M1.(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

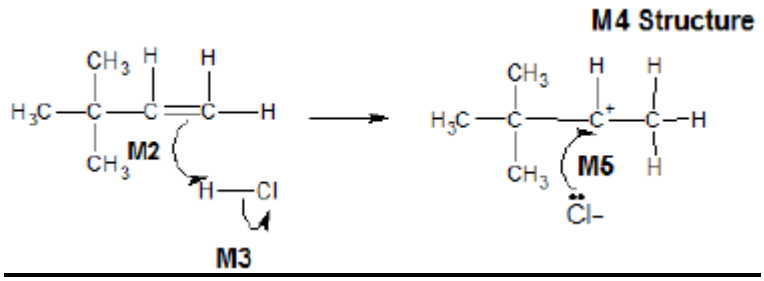
OR

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"

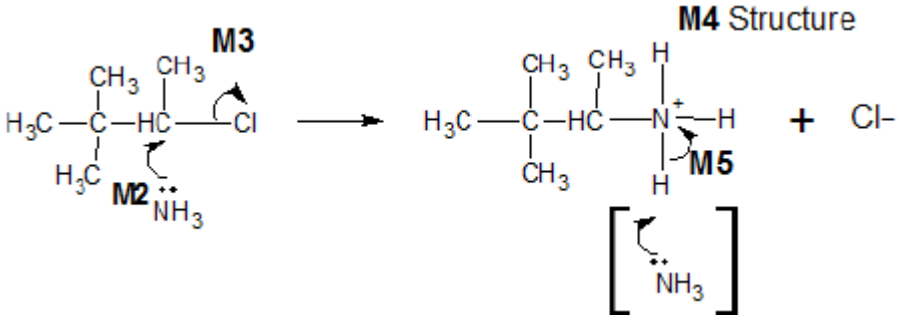
For ***M5****, credit attack on a partially positively charged carbocation structure, but penalise* ***M4***

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 <u>bromide (ion) or Br^- or NaBr or HBr</u>
- 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*

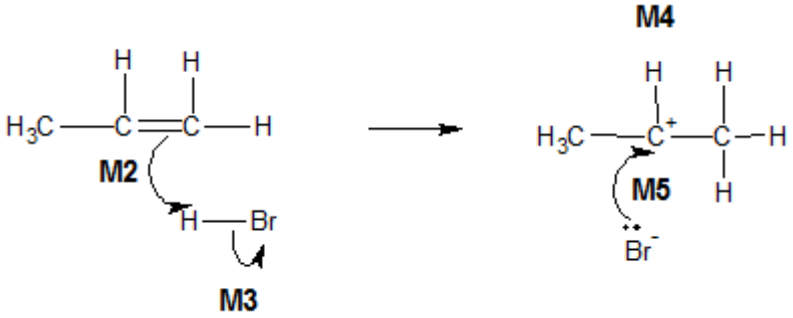
4

[19]

M2.(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

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

Accept the correct use of sticks

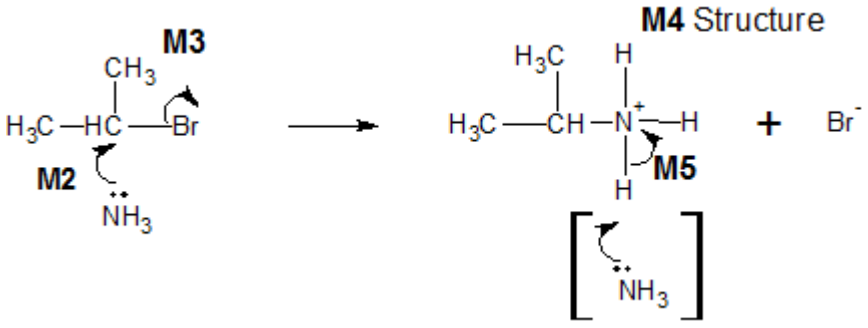
NB These are double-headed arrows

5

(b) **M1 Nucleophilic substitution**

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"

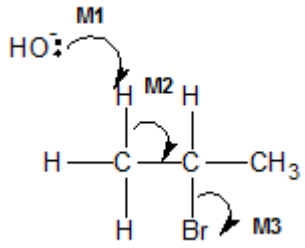
Credit polyprop-1-ene and polypropylene

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]

M3.(a) (Compounds with the) same molecular formula but different structural / displayed / skeletal formula

1

(b) (basic) elimination

1

Mechanism points:

Correct arrow from lone pair on :OH^- to H on C adjacent to C–Br

1

Correct arrow from C–H bond to C–C

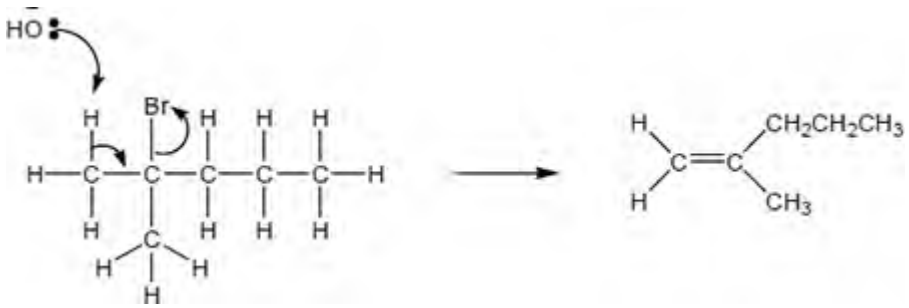
1

Correct arrow from C–Br bond to Br

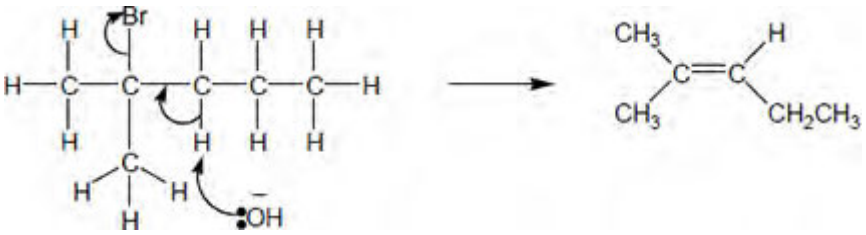
1

Structure of chosen product

1



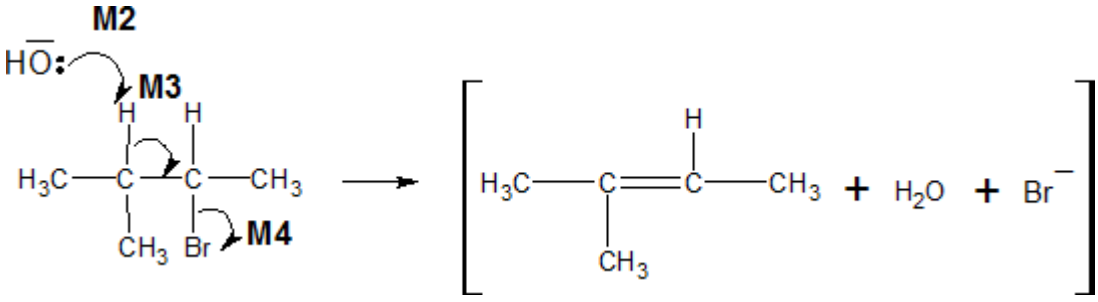
OR



[6]

M4.(a) (i) M1 **Elimination**

M1 *Credit "base elimination" but no other prefix.*



*Penalise **M2** if covalent KOH*

*Penalise **M4** for formal charge on C or Br of C−Br or incorrect partial charges on C−Br*

M2 must show an arrow from the lone pair on the oxygen of a negatively charged hydroxide ion to a correct H atom

Ignore other partial charges

M3 must show an arrow from a correct C−H bond adjacent to the C−Br bond to a correct C-C bond. Only award if an arrow is shown attacking the H atom of a correct adjacent C−H bond in **M2**

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

M4 is independent provided it is from their original molecule, **BUT CE=0 for the mechanism (penalise M2, M3 and M4 only) if nucleophilic substitution mechanism is shown**

Maximum any 2 of 3 marks for the mechanism *for wrong organic reactant or wrong organic product (if shown).*

Credit the correct use of "sticks" for the molecule except for the C−H being attacked

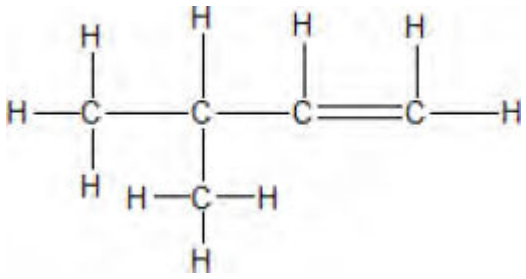
Award full marks for an E1 mechanism in which **M4** is on the correct carbocation

*Penalise **M4**, if an additional arrow is drawn from Br eg to K^+*

NB These are double-headed arrows

4

(ii) Displayed formula for 3-methylbut-1-ene



All bonds and atoms must be drawn out, but ignore bond angles

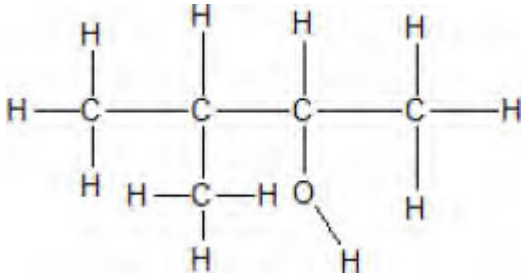
1

(iii) Position(al) (isomerism or isomer)

Penalise any other words that are written in addition to these.

1

(b) (i) Displayed formula for 3-methylbutan-2-ol



All bonds and atoms must be drawn out, but ignore bond angles.

1

(ii) Any **one** from

- Lower / decreased temperature **OR** cold
- Less concentrated (comparative) ***OR*** dilute KOH
- Water (as a solvent) / (aqueous conditions)

Ignore "pressure".

1

(iii) Nucleophilic substitution

Both words needed - credit phonetic spelling.

1

(iv) (Strong / broad) absorption / peak in the range **3230 to 3550** cm^{-1} or specified value in this range or marked correctly on spectrum

*Allow the words "dip" **OR** "spike" **OR** "trough" **OR** "low transmittance" as alternatives for absorption.*

1

[10]

M1.D

[1]

M2.C

[1]

M3.D

[1]

M4.A

[1]

M5.D

[1]

M6.D

[1]

M7.A

[1]

M8.A

[1]

M9.B

[1]

M10.C

[1]

M11.B

[1]

M12.C

[1]

M13.B

[1]

M14.D

[1]

M15.A

[1]

M16.D

[1]

M1.(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

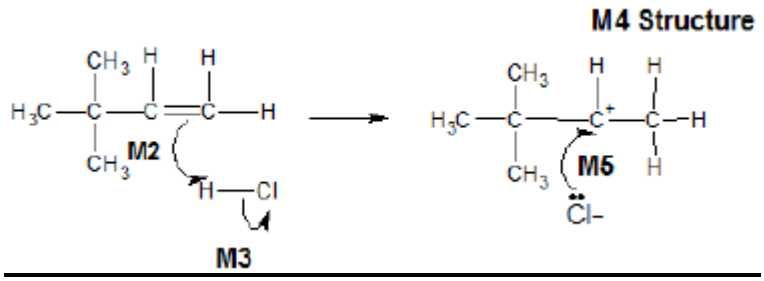
OR

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"

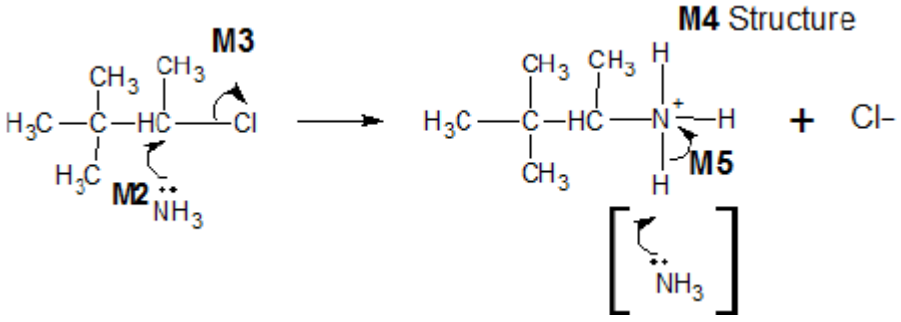
*For **M5**, credit attack on a partially positively charged carbocation structure, but penalise **M4***

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]

M2.(a) Structure for 3-methylbut-1-ene

$H_2C=CHCH(CH_3)_2$

Any correct structural representation.

Credit "sticks" and require the double bond.

1

(b) Structure for 2-methylpropan-2-ol

$(CH_3)_3COH$

Any correct structural representation.

Credit "sticks".

1

(c) Structure for propene

$H_2C=CHCH_3$

Any correct structural representation.

Credit "sticks" and require the double bond.

1

(d) Structure for 2-aminobutane

$CH_3CH_2CH(NH_2)CH_3$

Any correct structural representation.

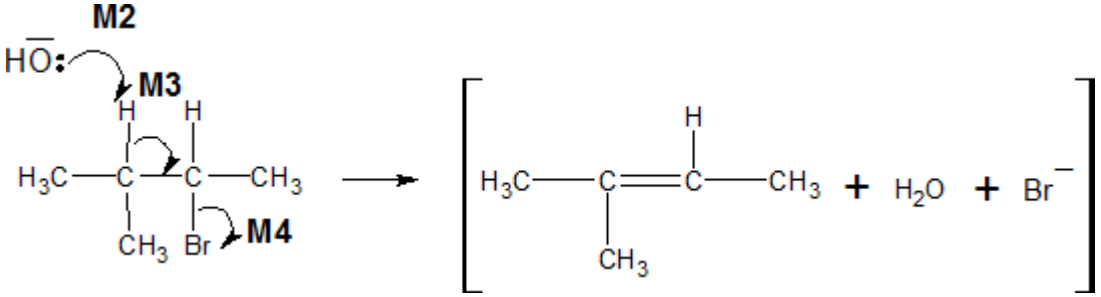
Credit "sticks".

1

[4]

M3.(a) (i) M1 **Elimination**

M1 *Credit "base elimination" but no other prefix.*



*Penalise **M2** if covalent KOH*

*Penalise **M4** for formal charge on C or Br of C−Br or incorrect partial charges on C−Br*

M2 must show an arrow from the lone pair on the oxygen of a negatively charged hydroxide ion to a correct H atom

Ignore other partial charges

M3 must show an arrow from a correct C−H bond adjacent to the C−Br bond to a correct C-C bond. Only award if an arrow is shown attacking the H atom of a correct adjacent C−H bond in **M2**

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

M4 is independent provided it is from their original molecule, **BUT CE=0 for the mechanism (penalise M2, M3 and M4 only) if nucleophilic substitution mechanism is shown**

Maximum any 2 of 3 marks for the mechanism *for wrong organic reactant or wrong organic product (if shown).*

Credit the correct use of "sticks" for the molecule except for the C−H being attacked

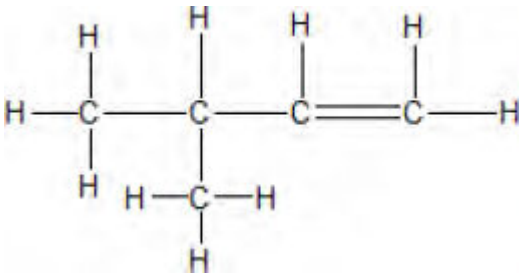
Award full marks for an E1 mechanism in which **M4** is on the correct carbocation

*Penalise **M4**, if an additional arrow is drawn from Br eg to K^+*

NB These are double-headed arrows

4

(ii) Displayed formula for 3-methylbut-1-ene



All bonds and atoms must be drawn out, but ignore bond angles

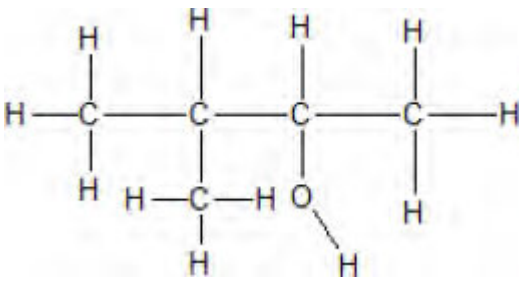
1

(iii) Position(al) (isomerism or isomer)

Penalise any other words that are written in addition to these.

1

(b) (i) Displayed formula for 3-methylbutan-2-ol



All bonds and atoms must be drawn out, but ignore bond angles.

1

(ii) Any **one** from

- Lower / decreased temperature **OR** cold
- Less concentrated (comparative) ***OR*** dilute KOH

- Water (as a solvent) / (aqueous conditions)
  Ignore "pressure".

1

(iii) Nucleophilic substitution
Both words needed - credit phonetic spelling.

1

(iv) (Strong / broad) absorption / peak in the range **3230 to 3550** cm^{-1} or specified value in this range or marked correctly on spectrum
*Allow the words "dip" **OR** "spike" **OR** "trough" **OR** "low transmittance" as alternatives for absorption.*

1

[10]

M4.C

[1]

M5.D

[1]

M6.D

[1]

M7.(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^+

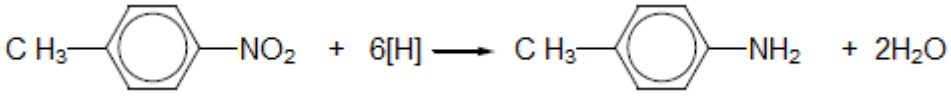
Ignore NaOH after Sn / HCl

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

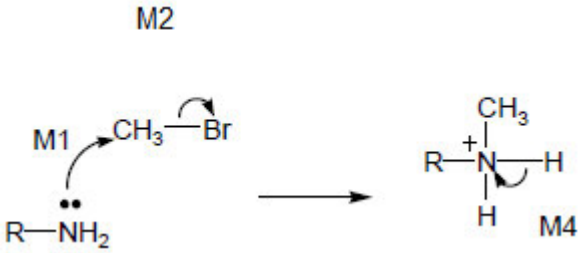
OR making hair conditioner

OR making fabric softener

OR making 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]

M1.(a) UV light

1

$CCl_4 \longrightarrow CCl_3\bullet + \bullet Cl$

1

(b) $Cl\bullet + O_3 \longrightarrow ClO\bullet + O_2$

1

$ClO\bullet + O_3 \longrightarrow Cl\bullet + 2O_2$

1

(c) M_r of CF_3Cl = 104.5

Moles freon = $1.78 \times 10^{-4} \times 10^3 / 104.5 = 1.70 \times 10^{-3}$

1

Number of molecules = $1.70 \times 10^{-3} \times 6.02 \times 10^{23} = 1.02 \times 10^{21}$

1

Molecules in 500 cm^3 = $(1.02 \times 10^{21} \times 500 \times 10^{-6}) / 100 = 5.10 \times 10^{15}$

Allow answer in the range 5.10–5.13 × 10^{15}

Answer must be given to this precision

1

[7]

M2.(a) (i) (Free-) radical substitution

Both underlined words are required

Penalise a correct answer if contradicted by an additional answer

1

(ii) **Initiation**

$F_2 \longrightarrow 2F\bullet$

Penalise absence of dot once only

First propagation

$F\bullet + CH_3F \longrightarrow \bullet CH_2F + HF$

Penalise + or − charges every time

Second propagation

$F_2 + \bullet CH_2F \longrightarrow CH_2F_2 + F\bullet$

Accept dot anywhere on CH_2F radical
Mark independently

Termination (must make 1,2-difluoroethane) $2 \bullet CH_2F \longrightarrow \underline{CH_2FCH_2F}$

Use of half-headed arrows must be correct to score, but if not correct then penalise once only in this clip

4

(iii) $CH_3\,CH_3 + \mathbf{5}F_2 \longrightarrow CF_3CHF_2 + \mathbf{5}HF$

$(C_2H_6)(C_2HF_5)$

1

(b) 1,1,1,2-tetrachloro-2,2-difluoroethane

Accept phonetic spelling eg "fluro, cloro"
*Penalise "flouro" and "floro", since **QoL***

OR

1,2,2,2-tetrachloro-1,1-difluoroethane

Ignore commas and hyphens

1

(c) (i) $\mathbf{2}O_3 \longrightarrow \mathbf{3}O_2$

ONLY this equation or a multiple
Ignore NO over the arrow
Other species must be cancelled

1

(ii) $O + NO_2 \longrightarrow NO + O_2$

ONLY this answer and NOT multiples
Ignore any radical dot on the O atom

1

[9]

M3.(a) **Initiation**

$Cl_2 \longrightarrow 2Cl\bullet$

Penalise absence of dot once only.

First propagation

$Cl\bullet + CH_3Cl \longrightarrow \bullet CH_2Cl + HCl$

Credit the dot anywhere on the radical.

Second propagation

$Cl_2 + \bullet CH_2Cl \longrightarrow CH_2Cl_2 + Cl\bullet$

Termination (must make 1,2-dichloroethane)

$2 \bullet CH_2Cl \longrightarrow CH_2ClCH_2Cl$

Penalise $C_2H_4Cl_2$

4

(b) (i) (chlorine free) radical

Ignore formula.

1

(ii) M1 $Cl\bullet + O_3 \longrightarrow ClO\bullet + O_2$

M2 $ClO\bullet + O_3 \longrightarrow Cl\bullet + 2O_2$

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

Credit the dot anywhere on the radical.

Penalise absence of dot once only.

Individual multiples acceptable but both need to be doubled if two marks are to be awarded.

2

[7]

M4.(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

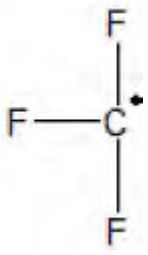
(ii) Ultra-violet / uv / sunlight

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 <u>at the end</u>
- has <u>not been used up</u>
- provides an alternative route / mechanism

3

[10]

M5.(a) (i) **M1 Initiation**

$Cl_2 \longrightarrow 2Cl\bullet$

Penalise absence of dot once only.

M2 First propagation

$Cl\bullet + CHF_3 \longrightarrow CF_3\bullet + HCl$

Penalise + or − charges <u>every time</u>.

M3 Second propagation

$Cl_2 + CF_3\bullet \longrightarrow CClF_3 + Cl\bullet$

Credit $CF_3\bullet$ with the radical dot above / below / to either side.

M4 Termination (must make C_2F_6)

$2\ CF_3\bullet \longrightarrow C_2F_6$ or CF_3CF_3

Mark independently.

4

(ii) ultra-violet / uv / sun light

OR (very) high temperature

OR 500 °C ≤ T ≤ 1000 °C

OR 773 K ≤ T ≤ 1273 K

1

(b) (i) Cl• **OR** chlorine atom / chlorine (free−) radical / Cl (atom)

Not 'chlorine' alone.

Credit 'Cl' alone on this occasion.

1

(ii) **2**O_3 ⟶ **3**O_2

Or multiples.

Ignore state symbols.

If the correct answer is on the line OR clearly identified below some working, then ignore any working.

1

[7]