AQA /

ASSESSMENT and
QUALIFICATIONS
ALLIANCE

Mark scheme
June 2003

GCE

Chemistry

Unit CHM4

1 The rate of the reaction between substance **A** and substance **B** was studied in a series of experiments carried out at the same temperature. In each experiment the initial rate was measured using different concentrations of **A** and **B**. These results were used to deduce the order of reaction with respect to **A** and the order of reaction with respect to **B**.

(a) What is meant by the term *order of reaction* with respect to **A**?

power of concentration term (in rate eqⁿ) (✓)
or index

or shown as x in $[\quad]^x$

(1 mark)

(b) When the concentrations of **A** and **B** were both doubled, the initial rate increased by a factor of 4. Deduce the **overall** order of the reaction.

2 (✓)

(1 mark)

(c) In another experiment, the concentration of **A** was increased by a factor of three and the concentration of **B** was halved. This caused the initial rate to increase by a factor of nine.

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

Order with respect to A .... 2 (✓)

Order with respect to B .... 0 (✓)

(ii) Using your answers from part (c)(i), write a rate equation for the reaction and suggest suitable units for the rate constant.
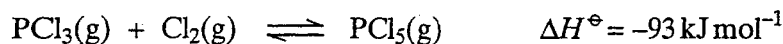
allow conseq
on c(i)

Rate equation .... (rate =) $k[A]^2$ (✓)

Units for the rate constant .... $mol^{-1} \, dm^3 \, s^{-1}$ (✓)

conseq on rate equation

(4 marks)

2 When a mixture of 0.345 mol of PCl_3 and 0.268 mol of Cl_2 was heated in a vessel of fixed volume to a constant temperature, the following reaction reached equilibrium.

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g) \qquad \Delta H^\ominus = -93\,kJ\,mol^{-1}$$

At equilibrium, 0.166 mol of PCl_5 had been formed and the total pressure was 225 kPa.

(a) (i) Calculate the number of moles of PCl_3 and of Cl_2 in the equilibrium mixture.

Moles of PCl_3 ... 0·345 − 0·166 = 0·179 (1) ⎱ (3 sig figs)

Moles of Cl_2 ... 0·268 − 0·166 = 0·102 (1) ⎰

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

.... 0·447 (1) .... (allow 2 sig figs)

conseq on (i)   (3 marks)

(b) Calculate the mole fraction and the partial pressure of PCl_3 in the equilibrium mixture.

Mole fraction of PCl_3 ... $\dfrac{0·179}{0·447}$ (1) = 0·4(00))

Partial pressure of PCl_3 ... PP = mol f^n × total P (1)

.... = 0·400 × 225 = 90(1) (kPa)

.... (1) (3 marks)

(c) (i) Write an expression for the equilibrium constant, K_p, for this equilibrium.

... $K_p = \dfrac{P_{PCl_5}}{P_{PCl_3} \times P_{Cl_2}}$ (1)   ignore brackets except [ ]

.... must show P

If K_p × in (i)
allow max 2 for
substitution of numbers
and conseq units

(ii) The partial pressures of Cl_2 and PCl_5 in the equilibrium mixture were 51.3 kPa and 83.6 kPa, respectively, and the total pressure remained at 225 kPa. Calculate the value of K_p at this temperature and state its units. ($1·81 \times 10^{-5}\ Pa^{-1}$)

... $K_p = \dfrac{83·6}{90·1 \times 51·3}$ = $1·8(1) \times 10^{-2}$ kPa^{-1}

.... (1) .... (1)

.... (1)

if 83·6 and 51·3 wrong way round, AE −1, answer = $6·81 \times 10^{-3}$ (4 marks)

(d) State the effect on the mole fraction of PCl_3 in the equilibrium mixture if

(i) the volume of the vessel were to be increased at a constant temperature,

.... increased (1)

(ii) the temperature were to be increased at constant volume.

.... increased (1)

(2 marks)

penalize pH given to 1 dp first time it would have scored only

3 (a) At 50 °C, the ionic product of water, K_w, has the value $5.48 \times 10^{-14} \, mol^2 \, dm^{-6}$.

    (i) Define the term K_w *or in words or below*

$$K_w = [H^+][OH^-] \Big\} \; (1) \text{ unless contradiction}$$

    (ii) Define the term pH

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

    (iii) Calculate the pH of pure water at 50 °C. Explain why pure water at 50 °C is still neutral even though its pH is not 7.

Calculation $[H^+] = \sqrt{5.48 \times 10^{-14}}$ (1)

$$= 2.34 \times 10^{-7}$$

$$\therefore pH = 6.63 \text{ or } 6.64 \; (1)$$

Explanation   pure water $\therefore [H^+] = [OH^-]$ (1)

                                                           (5 marks)

(b) At 25 °C, K_w has the value $1.00 \times 10^{-14} \, mol^2 \, dm^{-6}$. Calculate the pH at 25 °C of

    (i) a $0.150 \, mol \, dm^{-3}$ solution of sodium hydroxide,

$$[OH^-] = 0.150 \quad \therefore [H^+] = \frac{10^{-14}}{0.15} (1) = 6.66 \times 10^{-14}$$

or pOH = 0.82

$$\therefore pH = 13.18 \; (1)$$

or 13.17

    (ii) the solution formed when $35.0 \, cm^3$ of this solution of sodium hydroxide is mixed with $40.0 \, cm^3$ of a $0.120 \, mol \, dm^{-3}$ solution of hydrochloric acid.

$$\text{moles } OH^- = (35 \times 10^{-3}) \times 0.150 = 5.25 \times 10^{-3} \; (1)^a$$

$$\text{moles } H^+ = (40 \times 10^{-3}) \times 0.120 = 4.80 \times 10^{-3} \; (1)^b$$

$$\therefore \text{excess moles of } OH^- = 4.5 \times 10^{-4} \; (1)^c$$

$$\therefore [OH^-] = (4.5 \times 10^{-4}) \times \frac{1000}{75} \; (1)^d \; (1)^e$$

$$= 6.00 \times 10^{-3}$$

$$[H^+] = \frac{10^{-14}}{6.00 \times 10^{-3}} = 1.66 \times 10^{-12} \text{ or } pOH = 2.22$$

$$\therefore pH = 11.78 \; (1)^f$$

or 11.77

                                                           (8 marks)

(c)   In a $0.150 \, mol \, dm^{-3}$ solution of a weak acid HX at 25 °C, 1.80 % of the acid molecules are dissociated into ions.

(i)   Write an expression for K_a for the acid HX.

$$K_a = \frac{[H^+][X^-]}{[HX]} \quad (1)$$

(ii)   Calculate the value of K_a for the acid HX at this temperature and state its units.

$$[H^+] = 1.80 \times 10^{-2} \times 0.150 = 2.70 \times 10^{-3} \quad (1)$$

$$K_a = \frac{[H^+]^2}{[HX]} = \frac{(2.70 \times 10^{-3})^2}{0.150} = 4.86 \times 10^{-5} \, mol \, dm^{-3}$$

$$(1) \qquad (1)$$

$$(1)$$

$$\left[or \quad \frac{(2.70 \times 10^{-3})^2}{0.1473} = 4.95 \times 10^{-5} \right]$$

(5 marks)

18

Qu3	(a)	If K_w includes H_2O allow 6.63 if seen otherwise no marks likely	
	(b)(ii)	If no vol, max 4 for a, b, c, f	answer = 10.65
		If wrong volume, max 5 for a, b, c, e, f	
		If no subtraction max 3 for a, b, d.	
		If missing 1000 max 5 for a, b, c, d, f	answer = 8.78
		If uses excess as acid, max 4 for a, b, d, f,	answer = 2.22
		If uses excess as acid and no volume, max 2 for a,b,	(answer = 3.35)
	(c)	If wrong K_a in (i) max 2 in part (ii) for $[H^+]$ (1) and conseq units (1)	

but mark on fully from minor errors eg no [ ] or charges missing

4 (a) Outline a mechanism for the reaction of $CH_3CH_2CH_2CHO$ with HCN and name the product.

Mechanism

allow C_3H_7 if structure shown elsewhere

(1) M2
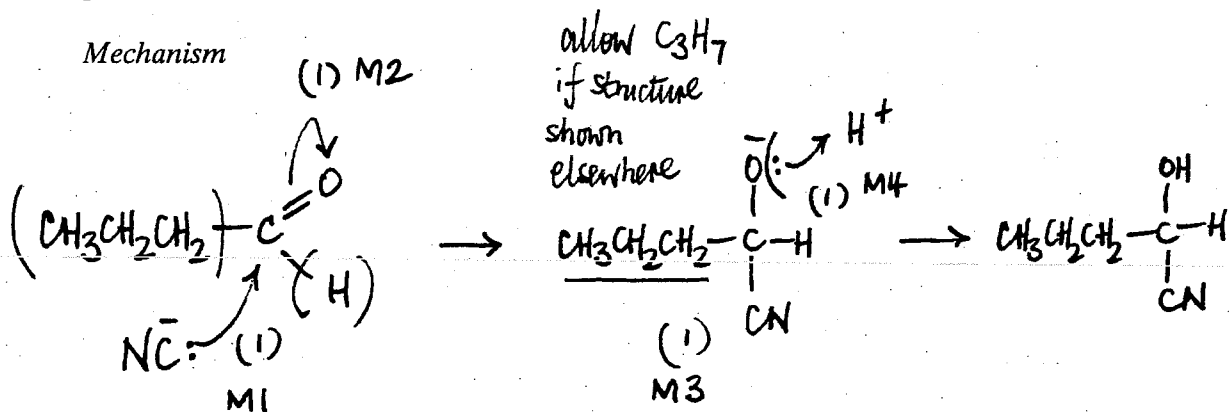
(penalize HCN splitting if wrong)

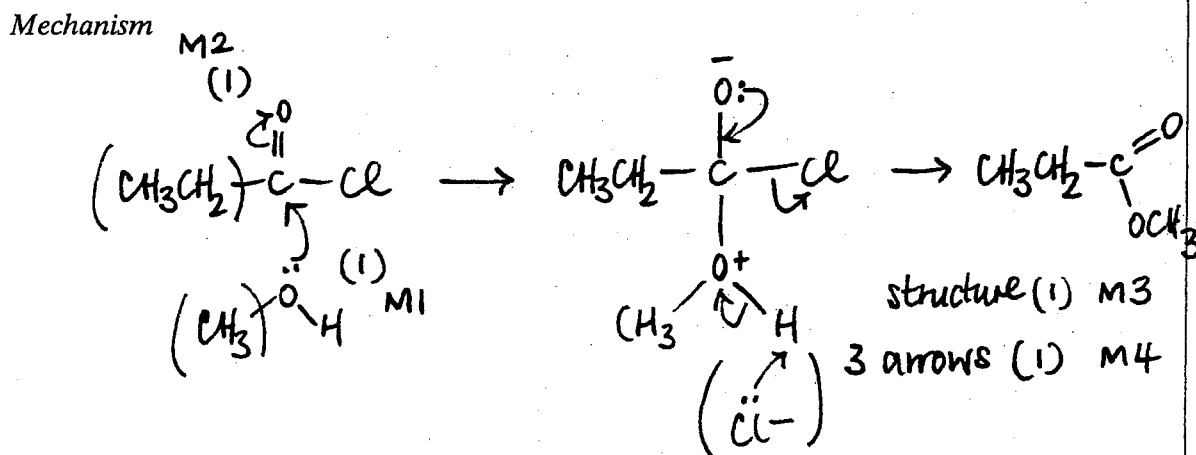Name of product ..... 2-hydroxy pentanenitrile (1) .....

(5 marks)

or 1-cyanobutan-1-ol

(b) Outline a mechanism for the reaction of CH_3OH with CH_3CH_2COCl and name the organic product.

Mechanism

M2 (1)

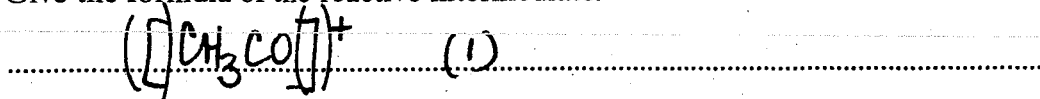structure (1) M3
3 arrows (1) M4

Name of organic product ..... methyl propanoate (1) .....

(5 marks)

(c) An equation for the formation of phenylethanone is shown below. In this reaction a reactive intermediate is formed from ethanoyl chloride. This intermediate then reacts with benzene.

$$\text{(benzene)} + CH_3COCl \xrightarrow{AlCl_3} \text{(benzene)}-COCH_3 + HCl$$
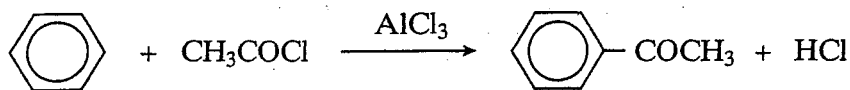
(i) Give the formula of the reactive intermediate.

.... $[CH_3CO]^+$ .... (1) ....

(ii) Outline a mechanism for the reaction of this intermediate with benzene to form phenylethanone.

$CH_3-C=O$ (1) M1
$\quad\quad\,\,^+$

(1) M2
COCH$_3$
M3 H
(1)

(4 marks)

$\dfrac{}{14}$
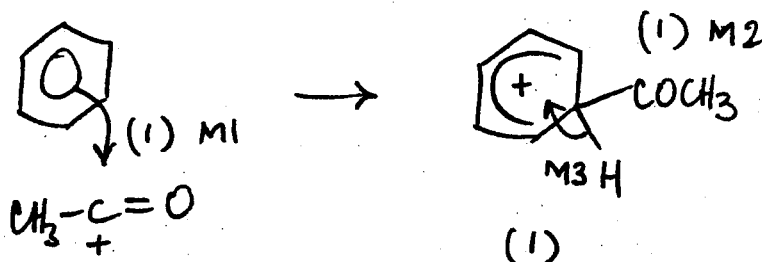
4	abc	extra curly arrows are penalised
	(a)	be lenient on position of negative sign on :CN⁻ but arrow must come from lp
	(a)/(b)	C=O alone loses M2 but can score M1 for attack on C⁺, similarly C—Cl
	(a)	allow 2-hydroxypentanonitrile or 2-hydroxypenta(ne)nitrile not ...pentylnitrile
	(b)	in M4, allow extra :Cl⁻ attack on H, showing loss of H⁺.
	(c)(i)	Allow formula in an "equation" (balanced or not); be lenient on the position of the + on the formula
	(c)(ii)	for M1 the arrow must go to the C or the + on the C don't be too harsh about the horseshoe, but + must not be close to the saturated C M3 must be final step not earlier; allow M3 even if structure (M2) is wrong

$\left(\text{allow } C_2H_5 \right)$

5 (a) The hydrocarbon **M** has the structure shown below.

$$CH_3CH_2-C=CH_2$$
$$\overset{|}{CH_3}$$

   (i) Name hydrocarbon **M**.

   .....**2-methylbut-1-ene**..... (1)   not...butan...

   (ii) Draw the repeating unit of the polymer which can be formed from **M**. State the type of polymerisation occurring in this reaction.

   Repeating unit

   $$(-)\overset{\overset{CH_3}{|}\,\overset{CH_2}{}}{\underset{\overset{|}{CH_3}}{C}}-CH_2(-) \quad (1) \qquad or \; 2\times$$

   Type of polymerisation ....**addition**..... (1)
                              or radical

   (iii) The reaction between **M** and benzene in the presence of HCl and AlCl$_3$ is similar to the reaction between ethene and benzene under the same conditions. Name the type of mechanism involved and draw the structure of the major product formed in the reaction between **M** and benzene.

   Name of mechanism ....**electrophilic substitution**..... (1)

   Major product

   $$\text{(benzene ring)}-\overset{\overset{CH_3}{|}}{\underset{\overset{|}{CH_3}}{C}}-CH_2CH_3 \qquad (1)$$

   (iv) Draw a structural isomer of **M** which shows geometrical isomerism.

   $$CH_3CH=CHCH_2CH_3 \qquad (1)$$

   (6 marks)

   (b) Draw the repeating unit of the polymer formed by the reaction between butanedioic acid and hexane-1,6-diamine. State the type of polymerisation occurring in this reaction and give a name for the linkage between the monomer units in this polymer.

   Repeating unit

   $$(-)\overset{\overset{O}{\|}}{C}-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-(CH_2)_6-\overset{\overset{H}{|}}{N}(-) \qquad \left(\text{see p11}\right)$$

   (1)   CONH   (1)

   Type of polymerisation ....**condensation**..... (1)

   Name of linkage (**poly**)**peptide** or (poly)**amide** (1)

   (4 marks)

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SECTION B

Answer **both** the questions in the space provided on pages 12 to 16 of this booklet.

6 Use the data given on the back of the Periodic Table on page 3 of this booklet to help you answer this question.
   Compounds **A** to **G** are all isomers with the molecular formula $C_6H_{12}O_2$

(a) Isomer **A**, $C_6H_{12}O_2$, is a neutral compound and is formed by the reaction between compounds **X** and **Y** in the presence of a small amount of concentrated sulphuric acid.
X and **Y** can both be formed from propanal by different redox reactions.
**X** has an absorption in its infra-red spectrum at $1750 \, cm^{-1}$.
Deduce the structural formulae of **A**, **X** and **Y**. Give suitable reagents, in each case, for the formation of **X** and **Y** from propanal and state the role of concentrated sulphuric acid in the formation of **A**.   (7 marks)

(b) Isomers **B**, **C**, **D** and **E** all react with aqueous sodium carbonate to produce carbon dioxide.
Deduce the structural formulae of the three isomers that contain an asymmetric carbon atom.
The fourth isomer has only three singlet peaks in its proton n.m.r. spectrum. Deduce the structural formula of this isomer and label it **E**.   (4 marks)

(c) Isomer **F**, $C_6H_{12}O_2$, has the structural formula shown below, on which some of the protons have been labelled.

$$\overset{a}{CH_3}-CH_2-O-CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{\underset{b}{C}}-CH_3$$
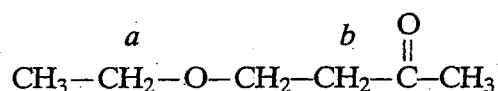
A proton n.m.r. spectrum is obtained for **F**. Using Table 1 on page 4 of this booklet, predict a value of δ for the protons labelled *a* and also for those labelled *b*. State and account for the splitting patterns of the peaks assigned to the protons *a* and *b*.   (6 marks)

(d) Isomer **G**, $C_6H_{12}O_2$, contains six carbon atoms in a ring. It has an absorption in its infra-red spectrum at $3270 \, cm^{-1}$ and shows only three different proton environments in its proton n.m.r. spectrum. Deduce a structural formula for **G**.   (2 marks)

Mark Scheme

5	(b)	allow outer horizontal bonds to be omitted
		allow HO-[..............]-H if [....] shows the repeating unit.; if brackets missing in the dimer, penalise one.
		penalise C_2H_4 or C_6H_{12} first time only
		allow CONH
		allow polypeptide or polyamide; peptide or amide **must** be spelled correctly

Turn over

7 (a) Outline a mechanism for the formation of ethylamine from bromoethane. State why the ethylamine formed is contaminated with other amines. Suggest how the reaction conditions could be modified to minimise this contamination. *(6 marks)*

   (b) Suggest one reason why phenylamine cannot be prepared from bromobenzene in a similar way. Outline a synthesis of phenylamine from benzene. In your answer you should give reagents and conditions for each step, but equations and mechanisms are not required. *(5 marks)*

END OF QUESTIONS

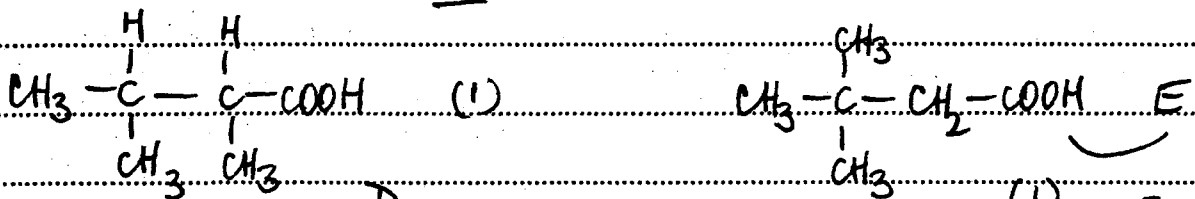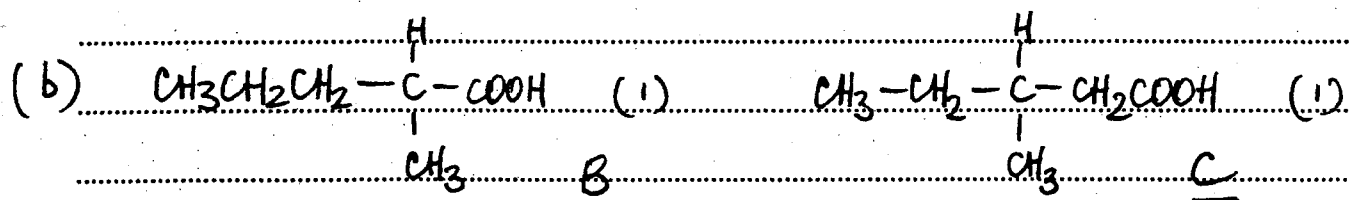| 6	(a)	first mark for C=O stated or shown in **X** (Ignore wrong names) **Y** <u>$CH_3CH_2CH_2OH$</u> allow C_3H_7 in **A** if **Y** correct. or vice versa Allow (1) for **A** if correct conseq to wrong **X** and **Y**
	(a)	other oxidising agents: acidified $KMnO_4$; Tollens; Fehlings
	(a)	other reducing agents: $LiAlH_4$; Na/ethanol ; Ni/H_2 ; Zn or Sn or Fe/HCl
	(b)	give (1) for carboxylic acid stated or COOH shown in <u>each</u> suggestion (1) for correct **E** any 2 out of 3 for **B, C** or **D**. allow C_3H_7 for either the **B** or **D** shown on the mark scheme i.e. a correct structure labelled **B, C** or **D** or **E** will gain 2.
	(c)	protons a – *quartet* must be correct to score *3 adjacent H* mark. Same for b
	(d)	allow (1) for any OH (alcohol) shown correctly in any structure – ignore extra functional groups. Structure must be completely correct to gain second mark

Question 6   (see also page 12)

(a)   X contains $\text{C}=\text{O}$ (1) ← if X and Y reversed lose this mark
     ∴ X is CH_3CH_2COOH (1)   but allow remaining max 6/7

     ∴ Y is $CH_3CH_2CH_2OH$ (1)

     ∴ A is $CH_3CH_2C\begin{array}{l}=O\\ \,\,\,OCH_2CH_2CH_3\end{array}$ (1)
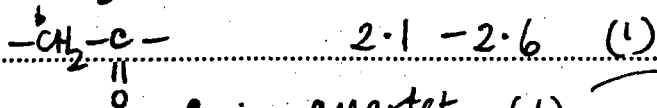
Propanal → X   reagent: acidified $K_2Cr_2O_7$ (1)

          → Y   reagent: $NaBH_4$ (1)

conc H_2SO_4 : catalyst (1)   [7 Total]

(b) $CH_3CH_2CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-COOH$ (1) $CH_3-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-CH_2COOH$ (1)
                    B   C

  $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-COOH$ (1) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-COOH$ E
           D   (1)   [4 marks]
      in any order

(c) $-O\overset{a}{C}H_2-$ 3·1 - 3·9 (1)

  $-\overset{b}{C}H_2-\underset{\underset{O}{||}}{C}-$ 2·1 - 2·6 (1)
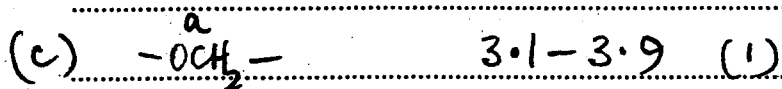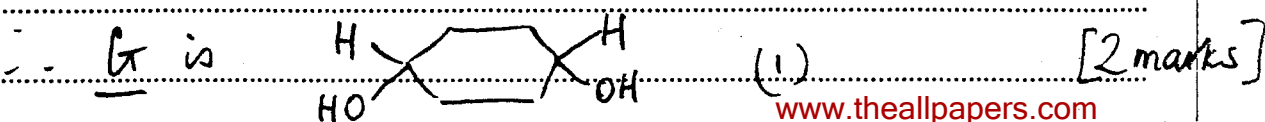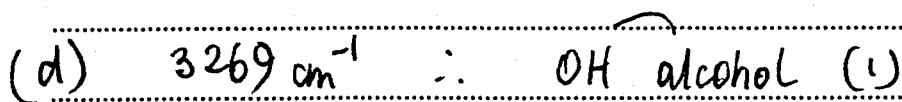
            a : quartet (1) ⌒ 3 adjacent H (1)
            b : triplet (1) ⌒ 2 adjacent H (1)

                                          [6 marks]

(d)   3269 cm⁻¹ ∴ OH alcohol (1)

     ∴ G is   [ring structure with HO and OH] (1)   [2 marks]

Question 7

(a)

$$CH_3CH_2-Br \quad \xrightarrow{\quad} \quad CH_3CH_2-\overset{+}{N}-H \quad (\longleftarrow :NH_3)$$

M1 (1) :NH₃   M2 (1)   M3 (1)   M4 (1)
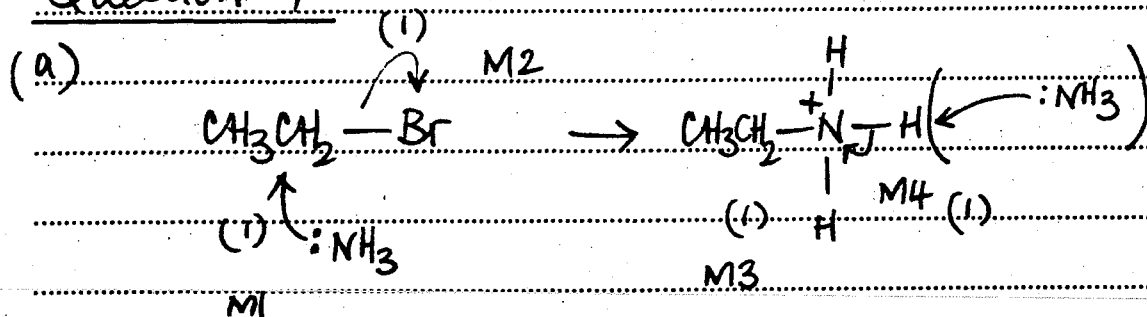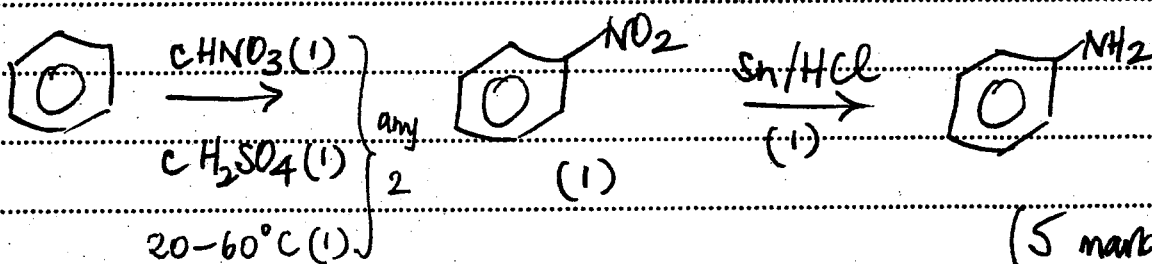
Further reaction/substitution / formation of II°/III° amines etc (1)

Use an excess of NH₃   (1)
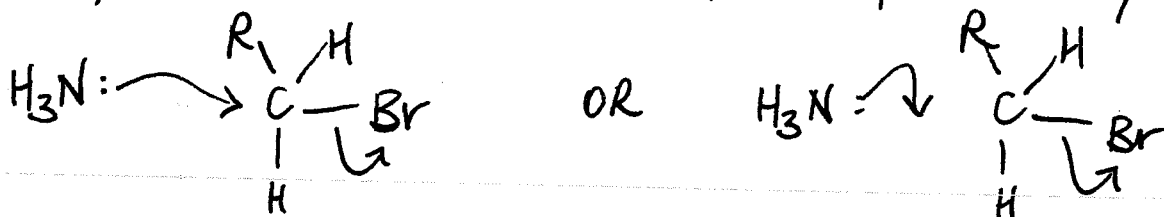
(6 marks)

(b) ⬡ repels nucleophiles (such as NH₃)   (1)

$$⬡ \quad \xrightarrow[C\,H_2SO_4\,(1) \atop 20-60°C\,(1)]{C\,HNO_3\,(1)} \quad ⬡-NO_2 \quad \xrightarrow[(1)]{Sn/HCl} \quad ⬡-NH_2$$

any 2   (1)

(5 marks)

[TOTAL 11]

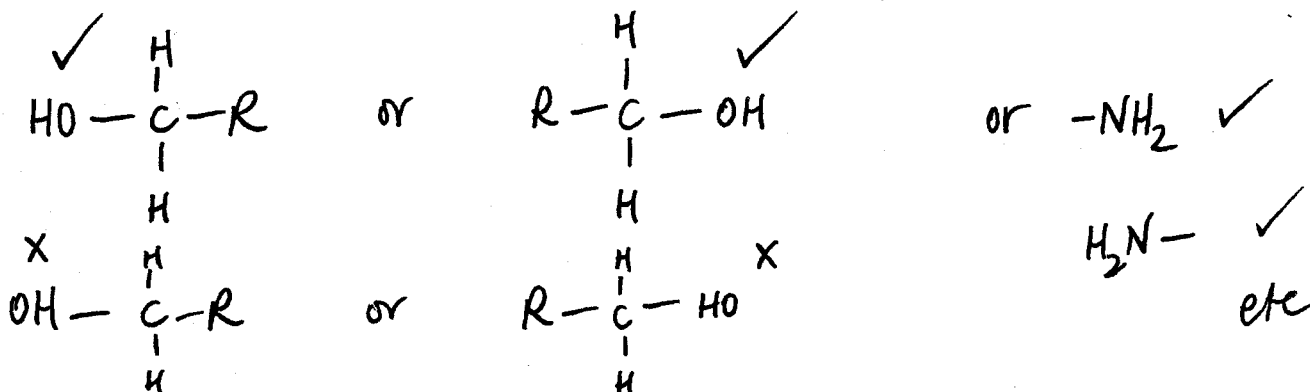| 7	(a)	allow SN1
		penalise :Br⁻ instead of NH₃ removing H⁺ for M4
		not contamination with *other amines* (this is in the question), not diamines
	(b)	allow because NH₃ is a nucleophile or benzene is (only) attacked by electrophiles or C-Br bond (in bromobenzene) is stronger/less polar or Br lp delocalized
	(b)	HNO₃ /H₂SO₄ without either conc scores (1) allow 20 – 60° for (1) (any 2 ex 3)
		allow name or structure of nitrobenzene
		other reducing agents: Fe or Sn with HCl (conc or dil or neither) not conc H₂SO₄or conc HNO₃ allow Ni/H₂ Not NaBH₄ or LiAlH₄ ignore wrong descriptions for reduction step eg hydrolysis or hydration

General Organic points for CHM 4

① <u>Curly arrows</u> must show movement of a pair of electrons
i.e. from bond to atom or from lp to atom/space e.

$$H_3N: \curvearrowright \overset{\displaystyle R \diagdown \;\; \diagup H}{\underset{\displaystyle H}{\overset{\displaystyle |}{C}} - Br}$$ OR $$H_3N: \curvearrowright \overset{\displaystyle R \diagdown \;\; \diagup H}{\underset{\displaystyle H}{\overset{\displaystyle |}{C}} - Br}$$

② <u>Structures</u>

penalize sticks $\left(\text{i.e.} \quad -\overset{|}{\underset{|}{C}}- \right)$ <u>once per paper.</u>

✓ $HO - \overset{\displaystyle H}{\underset{\displaystyle H}{\overset{\displaystyle |}{C}}} - R$ or $R - \overset{\displaystyle H}{\underset{\displaystyle H}{\overset{\displaystyle |}{C}}} - OH$ ✓ or $-NH_2$ ✓

✗ $OH - \overset{\displaystyle H}{\underset{\displaystyle H}{\overset{\displaystyle |}{C}}} - R$ or $R - \overset{\displaystyle H}{\underset{\displaystyle H}{\overset{\displaystyle |}{C}}} - HO$ ✗ H_2N- ✓

etc

<u>penalize once per paper</u>

<u>allow</u> $CH_3 -$ or $-CH_3$ or $\overset{\displaystyle CH_3}{\underset{\displaystyle |}{}}$ or $\overset{\displaystyle CH_3}{\underset{\displaystyle |}{}}$

  or $H_3C -$