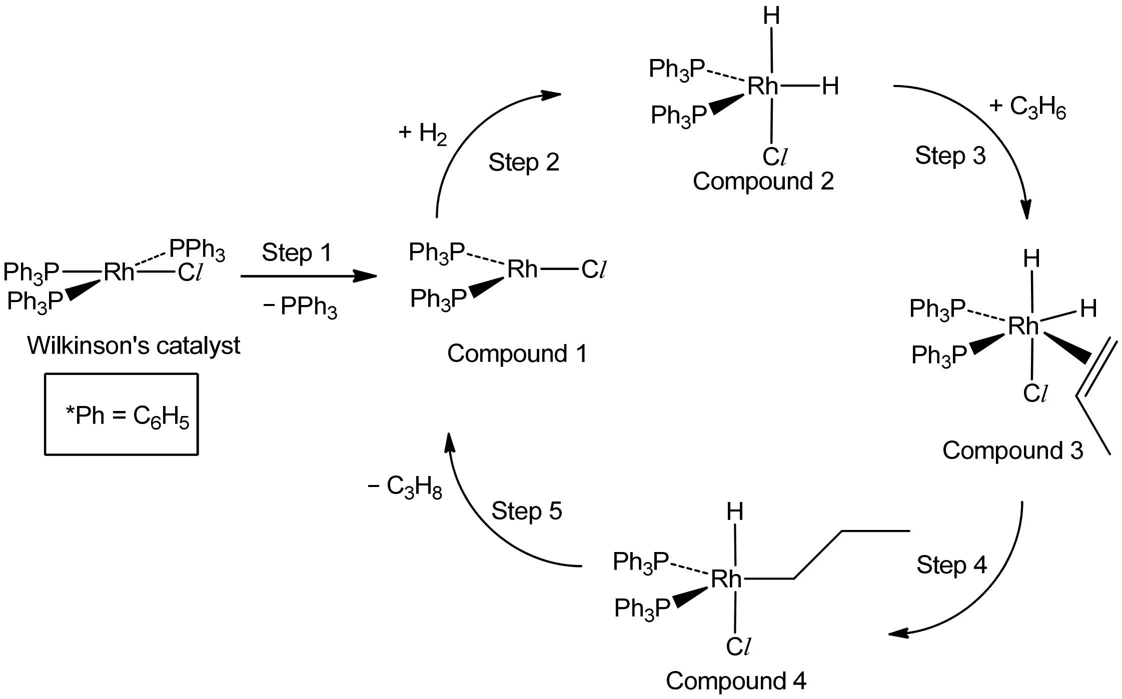
(b) **(i)** Using appropriate data from the *Data Booklet*, calculate the standard enthalpy change of reaction for the reaction given above. [2]

(ii) Based on your answer for **(b)(i)**, under what conditions would you expect the hydrogenation reaction to be spontaneous? [2]

(iii) Hence explain why a catalyst is still required for the hydrogenation. [2]

(c) A much more effective rhodium-based catalyst for the hydrogenation of alkenes was discovered in 1965. Wilkinson's catalyst, $Rh(PPh_3)_3Cl$, is added to the alkene dissolved in benzene and then stirred at ambient temperature with hydrogen gas being passed through the solution at atmospheric pressure. The hydrogenation was found to occur within minutes of stirring.

The diagram below shows the proposed mode of action for Wilkinson's catalyst for the hydrogenation of propene.



(i) Wilkinson's catalyst is one of the earliest examples of a transition metal complex behaving as a *homogeneous* catalyst. Explain what is meant by the word in italics. [1]

(ii) The oxidation state of Rh in Wilkinson's catalyst is +1. The phosphine ligands (PPh_3) are neutral ligands while the hydrogen atoms in compound 2 act as hydride ligands. Hence calculate the oxidation number of Rh in compound 2. [1]

(iii) Explain what is meant by the term *coordination number* and state the coordination number of Rh in Wilkinson's catalyst and in compound 3. [2]

(iv) Based on your answers for **(c)(ii)** and **(iii)**, state two properties of Rh that allows $Rh(PPh_3)_3Cl$, to behave as a homogeneous catalyst. Use the proposed mode of action above to illustrate your answers. [4]

[Total: 20]

2 **(a)** Describe the appearance of chlorine, bromine and iodine at room temperature and explain how the volatility of these elements varies down the group.

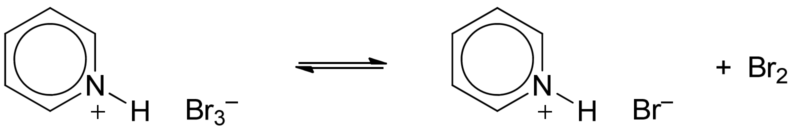
[3]

(b) A sample aqueous solution could contain either the chloride or bromide ion. Describe reactions you would carry out to confirm the identity of the ion, and write equations for reactions that occur, including state symbols.

[3]

Brominated organic compounds have found uses in drugs and fire retardants. They can be synthesized by reacting bromine with alkenes and arenes. Chemists have studied several alternative methods of bromination to avoid handling bromine directly.

An alternative bromine source is pyridinium tribromide, an ionic salt which produces bromine in the reaction mixture via the following equilibrium:



pyridinium tribromide

(c) **(i)** Explain one advantage of using pyridinium tribromide instead of bromine in organic synthesis reactions.

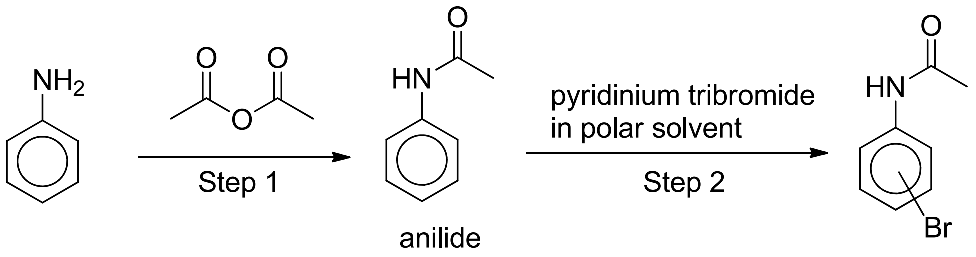
[1]

(ii) Draw the structure of the tribromide ion, Br_3^-, showing its shape. [1]

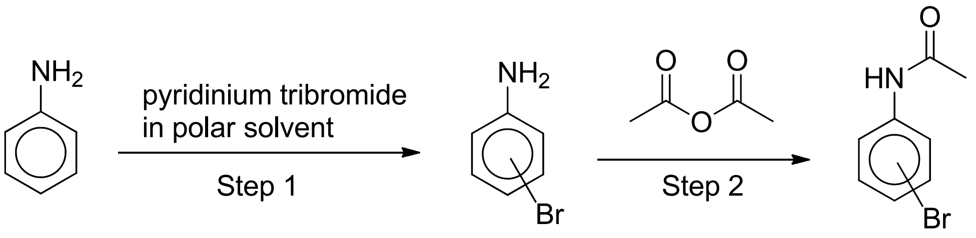
Pyridinium tribromide can be used in the synthesis of mono-brominated anilide. There are two potential routes to this synthesis starting from phenylamine.

In the diagram below, the line connecting Br to the benzene ring indicates that Br is attached to one of the carbons in the benzene ring.

Route 1:



Route 2:



(iii) What types of reaction are Step 1 and Step 2 of **Route 1**? [2]

(iv) **Route 1** is the preferred route for the synthesis because it produced mostly mono-brominated anilide while **Route 2** produced mostly multi-brominated anilide. Explain this observation as fully as you can. You may assume pyridinium tribromide in polar solvent has the same reactivity as aqueous bromine.

[2]

(v) 4-bromoanilide is obtained from Step 2 of **Route 1** at 88% yield. Suggest why it is the major product in this step instead of 2-bromoanilide.

[1]

(vi) Describe and explain the relative basicities of the three nitrogen-containing compounds in **Route 2**.

[3]

(d) Equilibrium systems involving tribromide have been studied extensively, one of which is shown below.

$$Br_2 + Br^- \rightleftharpoons Br_3^-$$

At 25 °C, the K_C value for the above equilibrium is 100. When 16.0 mg of liquid bromine was dissolved in 150 cm^3 of a 0.500 mol dm^{-3} solution of sodium bromide, the reaction is "virtually complete".

(i) Calculate the initial concentration of Br_2 added and, together with the information given, explain why the reaction is "virtually complete".

[2]

(ii) Using your answer in **(d)(i)**, estimate the concentrations of bromide and tribromide in the mixture at equilibrium.

[1]

(iii) Hence, deduce the concentration of Br_2 in the mixture at equilibrium, without solving quadratic equations.

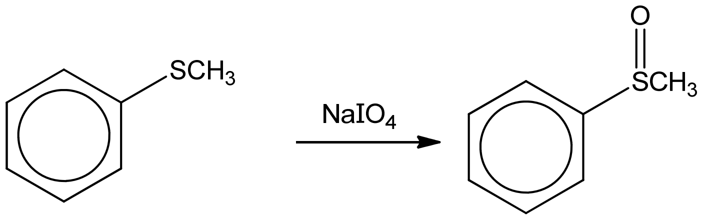
[1]

[Total: 20]

3 This question is about reactions of Period 3 elements or their compounds.

(a) Sodium iodate, $NaIO_4$ (M_r = 214), is a powerful oxidising agent that can be used to oxidise thioethers into sulfoxides with excellent yield.

Thioanisole (M_r = 124.1) is a thioether. In a reaction between thioanisole and 0.500 mol dm^{-3} solution of sodium iodate, it was found that the reaction yielded 9.82 g of the corresponding methyl phenyl sulfoxide. The percentage yield of the reaction was determined to be 91.3%.



thioanisole

methyl phenyl sulfoxide

(i) Calculate the mass of thioanisole that was used in the above reaction. [2]

The oxidation state of iodine in the product was +5, and the reacting mole ratio of thioanisole to sodium iodate was 1:1.

(ii) Determine the volume of sodium iodate, in cm^3, that was used in the above reaction. [1]

(iii) Explain why the reacting mole ratio is 1:1. [1]

(b) Thioethers can be synthesised by the reaction of a thiol (containing the –SH functional group) with an alkene. When methanethiol, CH_3SH, is reacted with ethene, the thioether ethyl methyl sulfide is obtained.

$$CH_2{=}CH_2 \xrightarrow{CH_3SH} CH_3{-}CH_2{-}SCH_3$$

ethyl methyl sulfide

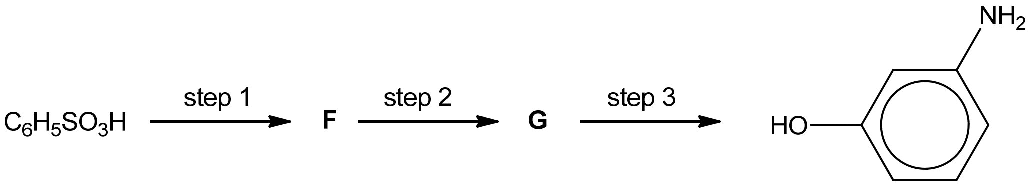
(i) Name the type of reaction that occurs when synthesising thioethers in this way. [1]

(ii) Suggest a mechanism for this reaction, showing all charges and using curly arrows to show the movement of electron pairs, and clearly indicating the rate-determining step. [2]

(iii) Draw the structure of the major product obtained when the starting alkene is replaced by propene. [1]

(c) Benzenesulfonic acid, $C_6H_5SO_3H$, was once widely used in the production of phenol. The process simply required heating the benzenesulfonic acid with aqueous sodium hydroxide, replacing the $–SO_3H$ group with –OH.

Suggest the reagents and conditions you would use in a three-step synthesis of 3-aminophenol starting from benzenesulfonic acid, identifying **F** and **G**. The reactivity of the $–SO_3H$ group and its influence as a side-chain of benzene is similar to that of a $–NO_2$ group.



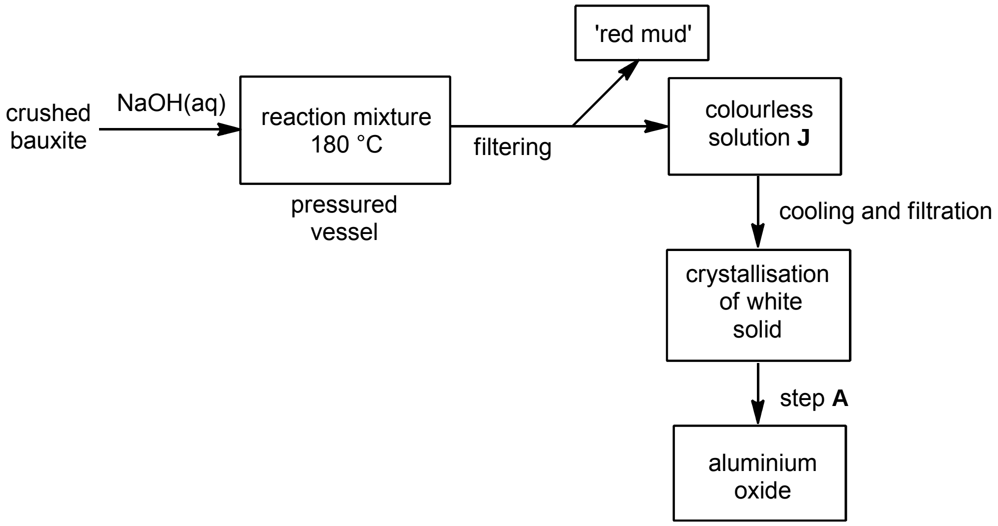
3-aminophenol

[5]

(d) The chlorides of the elements from sodium to phosphorus (each in their highest possible oxidation state) are separately added to water. Sketch a graph to show the trend in pH of the resulting mixtures. Label your graph with the full formula of each of the relevant chlorides.

[2]

(e) The Bayer process, outlined below, involves extracting aluminium oxide from bauxite, which also contains the metal oxide titanium dioxide, TiO_2, and compounds of iron(III) as impurities.



(i) State the identity of solution **J**. [1]

(ii) Explain, in terms of the nature of the oxides, how the addition of aqueous sodium hydroxide is able to separate the aluminium oxide from the titanium dioxide impurity. Write equations with state symbols for the reactions you describe.

[2]

(iii) Suggest the identity of the compound responsible for the colour of the 'red mud'. [1]

(iv) Upon cooling, solution **J** forms a white solid and sodium hydroxide solution as the only products. Aluminium oxide is then recovered via step **A**. Suggest the reagents and/or conditions required to carry out step **A**, giving an equation for the reaction.

[1]

[Total: 20]

4 (a) Sulfur dioxide and oxygen are used in the manufacture of sulfuric acid. In an experimental set-up, two sealed 30 dm^3 cylinders containing sulfur dioxide and oxygen separately at 450 ^oC, have a pressure of 4.0 atm and 2.0 atm respectively. The cylinders are combined and the two gases are allowed to react according to the equation

$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g)$$

At equilibrium at 450 ^oC, 90% of the SO_2 is converted into SO_3.

(i) For the mixture at equilibrium, calculate:

I the total pressure;
II the mole fraction of oxygen; and
III the number of moles of gas.

[4]

(ii) State and explain how you would expect the actual total pressure to be different from your answer in **(a)(i).**

[1]

(b) When antimony(V) fluoride, SbF_5, dissolves in hydrogen fluoride HF, the following reaction occurs

$$2HF + SbF_5 \rightarrow H_2F^+ + SbF_6^-$$

In H_2F^+, the proton is extremely weakly bound, making H_2F^+ a stronger acid than pure sulfuric acid, and is therefore called a superacid.

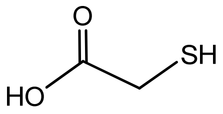
(i) Use VSEPR theory to predict the shape of the H_2F^+ ion. [1]

(ii) Identify the Brønsted acid and Brønsted base in the HF/SbF_5 reaction. [1]

(iii) The Lewis classification of acids and bases is broader and encompasses many more substances than the Brønsted-Lowry theory. A Lewis acid is an electron pair acceptor, while a Lewis base is an electron pair donor. Identify the Lewis acid and Lewis base in the HF/SbF_5 reaction.

[1]

(c) Thioglycolic acid is a sulfur-containing organic acid used to break disulfide bonds during hair perms. It has the structure shown below.



thioglycolic acid

The successive pK_a values of thioglycolic acid are 3.67 and 10.31, and sulfur has almost the same electronegativity as carbon.

(i) Draw the predominant form of thioglycolic acid present in aqueous solution at pH 7. [1]

(ii) Suggest a reason why the second pK_a of thioglycolic acid is higher than the first pK_a. You may use the symbol H_2A to represent thioglycolic acid.

[2]

(iii) Calculate the ratio of concentrations of the di-anion, A^{2-}, and mono-anion, HA^{-}, of thioglycolic acid present at pH 9.3. You may assume that these are the only two sulfur-containing species present at this pH.

[1]

(iv) Explain whether the solution in **(c)(iii)** is an effective buffer solution. [1]

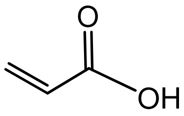
(v) The pK_a of phenolphthalein is 9.3. Explain whether phenolphthalein is a suitable indicator for detecting the **second** equivalence point of the titration of thioglycolic acid with aqueous sodium hydroxide.

[1]

(d) For all its health benefits, the effect of eating asparagus on the odour of urine has long been observed. It was once thought that the compound responsible for the smell in so-called 'asparagus-pee' was methanethiol, CH_3SH. In a more recent study, two other sulfur-containing compounds, **A** and **B**, were detected in 'asparagus-pee', rather than methanethiol itself.

(i) When hydrolysed in water, **A** releases propenoic acid and methanethiol, hence the earlier suspicion of this compound.

A + H_2O ⟶



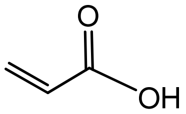
+ CH_3SH

propenoic acid

Draw the displayed formula of **A**. [1]

(ii) **B** can be prepared in the laboratory from propenoic acid by the following route.

<u>Step 1</u>



+ H_2S ⟶ **X**

<u>Step 2</u>

X + CH_3I ⟶ **Y**

<u>Step 3</u>

Y + CH_3SH $\xrightarrow{\text{condensation}}$ **B** + H_2O

X, Y, and **B** do not contain any chiral carbon. Only **X** and **Y** produce effervescence with Na_2CO_3, but not **B**.

Suggest structures for **X, Y,** and **B,** and state the type of reaction occurring in Step 1 and Step 2.

[5]

[Total: 20]

5 **(a)** Ruthenium and strontium are elements in the fifth period of the Periodic Table.

Element	**Ruthenium**	**Strontium**
Electronic configuration	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^7 5s^1$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$
Melting point/°C	2334	777

(i) Explain the difference in the melting points of ruthenium and strontium. [2]

(Ii) Sketch the trend of the successive ionisation energies of the first 10 electrons of a strontium atom and explain the trend observed. [3]

(b) The standard electrode potential for the reduction of Ru^{3+} to Ru^{2+} is shown below.

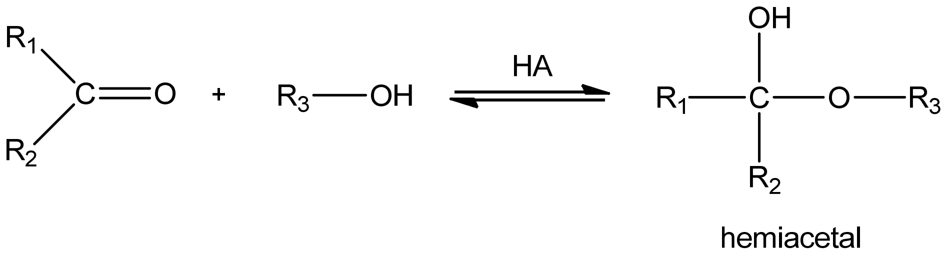
$$Ru^{3+}(aq) + e^- \rightleftharpoons Ru^{2+}(aq) \qquad E^\ominus = +0.23\text{ V}$$

(i) What do you understand by the term *standard electrode potential* of a half-cell? [1]

(ii) By using relevant $E^\ominus$ values from the *Data Booklet*, show that the reaction between $Ru^{3+}(aq)$ and Zn(s) is feasible. Construct a balanced equation, including state symbols, for the reaction. [2]

(iii) When aqueous ruthenium(III) chloride is treated with zinc and aqueous ammonia, orange crystals of a complex of ruthenium are formed. The crystals contain 36.9% of ruthenium by mass, the remainder consisting of hydrogen, nitrogen and chlorine. Suggest a formula for the orange crystals. [2]

(c) Aldehydes and ketones can react with alcohols to form hemiacetals in the presence of an acid catalyst via nucleophilic addition.



The mechanism for the reaction of benzaldehyde with methanol is thought to proceed as described below:

- The oxygen of the carbonyl group is first protonated by HA catalyst via an acid-base reaction to activate the carbonyl group.
- The alcohol is then added to the activated carbonyl group.
- Lastly, deprotonation gives the hemiacetal and regenerates the catalyst.

(i) Suggest a mechanism for this reaction, showing all charges and using curly arrows to show the movement of electron pairs. [3]

(ii) Hemiacetal **R** can be formed from the reaction of **P**, $C_9H_8O_3$, with acidified ethanol.

Both **P** and **R** yield a colourless gas which forms a white precipitate with limewater when warmed with aqueous sodium carbonate.

With alkaline aqueous iodine, **P** gives a yellow precipitate. Treating **P** with methanolic sodium borohydride yields compound **Q**, $C_9H_{10}O_3$. **Q** reacts with aqueous sodium hydroxide to yield compound **S**.

Use the information above to deduce the structures of compounds **P**, **Q**, **R** and **S**, explaining all the reactions involved.

[7]

[Total: 20]