AQA A-LEVEL CHEMISTRY · 7405

CHEMISTRY



MARK SCHEME

3.3.11 AMINES

SCORE	PERCENTAGE
/121	%

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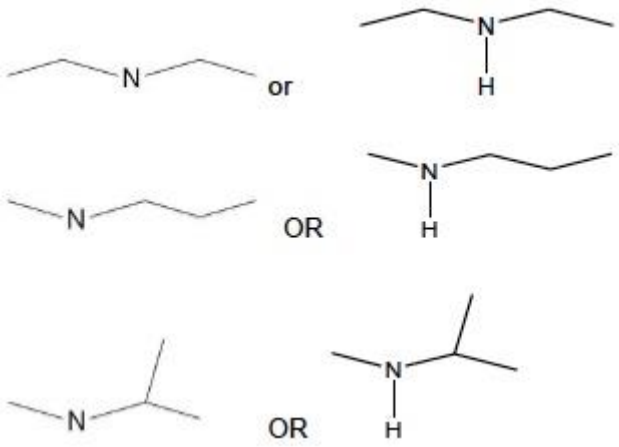
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Q1.

(a) C B A this order only

1

(b) Any three from

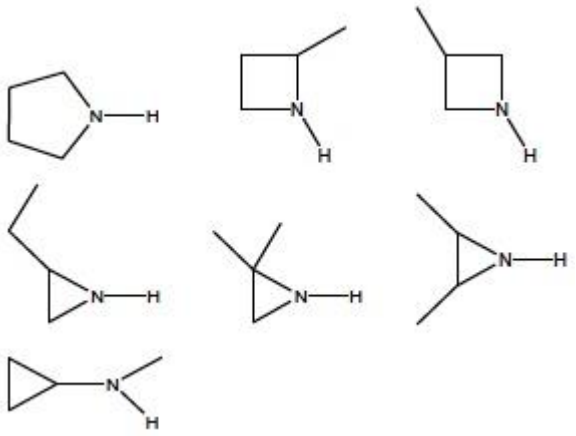


Must be skeletal *– allow with or without H on N*

All 3 correct score 2 (or one if not skeletal)

Any two correct score 1 (or zero if not skeletal)

Allow cyclic II° amines but NOT amines also containing other functional groups



2

(c) With halogenoalkane:

further reaction (of primary amines)

OR

Impure product/mixture of products/lower atom economy

Ignore bi-product / yield

1

With nitriles

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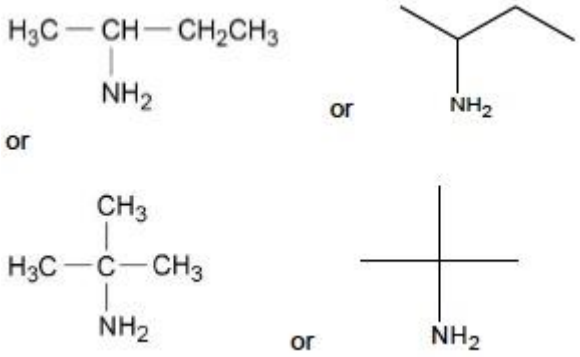
No further reaction

OR

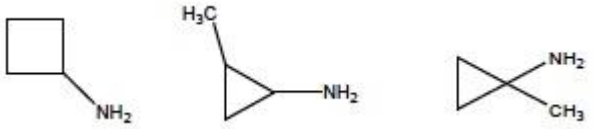
Single product / higher atom economy

1

(d)



Allow cyclic I° amines but NOT amines also containing other functional groups



1

(e) $CH_3CH_2CH_2NH_2 + H_2O \rightleftharpoons CH_3CH_2CH_2NH_3^+ + OH^-$

Allow simple arrow

Not C_3H_7

1

(green) turns blue

Allow blue-green, blue-purple

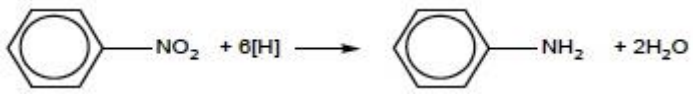
1

(f) $C_6H_5NO_2 + 6[H] \rightarrow C_6H_5NH_2 + 2H_2O$

Not H2

Not molecular formulae

OR



1

$C_6H_5NH_2$ present as ionic salt OR $C_6H_5NH_3^+$ (Cl^-) OR phenyl ammonium (chloride)

Allow present as an ion

But not phenylammonium hydroxide

1

[10]

Q2.

C

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[1]

Q3.

(a) (Strength depends on availability of) <u>lone pair on N</u> (atom)

M1

E N (next to ring): (lp) <u>delocalised</u> into ring

M2

(lp) less available (to donate to or to accept a H^+)

M3

F or **G**: N (next to alkyl): (positive) inductive effect/electrons pushed to N

M4

(lp) more available (to donate to or to accept a H^+)

M5

order of increasing base strength **E<G<F**

*Or **F** is most basic **and E** is least basic*

M6

(b) Intermediate compounds

Product of step 1 $C_6H_5CH_1Cl$

Allow $C_6H_5CH_2Br$

Product of step 2 $C_6H_5CH_2CN$

In steps 2 and 3, only allow marks for reagents/conditions if intermediate compounds are correct or close.

Reagents/conditions

Step 1
Cl_2 & UV

Allow Br_2 & UV

Step 2
KCN alcoholic & aq (both reqd)

Ignore temperature

Step 3
H_2 / Ni or Pt or Pd

Allow $LiAlH_4$ in (dry) ether – (with acid CE, followed by acid allow)

Not $NaBH_4$ and not Sn/HCl or Fe/HCl

2

[11]

Q4.

C

[1]

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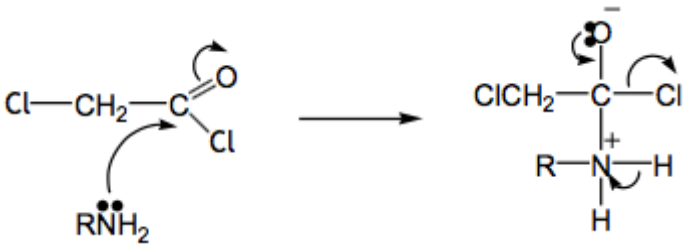
Q5.

(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° amine OR III° amine

Ignore N- substituted

1

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

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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]

Q6.

(a) M1 <u>Lone pair</u> on N labelled b <u>more available / more able to be donated</u> 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:*

<u>delocalized</u> into_(benzene) <u>ring</u>

QoL

1

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

methyl / alkyl groups <u>electron releasing or donating</u> 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]

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Q7.

(a) **M1** Benzene is more stable than cyclohexatriene

more stable than cyclohexatriene must be stated or implied

If benzene more stable than cyclohexene, then penalise M1 but mark on

If benzene less stable: can score M2 only

1

M2 Expected $\Delta H^{\ominus}$ hydrogenation of C_6H_6 is 3(–120)

= –360 kJ mol^{-1}

Allow in words e.g. expected $\Delta H^{\ominus}$ hydrog is three times the $\Delta H^{\ominus}$ hydrog of cyclohexene

1

M3 Actual $\Delta H^{\ominus}$ hydrogenation of benzene is

152 kJ mol^{-1} (less exothermic)

or 152 kJ mol^{-1} different from expected

Ignore energy needed

1

M4 Because of delocalisation or electrons spread out or resonance

1

(b) **No mark for name of mechanism**

Conc HNO_3

If either or both conc missing, allow one;

1

Conc H_2SO_4

this one mark can be gained in equation

1

$2\ H_2SO_4 + HNO_3 \rightarrow 2\ HSO_4^- + NO_2^+ + H_3O^+$

OR

$H_2SO_4 + HNO_3 \rightarrow HSO_4^- + NO_2^+ + H_2O$

OR via two equations

$H_2SO_4 + HNO_3 \rightarrow HSO_4^- + H_2NO_3^+$

$H_2NO_3^+ \rightarrow NO_2^+ + H_2O$

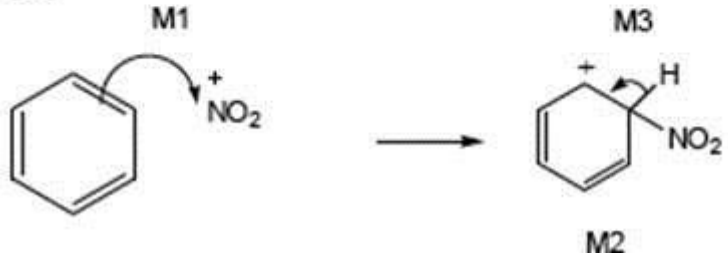
Allow + anywhere on NO_2^+

1

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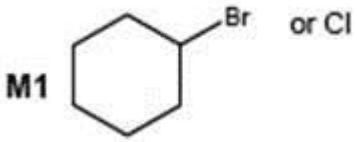
OR



M1 arrow from within hexagon to N or + on N
Allow NO_2^+ in mechanism
horseshoe must not extend beyond C2 to C6 but can be smaller
+ not too close to C1
M3 arrow into hexagon unless Kekule
allow M3 arrow independent of M2 structure
ignore base removing H in M3
+ on H in intermediate loses M2 not M3

3

(c) **If intermediate compound V is wrong or not shown, max 4 for 8(c)**



or chlorocyclohexane or bromocyclohexane

1

Reaction 3

M2 HBr

1

M3 Electrophilic addition

Allow M2 and M3 independent of each other

1

Reaction 4

M4 Ammonia if wrong do not gain M5

1

Allow M4 and M6 independent of each other

M5 Excess ammonia or sealed in a tube or under pressure

1

If CE e.g. acid conditions, lose M4 and M5

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M6 Nucleophilic substitution

1

(d) Lone or electron pair on N

No marks if reference to ''lone pair on N'' missing

1

Delocalised or spread into ring in U

1

Less available (to accept protons) or less able to donate (to H^+)

1

[19]

Q8.

D

[1]

Q9.

(a) (i) conc HNO_3

1

conc H_2SO_4

allow 1 for both acids if either conc missing

1

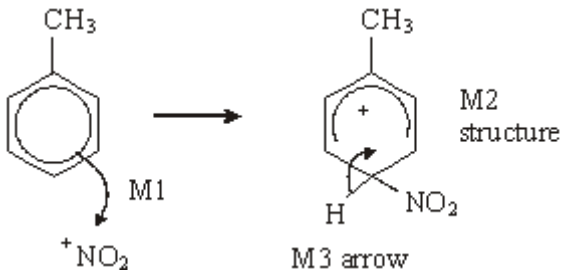
$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$

or $HNO_3 + H_2SO_4 \rightarrow NO_2^+ + H_2O + HSO_4^-$

1

(iii) electrophilic substitution CH_3

1



horseshoe must not extend beyond C2 to C6 but can be smaller
+ must not be too close to Cl

3

(b) Sn or Fe / HCl (conc or dil or neither)
or Ni / H_2 not $NaBH_4$ $LiAlH_4$

1

(c) (i) NH_3

1

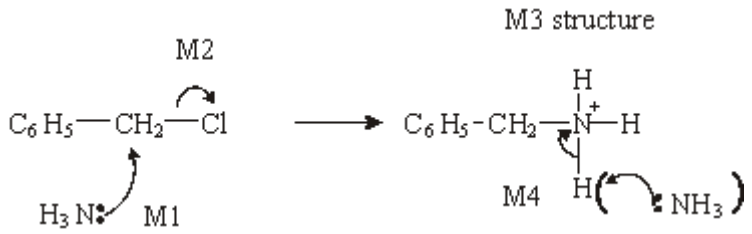
Use an excess of ammonia

1

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(ii) nucleophilic substitution

1



4

[15]

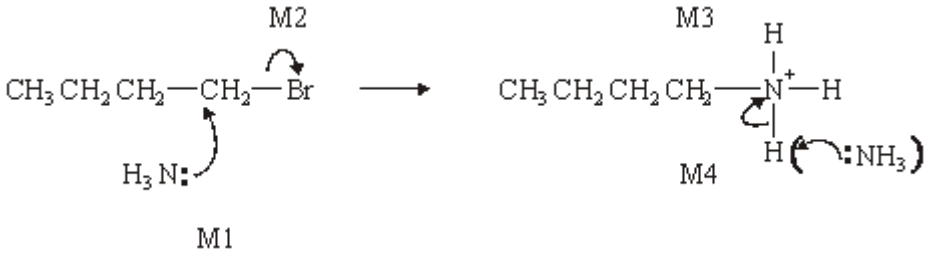
Q10.

B

[1]

Q11.

(a) Nucleophilic substitution



1

M1, M2 and M4 for arrows, M3 for structure of cation

(Allow M2 alone first, i.e. SN1 formation of carbocation)

(Penalise M4 if Br^- used to remove H^+)

4

(b) Step 1 $CH_3CH_2CH_2CN$ 1

$CH_3CH_2CH_2Br + KCN \rightarrow CH_3CH_2CH_2CN + KBr$ balanced

1

(or CN^-) (or Br^-)
(*not HCN*)

1

Step 2 $CH_3CH_2CH_2CN + 2H_2 \rightarrow CH_3CH_2CH_2CH_2NH_2$
(or 4[H])

1

(c) (i) Lone pair (on N) (in correct context)

1

R group increases electron density / donates electrons /pushes electrons / has positive inductive effect

1

(ii) Any strong acid (but not concentrated)
or any amine salt or ammonium salt of a strong acid

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1

(d) $CH_3CH_2N(CH_3)_2$

1

[12]

Q12.

(a) Cyclohexane evolves 120 kJ mol^{-1}

$\therefore$ (expect triene to evole) 360 kJ mol^{-1} **(1)** or 3 × 120

360 – 208 = 152 kJ **(1)** NOT 150

152 can score first 2

*QofL: benzene lower in energy / <u>more</u> (stated) stable **(1)***
Not award if mentions energy required for bond breaking

*due to <u>delocalisation</u> **(1)** or explained*

4

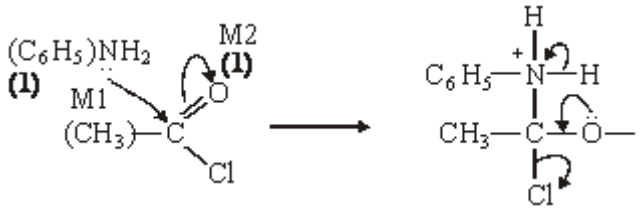
(b) (i) phenylamine weaker **(1)**

if wrong no marks

lone pair on N (less available) **(1)**
delocalised into ring **(1)** or "explained"

3

(ii) addition – elimination **(1)**



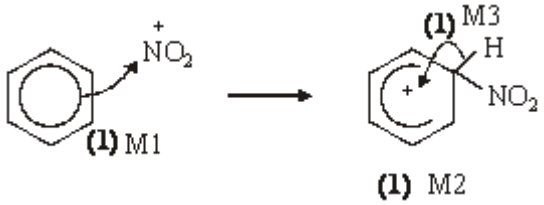
*structure **(1)** M3*
*3 arrows **(1)** M4*

N-phenyl ethanamide **(1)**

6

(iii) conc HNO_3 **(1)**
conc H_2SO_4 **(1)**

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



6

(iv) peptide / amide **(1)**

NaOH (aq) **(1)**

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HCl conc or dil or neither
H_2SO_4 dil NOT conc
NOT just H_2O

2

Notes

(a)
- 360 or 3 × 120 or in words **(1)**;
- 152 NOT 150 **(1)**; (152 can get first two marks)
- **Q of L** benzene more 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)**

(b) (ii) 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
 alone loses M2

(iii) **No marks for name of mechanism in this part**
if conc missing can score one for both acids (or in equation)
allow two equations

allow $HNO_3 + H_2SO_4 \rightarrow NO^{2+} + HSO_4^- + H_2O$
ignore side chain in mechanism even if wrong
arrow for M1 must come from niside hexagon
arrow to NO_2^+ must go to N but be lenient over position of +
+ must not be too near "tetrahedral" Carbon
horseshoe from carbons 2-6 but don't be too harsh

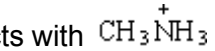
(iv) reagent allow NaOH
HCl conc or dil or neither
H_2SO_4 dil or neither but not conc
not just H_2O

[21]

Q13.

(a) (i) H+ or proton acceptor **(1)**
$CH_3NH_2 + H_2O$ (⇌) $CH_3^+NH_3$ (+) OH^- **(1)**

(ii) CH_3NH_3Cl or HCl **(1)**
Or any ammonium compound or strong acid
name or formula

(iii) extra OH^- reacts with 
or reaction / equilibrium moves to left
or ratio salt / base remains almost constant **(1)**
Any 2

5

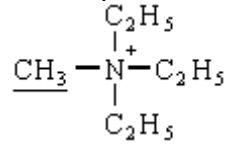
(b) lone pair (on N accepts H^+) **(1)**
CH_3 increases electron density (on N)
donates / pushes electrons

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has positive inductive effect **(1)**

2

(c) nucleophilic substitution **(1)**



(1)

2

[9]

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Q1.

(a) This was answered correctly by almost two-thirds of the students. The most common error was to confuse B and C.

(b) This question discriminated well and the best students drew three correct skeletal formulas. Cyclic secondary amines were accepted as long as there was no other functional group present, and one cyclic amine was sometimes included in place of the isomer with the branched propyl group. A common error was to draw primary amines based on branched alkyl groups.

(c) Both marks were gained by the 28.9% of the students who stated that further substitution reactions would occur following the formation of a primary amine from a halogenoalkane, and also that no further reaction would occur when primary amines were formed from nitriles. The second mark was less often gained, sometimes because students made no comment about nitriles at all.

(d) This was answered well although 12.4% of the students did not attempt the question.

(e) Many students were able to write a correct equation for the reaction between propylamine and water. However, some incorrectly suggested that the weak base would turn the indicator purple. Examiners noted that the use of litmus was sometimes described instead of Universal Indicator. The frequency with which this occurred suggests that some students do not necessarily make a distinction between U. I. and litmus.

(f) A good proportion of students gained the first mark for a correct equation. Only 7.7% could describe the formation of the phenylammonium ion and so explain the solubility of phenylamine in the aqueous acidic solution.

Q2.

A was the commonest incorrect response. 58.3% of students realised that electron-releasing alkyl groups increase the availability of the lone pair on N, making amines more basic than ammonia (D).

Q3.

(a) The full range of marks was seen and included some excellent answers. Other responses did not contain accurate descriptions of the effect of the attached groups on the availability of the lone pair on the nitrogen atom. The idea that, for nitrogen atoms directly attached to the benzene ring, the lone pair was delocalised into the ring was often poorly explained. The (positive) inductive effect of alkyl groups was much better described.

(b) Some excellent answers were seen, but overall this was not answered well. The fact that about 8% of students made no attempt at this part of the question perhaps indicated that a small number of students were short of time. Some students, confused by the presence of a benzene ring, started with nitration. This rarely led to any marks. For those who chose the correct route, the two intermediates were often correctly identified. The use of chlorine or bromine in UV in the first step was usually well known but use of the reagent KCN in a mixed aqueous/alcoholic solvent was less often correct in the next step. The expected reducing agent/condition for the

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final step was hydrogen with a nickel or platinum catalyst. $LiAlH_4$ in dry ether is not required knowledge for this specification, but was an acceptable answer.

Q5.

The IUPAC name in part (a)(i) proved harder than expected with answers including 1-chloro or ethyl. The mechanism in part (a)(ii) was well known with over half of students gaining full marks. There was a wide range of answers to part (d) with both the number of hydrogens and the overall M_r proving harder than expected, but, even so, nearly half of all students scored both marks. Many students knew (e) was tertiary but some thought it was an amide rather than an amine.

Part (f)(i) was generally well done and in the correct responses there was a fairly even distribution between those describing why b is a stronger base or why a is a weaker base. Part (f)(ii) proved more difficult and only the best students scored any marks. The term salt was given in the question and so just that link was not credited. Few stated that the ionic character of the salt would make it more water-soluble than lidocaine itself.

Q6.

Very few students scored all three marks for part (a). The ability of either nitrogen atom to be protonated depended on the availability of the lone pair and this needed to be mentioned for the first mark. The inductive effect of the alkyl groups on the nitrogen labelled b was the most often scored mark. Many failed to mention that the lone pair on the nitrogen labelled a would be delocalised into the benzene ring, often stating that the benzene rings are electron withdrawing or simply that there were delocalised electrons present.

Part (b) was poorly answered with a structural formula sometimes being given or alternatively a molecular formula but with an incorrect number of hydrogen atoms. The number of ^{13}C peaks was also found difficult and eight was a common wrong answer.

Q7.

In part (a), although most candidates scored at least half marks, some candidates did not use the data as requested. Some answers also referred to cyclohexatriene but went on to talk about one double bond.

Part (b) was well done, especially the mechanism. The most common errors were to omit *concentrated* for either or both acids or to omit the positive charge on the $H_2NO_3^+$ when writing two equations.

The synthesis in part (c) was a stretch and challenge question and was, as expected, very discriminating. There were some excellent answers but also many which failed to score.

Many candidates were unable to identify V and those who did often named it as a halobenzene even if they drew a correct structure. Preparation of the amine by nucleophilic substitution using an excess of ammonia was credited in Reaction 4 even if the answers to V and Reaction 3 were wrong.

A surprising number of candidates thought a base was a proton donor. Some otherwise good answers did not score as they failed to mention the lone pair on the nitrogen atom.

Many also simply stated that amine U contained delocalised electrons but failed to explain how involvement of the lone pair on nitrogen with these electrons lowered the base strength.

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Q9.

Part (a) was answered well by most candidates, but many did not note that both acids used in nitration are concentrated. Weaker candidates were unable to name the mechanism correctly and several lost marks by drawing the curly arrow going to the oxygen rather than the nitrogen of NO_2^+, by drawing the intermediate structure carelessly with the + charge shown too close to the tetrahedral carbon or by drawing the curly arrow showing the loss of H^+ the wrong way round.

Surprisingly, part (b) was badly answered: many incorrectly suggested $NaBH_4$ and in part (c) the need for an excess of ammonia was not well known. The first stage in the mechanism was answered well, but many were unable to show loss of H^+ correctly from the protonated amine.

Q11.

Although nucleophilic substitution reactions of haloalkanes appear both in CHM3 and in CHM4, a disappointing number of candidates was unable to name the mechanism correctly. Too many also showed the ammonia molecule with a negative charge. Curly arrows were drawn well by most except the careless. In part (b), a large number suggested that the reagent required in Step 1 was HCN rather than an ionic cyanide such as KCN. The equation in Step 2 was usually correct.
Part (c)(i) was usually well known although the simple statement “because of the inductive effect” was insufficient since it does not make it clear that the alkyl group has a positive inductive effect. A surprising number of candidates wrote NaOH rather than a strong acid or an ammonium or amine salt in part (c)(ii). Part (d) was answered correctly only by the better candidates.

Q12.

In part (a), not all candidates noted the requirement in the question to “Use the data”. The numerical difference of 152 kJ mol^{-1} between the expected enthalpy of hydrogenation of -360 kJ mol^{-1} and the actual value of –208 kJ mol^{-1} was rarely noted. Weaker candidates also thought that the data given was of the energy required to cause the reaction, rather than that evolved in the reaction. In part (b), weaker candidates muddled the expected addition-elimination reaction of an acid chloride and an amine with a Friedel Craft’s substitution in the benzene ring and frequently gained no marks for the section. The correct name for the product, N-phenylethanamide was rarely seen. Part (c) was better answered; most candidates were able to discuss nitration correctly and the mechanism was better answered than that in part (b)(ii). The amide or peptide link was not always named correctly in part (iv) and many did not state that acidic or alkaline hydrolysis is required to break the bond.

Q13.

Most were able to state in part (a) that a Brønsted-Lowry base is a proton acceptor, but writing an equation to illustrate this proved more difficult. Most of the better candidates were able to deduce that the basic buffer could be created by adding either a salt of methylamine with a strong acid such as hydrochloric or by adding the acid itself, but giving a qualitative explanation of the action of a basic buffer proved difficult for most candidates.

In part (b), the increase of electron density on the nitrogen and the greater availability of the lone pair were not always made clear.

Part (c) was rarely answered correctly. The use of a large excess of bromoethane was not noted and most answers gave the cation $[CH_3(C_2H_5)NH_2]^+$ which is formed after one substitution rather than the quaternary ammonium salt required.

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