Version 1.0: 1006

ASSESSMENT and QUALIFICATIONS ALLIANCE

General Certificate of Education

Chemistry 6421

CHM4 Further Physical and Organic Chemistry

Mark Scheme

2006 examination – June series

Mark schemes are prepared by the Principal Examiner and considered, together with the relevant questions, by a panel of subject teachers. This mark scheme includes any amendments made at the standardisation meeting attended by all examiners and is the scheme which was used by them in this examination. The standardisation meeting ensures that the mark scheme covers the candidates' responses to questions and that every examiner understands and applies it in the same correct way. As preparation for the standardisation meeting each examiner analyses a number of candidates' scripts: alternative answers not already covered by the mark scheme are discussed at the meeting and legislated for. If, after this meeting, examiners encounter unusual answers which have not been discussed at the meeting they are required to refer these to the Principal Examiner.

It must be stressed that a mark scheme is a working document, in many cases further developed and expanded on the basis of candidates' reactions to a particular paper. Assumptions about future mark schemes on the basis of one year's document should be avoided; whilst the guiding principles of assessment remain constant, details will change, depending on the content of a particular examination paper.

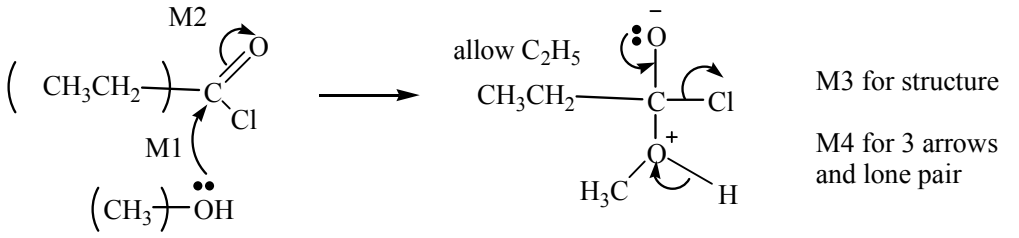
CHM4

SECTION A

Question 1

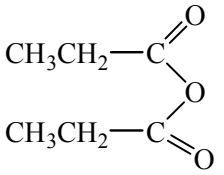
(a) $CH_3OH + CH_3CH_2COOH \rightarrow CH_3CH_2COOCH_3 + H_2O$ 1

(b) (nucleophilic) addition-elimination NOT acylation 1



4

ignore use of Cl^- to remove H^+

(c) 

allow C_2H_5 and $-CO_2-$

allow $CH_3CH_2COOCOCH_2CH_3$ 1

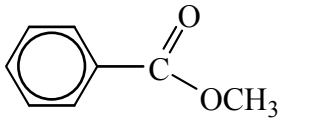
or $(CH_3CH_2CO)_2O$

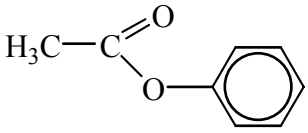
(d) (i) faster/not reversible/bigger yield/purer product/no(acid) (catalyst) required 1

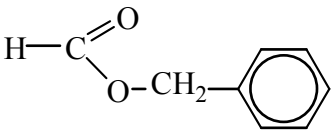
(ii) anhydride less easily hydrolysed or reaction less violent/exothermic
no (corrosive) (HCl) fumes formed or safer or less toxic/dangerous any one 1
expense of acid chloride or anhydride cheaper

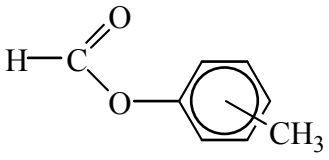
(e) (i) $C_8H_8O_2$ 1

(ii) any **two** from Allow $-CO_2-$ allow C_6H_5









2

Total 12

Question 2

(a) (i) Increase (if wrong no further marks in part (i) 1

higher P gives lower yield or moves to left 1

Eqm shifts to reduce P or eqm favours side with fewer moles 1

(ii) Endothermic if wrong no further marks in part (ii) 1

increase T increases yield or moves to right 1

Eqm shifts to reduce T or eqm favours endothermic direction 1

(b) (i) Moles of iodine = 0.023 If wrong no marks in (i) 1

Moles of HI = 0.172 1

If × 2 missed, max 1 in part (iv)

(ii) $K_c = \dfrac{[H_2][I_2]}{[HI]^2}$ must be square brackets (penalise once in paper)

- if round, penalise but mark on in (iv) 1

if K_c wrong, no marks in (iv) either but mark on from a minor slip in formula

(iii) V cancels in K_c expression or no moles same on top and bottom of expression 1

or total moles reactants = moles products, i.e. total no of moles does not change

(iv) $K_c = \dfrac{(0.023)^2}{(0.172)^2}$ Conseq on (i) 1

$= 0.0179$ or 1.79×10^{-2} Allow 0.018 or 1.8×10^{-2} 1

(v) $K_c = 55.9$ or 56 Conseq i.e. (answer to (iv))$^{-1}$ 1

Total mark 13

Question 3

(a) $-\log [H^+]$ ecf if [ ] wrong and already penalised 1

4.57×10^{-3} allow 4.6×10^{-3} ignore units 1

(b) (i) $K_a = \dfrac{[H^+][X^-]}{[HX]}$ allow HA etc not $\dfrac{[H^+]^2}{[HX]}$ but mark on 1

If expression wrong allow conseq
units in (ii) but no other marks in (ii)

(ii) $\dfrac{[H^+]^2}{[HX]} = \dfrac{(4 \cdot 57 \times 10^{-3})^2}{[0 \cdot 150]}$ If use 4.6×10^{-3} 1

$= 1.39 \times 10^{-4}$ $K_a = 1.4(1) \times 10^{-4}$

allow $1.39 – 1.41 \times 10^{-4}$ and pKa = 3.85 1

mol dm^{-3} 1

(iii) $pK_a = 3.86$ Penalise dp of final answer < or > 2 in pH once in paper 1

(c) (i) $\dfrac{30}{1000} \times 0.480 = 0.0144$ or $1.4(4) \times 10^{-2}$ Mark is for answer (M1) 1

(ii) $\dfrac{18}{1000} \times 0.350 = 0.0063$ or 6.3×10^{-3} Mark is for answer (M2) 1

(iii) $0.0144 – 2(0.0063) = 1.80 \times 10^{-3}$ M3 is for (i) - 2(ii) 1

If x 2 missed, CE i.e. lose M3 and the next mark gained

(iv) $1.80 \times 10^{-3} \times \dfrac{1000}{48} = 0.0375$ (0.038) M4 is for answer 1

If vol is not 48×10^{-3} (unless AE) lose M4 and next mark gained

If vol is 48 - this is AE – i.e. lose only M4

If multiply by 48×10^{-3} this is AE – i.e. lose only M4

(v) $10^{-14} / 0.0375$ ($10^{-14} / 0.038$) M5 for $K_w/[OH^-]$ 1

(= 2.66×10^{-13}) (= 2.63×10^{-13}) or pOH

or pOH = 1.426 (or pOH = 1.420)

If no attempt to use K_w or pOH lose both M5 and M6

pH = 12.57 (12.58) M6 1

Allow M6 conseq on AE in M5 if method OK

Total mark 13

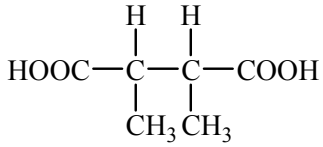
Question 4

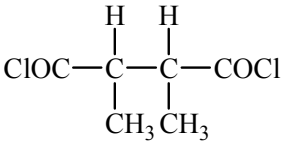
(a) (i) $CH_3CH=CHCH_3$ 1

Addition or radical **(QoL)** 1

(ii) $CH_3CH(OH)CH(OH)CH_3$ or with no brackets 1

butan(e)-2,3-diol or 2,3-butan(e)diol 1



allow  1

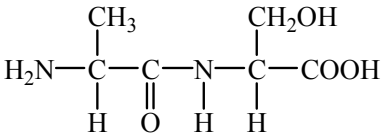
2,3-dimethylbutan(e)dioic acid ignore -1,4- 2,3-dimethylbutan(e)dioyl chloride 1

condensation (**QoL**) 1

(iii) NaOH or HCl etc or Na_2CO_3 **NOT** water nor acidified water nor weak acids 1

Allow conc sulphuric/nitric

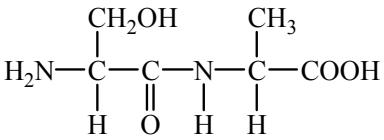
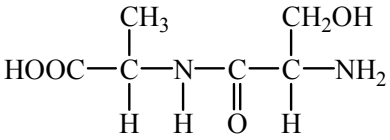
(b) Structure 1 Allow -CONH- and -COHN-



Allow zwitterions

NOT polypeptides/repeating units 1

Structure 2 either of

 or  1

(c) (i) $CH_3CH_2CH_2Br$ allow –Cl, -I 1

(ii) CH_3CH_2CN 1

(iii) (nucleophilic) substitution or from $CH_3CH_2CH_2Br$ if reduction written here, no further marks 1

further substitution/reaction occurs or other products are formed Allow reduction forms only one product 1

one of Allow salts including NH_4Br

$(CH_3CH_2CH_2)_2NH$ Allow HBr

$(CH_3CH_2CH_2)_3N$ 1

$(CH_3CH_2CH_2)_4N^+ Br^-$

Total mark 15

Question 5

(a) k = rate/$[CH_3CH_2COOCH_3][H^+]$ 1

or

$$= \frac{1 \cdot 15 \times 10^{-4}}{(0.150)(0.555)}$$

= 1.38×10^{-3} to 1.4×10^{-3} 1

$mol^{-1}dm^3s^{-1}$ 1

(b) ans = rate constant × (½ × 0.150) × (½ × 0.555) ignore units 1

= rate constant × 0.0208

2.88×10^{-5} (1.38×10^{-3} gives 2.87×10^{-5})

Allow $2.87 – 2.91 \times 10^{-5}$ (1.4×10^{-3} gives 2.91×10^{-5})

(c) $[H^+]$ = rate/ $k[CH_3COOCH_2CH_3]$ 1

$$= \frac{4.56 \times 10^{-5}}{(8 \cdot 94 \times 10^{-4})(0 \cdot 123)}$$

= 0.415 (0.4146) 1

pH = 0.38 mark independently $[H^+]$ = 0.41 gives pH = 0.39 1

Total Mark 7

SECTION B

Question 6

(a) $CH_3COCl + AlCl_3 \longrightarrow CH_3\overset{+}{C}O + AlCl_4^-$ 2

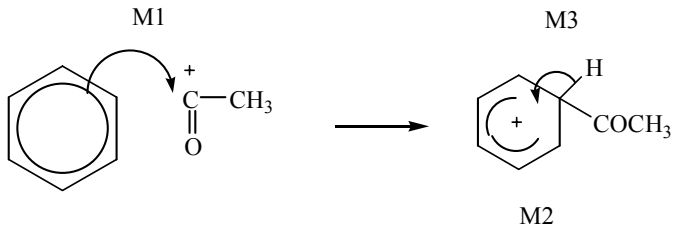
(1) equation (1)

penalise wrong alkyl group once at first error

position of + on electrophile can be on O or C or outside [ ]

penalise wrong curly arrow in the equation or lone pair on $AlCl_3$ else ignore

Electrophilic_substitution NOT F/C acylation 1



horseshoe must not extend beyond C2 to C6 but can be smaller 3

+ not too close to C1

M3 arrow into hexagon unless Kekule

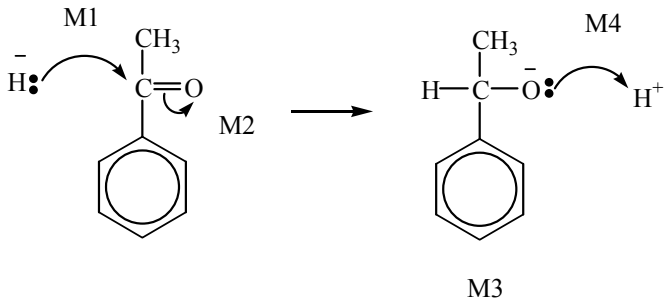
allow M3 arrow independent of M2 structure

M1 arrow from within hexagon to C or to + o n C

+ must be on C of $\overset{+}{R}CO$

(6 marks)

(b) Nucleophilic_addition NOT reduction 1



M2 not allowed independent, but can allow M1 for attack of H^- on C+ formed 4

1-phenylethan(-1-)ol or (1-hydroxyethyl)benzene 1

(6 marks)

(c) dehydration or elimination 1

(conc) H_2SO_4 or (conc) H_3PO_4 allow dilute and Al_2O_3 1

Do not allow iron oxides

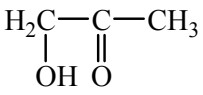
(2 marks)

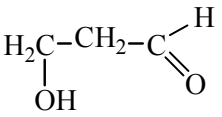
(Total 14 marks)

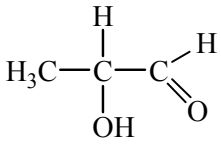
Question 7

(a) **X** **(**O-H) (alcohols) penalise acid or missing "alcohol" 1

Y C=O allow carbonyl 1





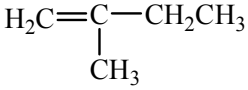


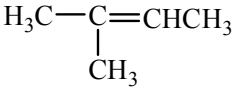
NOT acid

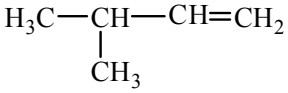
3

A 1

(6 marks)

(b) 



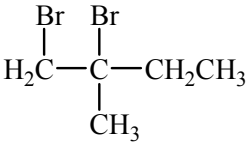


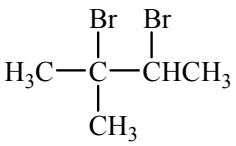
3

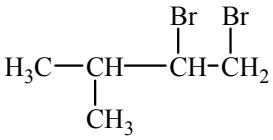
Allow conseq dibromocompounds following incorrect unbranched alkenes

NOT allow dibromocompound consequent on a duplicate alkene

NOT allow monobromocompounds if HBr added







3

6:3:1 either next to correct structure or to none 1

Allow a mark for identifying correct dibromocompound with three peaks even if integration ratio is wrong 1

if 6:3:1 missing or wrong, no marks for splitting

Only award a mark for splitting if it is clear which integration number it refers to

6 singlet or drawn 1

3 doublet or drawn 1

1 quartet/quadruplet or drawn 1

(max 10 marks)

(Total 16 marks)