



ASSESSMENT and
QUALIFICATIONS
ALLIANCE

Mark scheme January 2002

GCE

Chemistry

Unit CHM4

SECTION A

Answer **all** the 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	0.15	0.24	0.45×10^{-5}
2	0.30	0.24	0.90×10^{-5}
3	0.60	0.48	7.20×10^{-5}

- (i) Show how the data in the table can be used to deduce that the reaction is first-order with respect to A. *stated or shown numerically*

(Experiments 1 → 2), [A] doubled, ([B] constant),
rate doubled (1)

- (ii) Deduce the order with respect to B.

2 (1)
or shown as ... [B]²

(2 marks)

- (b) The following data were obtained in a second series of experiments on the rate of the reaction between compounds **C** and **D** at a constant temperature.

Experiment	Initial concentration of C/mol dm ⁻³	Initial concentration of D/mol dm ⁻³	Initial rate/mol dm ⁻³ s ⁻¹
4	0.75	1.50	9.30×10^{-5}
5	0.20	0.10	To be calculated

The rate equation for this reaction is

$$\text{rate} = k[\text{C}]^2[\text{D}]$$

- (i) Use the data from Experiment 4 to calculate a value for the rate constant, k , at this temperature. State the units of k .

Value for k $k = \frac{9.30 \times 10^{-5}}{(0.75)^2 \times (1.50)} = \frac{1.10}{(1)} \times 10^{-4}$

..... (1)

Units of k $\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$ (1)

.....

conseq
on (i)

- (ii) Calculate the value of the initial rate in Experiment 5.

rate = $(1.10 \times 10^{-4}) \times (0.20)^2 \times (0.10)$

.....

= $4.4(1) \times 10^{-7}$ (mol dm⁻³ s⁻¹)

..... (1) ignore units

↑ for the answer

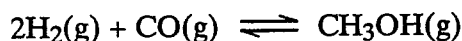
(4 marks)

Upside down expression for k scores zero in (i) for 9073
but rate = $9073 \times (0.2)^2 \times (0.1) = 36(3)$
conseq scores (1) in (ii)

TURN OVER FOR THE NEXT QUESTION

6

- 2 Hydrogen and carbon monoxide were mixed in a 2:1 mole ratio. The mixture was allowed to reach equilibrium according to the following equation at a fixed temperature and a total pressure of 1.75×10^4 kPa.



- (a) The equilibrium mixture contained 0.430 mol of carbon monoxide and 0.0850 mol of methanol.

- (i) Calculate the number of moles of hydrogen present in the equilibrium mixture.

$$0.86 \quad (1)$$

- (ii) Hence calculate the mole fraction of hydrogen in the equilibrium mixture.

(conseq on (i))
$$\text{total moles} = 0.86 + 0.43 + 0.085 = 1.375 \quad (1)$$

$$\therefore \text{mole fraction of H}_2 = \frac{0.86}{1.375} = 0.625 \quad (1)$$

(0.62-0.63)

- (iii) Calculate the partial pressure of hydrogen in the equilibrium mixture.

(conseq on (ii))
$$p_p = \text{mole fract}^n \times \text{total } P \quad (1)$$

$$= 0.625 \times 1.75 \times 10^4$$

$$= 1.09 \times 10^4 \quad (\text{kPa}) \quad (1)$$

$$\text{or } 1.1(0)$$

(5 marks)

- (b) In a different mixture of the three gases at equilibrium, the partial pressure of carbon monoxide was 7550 kPa, the partial pressure of hydrogen was 12300 kPa and the partial pressure of methanol was 2710 kPa.

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

$$K_p = \frac{P_{\text{CH}_3\text{OH}}}{P_{\text{H}_2}^2 \times P_{\text{CO}}} \quad (1) \quad \text{penalize []}$$

- (ii) Calculate the value of the equilibrium constant, K_p , for the reaction under these conditions and state its units.

not conseq to wrong K_p expression

$$K_p = \frac{2710}{(12300)^2 \times (7550)} = \frac{2.37 \times 10^{-9}}{(2.4)} \quad (1) \quad \left[\begin{array}{l} \text{or} \\ 2.37 \times 10^{-15} \\ P_a^{-2} \end{array} \right]$$

$$\text{Units } kPa^{-2} \quad (1)$$

(3 marks)

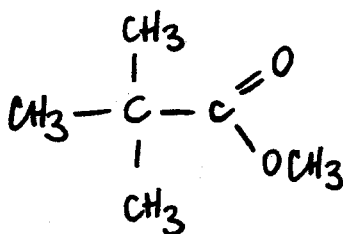
- (c) Two isomeric esters **E** and **F** formed from methanol have the molecular formula $C_6H_{12}O_2$

Isomer **E** has only 2 singlet peaks in its proton n.m.r. spectrum.

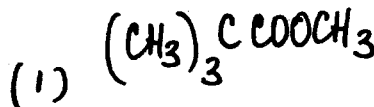
Isomer **F** is optically active.

Draw the structures of these two isomers.

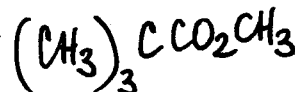
Isomer **E**



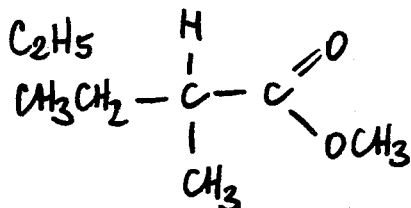
allow



or



Isomer **F**

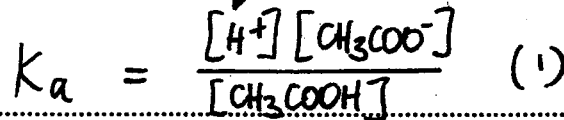


(1)

(2 marks)

- 3 The value of the acid dissociation constant, K_a , for ethanoic acid is $1.74 \times 10^{-5} \text{ mol dm}^{-3}$ at 298 K.

- (a) (i) Write an expression for K_a for ethanoic acid.



- (ii) Calculate the pH at 298 K of a $0.220 \text{ mol dm}^{-3}$ solution of ethanoic acid.

$$(1) \quad K_a = \frac{[H^+]^2}{[CH_3COOH]} \quad (1)$$

$$(2) \quad [H^+] = \sqrt{1.74 \times 10^{-5} \times 0.220} = 1.96 \times 10^{-3} \quad (1)$$

$$(3) \quad pH = -\log_{10} [H^+] \quad (1) \quad [\text{can score independently}]$$

$$(4) \quad = 2.71 \quad (1)$$

(5 marks)

2dp essential.

- (b) A sample of the $0.220 \text{ mol dm}^{-3}$ solution of ethanoic acid was titrated against sodium hydroxide solution.

- (i) Calculate the volume of a $0.150 \text{ mol dm}^{-3}$ solution of sodium hydroxide required to neutralise 25.0 cm^3 of the ethanoic acid solution.

$$\text{moles acid} = \frac{25}{1000} \times 0.220 \quad (1) = 5.50 \times 10^{-3}$$

$$= \frac{x}{10^3} \times 0.150$$

$$\therefore x = \frac{25 \times 0.220}{0.150} \quad \text{or} \quad 5.50 \times 10^{-3} \times \frac{1000}{0.150}$$

$$= 36.7 \text{ cm}^3 \quad (\text{or } 36.6) \quad (1)$$

(or 37)

(NOT 36
not 37.0)

(units must match)

If forget $\sqrt{\quad}$
can score
(1) and (3)
for
pH = 5.42

(ii) From the list below, select the best indicator for this titration and explain your choice.

Name of indicator	pH range
bromophenol blue	3.0 - 4.6
methyl red	4.2 - 6.3
bromothymol blue	6.0 - 7.6
thymol blue	8.0 - 9.6

Indicator thymol blue (1)
 Explanation weak acid - strong base (1)
equivalence at pH > 7 (1)
or high pH
 (5 marks)

(c) A buffer solution is formed when 2.00 g of sodium hydroxide are added to 1.00 dm³ of a 0.220 mol dm⁻³ solution of ethanoic acid. Calculate the pH at 298 K of this buffer solution.

If wrong Mr: CE ∴ lose marks (1) and (2) then mark on consequentially → max 4

- (1) mol NaOH added = $\frac{2.0}{40.0} = 0.050$ (1)
- (2) mol CH₃COOH left = $0.220 - 0.050 = 0.170$ (1)
- (3) mol CH₃COO⁻ formed = 0.050 (1)
- (4) $[H^+] = K_a \frac{[acid]}{[salt]}$ or $pH = pK_a + \log \frac{[A^-]}{[HA]}$ etc. (1)
- (5) $[H^+] = 1.74 \times 10^{-5} \times \frac{(0.170)}{(0.05)}$ $pH = 4.76 + \log \left(\frac{0.05}{0.17} \right)$ (1)
- (6) pH = 4.23 (1) ← correct answer gets ✓✓✓ ✓✓✓

can score these in (5)

If expression wrong; no marks 4/5/6

(6 marks)

Mark (5) is for use of correct values of (acid moles) and (salt moles)
 if one wrong allow pH conseq
 if both wrong, no further marks.

eg. if candidate forgets subtraction in (2) he loses (2) and (5) but can score (1)(3)(4)(6) = ^{max} 4 for pH = 4.12

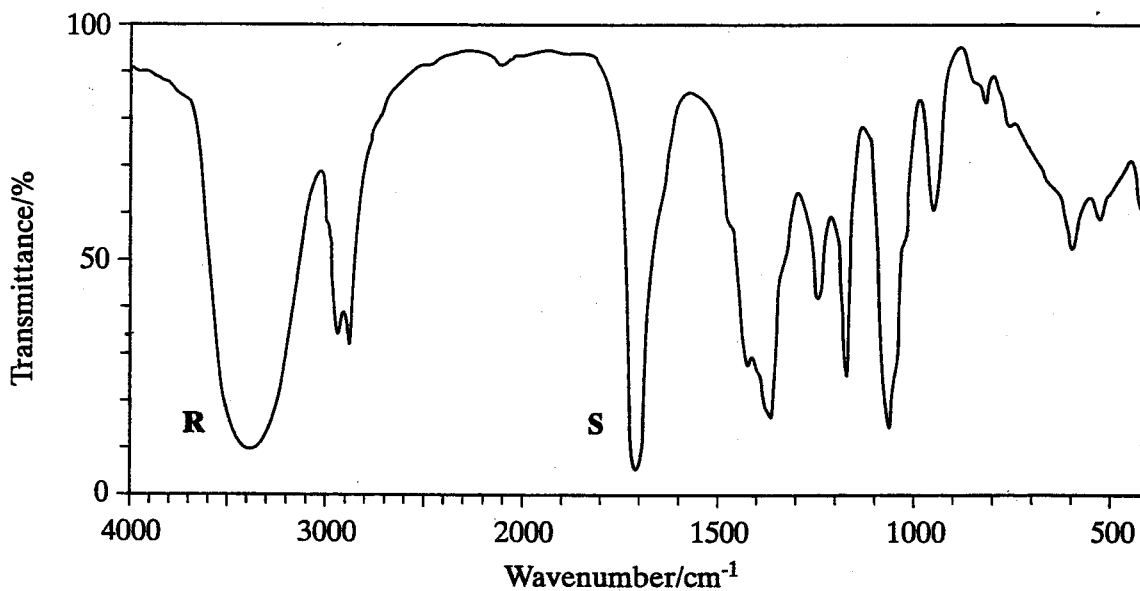
if $\frac{[acid]}{[salt]}$ upside down; answer 5.29 scores 3 for (1)(2)(3)

Turn over

4 Spectral data for use in this question are printed on the reverse of the Periodic Table provided.

Compound **Q** has the molecular formula $C_4H_8O_2$

(a) The infra-red spectrum of **Q** is shown below.



Identify the type of bond causing the absorption labelled **R** and that causing the absorption labelled **S**.

R O-H (alcohols) (1)

S C=O or carbonyl (1)

(2 marks)

(b) **Q** does not react with Tollens' reagent or Fehling's solution. Identify a functional group which would react with these reagents and therefore cannot be present in **Q**.

..... aldehyde (1) -CHO or RCHO

(1 mark)

(c) Proton n.m.r. spectra are recorded using a solution of a substance to which tetramethylsilane (TMS) has been added.

(not solvent, not cheap)

(i) Give two reasons why TMS is a suitable standard.

any
2 x (1) { Reason 1 TMS inert or non-toxic or volatile/easily removed
Reason 2 single (intense) peak or peak/signal upfield of others
..... peak of 12 protons
..... highly shielded
..... has 12 equivalent protons
..... more shielded
..... all protons in same environment
..... peak away from others

- (ii) Give an example of a solvent which is suitable for use in recording an n.m.r. spectrum. Give a reason for your choice.

Solvent CDCl_3 or CCl_4 (1) (NOT D_2O)

Reason proton free (1)

allow no hydrogens (atoms)

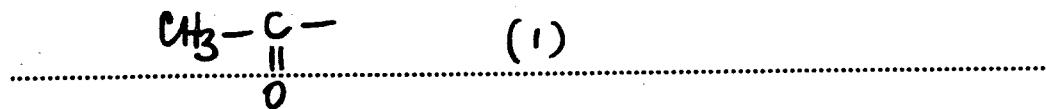
not $\left. \begin{array}{l} \text{H}^+ \\ \text{hydrogen ions} \end{array} \right\}$ (4 marks)

- (d) The proton n.m.r. spectrum of Q shows 4 peaks. The table below gives δ values for each of these peaks together with their splitting patterns and integration values.

δ/ppm	2.20	2.69	3.40	3.84
Splitting pattern	singlet	triplet	singlet	triplet
Integration value	3	2	1	2

What can be deduced about the structure of Q from the presence of the following in its n.m.r. spectrum?

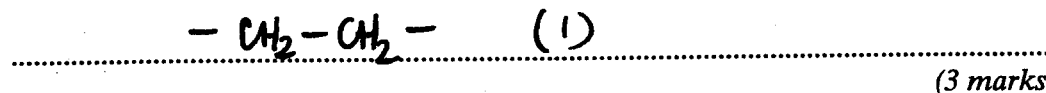
- (i) The singlet peak at $\delta = 2.20$



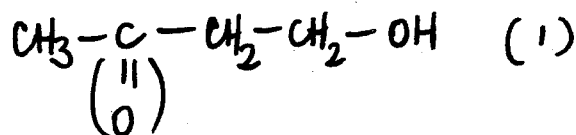
- (ii) The singlet peak at $\delta = 3.40$



- (iii) Two triplet peaks



- (e) Using your answers to parts (a), (b) and (d), deduce the structure of compound Q.



(1 mark)

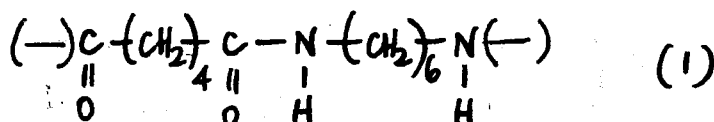
5 (a) Synthetic polyamides are produced by the reaction of dicarboxylic acids with compounds such as $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$

(i) Name the compound $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$

(allow
amine)

hexane-1,6-diamine or 1,6-diaminohexane (1)
or 1,6 hexan(e)diamine

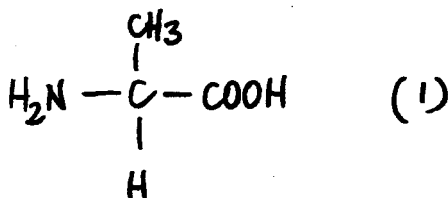
(ii) Give the repeating unit in the polyamide nylon 6,6.



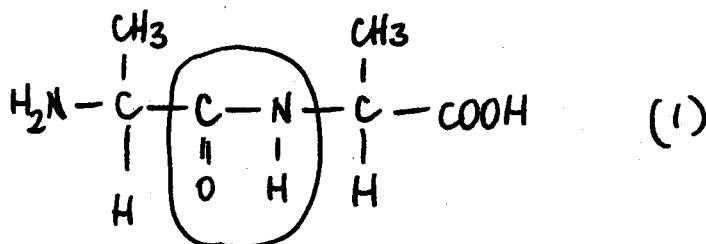
(2 marks)

(b) Synthetic polyamides have structures similar to those found in proteins.

(i) Draw the structure of 2-aminopropanoic acid.



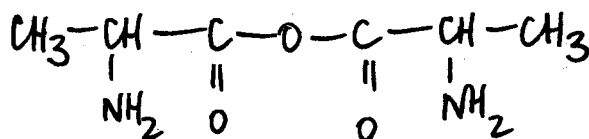
(ii) Draw the organic product formed by the condensation of two molecules of 2-aminopropanoic acid.



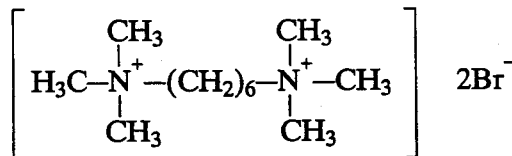
(2 marks)

peptide link essential: the rest is consequential on 6(i)
(allow CONH)

allow anhydride



- (c) Compounds like $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$ are also used to make ionic compounds such as **X**, shown below.



Compound X

- (i) **X** belongs to the same type of compound as $(\text{CH}_3)_4\text{N}^+\text{Br}^-$
Name this type of compound.

allow quaternary
quaternary ammonium salt (1)

(not ion
} not compound
bromide

- (ii) State a reagent which could produce **X** from $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$ and give a necessary condition to ensure that **X** is the major product.

Reagent CH_3Br or bromomethane (1)

Condition excess (CH_3Br) (1)

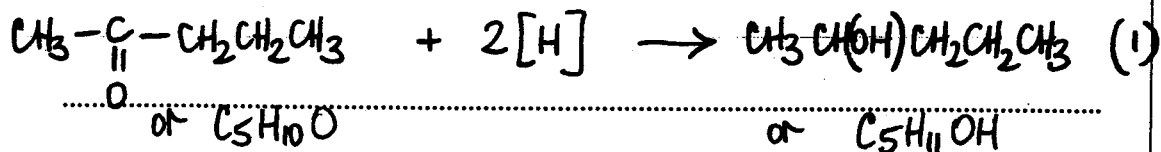
[penalize CH_3Cl
but allow
excess for
any halomethane.]

- (iii) Name the mechanism involved in this reaction to form **X**.

nucleophilic substitution (1)

(4 marks)

- 6 (a) (i) Write an equation for the reduction of pentan-2-one by aqueous NaBH_4 to form pentan-2-ol.
Use $[\text{H}]$ to represent the reductant.

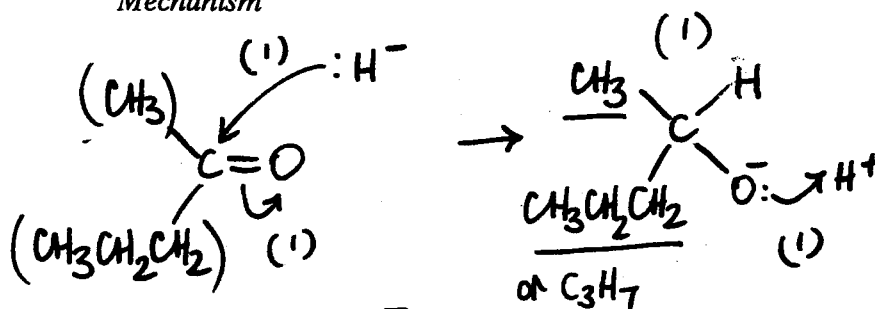


- (ii) Name and outline a mechanism for this reduction.

QOL

Name of mechanism nucleophilic addition (1)

Mechanism



[C=O alone loses this mark]

if structure shown in (i)

- (iii) State why the pentan-2-ol produced in this reaction is not optically active.

racemate
racemic mixture formed (1)

or explained eg 2 enantiomers in equal amounts

(7 marks)

- (b) Predict the m/z values of the two most abundant fragments in the mass spectrum of pentan-2-one.

Fragment 1 } 43 ; 43 } any two x (1)
Fragment 2 } 71 ; 15 }

(2 marks)

SECTION B

Answer the question below in the space provided on pages 13 to 16 of this booklet.

- 7 (a) The term *acylation* can be applied to the reaction of ethanoyl chloride with ethylamine and also to the reaction of ethanoyl chloride with benzene in the presence of a catalyst.

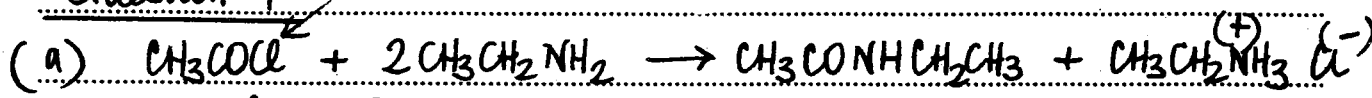
For each of these reactions, write an equation for the overall reaction and name the organic product. Name and outline a mechanism for each reaction and identify a suitable catalyst for the reaction with benzene. (15 marks)

- (b) In the industrial manufacture of aspirin, ethanoic anhydride is used as an acylating agent rather than ethanoyl chloride. Give **two** reasons why ethanoic anhydride is preferred. Describe a simple test to distinguish between a sample of ethanoic anhydride and one of ethanoyl chloride. Write equations for any reactions occurring. (7 marks)

- (c) Ethylamine can be prepared in a two-step synthesis from bromomethane or in a one-step synthesis from bromoethane. Give the reagents and conditions for all the reaction steps involved in these syntheses. State one possible disadvantage for each of these two synthetic routes. (8 marks)

END OF QUESTIONS

Question 7 if "ethyl chloride" see extra sheet

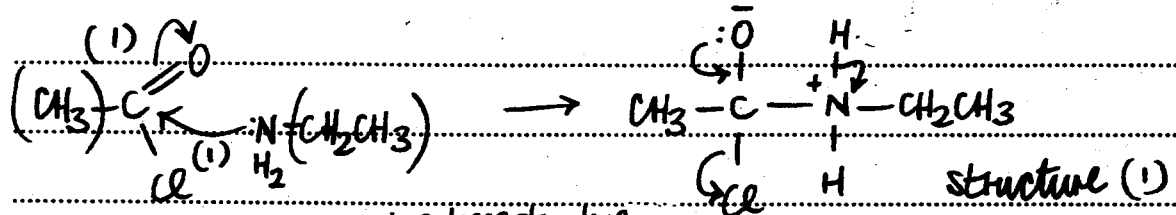


not molecular formula

(N)ethyl ethanamide (1)

eqⁿ (1) only an if structure c product correct

addition-elimination (1)

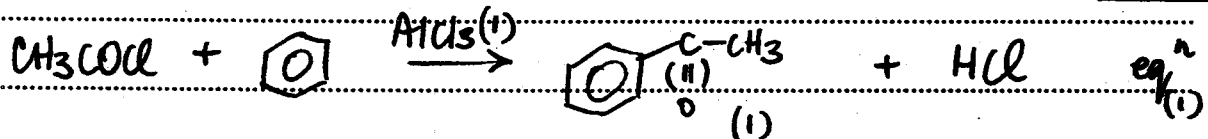


wrong amine loses structure mark

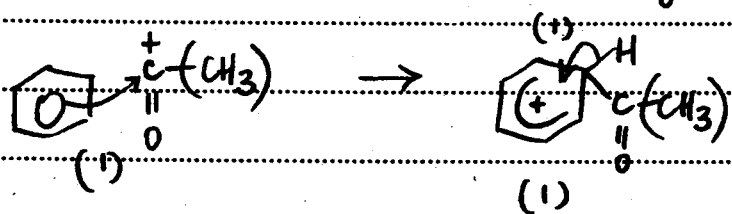
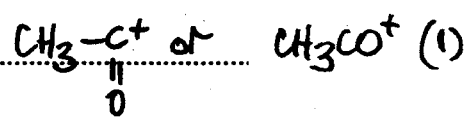
NH₃ loses first mark gained and structure.

3 arrows (1)

[max 8]



phenyl ethanone (1)



electrophilic substitution (1)

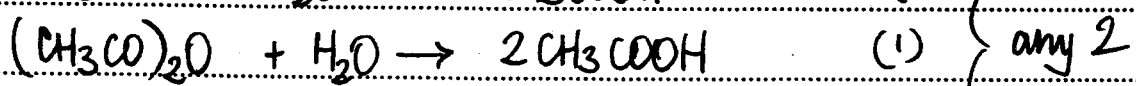
[max 8/9] → [max 15]

(b) Any two from cheaper / less toxic / less corrosive / rigorous or exothermic / less easily hydrolysed (2)

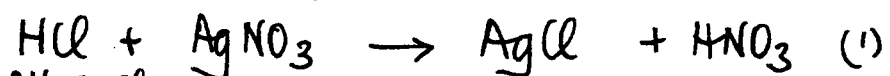
TEST: Add (to) H₂O (1) or alcohol or ammonia OR add (aqueous) AgNO₃ (1) [NOT Na₂CO₃]

anhydride: no fumes (1) or vigorous reaction

chloride: (misty) fumes (1) or pH test on gas described



or inic

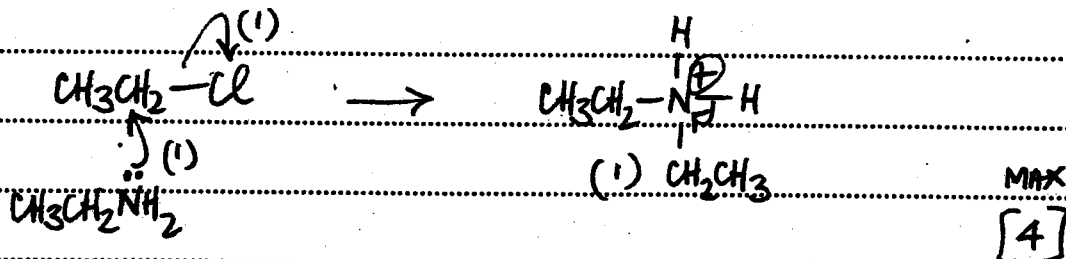


[7]

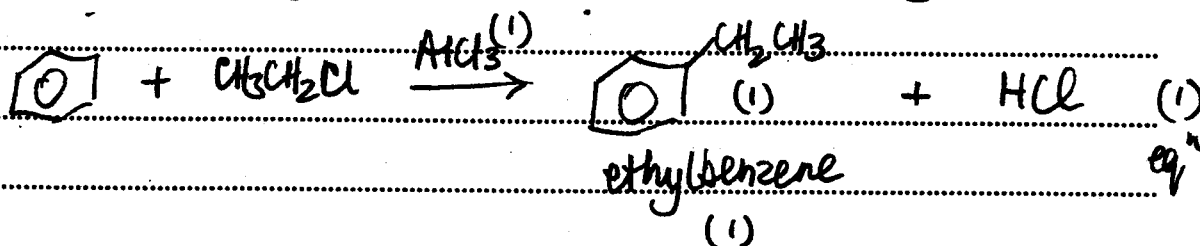
7(a) EXTRA

if $\text{CH}_3\text{CH}_2\text{Cl}$ given for ethanoyl chloride (max 12/15)

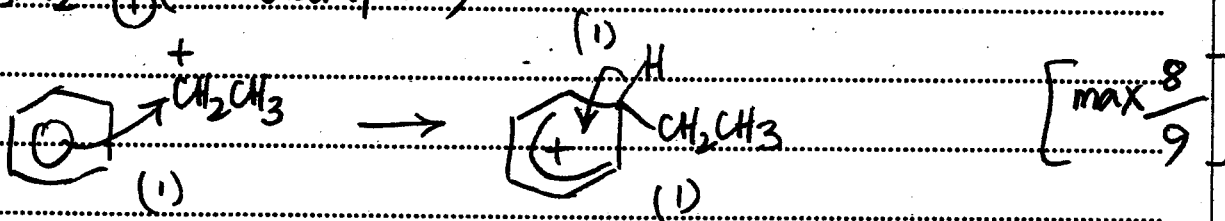
ie. eqⁿ / name no marks out of 3
 with amine mechanism nucleophilic substitution (1)



with benzene (ie alkylation rather than expected acylation)

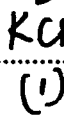
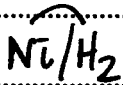


electrophilic substitution (1)

 CH_3CH_2^+ (is electrophile)

(b) If ethanoyl chloride further written as $\text{CH}_3\text{CH}_2\text{Cl}$
 allow test marks if correct description.

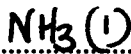
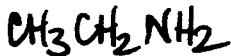
7(c)

NOT HCN / acidified KCN (and lose condition mark)
(aq) / alc or reflux (not just heat)
(1)

or Na/EtOH

or LiAlH_4 [NOT NaBH_4
or Sn/HCl]

(allow correct reducing agent on any nitrile)

Disadvantage: KCN toxic / 2 steps \therefore lower yield likely (1)
or H_2 dangerous not cost/timeexcess (1) or heat in sealed tube
or high pressure(condition:
not just
conc)Disadvantage: further reactions possible (1)
or high P expensive

[8]