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	0.32×10^{-3}
2	0.36	0.15	2.88×10^{-3}
3	0.72	0.30	11.52×10^{-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	5.0×10^{-2}	2.0×10^{-2}	6.5×10^{-4}
5	6.5×10^{-2}	3.4×10^{-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)

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

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 • 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). • 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). • 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. 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. If effect missing, e.g. answer states "equm shifts to right", mark on. 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)

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

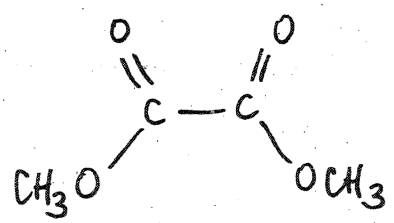
$= 0.0374$ (1)

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)

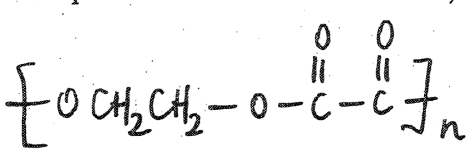
(d) Draw the structure of the organic product formed in each case when, in the presence of a small amount of concentrated sulphuric acid, ethanedioic acid reacts with

(i) an excess of methanol,



(1)

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



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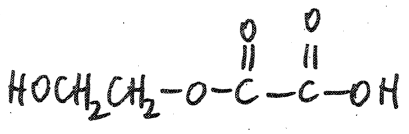

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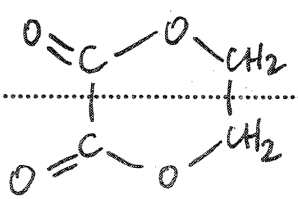


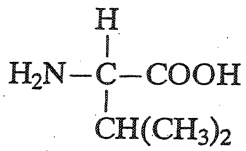
(1)

(2 marks)

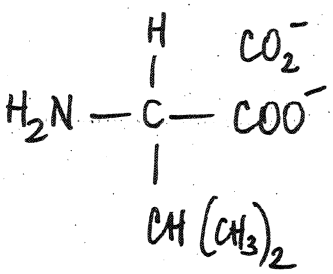
15

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

4 (a) Consider the following amino acid.



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



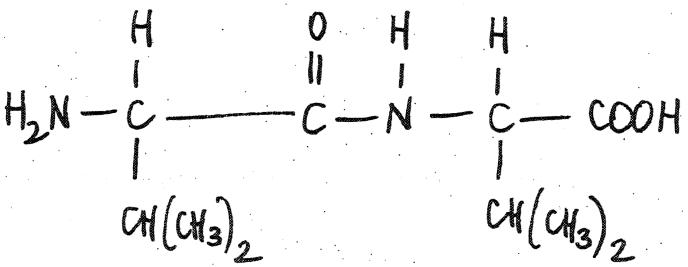
ignore Na^+ unless covalently bonded.

(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)

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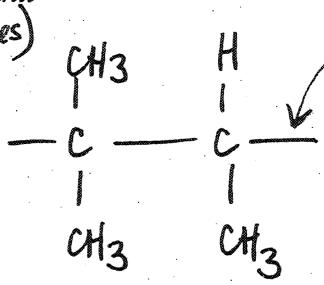
(b) Consider the hydrocarbon **G**, $(CH_3)_2C{=}CHCH_3$, which can be polymerised.

(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)

must show linking bonds



(1)

allow n

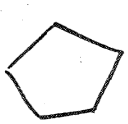
(ii) Draw the structure of an isomer of **G** which shows geometrical isomerism.

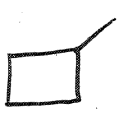
double bond must be shown

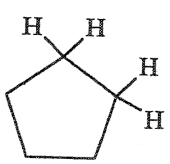
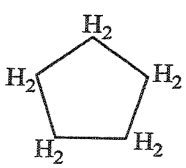
$CH_3CH=CHCH_2CH_3$ (1)

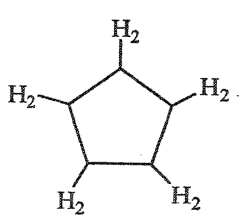
C_2H_5

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



(1) or  etc

allow  or 

but not 

etc

(4 marks)

7

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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)

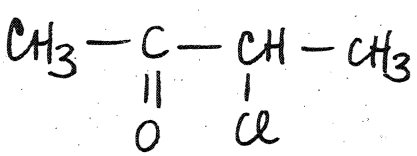
(b)	(ii)	must have 3 different elements, i.e. not $C_3H_7^+$ but allow balanced equation including $C_3H_7^+$ for the equation mark.
	(ii)	if fragment ion completely wrong (not m/z = 43) no further marks

(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**.

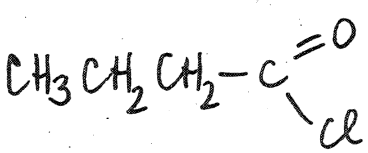


(1)

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)

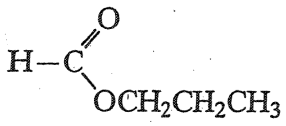
or

$CH_3CH_2CH_2COCl$

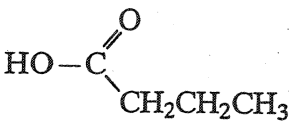
(1 mark)

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.

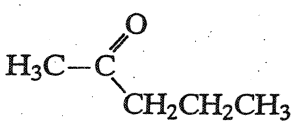
Reagent $NaHCO_3$ (1)

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

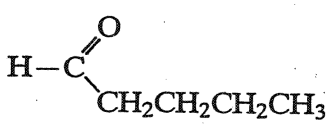
Observation with ***D*** effervescence (1)

(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.

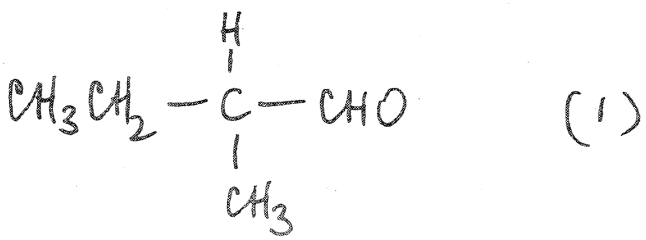
Reagent Tollens' or Fehling's (1)

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 mark)

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 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)

$(C_6H_5)NH_2$ M2 (1)

(1) M1

$(CH_3)-C(=O)-Cl \rightarrow C_6H_5-\overset{+}{N}(H)-C(-O^-)(-CH_3)-Cl$

structure (1) M3

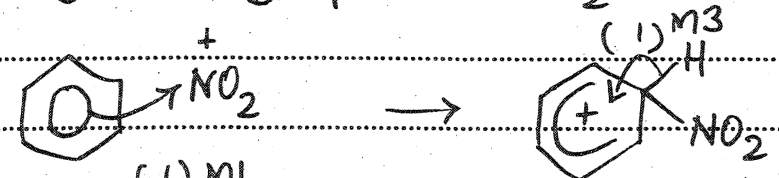
3 arrows (1) M4

N-phenyl ethanamide (1) [6 marks]

(iii) conc HNO_3 (1)

conc H_2SO_4 (1)

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



(1) M1 (1) M3 (1) M2

[6 marks]

(iv) peptide / amide (1)

NaOH (aq) (1) NOT just H_2O [2 marks]

HCl conc or dil or neither

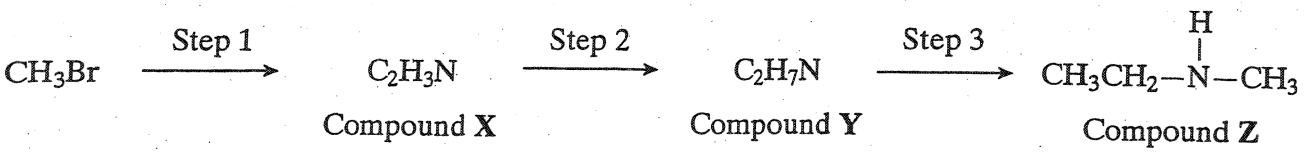
H_2SO_4 dil NOT conc

PLEASE TURN OVER

Qu7 notes to accompany mark scheme

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

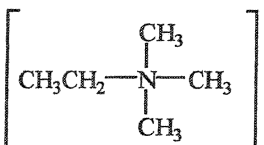
State the **type** of compound of which **Z** is an example.

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)							