AQA

ASSESSMENT and QUALIFICATIONS ALLIANCE

# Mark scheme January 2004

# GCE

## Chemistry

## Unit CHM4



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## SECTION A

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

**1** (a) The following data were obtained in a series of experiments on the rate of the reaction between compounds **A** and **B** at a constant temperature.

| Experiment | Initial concentration of **A**/mol dm$^{-3}$ | Initial concentration of **B**/mol dm$^{-3}$ | Initial rate/mol dm$^{-3}$ s$^{-1}$ |
|---|---|---|---|
| 1 | 0.12 | 0.15 | $0.32 \times 10^{-3}$ |
| 2 | 0.36 | 0.15 | $2.88 \times 10^{-3}$ |
| 3 | 0.72 | 0.30 | $11.52 \times 10^{-3}$ |

(i) Deduce the order of reaction with respect to **A**.

2 (1)

(ii) Deduce the order of reaction with respect to **B**.

0 (1)

*(2 marks)*

(b) The following data were obtained in a series of experiments on the rate of the reaction between NO and $O_2$ at a constant temperature.

| Experiment | Initial concentration of NO/mol dm$^{-3}$ | Initial concentration of $O_2$/mol dm$^{-3}$ | Initial rate/mol dm$^{-3}$ s$^{-1}$ |
|---|---|---|---|
| 4 | $5.0 \times 10^{-2}$ | $2.0 \times 10^{-2}$ | $6.5 \times 10^{-4}$ |
| 5 | $6.5 \times 10^{-2}$ | $3.4 \times 10^{-2}$ | To be calculated |

The rate equation for this reaction is

$$rate = k[NO]^2[O_2]$$

(i) Use the data from experiment 4 to calculate a value for the rate constant, $k$, at this temperature, and state its units.

*Value of k* $k = \frac{rate}{[NO]^2[O_2]} = \frac{6.5 \times 10^{-4}}{(5.0 \times 10^{-2})^2 (2.0 \times 10^{-2})} = 13$

(1) (1)

*Units of k* $mol^{-2}\ dm^6\ s^{-1}$

(1)

(ii) Calculate a value for the initial rate in experiment 5.

$rate = 13 (6.5 \times 10^{-2})^2 (3.4 \times 10^{-2})$

$= 1.9 \times 10^{-3}$ $(mol\ dm^{-3}\ s^{-1})$

(1)

*(4 marks)*

| | |
|---|---|
| (b) | If $k$ wrong, the mark in (ii) may be gained conseq for their $k \times 1.437 \times 10^{-4}$ |

6

**TURN OVER FOR THE NEXT QUESTION**

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2 At high temperatures, $SO_2Cl_2$ dissociates according to the following equation.

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g) \qquad \Delta H^{\ominus} = +93 \text{ kJ mol}^{-1}$$

When 1.00 mol of $SO_2Cl_2$ dissociates, the equilibrium mixture contains 0.75 mol of $Cl_2$ at 673 K and a total pressure of 125 kPa.

(a) Write an expression for the equilibrium constant, $K_p$, for this reaction.

$K_p = \dfrac{p_{SO_2} \times p_{Cl_2}}{p_{SO_2Cl_2}}$ (1)

*(1 mark)*

(b) Calculate the total number of moles of gas present in the equilibrium mixture.

$0.25 + 0.75 + 0.75 = 1.75$

(1) (1)

*(2 marks)*

(c) (i) Write a general expression for the partial pressure of a gas in a mixture of gases in terms of the total pressure.

$p$ = Total pressure × mol fraction (1)

(ii) Calculate the partial pressure of $SO_2Cl_2$ and the partial pressure of $Cl_2$ in the equilibrium mixture.

*Partial pressure of $SO_2Cl_2$* $125 \times \dfrac{0.25}{1.75} = 17.9$ kPa

(1) (1)

*Partial pressure of $Cl_2$* $125 \times \dfrac{0.75}{1.75} = 53.6$ kPa

(1) (1)

*(5 marks)*

(d) Calculate a value for the equilibrium constant, $K_p$, for this reaction and give its units.

$K_p = \dfrac{53.6 \times 53.6}{17.9} = 161$ kPa

(1) (1)

(1)

*(3 marks)*

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(e) State the effect, if any, of an increase in temperature on the value of $K_p$ for this reaction. Explain your answer.

*Effect on $K_p$* increase (1)

*Explanation* increase T sends equilibrium in endothermic direction (1)

*(2 marks)*

(f) State the effect, if any, of an increase in the total pressure on the value of $K_p$ for this reaction.

no effect (1)

*(1 mark)*

14

| | | |
|---|---|---|
| (a) | If $K_p$ has [ ] lose mark in (a) but allow full marks in (d) | |
| | If $K_p$ wrong/upside down etc, allow max 2 in (d) for substitution of numbers [1] and consequential units [1] | |
| (b) | Mark for moles of $SO_2Cl_2$ can be scored in part (c)(ii) if not gained in (b) | |
| | 1.75 gets [2] | |
| | If moles of $SO_2Cl_2$ = 1, this is a Chemical Error, hence a 2 mark penalty<br>• If total moles given in (b) = 1.75, this scores [2] in (b); but if the no moles of $SO_2Cl_2$ = 1 in (c)(ii), lose both marks in (c)(ii) for pp of $SO_2Cl_2$ = (1/1.75) × 125, i.e. the 2 mark penalty is in (c)(ii).<br>• If total moles given in (b) = 2.5, score zero in (b), but can gain full marks in (c)(ii) consequentially, i.e. the 2 mark penalty is in (b).<br>• If moles of $SO_2Cl_2$ = 1 and total in (b) does not equal 2.5, still lose both in (b) but can get all 4 conseq in (c)(ii) for 1/x etc and 0.75/x etc | |
| (c) | (i) | Allow "Total pressure = sum of partial pressures" for [1] or $p_A = x_A \times p_{tot}$ |
| | (ii) | First mark is for mole fraction.<br>If either number in either mole fraction is not consequential on (b), then lose both marks for that partial p. |
| (d) | If $pCl_2$ is not equal to $pSO_2$ or any number used in $K_p$ is not conseq on (c)(ii), allow units only | |
| | SIG FIGS; must be 3 sig figs in (b) but then allow 2 sig figs in (c) and (d); (ignore extra figs) but penalise incorrect rounding | |
| (e) | If effect wrong, no marks for explanation.<br>If effect missing, e.g. answer states "equm shifts to right", mark on.<br>In the explanation, the word "endothermic" (or its equivalent) is essential. | |

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Penalise 2sig figs once in the question but pH must also be to 2 dp
Penalise missing [ ] once in question.

**3** (a) The pH of a 0.120 mol dm$^{-3}$ solution of the weak monoprotic acid, HX, is 2.56 at 298 K.

(i) Write an expression for the term *pH*.

$pH = -\log [H^+]$ (1)

(ii) Write an expression for the dissociation constant, $K_a$, for the weak acid HX and calculate its value at 298 K.

*Expression for $K_a$* $K_a = \dfrac{[H^+][X^-]}{[HX]}$ (1)

*Calculation* $pH = 2.56 \therefore [H^+] = 2.75 \times 10^{-3}$ (1)

$K_a = \dfrac{[H^+]^2}{[HX]} = \dfrac{(2.75 \times 10^{-3})^2}{0.12} = 6.32 \times 10^{-5}$ (mol dm$^{-3}$) (1)

or $[H^+] = [X^-]$ (1)

*(5 marks)*

(b) (i) Write an expression for the ionic product of water, $K_w$, and give its value at 298 K.

*Expression for $K_w$* $K_w = [H^+][OH^-]$ (1)

*Value of $K_w$* $(1.0 \times) 10^{-14}$ (mol$^2$ dm$^{-6}$) (1)
ignore units

(ii) Hence, calculate the pH of a 0.0450 mol dm$^{-3}$ solution of sodium hydroxide at 298 K.

$[H^+] = \dfrac{1.0 \times 10^{-14}}{0.045} = 2.22 \times 10^{-13}$ (1)

or $pOH = 1.35$

$\therefore pH = 12.65$ (1)

must be 2dp in final answer.

*(4 marks)*

In (a)(ii):

| | |
|---|---|
| depending on approximations made, values of $K_a$ = | $10^{-5}$ × |
| using [HX] = 0.12 | 6.30 – 6.32 |
| using [HX] = 0.12 – 2.75... | 6.45 – 6.47 |
| using 2.8 and [HX] = 0.12 | 6.53 |
| using 2.8 and [HX] = 0.12 – 2.8 | 6.69 |

Upside down Ka

(c) A titration curve is plotted showing the change in pH as a 0.0450 mol dm$^{-3}$ solution of sodium hydroxide is added to 25.0 cm$^3$ of a solution of ethanedioic acid, $H_2C_2O_4$
The titration curve obtained has two equivalence points (end points).

(i) Write an equation for the reaction which is completed at the **first** equivalence point.

$H_2C_2O_4 + OH^- \longrightarrow HC_2O_4^- + H_2O$ (1)

(ii) When the **second** equivalence point is reached, a total of 41.6 cm$^3$ of 0.0450 mol dm$^{-3}$ sodium hydroxide has been added.
Calculate the concentration of the ethanedioic acid solution.

mol $OH^-$ $= (41.6 \times 10^{-3}) \times 0.0450$ (1) $= 1.87 \times 10^{-3}$

$\therefore$ mol $H_2C_2O_4$ $= 9.36 \times 10^{-4}$ (1)

$[H_2C_2O_4] = 9.36 \times 10^{-4} \times 10^3/25$

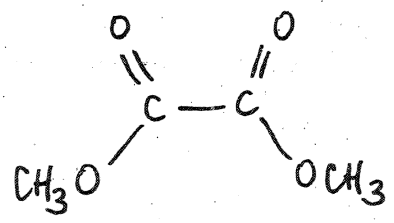
$= 0.0374$ (1)

| |
|---|
| if moles of $H_2C_2O_4$ not equal to half moles of $OH^-$, no further marks gained |
| if mol $OH^-$ = $1.9 \times 10^{-3}$; hence mol $H_2C_2O_4$ = $9.5 \times 10^{-4}$; $[H_2C_2O_4]$ = 0.038 |

*(4 marks)*

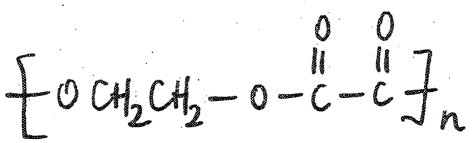
(d) Draw the structure of the organic product formed in each case when, in the presence of a small amount of concentrated sulphuric acid, ethanedioic acid reacts with

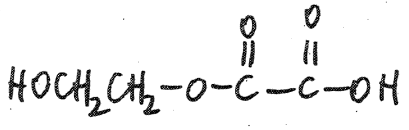
(i) an excess of methanol,

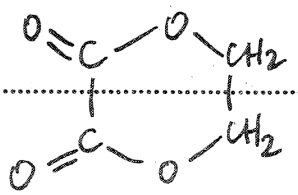


(1)

(ii) an equimolar amount of ethane-1,2-diol.



or 

or 

(1)

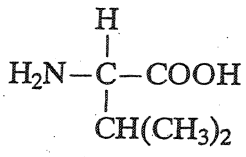
*(2 marks)*

15

| | | |
|---|---|---|
| (d) | (i) | must be diester<br>allow $CH_3OOCCOOCH_3$ or $CH_3O_2CCO_2CH_3$ and similarly in (ii) |
| | (ii) | must be 1:1 proportion<br>allow repeating unit alone (i..e. n not essential) |

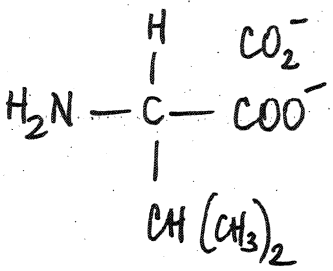
Turn over

4 (a) Consider the following amino acid.



(i) Draw the structure of the amino acid species present in a solution at pH 12.

ignore $Na^+$ unless covalently bonded.

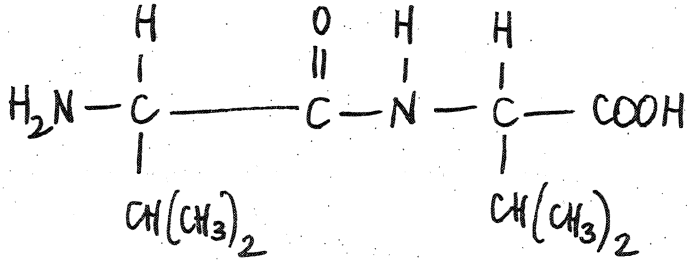


(1)

(ii) Draw the structure of the dipeptide formed from two molecules of this amino acid.

must be dipeptide, not polymer nor anhydride

allow –CONH– or –COHN–



(1)

allow zwitterion

(iii) Protein chains are often arranged in the shape of a helix. Name the type of interaction that is responsible for holding the protein chain in this shape.

QL hydrogen bonding (1)

allow with dipole-dipole or v derWaals, but not dipole-dipole etc alone

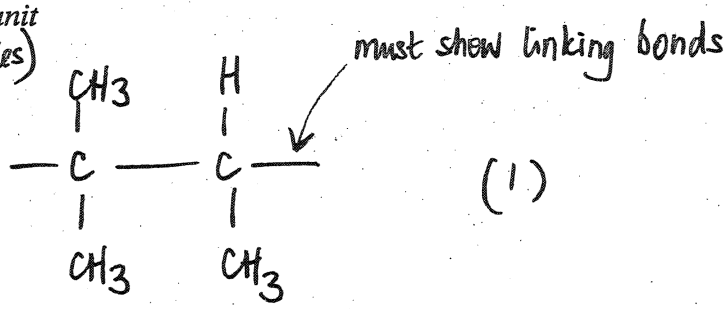
*(3 marks)*

(b) Consider the hydrocarbon **G**, $(CH_3)_2C{=}CHCH_3$, which can be polymerised.

(i) Name the type of polymerisation involved and draw the repeating unit of the polymer.

*Type of polymerisation* addition(al)(1)

*Repeating unit* (not multiples)

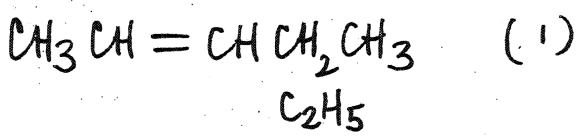



(1)

allow n

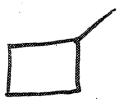
(ii) Draw the structure of an isomer of **G** which shows geometrical isomerism.

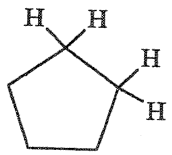
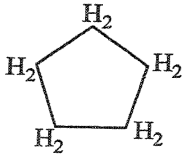
double bond must be shown

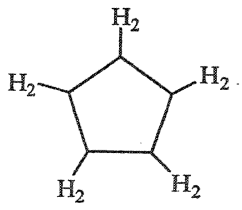



(1)

(iii) Draw the structure of an isomer of **G** which does not react with bromine water.

(1) or  etc

allow  or  etc

but not 

*(4 marks)*

7

5 Compound **Q** has the molecular formula $C_4H_7ClO$ and does not produce misty fumes when added to water.

(a) The infra-red spectrum of **Q** contains a major absorption at 1724 $cm^{-1}$. Identify the bond responsible for this absorption.

C=O (1) or "carbonyl"

*(1 mark)*

(b) The mass spectrum of **Q** contains two molecular ion peaks at $m/z$ = 106 and $m/z$ = 108. It also has a major peak at $m/z$ = 43.

(i) Suggest why there are two molecular ion peaks.

Allow $^{35}Cl$ and $^{37}Cl$ without word isotope - but must be correct isotopes.

Cl has (2) isotopes (1)

(ii) A fragment ion produced from **Q** has $m/z$ = 43 and contains atoms of **three** different elements. Identify this fragment ion and write an equation showing its formation from the molecular ion of **Q**.

*Fragment ion* $CH_3-\overset{+}{C}=O$ must be an ion * (1)

*Equation* $C_4H_7ClO^{+\bullet} \longrightarrow CH_3\overset{+}{C}O + C_2H_4Cl^{\bullet}$ (1)

*(3 marks)*

* allow $C_2H_3O^+$ or any form of it (i.e. $CH_2CHO^+$ or $CH_2COH^+$)
in equation, be generous with position of + or •

(c) The proton n.m.r. spectrum of **Q** was recorded.

(i) Suggest a suitable solvent for use in recording this spectrum of **Q**.

$CDCl_3$ or $CCl_4$ (1) or $D_2O$, $C_6D_6$ etc

(ii) Give the formula of the standard reference compound used in recording proton n.m.r. spectra.

$Si(CH_3)_4$ (1) or $SiC_4H_{12}$

*(2 marks)*

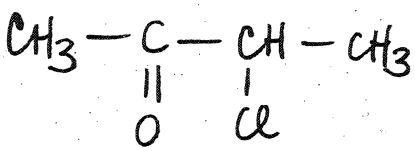
| | | |
|---|---|---|
| (b) | (ii) | must have 3 different elements, i.e. not $C_3H_7^+$ but allow balanced equation including $C_3H_7^+$ for the equation mark. |
| | (ii) | if fragment ion completely wrong (not m/z = 43) no further marks |

(d) The proton n.m.r. spectrum of **Q** shows three peaks. Complete the table below to show the number of adjacent, non-equivalent protons responsible for the splitting pattern.

| | Peak 1 | Peak 2 | Peak 3 |
|---|---|---|---|
| Integration value | 3 | 3 | 1 |
| Splitting pattern | doublet | singlet | quartet |
| Number of adjacent, non-equivalent protons | 1 | 0 | 3 |

(1) *(1 mark)*

(e) Using the information in parts (a), (b) and (d), deduce the structure of compound **Q**.

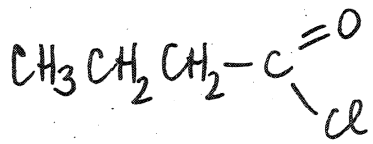


(1)

or $CH_3COCHClCH_3$

*(1 mark)*

(f) A structural isomer of **Q** reacts with cold water to produce misty fumes. Suggest a structure for this isomer.



or $(CH_3)_2CHCOCl$ (1)

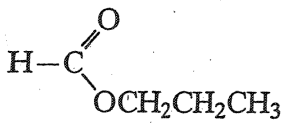
or

$CH_3CH_2CH_2COCl$

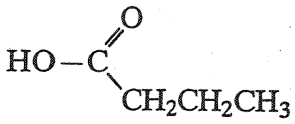
*(1 mark)*

9

**6** (a) Consider the following pair of isomers.



**C**



**D**

(i) Name compound **C**.

Propyl methanoate (1)

(ii) Identify a reagent which could be used in a test-tube reaction to distinguish between **C** and **D**. In each case, state what you would observe.

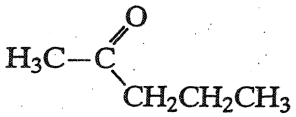
*Reagent* $NaHCO_3$ (1)

*Observation with* ***C*** no reaction (1)

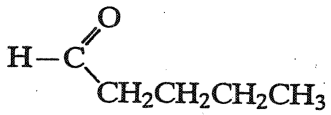
*Observation with* ***D*** effervescence (1)

*(4 marks)*

(b) Consider the following pair of isomers.



**E**



**F**

(i) Name compound **E**.

pentan-2-one (1)

(ii) Identify a reagent which could be used in a test-tube reaction to distinguish between **E** and **F**. In each case, state what you would observe.

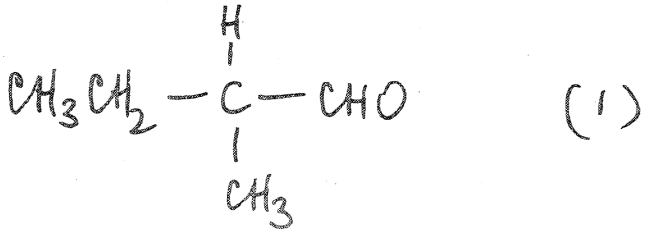
*Reagent* Tollens' or Fehling's (1)

*Observation with* ***E*** no reaction (1)

*Observation with* ***F*** silver mirror or red ppt (1)

*(4 marks)*

(c) Draw the structure of the chain isomer of **F** which shows optical isomerism.



(1)

*(1 marks)*

9

**Qu 6**

| (a) | (i) | not propanyl |
|---|---|---|

- A wrong reagent or no reagent scores zero
- An incomplete reagent such as silver nitrate for Tollens, or potassium dichromate loses the reagent mark, but can get both observation marks.
- penalise observations which just say *colour change occurs* or only state starting colour.

(ii) for **C** and **D** NOT Tollens

| Test | an identified (hydrogen) carbonate | acidified $K_2Cr_2O_7$ | acidified $KMnO_4$ | correct metal | UI or stated indicator | $PCl_5$ |
|---|---|---|---|---|---|---|
| observation with **C** | no reaction | goes green | goes colourless | no reaction | no change | no reaction |
| observation with **D** | bubbles or $CO_2$ | no change | no change | bubbles or $H_2$ | red or correct colour<br>pH 3 – 6.9 | (misty) fumes |

| (b) | (i) **pentan-2-one or 2-pentanone** but not pent-2-one or pentyl |
|---|---|
| (ii) | for **E** and **F** |

| Test | Tollens | Fehlings or Benedicts | iodoform or $I_2$/NaOH | acidified $K_2Cr_2O_7$ | Schiff's |
|---|---|---|---|---|---|
| observation with **E** | No reaction | no reaction | yellow (ppt) | no change | no reaction |
| observation with **F** | silver or mirror or grey or ppt | red or ppt not red solution | no reaction | goes green | goes pink |

| (c) | must be an aldehyde. Allow $C_2H_5$ for $CH_3CH_2$ otherwise this is the only answer. |
|---|---|

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## Question 7 (see also notes)

(a) cyclohexene evolves 120 kJ mol

∴ (expect triene to evolve) 360 kJ mol$^{-1}$ (1) or 3 × 120

360 − 208 = 152 kJ (1) NOT 150 (152 can score 2)

QofL: benzene lower in energy / stated more stable (1) [not award if mentions energy required for bond breaking]

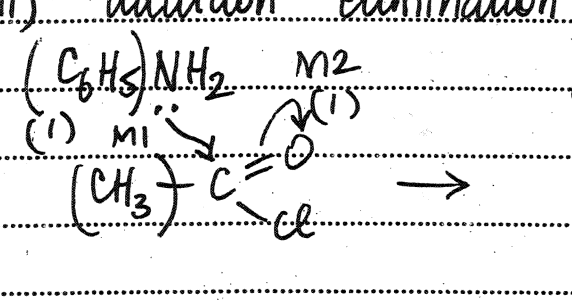
due to delocalization (1) or explained [4 marks]

(b)(i) phenylamine weaker (1) if wrong – no marks

lone pair on N (less available) (1)

delocalized into ring (1) or "explained" [3 marks]

(ii) addition – elimination (1)




structure (1) M3

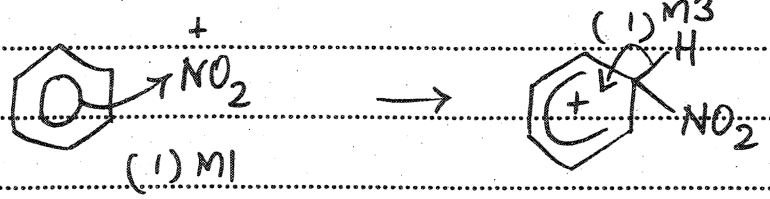
3 arrows (1) M4

N-phenyl ethanamide (1) [6 marks]

(iii) conc HNO$_3$ (1)

conc H$_2$SO$_4$ (1)

$HNO_3 + 2H_2SO_4 \longrightarrow {}^{+}NO_2 + H_3O^{+} + 2HSO_4^{-}$ (1)




(1) M2 [6 marks]

(iv) peptide / amide (1)

NaOH (aq) (1) NOT just H$_2$O [2 marks]

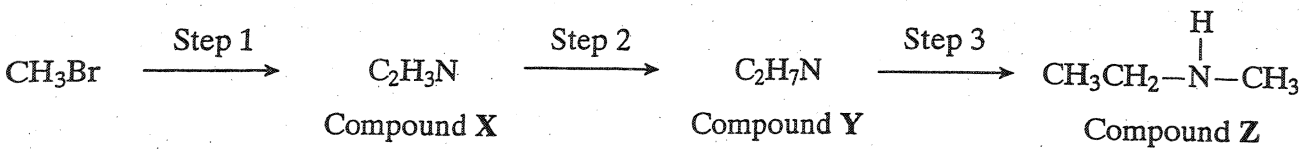
HCl conc or dil or neither

H$_2$SO$_4$ dil NOT conc

**Qu7 notes to accompany mark scheme**

| | | | |
|---|---|---|---|
| (a) | | ▪ 360 or 3×120 or in words [1];<br>▪ 152 NOT 150 [1]; (152 can get first two marks)<br>▪ **Qof L** benzene <u>more</u> stable but not award if ΔH values used to say that more energy is required by benzene for hydrogenation compared with the triene or if benzene is only compared with cyclohexene [1];<br>▪ delocalisation or explained [1] | 4 |
| (b) | (i) | phenylamine weaker [1] if wrong no marks<br>lone pair or electrons on N [1]<br>electrons delocalised into the ring or explained [1] | 3 |
| | (ii) | **<u>N</u>**-phenylethanamide or N-phenylacetamide or acetanilide<br>mechanism: if shown as substitution can only gain M1<br>if $CH_3CO+$ formed can only gain M1<br>lose M4 if $Cl^-$ removes $H^+$<br>be lenient with structures for M1 and M2 but must be correct for M3<br>  alone loses M2 | 6 |
| | (iii) | **<u>NO mark for name of mechanism in this part</u>**<br>if conc missing can score one for both acids (or in equation)<br>allow two equations<br>allow $HNO_3 + H_2SO_4 \longrightarrow NO_2^+ + HSO_4^- + H_2O$<br>ignore side chain in mechanism even if wrong<br>arrow for M1 must come from inside hexagon<br>arrow to $NO_2^+$ must go to N but be lenient over position of +<br>+ must not be too near to "tetrahedral" Carbon<br>horseshoe from carbons 2-6 but don't be too harsh | 6 |
| | (iv) | reagent allow NaOH<br>HCl conc or dil or neither<br>$H_2SO_4$ dil or neither but not conc<br>not just $H_2O$ | 2 |
| | | ringed total at end (max 21) | |

**8** Compound **Z** can be formed via compounds **X** and **Y** in the three step synthesis shown below.




Identify compounds **X** and **Y** and give reagents and conditions for Steps 1 and 2.

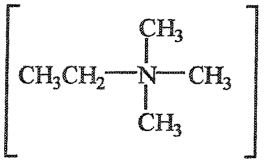
State the **type** of compound of which **Z** is an example.

Compound **Z** reacts with a large excess of bromomethane to form a solid product. Draw the structure of this product and name the type of mechanism for this reaction.

*(9 marks)*

**END OF QUESTIONS**

**Qu8 Replacement mark scheme**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **X** is $CH_3CN$ or ethanenitrile or ethanonitrile or methyl cyanide or cyanomethane or ethyl nitrile or methanecarbonitrile **not** ethanitrile but contradiction of name and structure loses mark | | | | | | | 1 |
| **Y** is $CH_3CH_2NH_2$ or ethylamine or aminoethane or ethanamine | | | | | | | 1 |
| Step 1 | reagent | KCN not HCN or KCN/HCl | | | | | 1 |
| | condition | (aq)/alcohol - only allow condition if reagent correct or incomplete | | | | | 1 |
| Step 2 | reagent | $H_2$ | $LiAlH_4$ | Na | Zn/Fe/Sn | Not $NaBH_4$ | 1 |
| | condition | Ni/Pt/Pd | ether | ethanol | HCl | | 1 |
| **Z** is a amine or aminoalkane or in named amine even if incorrect name for **Z** | | | | | | | 1 |
| secondary (only award if amine correct) | | | | | | | 1 |
|  + $(Br^-)$ + can be on N or outside brackets as shown | | | | | | | 1 |
| nucleophilic substitution | | | | | | | 1 |
| ringed total at end (**max 9/10**) | | | | | | | |