M1.(a) (i) **Initiation**

$Br_2 \longrightarrow 2Br\bullet$

First propagation

$Br\bullet + CHF_3 \longrightarrow \bullet CF_3 + HBr$

Second propagation

$Br_2 + \bullet CF_3 \longrightarrow CBrF_3 + Br\bullet$

Termination

$2\bullet CF_3 \longrightarrow C_2F_6$ ***OR*** CF_3CF_3

OR

$2Br\bullet \longrightarrow Br_2$

OR

$Br\bullet + \bullet CF_3 \longrightarrow CBrF_3$

Penalise absence of dot once only

Credit the dot anywhere on the radical

4

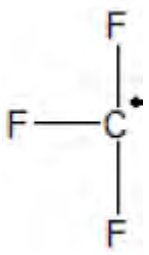
(ii) Ultra-violet / uv / sunlight

OR

T > 100°C OR high temperature

1

(b) (i)



Displayed formula required with the radical dot on carbon

1

(ii) (The) C–Br (bond) breaks more readily / is weaker than (the) C–Cl (bond) (or converse)

OR

The C–Br bond enthalpy / bond strength is less than that for C–Cl (or converse)

*Requires **a comparison** between the two bonds*

Give credit for an answer that suggests that the UV

frequency / energy may favour C–Br bond breakage rather than C–Cl bond breakage

Ignore correct references either to size, polarity or electronegativity

Credit correct answers that refer to, for example "the bond between carbon and bromine requires less energy to break than the bond between carbon and chlorine"

1

(iii) **M1**

$Br\bullet + O_3 \longrightarrow BrO\bullet + O_2$

M2

$BrO\bullet + O_3 \longrightarrow Br\bullet + 2O_2$

***M1** and **M2** could be in either order*

Credit the dot anywhere on the radical

Penalise absence of dot once only

Penalise the use of multiples once only

M3 One of the following

They / it / the bromine (atom)

- does not appear in the overall equation
- is regenerated
- is unchanged at the end
- has not been used up
- provides an alternative route / mechanism

3

[10]

M2.(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

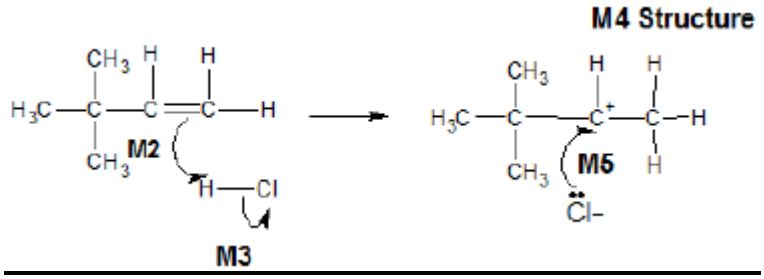
OR

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 <u>their</u> 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.

<u>Maximum 3 of 4 marks for a correct mechanism</u> *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"

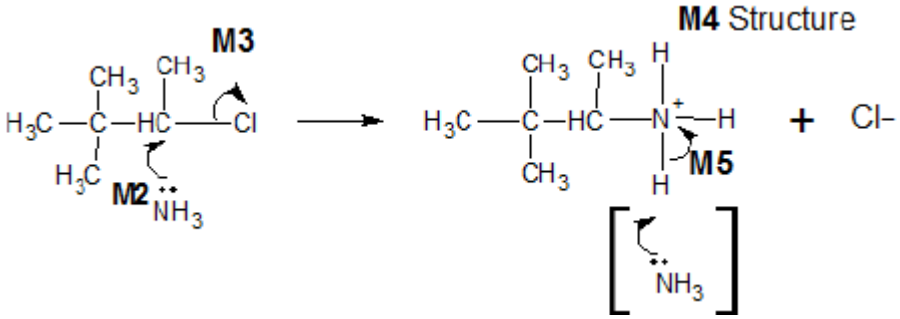
*For **M5**, credit attack on a partially positively charged carbocation structure, but penalise **M4***

5

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

*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 <u>their original molecule</u>
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]

M3.(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^+

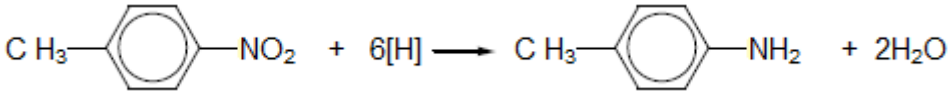
Ignore NaOH after Sn / HCl

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

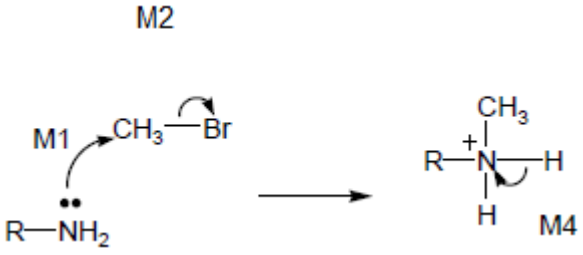
OR <u>making</u> hair conditioner

OR <u>making</u> 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

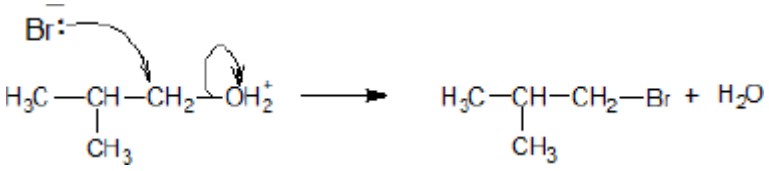
[11]

M4.(a) (i) **M1** double-headed curly arrow from the lone pair of the bromide ion to the C atom of the CH_2

Penalise additional arrows.

M2 double-headed arrow from the bond to the O atom

As follows



2

(ii) **M1** <u>nucleophilic substitution</u>

M1 *both words needed (allow phonetic spelling).*

M2 1-bromo(-2-)methylpropane

M2 *Require correct spelling in the name but ignore any hyphens or commas.*

2

(b) **M1** hydrolysis

*For **M1** give credit for 'hydration' on this occasion only.*

M2 <u>C≡N</u> with absorption range <u>2220–2260</u> (cm^{-1})

*Credit 1 mark from **M2** and **M3** for identifying C≡N **and** either O–H(acids) **or** C=O **or** C–O without reference to wavenumbers or with incorrect wavenumbers.*

M3 O–H(acids) with absorption range 2500–3000 (cm^{-1})

OR

C=O with absorption range 1680–1750 (cm^{-1})

OR

C–O with absorption range 1000–1300 (cm^{-1})

*Apply the list principle to **M3***

3

(c) (i) **M1** Yield / product **OR** ester increases / goes up / gets more

***M2** (By Le Chateliers principle) the position of equilibrium is driven / shifts / moves to the right / L to R / in the forward direction / to the product(s)*

M3 – requires a correct statement in M2

(The position of equilibrium moves)

to oppose the increased concentration of ethanol

to oppose the increased moles of ethanol

to lower the concentration of ethanol

to oppose the change and decrease the ethanol

*If no reference to **M1**, marks **M2** and **M3** can still score BUT if **M1** is incorrect CE=0*

*If there is reference to 'pressure' award **M1** ONLY.*

3

(ii) ***M1***

Catalysts provide an alternative route / pathway / mechanism

OR

surface adsorption / surface reaction occurs

*For **M1**, not simply 'provides a surface' as the only statement.*

***M1** may be scored by reference to a specific example.*

M2

that has a lower / reduced activation energy

OR

<u>lowers / reduces the activation energy</u>

*Penalise **M2** for reference to an increase in the energy of the molecules.*

*For **M2**, the student may use a definition of activation energy without referring to the term.*

*Reference to an increase in successful collisions in unit time <u>alone</u> is not sufficient for **M2** since it does not explain why this has occurred.*

2

[12]