**Q1.**          (a)     Methylamine is a weak Brønsted-Lowry base and can be used in aqueous solution with one other substance to prepare a basic buffer.

(i)      Explain the term *Br*ø*nsted-Lowry base* and write an equation for the reaction of methylamine with water to produce an alkaline solution.

*Brønsted-Lowry base* ..........................................................................

*Equation* ..............................................................................................

(ii)     Suggest a substance that could be added to aqueous methylamine to produce a basic buffer.

.............................................................................................................

(iii)     Explain how the buffer solution in part (a)(ii) is able to resist a change in pH when a small amount of sodium hydroxide is added.

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**(5)**

(b)     Explain why methylamine is a stronger base than ammonia.

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**(2)**

(c)     A cation is formed when methylamine reacts with a large excess of bromoethane. Name the mechanism involved in the reaction and draw the structure of the cation formed.

*Name of mechanism* ....................................................................................

*Structure*

**(2)**

**(Total 9 marks)**

**Q2.**          (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)**

(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)**

**(Total 11 marks)**

**Q3.**          Compound **Z** can be formed via compounds **X** and **Y** in the three step synthesis shown below.



Identify compounds **X** and **Y** and give reagents and conditions for Steps 1 and 2.

State the **type** of compound of which **Z** is an example.

Compound **Z** reacts with a large excess of bromomethane to form a solid product. Draw the structure of this product and name the type of mechanism for this reaction.

**(Total 9 marks)**

**Q4.**          (a)     Name and outline a mechanism for the formation of butylamine, CH3CH2CH2CH2NH2, by the reaction of ammonia with 1-bromobutane, CH3CH2CH2CH2Br.

*Name of mechanism* ....................................................................................

*Mechanism*

**(5)**

(b)     Butylamine can also be prepared in a two-step synthesis starting from 1-bromopropane, CH3CH2CH2Br. Write an equation for each of the two steps in this synthesis.

*Step 1*

......................................................................................................................

*Step 2*

......................................................................................................................

**(3)**

(c)     (i)      Explain why butylamine is a stronger base than ammonia.

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(ii)     Identify a substance that could be added to aqueous butylamine to produce a basic buffer solution.

.............................................................................................................

**(3)**

(d)     Draw the structure of a tertiary amine which is an isomer of butylamine.

**(1)**

**(Total 12 marks)**

**Q5.**          The following reaction scheme shows the formation of two amines, **K** and **L**, from methylbenzene.



(a)     (i)      Give the reagents needed to carry out Step 1. Write an equation for the formation from these reagents of the inorganic species which reacts with methylbenzene.

*Reagents* ............................................................................................

*Equation* .........….................................................................................

(ii)     Name and outline a mechanism for the reaction between this inorganic species and methylbenzene.

*Name of mechanism .*...........................................................................

Mechanism

**(7)**

(b)     Give a suitable reagent or combination of reagents for Step 2.

......................................................................................................................

**(1)**

(c)     (i)      Give the reagent for Step 4 and state a condition to ensure that the primary amine is the major product.

*Reagent* .............................................................................................

*Condition .*.......................................................….................................

(ii)     Name and outline a mechanism for Step 4.

*Name of mechanism* ...........................................................................

*Mechanism*

**(7)**

(d)     Explain why amine **K** is a weaker base than ammonia.

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**(2)**

(e)     Draw the structure of the organic compound formed when a large excess of bromomethane reacts with amine **L**.

**(1)**

(f)      Draw the structure of the organic compound formed when ethanoyl chloride reacts with amine **L** in an addition–elimination reaction.

**(1)**

**(Total 19 marks)**

**Q6.**          Consider the following reaction sequence.



(a)     For Step 1, name the mechanism and give the reagents involved.

*Name of mechanism .*...................................................................................

*Reagents* ......................................................................................................

**(3)**

(b)     For Step 2, give a reagent or combination of reagents. Write an equation for this reaction using [H] to represent the reductant.

*Reagent(s)* ...................................................................................................

*Equation .*......................................................................................................

**(2)**

(c)     Give the *m/z* value of a major peak which could appear in the mass spectrum of methylbenzene, but not in the spectrum of either **E** or **F**.

......................................................................................................................

**(1)**

(d)     Draw the structure of the species formed by **F** in an excess of hydrochloric acid.

**(1)**

(e)     Compounds **G** and **H** are both monosubstituted benzenes and both are isomers of **F**.
**G** is a primary amine and **H** is a secondary amine. Draw the structures of **G** and **H** below.

**G**

**H**

**(2)**

**(Total 9 marks)**

**Q7.**          (a)     Name the compound (CH3)2NH

......................................................................................................................

**(1)**

(b)     (CH3)2NH can be formed by the reaction of an excess of CH3NH2 with CH3Br. Name and outline a mechanism for this reaction.

*Name of mechanism* ....................................................................................

*Mechanism*

**(5)**

(c)     Name the type of compound produced when a large excess of CH3Br reacts with CH3NH2 Give a use for this type of compound.

*Type of compound* ......................................................................................

*Use ..*............................................................................................................

**(2)**

(d)     Draw the structures of the two compounds formed in the reaction of CH3NH2 with ethanoic anhydride.

**(2)**

**(Total 10 marks)**

**Q8.**          (a)     The repeating units of two polymers, **P** and **Q**, are shown below.



(i)      Draw the structure of the monomer used to form polymer **P**. Name the type of polymerisation involved.

*Structure of monomer*

*Type of polymerisation* .......................................................................

(ii)     Draw the structures of **two** compounds which react together to form polymer **Q**. Name these **two** compounds and name the type of polymerisation involved.

*Structure of compound 1*

*Name of compound 1* .........................................................................

*Structure of compound 2*

*Name of compound 2* ........................................................................

*Type of polymerisation* .......................................................................

(iii)     Identify a compound which, in aqueous solution, will break down polymer **Q** but not polymer **P**.

.............................................................................................................

**(8)**

(b)     Draw the structures of the **two** dipeptides which can form when one of the amino acids shown below reacts with the other.



          *Structure 1*                                              *Structure 2*

**(2)**

(c)     Propylamine, CH3CH2CH2NH2, can be formed either by nucleophilic substitution or by reduction.

(i)      Draw the structure of a compound which can undergo nucleophilic substitution to form propylamine.

(ii)     Draw the structure of the nitrile which can be reduced to form propylamine.

(iii)     State and explain which of the two routes to propylamine, by nucleophilic substitution or by reduction, gives the less pure product. Draw the structure of a compound formed as an impurity.

*Route giving the less pure product .*....................................................

*Explanation* .........................................................................................

.............................................................................................................

*Structure of an impurity*

**(5)**

**(Total 15 marks)**

**Q9.**          Haloalkanes are useful compounds in synthesis.
Consider the three reactions of the haloalkane **A** shown below.



(a)     (i)      Draw a **branched-chain** isomer of **A** that exists as optical isomers.

**(1)**

(ii)Name the type of mechanism in Reaction **1**.

.............................................................................................................

**(1)**

(iii)Give the full IUPAC name of compound **B**.

.............................................................................................................

**(1)**

(b)The infrared spectra shown below are those of the four compounds, **A**, **B**, **C** and **D**.
Using **Table 1** on the Data Sheet, write the correct letter in the box next to each spectrum.

(i)

|  |  |
| --- | --- |
|  |  |

(ii)

|  |  |
| --- | --- |
|  |  |

(iii)

|  |  |
| --- | --- |
|  |  |

(iv)

|  |  |
| --- | --- |
|  |  |

**(4)**

(c)Draw the repeating unit of the polymer formed by **B** and name the type of polymerisation involved.

Repeating unit

Type of polymerisation .................................................................................

**(2)**

(d)     (i)      Outline a mechanism for Reaction **3**.

**(4)**

(ii)     State the conditions used in Reaction **3** to form the maximum amount of the primary amine, **D**.

.............................................................................................................

**(1)**

(iii)Draw the structure of the secondary amine formed as a by-product in Reaction **3**.

**(1)**

(e)**D** is a primary amine which has three peaks in its 13C n.m.r. spectrum.

(i)An isomer of **D** is also a primary amine and also has three peaks in its 13C n.m.r. spectrum. Draw the structure of this isomer of **D**.

**(1)**

(ii)Another isomer of **D** is a tertiary amine. Its 1H n.m.r. spectrum has three peaks. One of the peaks is a doublet. Draw the structure of this isomer of **D**.

**(1)**

**(Total 17 marks)**

**Q10.**          The compound (CH3CH2)2NH can be made from ethene in a three-step synthesis as shown below.



(a)     Name the compound (CH3CH2)2NH

......................................................................................................................

**(1)**

(b)     Identify compounds **F** and **G**.

Compound **F** ...............................................................................................

Compound **G** ...............................................................................................

**(2)**

(c)     For the reactions in Steps **1**, **2** and **3**,

•    give a reagent or reagents

•    name the mechanism.

Balanced equations and mechanisms using curly arrows are **not** required.

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**(6)**

(d)     Identify **one** organic impurity in the product of Step **3** and give a reason for its formation.

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......................................................................................................................

**(2)**

**(Total 11 marks)**

**Q11.**          The hydrocarbons benzene and cyclohexene are both unsaturated compounds.
Benzene normally undergoes substitution reactions, but cyclohexene normally
undergoes addition reactions.

(a)     The molecule cyclohexatriene does not exist and is described as hypothetical.
Use the following data to state and explain the stability of benzene compared with the hypothetical cyclohexatriene.



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*(Extra space)* ...............................................................................................

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**(4)**

(b)     Benzene can be converted into amine **U** by the two-step synthesis shown below.



The mechanism of Reaction **1** involves attack by an electrophile.

Give the reagents used to produce the electrophile needed in Reaction **1**.

Write an equation showing the formation of this electrophile.

Outline a mechanism for the reaction of this electrophile with benzene.

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*(Extra space)* ................................................................................................

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**(6)**

(c)     Cyclohexene can be converted into amine **W** by the two-step synthesis shown below.



Suggest an identity for compound **V**.

For Reaction **3**, give the reagent used and name the mechanism.

For Reaction **4**, give the reagent and condition used and name the mechanism.

Equations and mechanisms with curly arrows are **not** required.

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*(Extra space)* ...............................................................................................

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**(6)**

(d)     Explain why amine **U** is a weaker base than amine **W**.

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*(Extra space)* ................................................................................................

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......................................................................................................................

**(3)**

**(Total 19 marks)**

**Q12.**          The amide or peptide link is found in synthetic polyamides and also in naturally
occurring proteins.

(a)     (i)      Draw the repeating unit of the polyamide formed by the reaction of propanedioic acid with hexane-1,6-diamine.

**(2)**

(ii)     In terms of the intermolecular forces between the polymer chains, explain why polyamides can be made into fibres suitable for use in sewing and weaving, whereas polyalkenes usually produce fibres that are too weak for this purpose.

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*(Extra space)* ......................................................................................

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**(3)**

(b)     (i)      Name and outline a mechanism for the reaction of CH3CH2COCl with CH3NH2

Name of mechanism............................................................................

Mechanism

**(5)**

(ii)     Give the name of the product containing an amide linkage that is formed in the reaction in part (b) (i).

.............................................................................................................

**(1)**

(c)     The dipeptide shown below is formed from two different amino acids.



Draw the structure of the alternative dipeptide that could be formed by these two amino acids.

**(1)**

(d)     The amino acids serine and aspartic acid are shown below.



(i)      Give the IUPAC name of serine.

.............................................................................................................

**(1)**

(ii)     Draw the structure of the species formed when aspartic acid reacts with aqueous sodium hydroxide.

**(1)**

(iii)     Draw the structure of the species formed when serine reacts with dilute hydrochloric acid.

**(1)**

(iv)    Draw the structure of the species formed when serine reacts with an excess of bromomethane.

**(1)**

**(Total 16 marks)**

**Q13.**This question is about the primary amine CH3CH2CH2NH2

(a)     The amine CH3CH2CH2NH2 reacts with CH3COCl

Name and outline a mechanism for this reaction.

Give the IUPAC name of the organic product.

........................................................................................................................

........................................................................................................................

**(6)**

(b)     Isomers of CH3CH2CH2NH2 include another primary amine, a secondary amine and a tertiary amine.

(i)      Draw the structures of these **three** isomers.
Label each structure as primary, secondary or tertiary.

**(3)**

(ii)     Use **Table 1** on the Data Sheet to explain how you could use infrared spectra in the range outside the fingerprint region to distinguish between the secondary amine and the tertiary amine.

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**(2)**

(c)     The amine CH3CH2CH2NH2 can be prepared by two different routes.

Route **A** is a two-stage process and starts from CH3CH2Br.

Route **B** is a one-stage process and starts from CH3CH2CH2Br.

(i)      Identify the intermediate compound in Route **A**.

Give the reagents and conditions for both stages in Route **A** and the single stage in Route **B**.

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**(7)**

(ii)     Give **one** disadvantage of Route **A** and **one** disadvantage of Route **B**.

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...............................................................................................................

...............................................................................................................

...............................................................................................................

**(2)**

**(Total 20 marks)**

**M1.**          (a)     (i)      H+ or proton acceptor **(1)**CH3NH2 + H2O () CH3+NH3 (+) OH– **(1)**

(ii)     CH3NH3Cl 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)**CH3 increases electron density (on N)
       donates / pushes electrons
       has positive inductive effect **(1)**

**2**

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

**2**

**[9]**

**M2.**          (a)



          Further reaction / substitution / formation of 2° / 3° amines etc **(1)**use an excess of NH3 **(1)**

**6**

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

****

**5**

          **Notes**

(a)     allow SN1
penalise: Br– intead of NH3 removing H+ for M4
not contamination with *other amines* (this is in the question) not diamines

(b)     allow because NH3 is a nuclephile or benzene is (only) attacked by electrophiles
or C–Br bond (in bromobenzene) is stronger / less polar or Br lp delocalized

          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 H2SO4 or conc HNO3                                 allow Ni/H2                                 Not NaBH4 or LiAlH4ignore wrong descriptions for reduction step e.g. hydrolysis or hydration

**[11]**

          Organic points

(1)     Curly arrows: must show movement of a pair of electrons,
i.e. from bond to atom or from lp to atom / space
e.g.



(2)     Structures

penalise sticks (i.e. ) once per paper



Penalise once per paper

          allow CH3– or –CH3 or  or CH3    or   H3C–

**M3.**         **X** is CH3CN or ethanenitrile or ethanonitrile or methyl cyanide or
cyanomethane or ethyl nitrile or methanecarbonitrile

***Not*** *ethanitrile
but contradiciton of name and structure lose marks*

**1**

          **Y** is CH3CH2NH2 or ethylamine or aminoethane or ethanamine

**1**

          Step 1: reagent      KCN not HCN/HCl
           condition      (aq)/alcohol - only allow condition if reagent
           correct or incomplete

**2**

          Step 2: reagent      H2                  LiAlH4        Na            Zn/Fe/Sn    Not NaBH4            condition      Ni/Pt/Pd        ether        ethanol     HCl

**2**

          **Z** is an amine or aminoalkane or named amine even if incorrect name for **Z**            secondary (only award if amine correct)

**1**

****   (Br–)+ can be on N or outside brackets as shown

**1**

          nucleophilic substitution

**1**

**[9]**

**M4.**          (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        CH3CH2CH2CN   1

CH3CH2CH2Br + KCN → CH3CH2CH2CN + KBr balanced

**1**

                            (or CN–) (or Br–)
                   (*not HCN*)

**1**

Step 2        CH3CH2CH2CN + 2H2 → CH3CH2CH2CH2NH2                     (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

**1**

(d)     CH3CH2N(CH3)2

**1**

**[12]**

**M5.**          (a)     (i)      conc HNO3

**1**

conc H2SO4

*allow 1 for both acids if either conc missing*

**1**

HNO3 + 2H2SO4 → NO2+ + H3O+ + 2HSO4–

or HNO3 + H2SO4 → NO2+ + H2O + HSO4–

**1**

(iii)     electrophilic substitution CH3

**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 / H2 not NaBH4 LiAlH4

**1**

(c)     (i)     NH3

**1**

Use an excess of ammonia

**1**

(ii)     nucleophilic substitution

**1**

****

**4**

(d)     lone pair on N less available (in correct context)

**1**

delocalised into the ring (Q of L)

**1**

(e)



*ignore Br*

*+ must be on N or outside a*

*square bracket*

**1**

(f)



**1**

**[19]**

**M6.**          (a)     electrophilic substitution;

**1**

          cone HNO3;

**1**

cone H2SO4 either or both cone missing scores one for both acids;

**1**

(b)     Sn or Fe/HCl (cone or dil or neither);

*(ignore extra NaOH)*

**1**

Sn or Fe/H2SO4 (dil or neither)

*(not HNO3 at all)*

or H2/Ni

*(not NaBH4/ LiAlH4 or Na/C2H5OH)*

**

**1**

(c)     77 or 92;

**1**

(d)



**1**

*(allow -NH3+)*

(e)     **G**

****

**1**

          **H**

****

**1**

**[9]**

**M7.**          (a)     dimethylamine

**1**

(b)     nucleophilic substitution

**1**

****

**4**

(c)     quaternary ammonium salt

**1**

(cationic) surfactant / bactericide / detergent / fabric softener or
conditioner/hair conditioner

**1**

(d)



*(allow CH3COOH or CH3COO– NH4+)*

**2**

**[10]**

**M8.**          (a)     (i)      CH3CH=CHCH3

**1**

Addition or radical (**QoL**)

**1**

(ii)     CH3CH(OH)CH(OH)CH3 or with no brackets

**1**

butan(e)–2,3–diol or 2,3–butan(e)diol

**1**

****

**1**

2,3–dimethylbutan(e)dioic acid       2,3–dimethylbutan(e)dioyl chloride

ignore –1,4–

**1**

condensation (**QoL**)

**1**

(iii)     NaOH or HCl etc or Na2CO3

*Allow conc sulphuric/nitric*

***NOT*** *water nor acidified water nor weak acids*

**1**

(b)     Structure 1



*Allow –CONH– and –COHN–*

*Allow zwitterions*

***NOT polypeptides/repeating units***

**1**

Structure 2 either of



**1**

(c)     (i)      CH3CH2CH2Br

*allow –Cl, –I*

**1**

(ii)     CH3CH2CN

**1**

(iii)     (nucleophilic) substitution or from CH3CH2CH2Br

*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
(CH3CH2CH2)2NH
(CH3CH2CH2)3N
(CH3CH2CH2)4N+ Br–

*Allow salts including NH4Br*

*Allow HBr*

**1**

**[15]**

**M9.**          (a)     (i)



*not allow C3H7*

*allow C2H5 bonded to C either way round*

**1**

(ii)     elimination

*allow base – elimination*

*but penalise any other qualification*

**1**

(iii)     Z-pent-2-ene or cis-pent-2-ene               either Z or cis is necessary
(allow Z-2-pentene or cis-2-pentene)

*with or without brackets around Z
with or without hyphens*

**1**

(b)     (i)      C

**1**

(ii)     A

**1**

(iii)     B

**1**

(iv)    D

**1**

(c)



*allow C2H5 bonded via C or H*

*must have both trailing bonds
ignore brackets or n*

**1**

addition or radical or step or chain growth

*QOL not additional*

**1**

(d)     (i)



*Allow SN1, i.e M2 first then attack of NH3 on carbocation.*

*Allow C2H5 in M3 bonded either way*

*Allow with or without NH3 to remove H+ in M4, but lose mark if Br– used.*

*ignore δ+ or δ– unless wrong*

*+ on central C instead of δ + loses M2*

**4**

(ii)     excess NH3

*ignore reflux*

*allow conc ammonia in sealed tube*

**1**

(iii)



*Allow C2H5 bonded either way*

**1**

(e)     (i)



**1**

(ii)



*NOT (C2H5)2NCH3 which is tertiary with 3 peaks but its spectrum has no doublet.*

**1**

**[17]**

**M10.**          (a)     diethylamine **OR** ethyl ethanamine **OR** ethyl aminoethane

*ignore N–*

**1**

(b)     For (b) and (c)

There are three valid routes for this synthesis called
Routes **A**, **B** and **C** below

•        Decide which route fits the answer best (this may not be the
best for part b) to give the candidate the best possible overall mark.

•        Mark part (b)

•        For this best route mark the mechanism and reagent independently

•        Migration from one route to another is not allowed

•        Either name or formula is allowed in every case.

•        Ignore conditions unless they are incorrect.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|   | **Route A** | **Route B** | **Route C** |   |
| F | CH3CH2Br or CH3CH2Cl | C2H6 | CH3CH2OH | **1** |
| G | CH3CH2NH2 ethylamine OR ethanamine OR aminoethane | CH3CH2Br ORCH3CH2Cl | CH3CH2Br ORCH3CH2Cl | **1** |

(c)

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|   |   | **Route A** | **Route B** | **Route C** |   |
| Step 1 | Reagent(s) | HBr **OR** HCl | H2/Ni (Not NaBH4) | H2O & H3PO4 **OR**H2O & H2SO4 | **1** |
| Mechanism | Electrophilic addition | addition (allow electrophilic **OR** catalytic but not nucleophilic) ignore hydrogenation | Electrophilic addition | **1** |

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Step 2 | Reagent(s) | NH3 | Cl2 **OR** Br2 | HBr OR KBr & H2SO4 **OR** PCl3 **OR** PCl5 **OR** SOCl2 | **1** |
| Mechanism | Nucleophilic substitution | (free) radical substitution | Nucleophilic substitution | **1** |

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Step 3 | Reagent(s) | CH3CH2Br **OR** CH3CH2Cl | CH3CH2NH2 **OR** NH3 but penalise excess ammonia here | CH3CH2NH2**OR** NH3 but penalise excess ammonia here | **1** |
| Mechanism | Nucleophilic substitution | Nucleophilic substitution | Nucleophilic substitution | **1** |

(d)     tertiary amine **OR** triethylamine **OR** (CH3CH2)3N
Quaternary ammonium salt
**OR** tetraethylammonium bromide **OR** chloride **OR** ion
**OR** (CH3CH2)4N+ (Br– **OR** Cl–)

**1**

further substitution will take place **OR**diethylamine is a better nucleophile than ethylamine

**1**

**[11]**

**M11.**          (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 ΔH~~ο~~ hydrogenation of C6H6 is 3(–120)

 = –360 kJ mol-1

*Allow in words e.g. expected ΔH~~ο~~ hydrog is three times the ΔH~~ο~~ hydrog of cyclohexene*

**1**

**M3** Actual ΔH~~ο~~ 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 HNO3

*If either or both conc missing, allow one;*

**1**

Conc H2SO4

*this one mark can be gained in equation*

**1**

2 H2SO4 + HNO3 → 2 HSO4– + NO2+ + H3O+

**OR**

H2SO4 + HNO3 → HSO4– + NO2+ + H2O

**OR via two equations**

H2SO4 + HNO3 → HSO4– + H2NO3+

H2NO3+ → NO2+ + H2O

*Allow + anywhere on NO2+*

**1**

****

*M1 arrow from within hexagon to N or + on N*

*Allow NO2+ 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*

**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]**

**M12.**         (a)     (i)



Allow –CONH- or - COHN -

*Mark two halves separately*

*lose 1 each for missing trailing bonds at one or both ends or error in peptide link or either or both of H or OH on ends*

**1**

*Not allow –(C6H12)–*

*Ignore n*

**1**

(ii)     **M1** in polyamides - H bonding

**1**

**M2** in polyalkenes - van der Waals forces

*Penalise forces between atoms or van der Waals bonds*

**1**

**M3** Stronger forces (of attraction) in polyamides
Or H bonding is stronger
(must be a comparison of correct forces to score M3)

*Do not award if refer to stronger bonds*

**1**

(b)     (i)      (nucleophilic) addition elimination



*Minus sign on NH2 loses* ***M1***

**1**

*M2 not allowed independent of* ***M1****, but allow* ***M1*** *for correct attack on C+*

*+ rather than + on C=O loses* ***M2***

*If Cl lost with C=O breaking, max 1 for* ***M1***

***M3*** *for correct structure with charges but*

*lp on O is part of* ***M4***

*only allow* ***M4*** *after correct/ very close M3*

*For M4, ignore NH3 removing H+ but lose*

***M4*** *for Cl removing H+ in mechanism,*

*but ignore HCl as a product*

**4**

(ii)     N-methylpropanamide

*Not N-methylpropaneamide*

**1**

(c)



*Allow –CONH– or –COHN–*

**1**

(d)     (i)      2-amino-3-hydroxypropanoic acid

**1**

(ii)



Must be salts of aspartic acid

*allow –CO2–*

*allow NH2–*

**1**

(iii)     Penalise use of aspartic acid once in d(iii) and d(iv)



*allow –CO2H*

*allow +NH3–*

*don’t penalize position of + on NH3*

**1**

(iv)    Penalise use of aspartic acid once in d(iii) and d(iv)

**(Br–)**

*allow –CO2–*

*must show C-N bond*

*don’t penalize position of + on N(CH3)3*

**1**

**[16]**

**M13.**(a)    (nucleophilic) addition-elimination

**1**

****

M4 for 3 arrows and lp

Allow wrong amine in M1 but penalise in M3

Allow C3H7 in M3

Minus sign on NH3 loses M1 (but not M4 if NH3 also shown here)

*• Allow attack by: NH2CH2CH2CH3*

*•  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 with charges 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 RNH2 removing H+ but lose M4 for Cl– removing H+ in mechanism,*

*• but ignore HCl shown as a product.*

**4**

N-propylethanamide must be this name even if wrong amine used

*NOT N-propylethaneamide*

**1**

(b)    (i)



Not allow ambiguous C3H7NH2
BEWARE No mark for the original amine CH3CH2CH2NH2

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

**1**

****

Allow C2H5

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

**1**

****

**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  CH3CH2CN 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        H2

                                          H loses M4 but mark on

                                                                       LiAlH4

*Apply list principle for extra reagents or catalysts.*

*M5 only scores after correct M4*

*Not NaBH4  not Sn or Fe / HCl*

*Allow (dil) acid after but not with LiAlH4*

*Penalise conc acid.*

**1**

M5                                        Ni or Pt or Pd

                                                                       ether

**1**

M6  Route **B**                         NH3

*With acid loses M6 & M7*

*Apply list principle for extra reagents or catalysts.*

**1**

M7                                        Excess NH3

*Ignore conc, ignore high P, ignore solvent.*

**1**

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

                                                                          Expensive LiAlH4                                                                          ignore acidified

                                             ***OR*** lower yield because 2 steps

*Allow H2 flammable / explosive etc.*

*Not just dangerous.*

*Ignore time reasons.*

**1**

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

*Allow impure product.*

**1**

**[20]**