Q7.

This question is about 2-bromopropane.

(a) Define the term electronegativity.

Explain the polarity of the C–Br bond in 2-bromopropane.

Electronegativity _____

_____

_____

Explanation _____

_____

_____

(3)

(b) Outline the mechanism for the reaction of 2-bromopropane with an **excess of ammonia**.

(4)

(c) Draw the skeletal formula of the main organic species formed in the reaction between a **large excess of 2-bromopropane** and ammonia.

Give a use for the organic product.

Skeletal formula

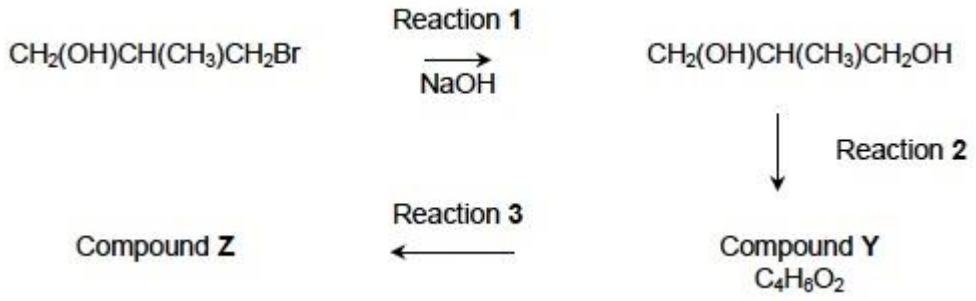
Use _____

(2)

(Total 9 marks)

Q8.

Halogenoalkanes are useful compounds in synthesis. A reaction pathway is shown.



(a) Give the IUPAC name for $CH_2(OH)CH(CH_3)CH_2Br$

(1)

(b) Reaction **1** occurs via a nucleophilic substitution mechanism.

Explain why the halogenoalkane is attacked by the nucleophile in this reaction.

(3)

(c) The infrared spectrum of Compound **Y** shows a significant absorption in the range 1680–1750 cm^{-1}

Draw the displayed formula of Compound **Y**.

(1)

(d) Compound **Z** has the empirical formula C_3H_4NO

Give the structure of Compound **Z**.

Suggest the reagent for Reaction **3**.

Structure

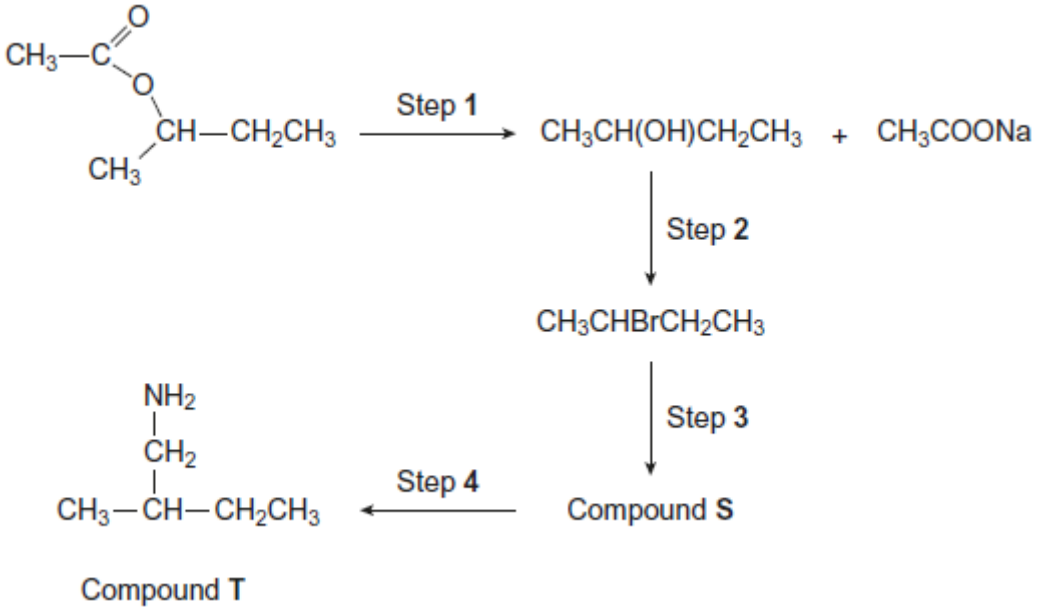
Reagent for Reaction **3** _____

(2)

(Total 7 marks)

Q9.

A four-step synthesis of compound **T** is shown.



(a) Give the reagent and conditions for Step **1**.
State how you could obtain a sample of the alcohol from the reaction mixture formed in Step **1**.

_____

_____

_____

_____

_____

(3)

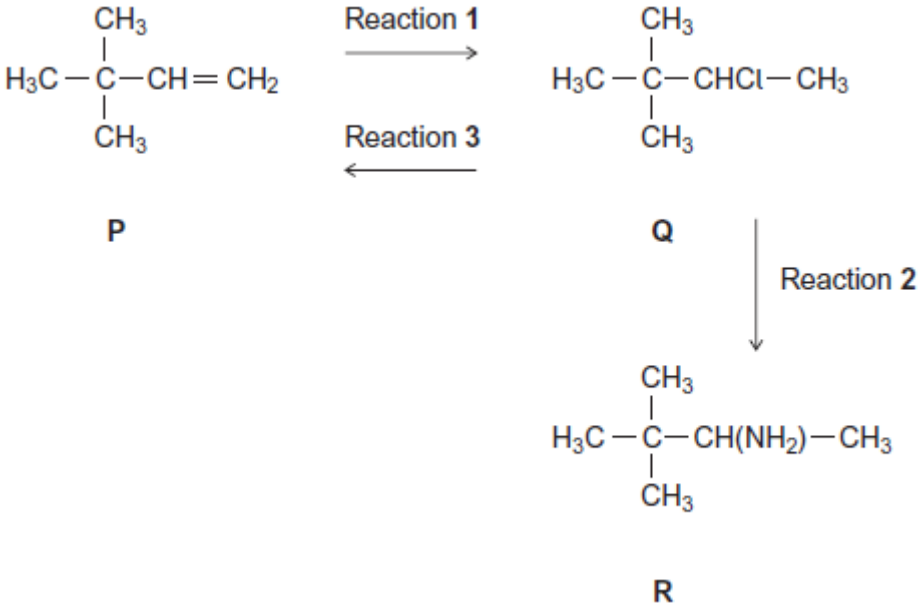
(b) Draw the structure of compound **S**.
For each of Steps **3** and **4**, give a reagent and one condition, other than heat.

(5)

(Total 8 marks)

Q10.

Consider the following scheme of reactions.



P **Q** **R**

(a) Give the IUPAC name for compound **P** and that for compound **Q**.

P _____

Q _____

(2)

(b) The conversion of **P** into **Q** in Reaction **1** uses HCl

Name and outline a mechanism for this reaction.

_____

(5)

(c) The conversion of **Q** into **R** in Reaction **2** uses NH_3

Name and outline a mechanism for this reaction.

_____

(5)

(d) State the type of reaction shown by Reaction **3**.

Identify a reagent for this reaction.

Give **one** condition necessary for a high yield of product when **Q** is converted into **P**.

(3)

(e) Hydrogen bromide (HBr) could be used in the overall conversion of **P** into **R**, instead of using HCl
Hydrogen bromide is made by the reaction of NaBr with concentrated phosphoric acid.
Concentrated sulfuric acid is **not** used to make HBr from NaBr

Write an equation for the reaction of NaBr with H_3PO_4 to produce HBr and Na_3PO_4 only.

Identify **two** toxic gases that are formed, together with HBr, when NaBr reacts with concentrated H_2SO_4

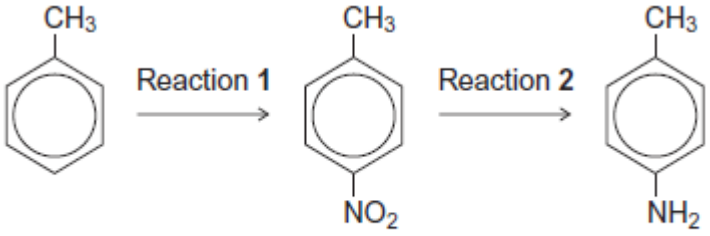
State the role of H_2SO_4 in the formation of these two toxic gases.

(4)

(Total 19 marks)

Q11.

Consider the following reaction sequence starting from methylbenzene.



J

(a) Name the type of mechanism for reaction **1**.

_____

(1)

(b) Compound **J** is formed by reduction in reaction **2**.

(i) Give a reducing agent for this reaction.

_____

(1)

(ii) Write an equation for this reaction. Use [H] to represent the reducing agent.

_____

(1)

(iii) Give a use for **J**.

_____

(1)

(c) Outline a mechanism for the reaction of bromomethane with an excess of compound **J**. You should represent **J** as RNH_2 in the mechanism.

(4)

(d) Compound **K** ($C_6H_5CH_2NH_2$) is a structural isomer of **J**.

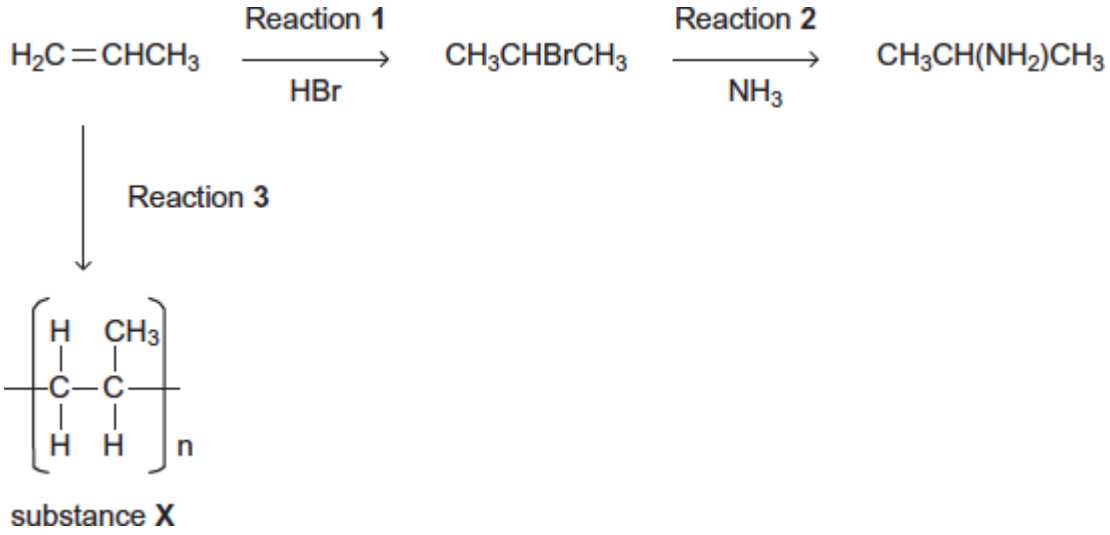
Explain why **J** is a weaker base than **K**.

(3)

(Total 11 marks)

Q12.

Consider the following reactions.



substance **X**

(a) Name and outline a mechanism for Reaction **1**.

Name of mechanism _____

Mechanism

(5)

(b) Name and outline a mechanism for Reaction **2**.

Name of mechanism _____

Mechanism

(5)

(c) State the type of reaction in Reaction **3**.
Give the name of substance **X**.

_____

_____

_____

(2)

(d) The haloalkane produced in Reaction **1** can be converted back into propene in an elimination reaction using ethanolic potassium hydroxide.

$$CH_3CHBrCH_3 \xrightarrow{KOH} H_2C{=}CHCH_3$$

Outline a mechanism for this conversion.

(3)
(Total 15 marks)

Mark Scheme

Q7.

(a) **M1** The (relative) tendency of an atom to attract a pair of electrons/ the electrons/ electron density in a covalent bond

1

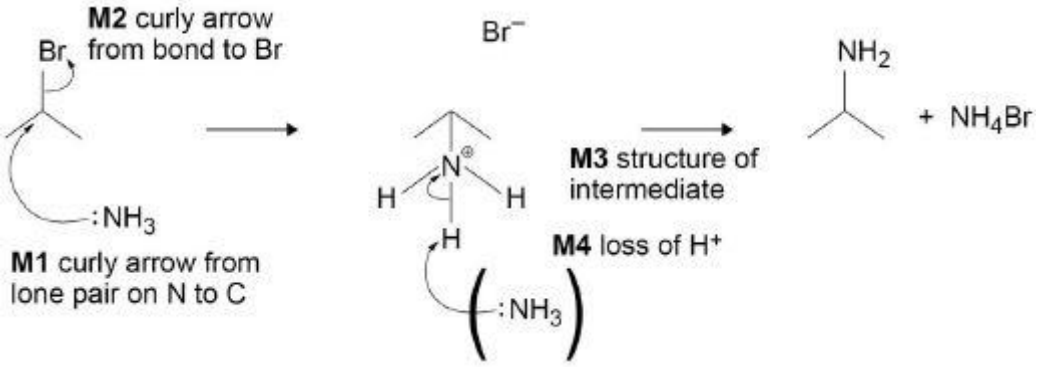
M2 Br is more electronegative than C (or vice versa)

1

M3 So Br is δ- and C is δ+

1

(b)



M4 Penalise loss of H^+ using Br^-

Allow S_n1

4

(c) **M1**

Allow + outside square brackets

1

M2 Use: (Hair) conditioner / (Cationic) surfactant / disinfectant

Allow fabric softener

1

[9]

Q8.

(a) 3-bromo-(2)-methylpropan-1-ol ONLY

3 and 1 are essential, 2 may be omitted, but any other number here is wrong

Ignore hyphens and commas

1

(b) Bromine is more electronegative than carbon

Allow difference in electronegativity if polarity of bond shown

M1

C is partially positive / electron deficient

M2 and M3 can be awarded from diagram that shows nucleophilic attack

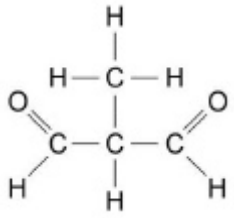
M2

Lone/electron pair (on the nucleophile) donated to the partially positive carbon

Allow lone pair attracted to / attacks the partially positive carbon

M3

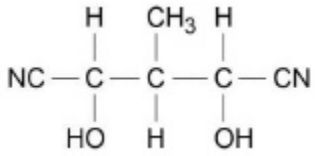
(c)



Must be displayed with all bonds shown

1

(d)



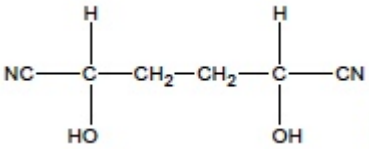
Not need be displayed

See General Marking instructions section 3.12 for penalties for incorrectly drawn bonds such as C–HO or C–NC etc.

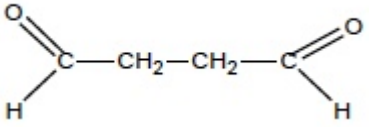
1

KCN & (dil) acid

Allow



from



Allow HCN

Ignore alcoholic solvents

Penalise conc. HCl, H_2SO_4 or any HNO_3

1

[7]

Q9.

(a) M1 NaOH

Only score M2 if M1 gained, but mark on from hydroxide. Mention of acid loses M1 & M2

1

M2 Aqueous/(warm)

Ignore alcoholic / conc / dil.

1

M3 (Fractional) distillation or described

Not just evaporation; not reflux

Allow chromatography

1

(b) M1 S is $CH_3CH(CN)CH_2CH_3$

Allow without brackets

1

Step 3

M2 KCN (mark on from CN^-)

Not HCN, not KCN with acid

1

M3 Alcoholic / (aqueous)

Allow ethanolic

Can only score M3 if M2 gained

1

Step 4

M4 H_2

$LiAlH_4$

Na

Can only score M5 if M4 gained

1

M5 Ni or Pt or Pd

Ethoxyethane or ether

$LiAlH_4$ with acid loses both M4 and M5

Ignore 'followed by acid'

Na

Ethanol

NOT $NaBH_4$ OR Sn/HCl

Penalise other extras as list

Ignore pressure or temperature

1

[8]

Q10.

(a) **P** 3,3−dimethylbut−1−ene

OR

accept 3,3−dimethylbutene

Ignore absence of commas, hyphens and gaps

Require correct spelling

Q 3−chloro−2,2−dimethylbutane

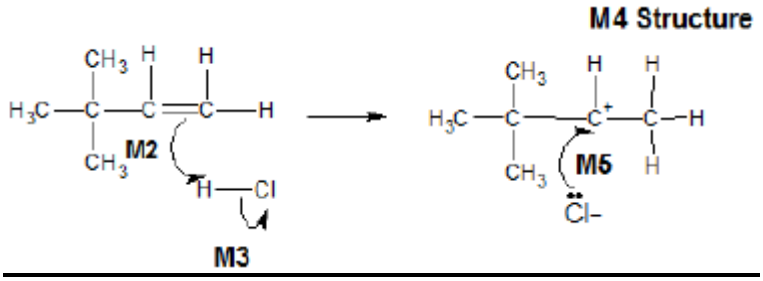
OR

accept 2−chloro−3,3−dimethylbutane

In Q, "chloro" must come before "dimethyl"

2

(b) **M1 Electrophilic addition**



M2 must show an arrow from the double bond towards the H atom of HCl
M3 must show the breaking of the H−Cl bond
M4 is for the structure of the carbocation
M5 must show an arrow from the lone pair of electrons on the negatively charged chloride ion towards the positively charged carbon atom on their carbocation.

NB The arrows here are double−headed

M1 *both words required*

For the mechanism

M3 *Penalise incorrect partial charge on H−Cl bond and penalise formal charges*

Ignore partial negative charge on the double bond.

Maximum 3 of 4 marks for a correct mechanism *using HBr or the wrong organic reactant or wrong organic product (if shown) or a primary carbocation*

Penalise once only in any part of the mechanism for a line and two dots to show a bond

Credit the correct use of "sticks"

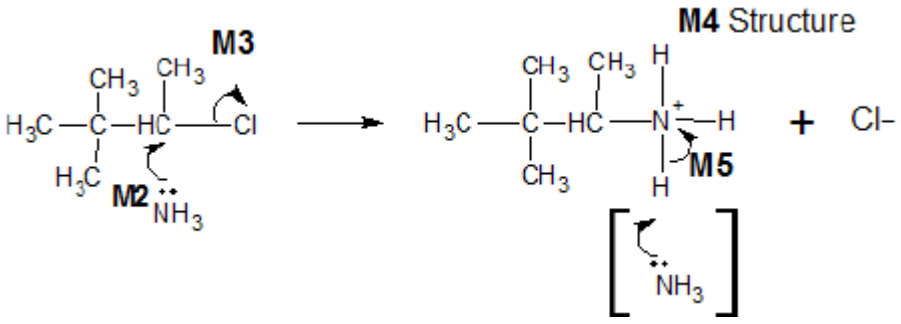
*For **M5**, credit attack on a partially positively charged carbocation structure, but penalise **M4***

5

(c) **M1 Nucleophilic substitution**

*For **M1**, both words required.*

Accept phonetic spelling



M2 must show an arrow from the lone pair of electrons **on the nitrogen atom** of an ammonia molecule to the correct C atom
M3 must show the movement of a pair of electrons from the C− Cl bond to the Cl atom. Mark **M3** independently provided it is from their original molecule
M4 is for the structure of the alkylammonium ion, which could be a condensed formula. A positive charge **must** be shown on, or close to, the N atom.
M5 is for an arrow from the N−H bond to the N atom
Award full marks for an S_N1 mechanism in which **M2** is the attack of the ammonia on the intermediate carbocation

NB These are double-headed arrows

For the mechanism

*Penalise **M2** if NH_3 is negatively charged.*

*Penalise **M3** for formal charge on C of the C−Cl or incorrect partial charges on C−Cl*

*Penalise **M3** for an additional arrow from the Cl to something else*

*The second mole of ammonia is not essential for **M5**; therefore ignore any species here*

Penalise once only for a line and two dots to show a bond

***Maximum 3 of 4 marks for the mechanism** for wrong organic reactant OR wrong organic product if shown*

Accept the correct use of "sticks"

5

(d) **M1** (base) elimination

***M1** Dehydrohalogenation*

M2 KOH **OR** NaOH
M3 Must be consequential on a correct reagent in **M2**, but if incomplete or inaccurate attempt at reagent (e.g. hydroxide ion), **penalise M2 only and mark on**

Any **one** from
- high temperature OR hot OR heat / boil under reflux
- concentrated
- alcohol / ethanol (as a solvent) / (ethanolic conditions)

***M3** not "reflux" alone*

***M3** if a temperature is stated it must be in the range 78C to 200 °C*

Ignore "pressure"

3

(e) **M1**

$3NaBr + H_3PO_4 \longrightarrow 3HBr + Na_3PO_4$

***M1** Credit correct ionic species in the equation*

M2 and M3
SO_2 **and** Br_2 identified
M4
Concentrated sulfuric acid
- is an oxidising agent
- oxidises the bromide (ion) or Br^- or NaBr or HBr
- is an electron acceptor

*In **M2** and **M3** the two gases need to be identified. If equations are used using sulfuric acid and the toxic gases are not identified clearly, allow one mark for the formulas of SO_2 and Br_2*
- *apply the list principle as appropriate but ignore any reference to HBr*
- *the marks are for identifying the two gases either by name or formula*

4

[19]

Q11.

(a) Electrophilic substitution

Both words needed
Ignore minor misspellings

1

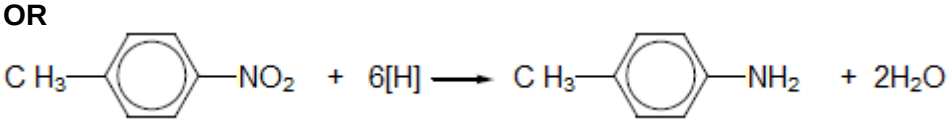
(b) (i) Sn / HCl
OR H_2 / Ni **OR** H_2 / Pt **OR** Fe / HCl **OR** Zn / HCl **OR** $SnCl_2$ / HCl

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) making dyes

OR making quaternary ammonium salts

OR making (cationic) surfactants

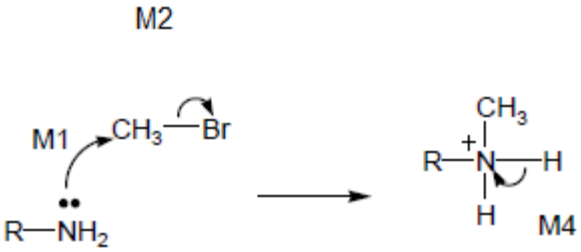
OR making hair conditioner

OR making fabric softener

OR <u>making</u> detergents

1

(c)



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

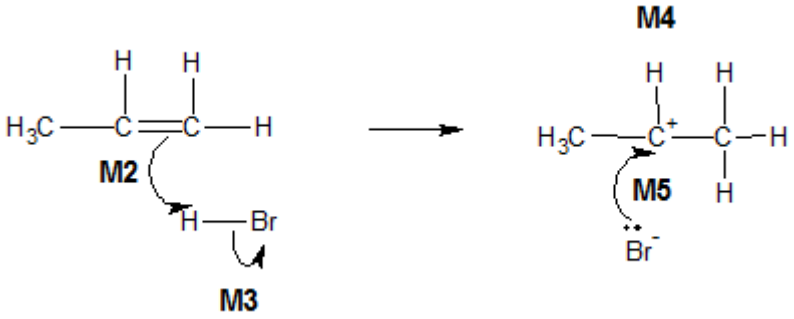
[11]

Q12.

(a) **M1 <u>electrophilic addition</u>**

*For **M1**, both words required*

Accept phonetic spelling



For the mechanism

***M2** Ignore partial negative charge on the double bond*

M2 must show an arrow from the double bond towards the H atom of the H–Br molecule

***M3** Penalise partial charges on H–Br bond if wrong way and penalise formal charges*

M3 must show the breaking of the H–Br bond

Penalise once only in any part of the mechanism for a line and two dots to show a bond

M5 must show an arrow from the lone pair of electrons on the negatively charged bromide ion towards the correct (positively charged) carbon atom

<u>Maximum any 3 of 4 marks for the mechanism</u> for wrong (organic) reactant OR wrong organic product (if shown) OR primary carbocation

Accept the correct use of sticks

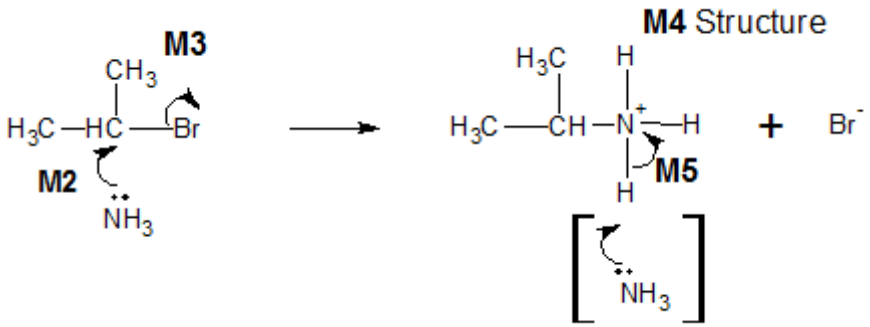
NB These are double-headed arrows

5

(b) **M1 <u>Nucleophilic substitution</u>**

*For **M1**, both words required*

Accept phonetic spelling



For the mechanism

*Penalise **M2** if NH_3 is negatively charged*

M2 must show an arrow from the lone pair of electrons **on the nitrogen atom** of an ammonia molecule to the correct C atom

*Penalise **M3** for formal charge on C of the C−Br or incorrect partial charges on C−Br*

*Penalise **M3** for an additional arrow from the Br to something else*

M3 must show the movement of a pair of electrons from the C–Br bond to the Br atom. Mark **M3** independently provided it is from their original molecule

*The second mole of ammonia is not essential for **M5**; therefore ignore any species here*

M4 is for the structure of the alkylammonium ion, which could be a condensed formula. A positive charge **must** be shown on / or close to, the N atom

Penalise once only for a line and two dots to show a bond

M5 is for an arrow from the N–H bond to the N atom

***Maximum any 3 of 4 marks for the mechanism** for wrong organic reactant **OR** wrong organic product if shown*

Award full marks for an S_N1 mechanism in which **M2** is the attack of the ammonia on the intermediate carbocation

Accept the correct use of "sticks"

NB These are double-headed arrows

5

(c) M1 (addition) polymerisation OR poly-addition

Ignore "additional"

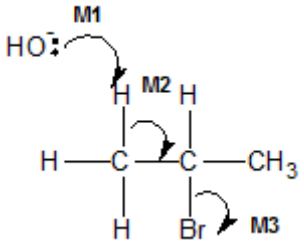
Credit polyprop-1-ene and polypropylene

M2 poly(propene) / polypropene

Penalise "condensation polymerisation"

2

(d)



*Penalise **M1** if covalent KOH*

M1 must show an arrow from the lone pair on the oxygen of a negatively charged hydroxide ion to a correct H atom

*Penalise **M3** for formal charge on C of C–Br or incorrect partial charges on C−Br.*

M2 must show an arrow from a correct C–H bond adjacent to the C–Br bond to the appropriate C–C bond. Only award if an arrow is shown attacking the H atom of a correct C−H bond in **M1**

Ignore other partial charges

Penalise once only in any part of the mechanism for a line and two dots to show a bond

M3 is independent provided it is from their original molecule, but **CE=0 if nucleophilic substitution**

Maximum any 2 of 3 marks *for wrong organic reactant*

Award full marks for an E1 mechanism in which **M3** is on the correct carbocation.

Accept the correct use of "sticks" for the molecule except for the C–H being attacked

NB These are double-headed arrows

3

[15]