Mark schemes

1

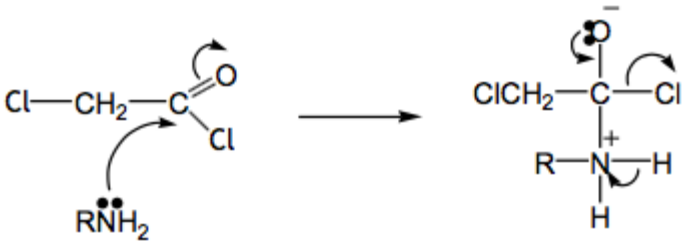
(a) (i) (2-)chloroethan (-1-) oyl chloride

2 not required but penalise 1- or other numbers at start. Ignore 1 in ethanoyl

Ignore hyphens, commas, spaces

1

(ii)



M1 for arrow from lp on N to C

(or to space half way between N and C)

If full amine drawn, ignore slips except in –NH_2

M2 for arrow from C=O bond to O

Not score M2 as an independent first step, but can allow M1 for attack on C+ produced

If Cl lost at this stage, Max 1 for M1

M3 for structure of ion including 2 charges

M4 for 3 arrows and lp on O

- may be scored in two steps

Ignore use of RNH_2 to remove H+ in M4, but penalise use of Cl^-

4

(b) Nucleophilic substitution

Allow minor spelling errors e.g. nucleophyllic

1

(c) 9

1

(d) M_r = 234(.0)

9.4 scores 2 marks

1

% H = 9.4(0)

M2 = $\frac{22}{M1} \times 100$

If M_r = 234 not shown, can score M1 if their answer × 234 = their no of H

1

(e) Tertiary amine OR 3^o amine OR III^o amine

Ignore N- substituted

1

(f) (i) If ***a*** given: CE=0, can only score if answer given is **b**

M1 lp on N^b or on **b**

M2 alkyl groups donate electron density or positive inductive effect or electron donating groups attached

M3 (lp on N^b) more available or protonated amine stabilised or better lp donor/H^+ acceptor

Ignore reference to nucleophiles

*NOTE – there is NO mark for **b** alone*

Alternatives

*M1 lp on N^a or on **a***

M2 lp or electrons (on N^a) <u>delocalised</u> into ring /towards O in C=O

M3 (lp on N^a) less available (to bond to H^+/accept proton)

1
1
1

(ii) Salt is ionic

Independent marks

1

(More) soluble (in blood/body fluids/water)

1

[15]

2 (a) Electrophilic substitution

Both words needed

Ignore minor misspellings

1

(b) (i) Sn / HCl
OR H_2 / Ni **OR** H_2 / Pt **OR** Fe / HCl **OR** Zn / HCl **OR** $SnCl_2$ / HCl

Ignore conc or dil with HCl,

Allow (dil) H_2SO_4 but not conc H_2SO_4

Not allow HNO_3 or H^+

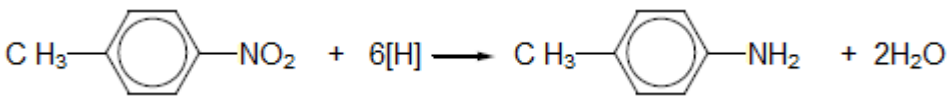
Ignore NaOH after Sn / HCl

Ignore catalyst

1

(ii) $CH_3C_6H_4NO_2 + 6[H] \rightarrow CH_3C_6H_4NH_2 + 2H_2O$

OR



Allow molecular formulae as structures given

$C_7H_7NO_2 + 6[H] \rightarrow C_7H_9N + 2H_2O$

Qu states use [H], so penalised $3H_2$

1

(iii) <u>making</u> dyes

OR <u>making</u> quaternary ammonium salts

OR <u>making</u> (cationic) surfactants

OR <u>making</u> hair conditioner

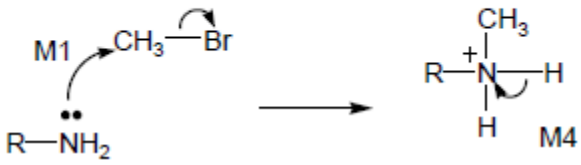
OR <u>making</u> fabric softener

OR <u>making</u> detergents

1

(c)

M2



M3

NO Mark for name of mechanism

Allow SN1

M1 for lone pair on N and arrow to C or mid point of space between N and C

M2 for arrow from bond to Br

M3 for structure of protonated secondary amine

M4 for arrow from bond to N or + on N

For M4: ignore RNH_2 or NH_3 removing H^+ but penalise Br^-

4

(d) <u>lone or electron pair on N</u>

If no mention of lone pair CE = 0

If lone pair mentioned but not on N then lose M1 and mark on

M1

1

in **J** spread / delocalised into ring (or not delocalised in K)

Ignore negative inductive effect of benzene

*Allow interacts with **Π** cloud for M2*

M2

1

less available (for protonation or donation in **J**)

M3

OR

in **K** there is a positive inductive effect / electron releasing)

M2

more available (for protonation or donation in **K**)

M3

1

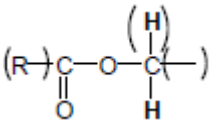
[11]

3

(a) M1 Ester **1**

If Ester 2, can score M3 only.

1

M2 peak at δ = 4.1 due to 

When marking M2 and M3, check any annotation of structures in the stem at the top of the page.

1

M3 (δ = 4.1 peak is) quartet as <u>adjacent / next to / attached to CH_3</u>

1

M4 Other spectrum quartet at δ = 2.1-2.6 (or value in this range)

1

(b) M1 <u>Quaternary</u> (alkyl) <u>ammonium salt / bromide</u>

1

M2 CH_3Br or bromomethane

Penalise contradictory formula and name.

1

M3 Excess (CH_3Br or bromomethane)

Mention of acid eg H_2SO_4 OR alkali eg NaOH loses both M2 and M3.

1

M4 Nucleophilic substitution

Can only score M3 if reagent correct.

Ignore alcohol or ethanol (conditions) or Temp.

1

(c)

	Bromine (penalise Br but mark on)	Acidified $KMnO_4$ (Penalise missing acid but mark on)

Wrong reagent = no marks.

If bromine colour stated it must be red, yellow, orange, brown or any combination, penalise wrong starting colour.

1

Benzene	no reaction / colour remains / no (visible) change	no reaction / colour remains / no (visible) change

Ignore 'clear', 'nothing'.

Allow colour fades slowly.

Allow 'nvc' for no visible change.

1

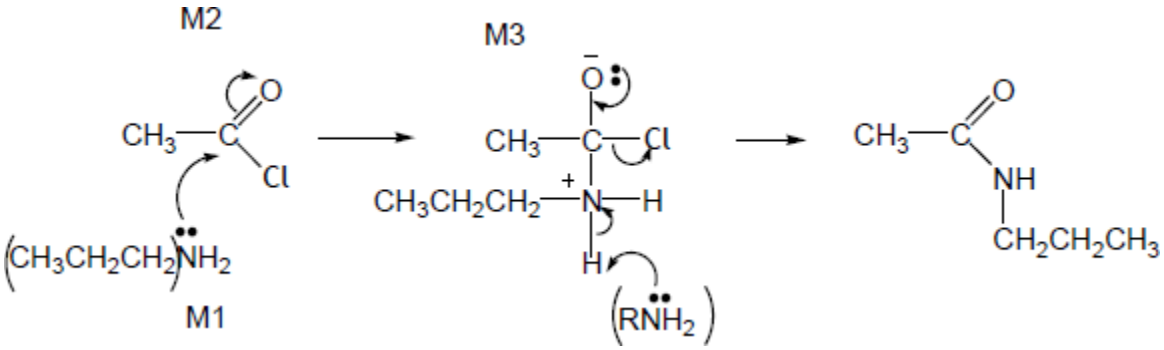
cyclohexene	(Bromine) decolourised	(Acidified $KMnO_4$) decolourised

1

[11]

4 (a) (nucleophilic) addition-elimination

1



M4 for 3 arrows and lp

Allow wrong amine in M1 but penalise in M3

Allow C_3H_7 in M3

Minus sign on NH_3 loses M1 (but not M4 if NH_3 also shown here)

- *Allow attack by: $NH_2CH_2CH_2CH_3$*
- *M2 not allowed independent of M1, but allow M1 for correct attack on C^+*
- *+ rather than δ+ on C=O loses M2*
- *If Cl lost with C=O breaking, max 1 for M1*
- *M3 for correct structure <u>with charges</u> but lone pair on O is part of M4*
- *3 arrows in M4 can be shown in two separate steps.*
- *If M3 drawn twice, mark first answer eg ignore missing + if missed off second structure*
- *Only allow M4 after correct / very close M3*
- *For M4, ignore RNH_2 removing H^+ but lose M4 for Cl^- removing H^+ in mechanism,*
- *but ignore HCl shown as a product.*

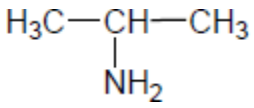
4

<u>N-propylethanamide</u> must be this name even if wrong amine used

NOT N-propylethaneamide

1

(b) (i)



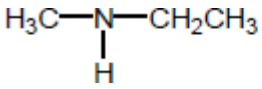
Primary

Not allow ambiguous $C_3H_7NH_2$

BEWARE No mark for the original amine $CH_3CH_2CH_2NH_2$

Label and structure must both be correct for each type to score the mark.

1

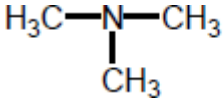


Secondary

Allow C_2H_5

Penalize wrong number of carbons but otherwise correct, first time only.

1



tertiary

1

(ii) Absorption at 3300−3500 (cm^{-1}) in spectrum

Allow trough, peak, spike.

Ignore absorption at 750 − 1100 for C–C bond in secondary - this is within fingerprint region.

Allow any number in this range.

If range missing, no further marks.

If range linked to tertiary, no further marks.

1

N–H (bond) (only) present in secondary amine or not present in tertiary amine

OR

This peak or N–H absorption (only) present in spectrum of secondary amine or not present in spectrum of tertiary amine

1

(c) (i) M1 Route **A**: stage 1 KCN

Apply list principle for extra reagents or catalysts
NOT HCN NOT KCN / acid Not KCN / HCN

1

M2 Aqueous or ethanolic

M2 only scores after correct M1
ignore warm; acid here loses M1 & M2

1

M3 Route **A** Intermediate CH_3CH_2CN or propanenitrile

If M3 intermediate wrong, max 2 for M1 & M2 ie no mark for stage 2

Name alone must be exactly correct to gain M1 but mark on if name close

But if M3 intermediate close, eg "nitrile" or wrong nitrile, can award marks in stage 2

correct formula gains M1 (ignore name if close)

If stage 1 correct and intermediate is missing, can award marks in stage 2

contradiction of name and formula loses mark

stage 1 wrong & intermediate missing, no marks.

1

M4 Route **A**: stage 2 H_2

H loses M4 but mark on

$LiAlH_4$

Apply list principle for extra reagents or catalysts.

M5 only scores after correct M4

Not $NaBH_4$ not Sn or Fe / HCl

Allow (dil) acid after but not with $LiAlH_4$

Penalise conc acid.

1

M5 Ni or Pt or Pd

ether

1

M6 Route **B** NH_3

With acid loses M6 & M7

Apply list principle for extra reagents or catalysts.

1

M7 Excess NH_3

Ignore conc, ignore high P, ignore solvent.

1

(ii) Route **A** disadv Toxic / poisonous KCN or cyanide or CN^- or HCN

Expensive $LiAlH_4$
ignore acidified

OR lower <u>yield</u> because 2 steps

Allow H_2 flammable / explosive etc.

Not just dangerous.

Ignore time reasons.

1

Route **B** disadv Further reaction / substitution likely

Allow impure product.

1

[20]

5

(a) M1 Lone pair on N labelled b more available / more able to be donated than lone pair on N labelled *a*

Ignore N(b) more readily accepts protons.

Ignore N(b) is stronger base.

1

M2 lp or electrons or electron density on N labelled *a:*

delocalized into (benzene) ring

QoL

1

M3 lp or electrons or electron density on N labelled *b:*

methyl / alkyl groups electron releasing or donating or (positive) inductive effect or push electrons or electron density

QoL

1

(b) $C_{19}H_{24}N_2$

Any order.

1

11

1

[5]

6

Measure pH with a meter

Chemical indicators not allowed for M1 (allow mark for M2 if student describes differences in pHs but not for differences in colours).

1

Methylamine would have a higher pH / ammonia would have a lower pH

Use of $CuSO_4$ not allowed.

1

[2]

7

(a) Sn / HCl ***OR*** Fe / HCl not conc H_2SO_4 nor any HNO_3

Ignore subsequent use of NaOH

Ignore reference to Sn as a catalyst with the acid

Allow H_2 (Ni / Pt) but penalise wrong metal

But NOT $NaBH_4$ $LiAlH_4$ Na / C_2H_5OH

1

Equation must use molecular formulae

$C_6H_4N_2O_4 + 12\ [H]$

12[H] and $4H_2O$ without correct molecular formula scores 1 out of 2

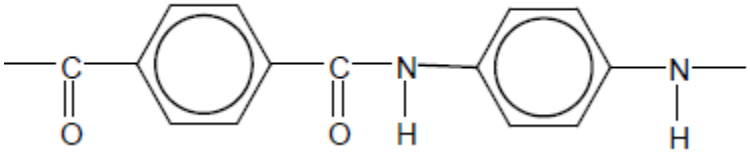
1

$\rightarrow C_6H_8N_2 + 4H_2O$

Allow .... + $6H_2$ if H_2 / Ni used

Allow −CONH− or −COHN− or $-C_6H_4-$

1



Mark two halves separately: lose 1 each for

- *error in diamine part*
- *error in diacid part*
- *error in peptide link*
- *missing trailing bonds at one or both ends*
- *either or both of H or OH on ends*

Ignore n

2

(b) H_2 (Ni / Pt) but penalise wrong metal

NOT Sn / HCl, $NaBH_4$ etc.

1

CH_2

1

In benzene 120°

1

In cyclohexane 109° 28’ or 109½°

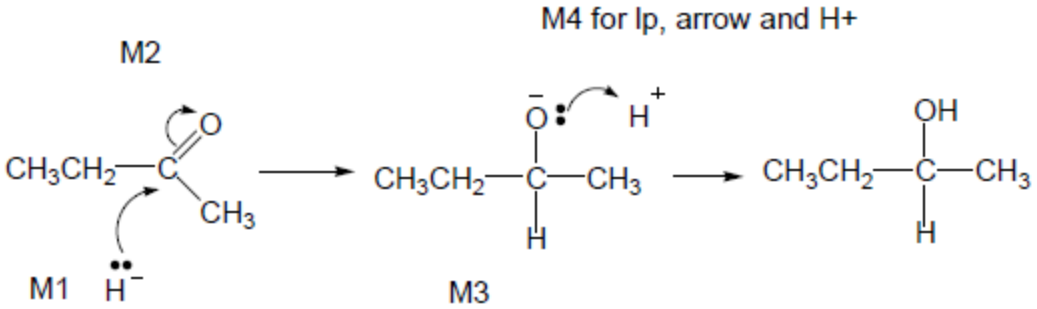
Allow 108° - 110°

If only one angle stated without correct qualification, no mark awarded

1

(c) (i) Nucleophilic addition

1



- *M2 not allowed independent of M1, but allow M1 for correct attack on C+*
- *+ rather than δ+ on C=O loses M2*
- *M3 is for correct structure including minus sign but lone pair is part of M4*
- *Allow C_2H_5*
- *M1 and M4 include lp and curly arrow*
- *Allow M4 arrow to <u>H</u> in H_2O (ignore further arrows)*

4

(ii) M1 Planar C=O (bond / group)

Not just planar molecule

1

M2 Attack (equally likely) from either side

Not just planar bond without reference to carbonyl

1

M3 (about product): Racemic mixture formed ***OR*** 50:50 mixture or each enantiomer equally likely

1

[17]