2.8 EXTRA QUESTIONS MS

1.

(i) $Cl_2 \rightarrow 2Cl\bullet$ / ½ $Cl_2 \rightarrow Cl\bullet$ **(1)** 1

(ii) $Cl\bullet + C_6H_5CH_3 \rightarrow C_6H_5CH_2\bullet + HCl$ **(1)**

$C_6H_5CH_2\bullet + Cl_2 \rightarrow Cl\bullet + C_6H_5CH_2Cl$ **(1)** 2

(iii) $C_6H_5CHCl_2$ / $C_6H_5CCl_3$ / $C_6H_5\ CHCHC_6\ H_5$ /
other correct possible answer **(1)** 1

[4]

2. (a) (i) (free–)radical substitution 1
(both words required for the mark)

(ii) uv light OR sunlight OR <u>high</u> temperature OR 150°C to 500°C 1

(iii) Propagation 1
(ignore "chain", "first", "second" in front of the word propagation)

(iv) Termination 1
$\cdot CH_2CH_3 + Br\cdot \longrightarrow CH_3CH_2Br$
OR $2\cdot CH_2CH_3 \longrightarrow C_4H_{10}$ 1
(penalise if radical dot is obviously on CH_3, but not otherwise)
(penalise $C_2H_5\cdot$)
(credit $2Br\cdot \longrightarrow Br_2$)
(ignore "chain" in front of the word termination)

(b) (i) <u>Fractional</u> distillation OR fractionation 1
(credit gas–liquid chromatography, GLC)

(ii) $CH_3CH_3 + 6Br_2 \longrightarrow C_2Br_6 + 6HBr$ 1
(credit C_2H_6 for ethane)

[7]

3. (a) (i) (free–) radical substitution 1
(both words required for the mark)
initiation $Cl_2 \rightarrow 2Cl\cdot$ 1
(credit correct half arrows, but penalise double headed arrows)

first propagation $CH_3Cl + Cl\cdot \rightarrow \cdot CH_2Cl + HCl$ 1
second propagation $\cdot CH_2Cl + Cl_2 \rightarrow CH_2Cl_2 + Cl\cdot$ 1
(penalise the absence of dots on radicals once only)
(penalise radical dot on Cl of CH_2Cl once only)

(ii) $CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$ 1
(penalise if any radicals appear in this equation)

(b) M1: mol C = 10.1/12.0 and mol Cl = 89.9/35.5 1

M2: Ratio 0.842 : 2.53 OR 1: 3 OR CCl3 1

M3: 237.0/Mr of CCl_3 = 237.0/118.5 = 2 Therefore C_2Cl_6 1
(correct answer gains full credit)

OR

M1: 237.0 × 10.1/100 and 237 × 89.9/100 1

M2: Ratio 23.9/12.0 : 213/35.5 OR 2 : 6 1

M3: C_2Cl_6 1
(correct answer gains full credit)

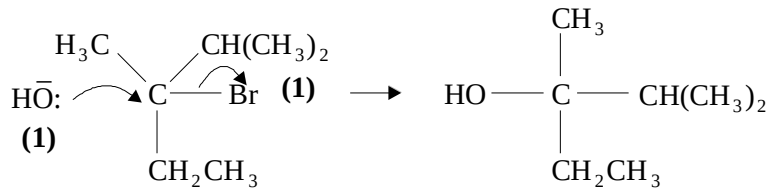
(c) any two from $CHBr_3$ or CBr_4 or $C_2H_2Br_4$ (or $CHBr_2CHBr_2$) or C_2Br_6 (or CBr_3CBr_3) 2
(ignore HBr or H_2)
(ignore equations and ignore names when given in addition to formulae)
(penalise names alone)

[10]

4. (a) (i) substitution or hydrolysis **(1)**

nucleophile **(1)**

(ii)



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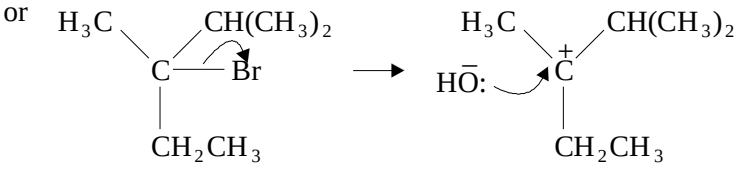

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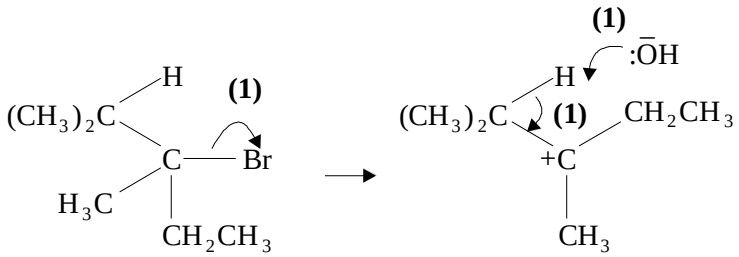
(b) (i) *Type of reaction* elimination **(1)**

Role of reagent base or proton acceptor **(1)**

(ii) *Structure of the alkene* $(CH_3)_2C{=}C(CH_3)CH_2CH_3$ **(1)**

Mechanism



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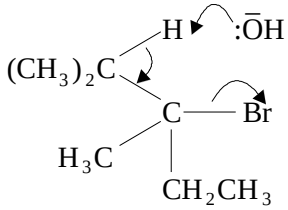


(iii) *Structure of second alkene* $(CH_3)_2CHC(CH_3){=}CHCH_3$ **(1)**

Name 3,4-dimethylpent-2-ene **(1)**

Structure of third alkene $(CH_3)_2CHC(C_2H_5){=}CH_2$ **(1)**

Name 2-ethyl-3-methylbut-1-ene**(1)** 10

[15]

5. (i) M1 curly arrow from lone pair of electrons on oxygen of hydroxide ion 1

(insist on a lone pair of electrons on the oxygen atom and a negative charge, but only credit this mark if the attack is to a correct H atom)

M2 curly arrow from the middle of the C–H bond to the middle of the C–C bond. 1

(only credit this mark if the arrow originates from the correct C–H bond and if an attempt has been made at M1)

M3 curly arrow from the middle of the C–Br bond towards/alongside the Br atom. 1

(credit M3 independently unless the bond breaking is contradicted by an additional arrow)

(penalise M3 curly arrow if the C–Br has a formal positive charge)

(ignore partial charges on the C–Br bond, but penalise if incorrect)

(credit full marks for an E1 mechanism, with M2 awarded for a correct curly arrow on the correct carbocation)

(award a maximum of two marks for an incorrect haloalkane)

(ignore products)

(ii) Haloalkane/C_2H_5Br is made from ethane
OR haloalkane is not (readily) available
OR haloalkane is expensive
OR it is (too) expensive/costly
OR (reaction) yield is too low/poor
OR it is too slow
OR a valid reference to nucleophilic substitution/alcohol formation occurring as an alternative reaction. 1

(ignore references to temperature or to energy consumption)

(do not credit statements which refer to the idea that this route is not chosen, because industry chooses another route e.g. cracking)

[4]

6.

(i) M1: potassium cyanide OR KCN OR sodium Cyanide OR NaCN; 1

(ignore conditions - dissolved in (aq) or (alc) or KOH(aq) all work) (penalise HCN)

M2: propanenitrile; 1

(credit propan-1-nitrile OR propan nitrile, but not propanitrile)

(ii) M1: ammonia OR NH_3; 1

(If formula is written, insist that it is correct)
(ignore conditions, but penalise acidic)

M2: ethylamine; 1

(credit aminoethane)

(iii) M1: curly arrow <u>from lone pair</u> on nitrogen of (correct formula for) ammonia towards/alongside C atom of C-Br; 1

(penalise M1 if formula of ammonia is wrong or has a negative charge or has no lone pair or arrow is from negative charge)

M2: curly arrow <u>from C-Br bond</u> towards/alongside side Br atom; 1

(credit M2 independently)
(penalise M2 if formal positive charge on C atom of C-Br)

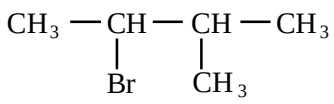
M3: correct structure of the ethylammonium ion; 1

(credit the structure drawn out with all four bonds around the nitrogen atom OR written as $C_2H_5NH_3^+$ OR $CH_3CH_2NH_3^+$)

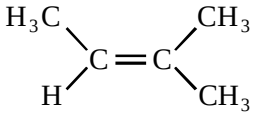
M4: curly arrow <u>from the middle of one of the H-N bonds</u> towards the positive <u>N atom</u>; 1

(possible to credit M4 on an incorrect ethylammonium ion with no positive charge)
(ignore use of ammonia or bromide ion etc. to remove proton from ethylammonium ion)
(If the wrong haloalkane is used, award MAX. 3 marks for the mechanism) (If S_N1 mechanism is used, give full credit in which M1 is for a curly arrow from the lone pair of the N atom of (correct formula for) ammonia towards/alongside the positive carbon atom of $CH_3CH_2^+$)

[8]

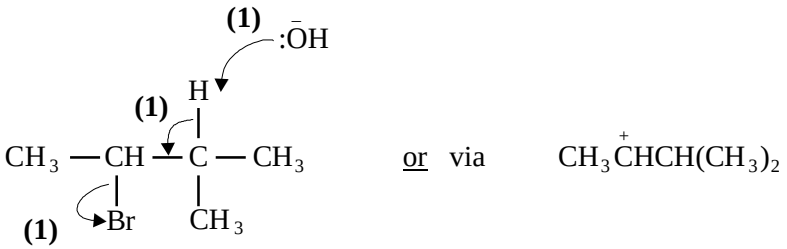
7. (a)  or $CH_3CHBrCH(CH_3)_2$ 1

(1)

(b) (i)  or $CH_3CH=C(CH_3)_2$

(1)

(ii) (nucleophilic) elimination



or via

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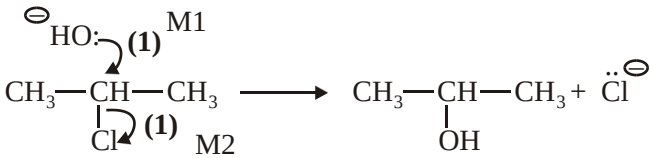
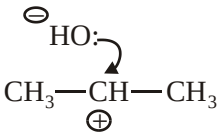
(c) 3–methylbut–1–ene **(1)** 1

[7]

8. (i) *Mechanism*:



Credit M1 for 

M1 and M2 independent

Curly arrows must be from a bond or a lone pair

Do not penalise sticks

Penalise M1 if Na—OH *precedes (penalise this once)*

Penalise incorrect $\delta+$ $\delta-$ for M2

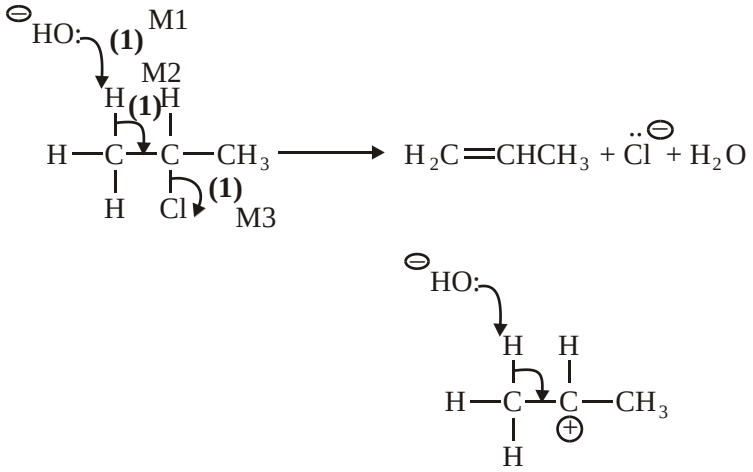
Penalise + on C atom for M2

Only allow M1 for incorrect haloalkane

Role of the hydroxide ion: nucleophile **(1)**
electron pair donor
lone pair donor

NOT nucleophilic substitution

(ii) *Mechanism*:



Only allow M1 and M2 for incorrect haloalkane unless RE on (i)

+ charge on H on molecule, penalise M1

M3 independent

M2 must be to correct C–C

M1 must be correct H atom

Credit M1 and M2 via carbocation mechanism

No marks after any attack of C ⊕ *by* OH^-

Role of the hydroxide ion: base **(1)** 7

proton acceptor

accepts H^+

[7]

9. (a) (i) *Structure*: $H_3C-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$ **(1)** [insist on C — OH bond]

No credit for propan-1-ol even when named correctly

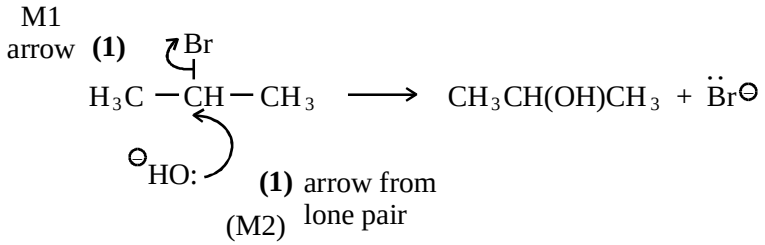
Credit propane-2-ol

Name: propan-2-ol **(1)**

Not 2-hydroxypropane

(ii) *Name of mechanism*: nucleophilic substitution **(1) (both words)**
(NOT S_N1 orS_N2)

Mechanism:



penalise incorrect polarity on C-Br (M1)
Credit the arrows even if incorrect haloalkane
If S_N1, both marks possible

i.e. M1 C — Br M2 HO correct carbocation

5

(b) (i) elimination **(1)**

(ii) base **(1)**
OR proton acceptor
NOT nucleophile (base)

2

[7]

10. (a) M1 NaOH OR KOH OR correct name 1

M2 aqueous or solution in water *(ignore heat, reflux etc.)* 1

(Penalise M1 for hydroxide ion alone, but mark on and credit M2)
(Credit M2 ONLY for H_2O as reagent and heat / warm / T=50 to 100^oC)
(NaOH(aq) scores M1 and M2 provided it is not contradicted)
(Penalise M2 if NaOH(aq) followed by concentrated or ethanol)
(Penalise M1 and M2 if followed by acid)

(b) Ethanolic OR alcoholic OR CH_3CH_2OH / CH_3OH solvent OR aqueous ethanol/alcohol 1
OR higher temperature *(must be comparative)*

(Ignore heat or heat under reflux)

(Credit part (c) independently from part (b))

(Penalise "ethanoic")

[3]

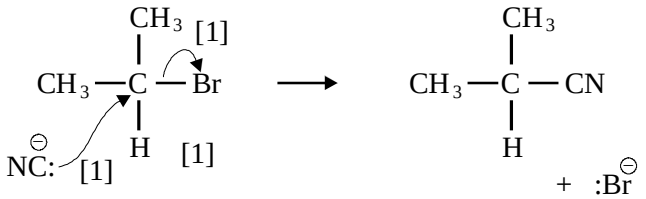
11. (i) 2–methylpropanenitrile **(1)**

(ii) Reagent KCN **(1)**

Conditions alcoholic/aq **(1)**

(iii) *Name of mechanism* nucleophilic substitution **(1)**

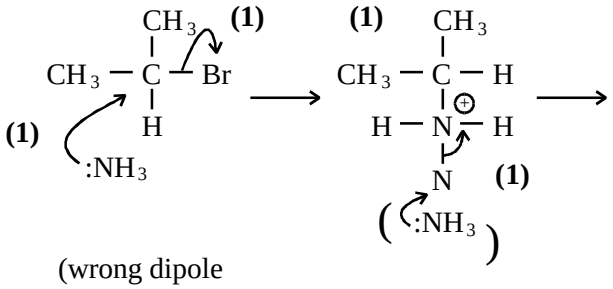
Mechanism



7

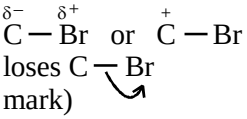
[7]

12. (a) *Name of mechanism*: nucleophilic substitution **(1)**
Mechanism:



(M3 is for correct carbocation - if used wrong halogenoalkane lose M3)

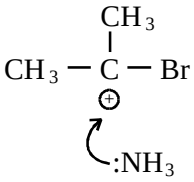
(wrong dipole



loses C — Br mark)

Marks S_N1 using same points

∴ M2 requires



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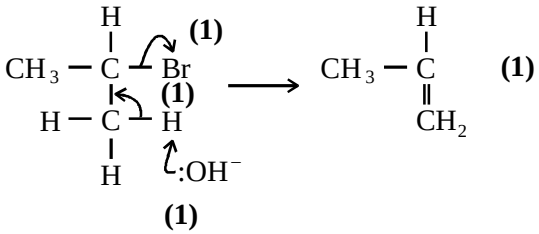
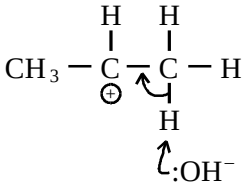
(b) *Role of potassium hydroxide*: Base **(1)**
Mechanism:



Mark E1 using same points

∴ M2/M3



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[10]

13. elimination **(1)** 1

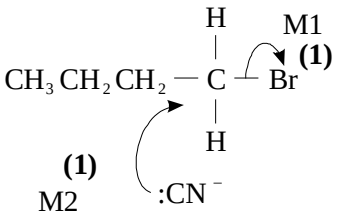
[1]

14. (i) $CH_3\ CH_2\ CH_2\ CH_2\ CN$ **(1)** Not $C_4\ H_9\ CN$

Pentanenitrile **(1)**

allow pentanonitrile, ignore numbers

(ii) Nucleophilic substitution **(1)**



SN1 mechanism

M1 formation of carbocation including C — Br

M2 attack by :CN–

allow mechanism showing 'Cl'

If '+' onC' lose M1

If K–CN shown lose M2

If $\delta^{-}c-^{\delta+}_{Bs}$ *lose M1*

(iii) C–F bond is strong (er) **(1)**
Must imply C–F is stronger than C–Br bond

ignore references to electronegativity, bond polarity etc.

6

[6]

15. (a) (base) elimination 1
(penalise other words before 'elimination' e.g. nucleophilic)

M1: curly arrow from lone pair of electrons on oxygen of hydroxide ion 1
(insist on a lone pair of electrons on the oxygen atom and a negative charge, but only credit this mark if the attack is to a correct H atom) 1

M2: curly arrow from the <u>middle of the C-H bond</u> to the <u>middle of the C–C bond</u> 1
(only credit this mark if the arrow originates from the correct C–H bond and if an attempt has been made at M1)

M3: curly arrow from the <u>middle of the C–Br bond</u> towards/alongside the Br atom
(credit M3 independently unless the bond breaking is contradicted by an additional arrow)
(penalise curly arrow if the C–Br has a formal positive charge)
(credit full marks for an E1 mechanism, with M2 awarded for a correct curly arrow on the correct carbocation)
(award a maximum of two marks for either an incorrect haloalkane or an incorrect organic product)
(maximum 2 marks for use of .sticks. for the haloalkane, unless RE from 2(b), when credit can be given)

(b) nucleophile or electron pair donor 1
(penalise 'base')

(c) $CH_3CH_2CH_2CH_2Br + 2NH_3 \rightarrow CH_3CH_2CH_2CH_2NH_2 + NH_4Br$ 2

(M1 correct product)
(M2 balanced equation using $2NH_3$ and leading to NH_4Br)
(penalise M1 for use of $C_4H_9NH_2$ or for incorrect haloalkane, but allow consequent correct balancing of equation with 2 moles of ammonia)

(1–)butylamine 1

(credit 1–aminobutane and butyl–1–amine)
(award QoL mark for correct spelling)

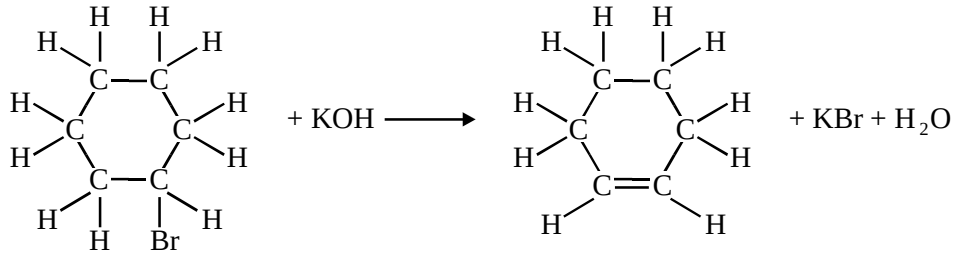
[8]

16. (i) potassium or sodium hydroxide (or other specific strong base) **(1)**

allow formula; ***not*** *just 'hydroxide'*

in ethanolic /alcoholic solution (independent of first mark) **(1)** 2

allow 'in ethanol', ***not*** *just 'ethanol'/ 'with ethanol'*
ignore references to heat / pressure

(ii) 

structure of cyclohexene showing double bond **(1)**

minimum structure needed is a ring with CH_2 units implied and double bond:
do not allow KOH over arrow

equation correct overall ie balanced
allow ionic equation **(1)** 2

(iii) elimination / dehydrohalogenation 1
ignore nucleophilic / electrophilic etc.

[5]

17.

(a) (i) $CH_3CH_2CH_2Br + KCN \rightarrow CH_3CH_2CH_2CN + KBr$ **(1)** 1

allow C_3H_7Br allow C_4H_7N

(ii) nucleophilic substitution / SN2 **(1)** 1

(b) CN^- **or** NC^- **(1)**

lone pair of electrons on C atom **(1)** 2

[4]

18. (a) 2-bromobutane; 1

(b) Elimination; 1

(penalise "nucleophilic" OR "electrophilic" before the word "elimination")

M1: curly arrow <u>from lone pair</u> on oxygen of hydroxide ion to H atom on <u>correct</u> C-H adjacent to C-Br; 1

(penalise M1 if KOH shown as covalent with an arrow breaking the bond)

M2: curly arrow <u>from single bond</u> of <u>adjacent C-H</u> <u>to adjacent single bond</u> C-C; 1

(only credit M2 if M1 is being attempted to correct H atom)

M3: curly arrow <u>from C-Br bond</u> to side of Br atom; 1

(credit M3 independently unless arrows contradict)
(Credit possible repeat error from 2(c)(iii) for M3)
(If the wrong haloalkane is used OR but-1-ene is produced, award MAX. 2 marks for the mechanism)
(If E1 mechanism is used, give full credit in which M1 and M2 are for correct curly arrows on the correct carbocation)

[5]

19. (a) (i) $CH_3Cl + 2Cl_2 \rightarrow CHCl_3 + 2HCl$ **(1)**

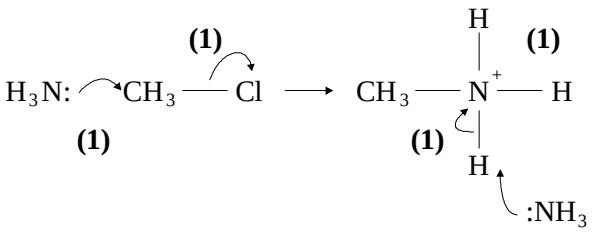
(ii) step in which radicals are used and formed **(1)**

(iii) $CH_3Cl + Cl\bullet \rightarrow \bullet CH_2Cl + HCl$ **(1)**

(iv) $\bullet CHCl_2 + Cl_2 \rightarrow CHCl_3 + Cl\bullet$ 4

(b) *Equation* $CH_3Cl + 2NH_3 \rightarrow CH_3NH_2 + NH_4Cl$ **(1)**

Mecanism



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[9]

20. $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$ **(1)**

Initiation: $Cl_2 \rightarrow 2Cl\cdot$ **(1)**

Propagation: $CH_4 + Cl\cdot \rightarrow CH_3\cdot + HCl$ **(1)**

$CH_3\cdot + Cl_2 \rightarrow CH_3Cl + Cl\cdot$ **(1)**

Termination: $Cl\cdot + Cl\cdot \rightarrow Cl_2$ **(1)**

or $CH_3\cdot + CH_3\cdot \rightarrow C_2H_6$ 5

[5]

21. Reaction 5 NH_3 **(1)** 1

For Reaction 4; credit dil H_2SO_4 OR H_2SO_4(aq) OR HCl (aq) but NOT steam and NOT NaOH(aq)

[1]

22. nucleophilic substitution 1

(both words needed)

Mechanism M1 curly arrow <u>from lone pair</u> on oxygen of hydroxide ion to C atom of C-Br 1

Mechanism M2 curly arrow <u>from C-Br bond</u> to side of Br atom 1

(a possible repeat error here from Question 4a)
(award a maximum of one mark for the wrong haloalkane)
(credit an SNl mechanism in which Ml will be a curly arrow <u>from the lone pair</u> on oxygen of the hydroxide ion to the correct positive <u>carbon</u> atom)

Y is susceptible to attack by hydroxide ions for one of the following reasons 1

- o the C-Br bond is polar
- o the carbon atom is partially positive (or shown as such)
- o the carbon atom is electron deficient

[4]

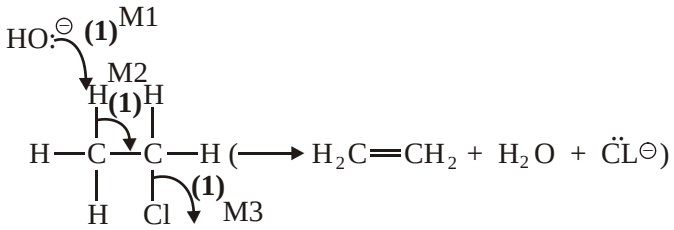
23. (a) <u>Reaction 2</u>: NaOH OR KOH **(1)** M1 alcohol (ic) OR ethanol (ic)**(1)** M2

ignore heat

Condition mark <u>linked to correct reagent</u> but award M2 if OH^- or base or alkali mentioned

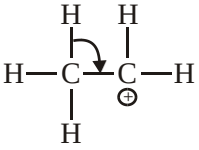
2

(b) <u>Mechanism</u>:



Award M3 (C—Cl) *independently*
M1 and M2 must be to / from correct places

E1 mechanism possible in which M2



<u>Name</u>: of mechanism = elimination **(1)**

NOT dehydrohalogenation

Ignore "base" OR "nucleophilic" before elimination

<u>Reason</u>: Reaction 2 has (very) low yield **(1)** 5

QoL OR chloroethane has to be made (from ethane)
OR chloroethane is expensive
OR chloroethane is not redily available

[7]

24. (a) Alcohol: Reaction = Substitution (/ hydrolysis) **(1)**
Ignore reference to nucleophilic, but electrophilic give zero

Alcohol: Role = nucleophile (/ lone pair donor) **(1)**

Alkene: reaction = elimination **(1)**
Ignore ref to nucleophilic or electrophilic

Alkene: base (/ proton acceptor) **(1)** 4

(b) Alcohol = butan-2-ol **(1)**
Not 2-hydroxybutane or but-2-ol

Appropriate structure for $CH_3CH(OH)\ CH_2CH_3$ **(1)**
Brackets not essential

S_N2 version	S_N1 version
$\overset{\delta+}{C}-\overset{\delta-}{Br}$ bond is polar	C–Br bond is polar **(1)**
Lone pair of OH^-	C–Br bond breaks **(1)**
Attacks the $C^{\delta+}$	forming carbocation / carbonium ion **(1)**

M1 can be scored from a diagram, M2 and M3 from written explanation only 5

[9]

25. (i) 2-chloro(-2-)methylpropane / (2)methyl 2 chloropropane **(1)** 1

(ii) appropriate unambiguous formula for **either** but-1-ene **or** but-2-ene **(1)**

appropriate unambiguous formula for the remaining structural isomer

allow 1 mark if candidate draws cis and trans but-2-ene **(1)** 2

(iii) unambiguous structure for 2-methylpropan-1-ol – may be from mechanism **(1)**

curly arrow / attack by OH^- curly arrow from lone pair or charge only **(1)**

do **not** allow if Na -OH

curly arrow from bond to Cl / dipole shown on C-Cl bond / intermediate showing 3 full and 2 partial bonds to C **(1)**

loss of Cl^- NaCl **or** $Na^+:Cl^-$ **(1)**

$^-$ **not** allowed 4

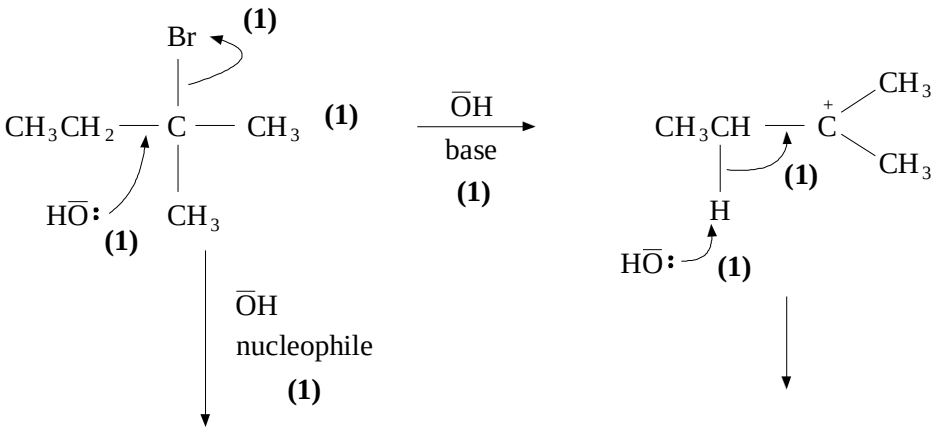
if S_N1 mechanism given:
first mark as above - independent
second mark for correct carbocation formed including curly arrow from C to Cl or $C^{S+}–Cl^{S-}$

third mark for hydroxide attack as above
final mark not available (wrong mechanism)

penalise missing proton once only

[7]

26.

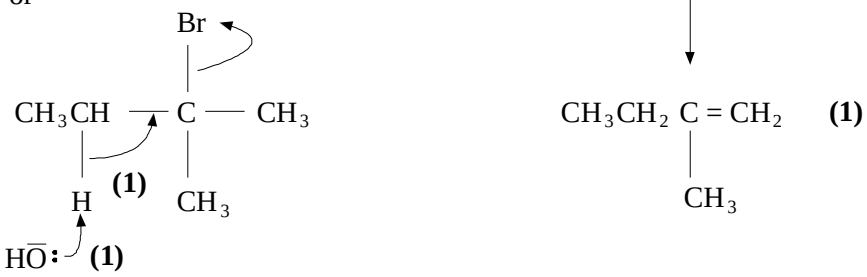


$CH_3CH=C(CH_3)_2$ **(1)**

$CH_3CH_2C(OH)(CH_3)_2$ **(1)** 2-methylbut-2-ene **(1)**

2-methylbutan-2-ol **(1)** also loss of H^+ from CH_3 **(1)**

or



(1)

2- methylbut - l - ene **(1)**

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[14]