M1.(a) **P**   3,3−dimethylbut−1−ene
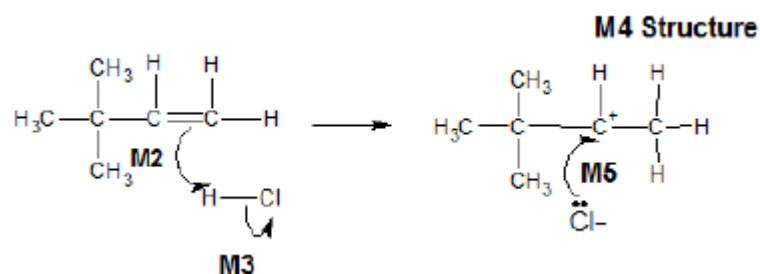   ***OR***
                   accept 3,3−dimethylbutene
                       Ignore absence of commas, hyphens and gaps
                       Require correct spelling

        Q   3−chloro−2,2−dimethylbutane
        OR
                   accept 2−chloro−3,3−dimethylbutane
                       In Q, "chloro" must come before "dimethyl"

2

   (b)   **M1 <u>Electrophilic addition</u>**

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
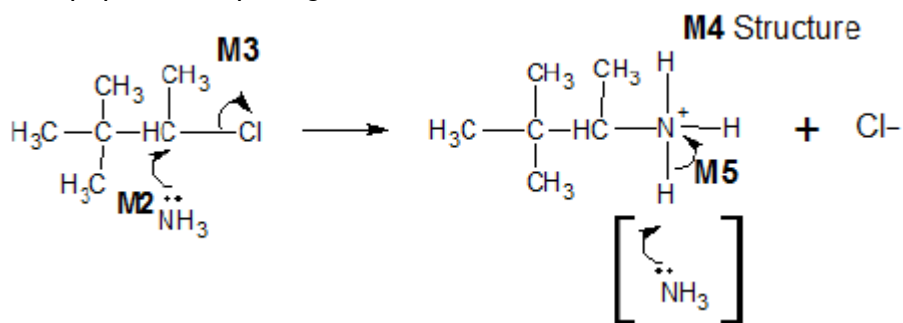   *Credit the correct use of "sticks"*
           *For **M5**, credit attack on a partially positively charged carbocation structure, but penalise **M4***

5

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

> *For **M1**, both words required.*
> *Accept phonetic spelling*

M4 Structure

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*
>
> <u>***Maximum 3 of 4 marks for the mechanism***</u> *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
•   <u>high</u> temperature OR <u>hot</u> OR <u>heat / boil under reflux</u>
•   <u>concentrated</u>
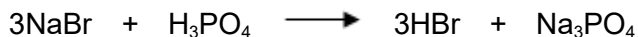•   <u>alcohol / ethanol (as a solvent) / (ethanolic conditions)</u>

Page 3

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

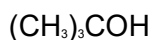**[19]**

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

$H_2C=CHCH(CH_3)_2$

Any correct structural representation.
Credit "sticks" and require the double bond.
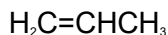
1

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

$(CH_3)_3COH$

Any correct structural representation.
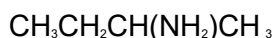*Credit "sticks".*

1

Page 4

(c)   Structure for propene

H₂C=CHCH₃
Any correct structural representation.
Credit "sticks" and require the double bond.

1

(d)   Structure for 2-aminobutane

CH₃CH₂CH(NH₂)CH₃
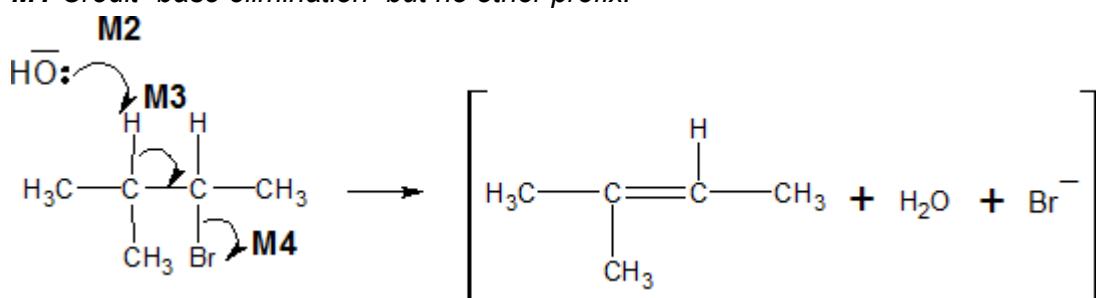*Any correct structural representation.*
Credit "sticks".

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 <u>lone pair on the oxygen</u> of a negatively charged hydroxide ion <u>to a correct</u> 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 <u>original molecule</u>, **BUT CE=0 <u>for the mechanism (penalise M2, M3 and M4 only)</u> if nucleophilic substitution mechanism is shown**
*<u>**Maximum any 2 of 3 marks for the mechanism**</u> for wrong organic reactant or wrong organic product (if shown).*
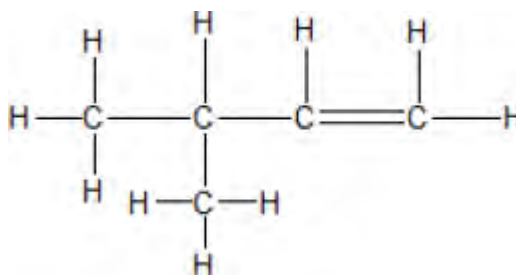*Credit the correct use of "sticks" for the molecule except for the C−H being attacked*

Page 5

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) <u>Displayed formula</u> for 3-methylbut-1-ene

All bonds and atoms must be drawn out, but ignore bond angles
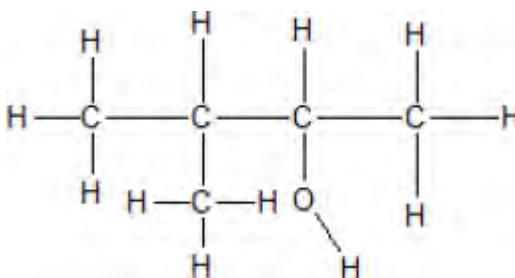
1

(iii) <u>Position(al)</u> (isomerism or isomer)

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

1

(b) (i) <u>Displayed formula</u> for 3-methylbutan-2-ol

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

1

(ii) Any **one** from

• <u>Lower / decreased</u> temperature **OR** <u>cold</u>

• <u>Less concentrated</u> (comparative) **OR** <u>dilute</u> KOH

Page 6

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

  1

(iii) <u>Nucleophilic substitution</u>
  Both words needed - credit phonetic spelling.

  1

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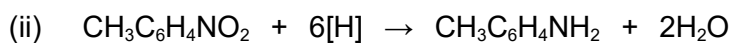
  1

(b) (i) Sn / HCl

Ignore conc or dil with HCl,

Allow (dil) H_2SO_4 but not conc H_2SO_4

Not allow HNO_3 or H^+

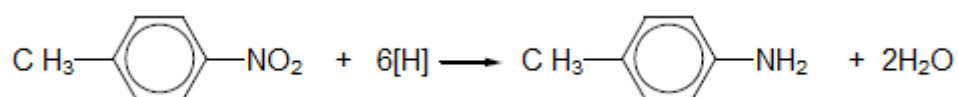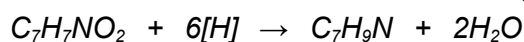*Ignore NaOH after Sn / HCl*

Ignore catalyst

1

(ii) $CH_3C_6H_4NO_2$ + 6[H] → $CH_3C_6H_4NH_2$ + $2H_2O$

OR

Allow molecular formulae as structures given

$C_7H_7NO_2$ + 6[H] → C_7H_9N + $2H_2O$

Qu states use [H], so penalised $3H_2$

1

(iii) <u>making</u> dyes

OR <u>making</u> quaternary ammonium salts

OR <u>making</u> (cationic) surfactants
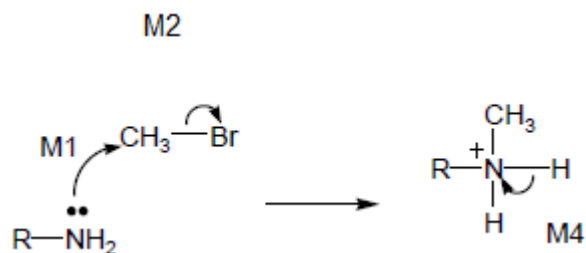
OR <u>making</u> hair conditioner

OR <u>making</u> fabric softener

OR <u>making</u> detergents

1

(c)

M2

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]