A-Level Chemistry

Free Radical Substitution

Mark Scheme

Time available: 59 minutes
Marks available: 54 marks

1. (a) (i) $CH_3Cl + 2Cl_2 \longrightarrow CHCl_3 + 2HCl$

IGNORE *state symbols*

ALLOW *multiples*

1

(ii) (Free-)radical substitution

This answer only

1

(iii) Initiation:

$Cl_2 \longrightarrow 2Cl\bullet$

Penalise absence of dot once only

1

1st Propagation step

$Cl\bullet + CH_2Cl_2 \longrightarrow \bullet CHCl_2 + HCl$

Penalise + and/or – charges every time

1

2nd Propagation step

$\bullet CHCl_2 + Cl_2 \longrightarrow CHCl_3 + Cl\bullet$

ALLOW *• anywhere on* $\bullet CHCl_2$ *but, if drawn out as a structure, then • must be on C*

1

Termination

$2 \bullet CHCl_2 \longrightarrow C_2H_2Cl_4$

Mark independently

ALLOW $\bullet CH_2Cl + \bullet CCl_3 \longrightarrow C_2H_2Cl_4$

IGNORE *state symbols throughout*

1

(b) (i) $CClF_3 \longrightarrow \bullet CF_3 + Cl\bullet$

ALLOW *• anywhere on* $\bullet CF_3$ *unless displayed*

1

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

Equations can be in either order

Penalise absence of • once only

1

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

ALLOW *• anywhere on* $\bullet ClO$

NOT $\bullet O_3$

1

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2. (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

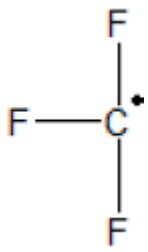
(ii) Ultra-violet / uv / sunlight

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

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

1

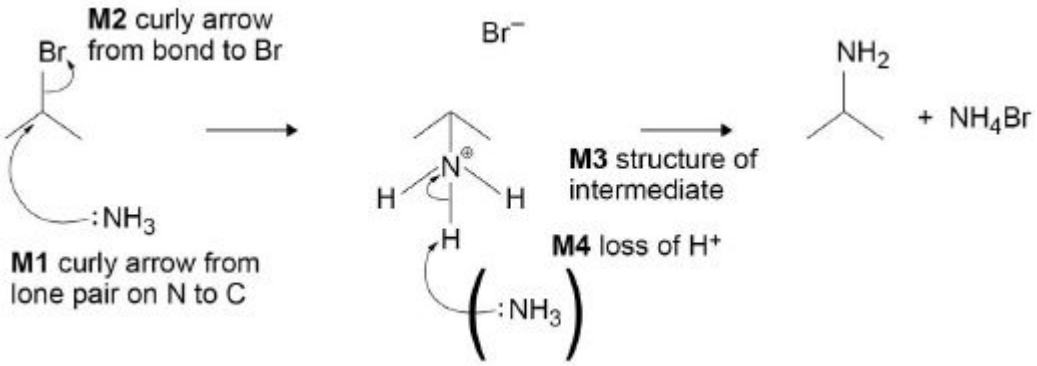
M2 Br is more electronegative than C (or vice versa)

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

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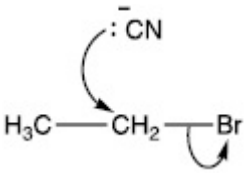
4. (a)



M1 arrow from lone pair on C of CN^- to the C of the CH_2 group

M2 arrow from the C–Br bond to the Br

*All arrows are double-headed. Penalise one mark from the total for **2.1** if half headed arrows are used.*

Do not penalise the "correct" use of "sticks"

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

Allow the minus sign to be anywhere on the CN^- ion

***M2** penalise formal charges or incorrect partial charges on C–Br bond*

*SN1: allow SN1 mechanism with **M1** for breakage of C–Br bond and **M2** for attack by CN^- on correct carbocation*

***Max 1 of 2 marks** for wrong organic reactant*

Ignore wrong organic product (if shown)

Extra arrows or incorrect covalent bonds:

Penalise the mark for breaking of C–Br bond for any extra arrows involving Br or covalent bond in KBr

Penalise the mark for attack by CN^- for any extra arrows involving CN or covalent bond in KCN

2

(b) propanenitrile

Ignore any gaps, hyphens, commas

Allow propane-1-nitrile

1

(c)

M1 $\frac{55(.0)}{108.9+65.1}$ (x 100) or $\frac{55(.0)}{174(.0)}$ (x 100) or $\frac{55(.0)}{55(.0)+119(.0)}$ (x 100)

1

M2 31.6(%) (must be 3sf)

1

31.6 scores 2 marks; 32 scores 1 mark

no ECF

[5]

5. (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

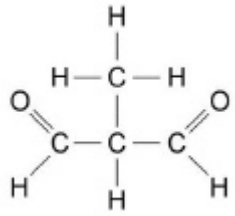
M2

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

Allow lone pair attracted to / attacks the partially positive carbon

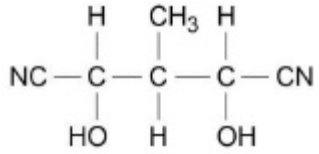
M3

(c)



Must be displayed with all bonds shown

1

(d) 

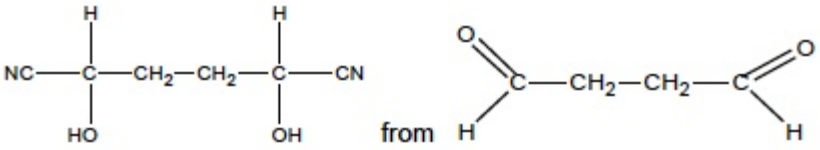
Not need be displayed

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



Allow HCN

Ignore alcoholic solvents

Penalise conc. HCl, H_2SO_4 or any HNO_3

1

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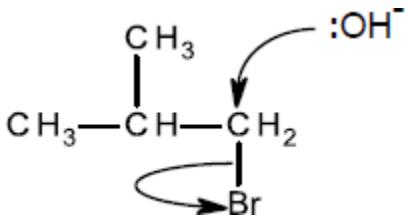
6. (a) **M1** nucleophilic substitution



*Penalise **M3** for formal charge on C and/or Br of C-Br or incorrect partial charges on C-Br*

*Max 1 out of 2 for **M2** & **M3** for incorrect reactant or product (ignore poorly drawn bond from C to OH group in product if shown)*

For SN^2

*penalise **M2** for any additional arrow(s) on NaOH*

*penalise **M3** for any additional arrow(s) to/from the Br to/from anything else*

1

M2 curly arrow from lone pair on O of OH^- to C of C-Br

1

M3 curly arrow from C-Br bond to the Br

1

If SN^1 mechanism given (loss of Br first followed by attack by OH^-) then:

***M2** curly arrow from C-Br bond to the Br*

***M3** curly arrow from lone pair on O of OH^- to positive C atom of correct carbocation*

*penalise **M2** for any additional arrow(s) to/from the Br to/from anything else*

*penalise **M3** for any additional arrow(s) on NaOH*

*If curly arrows represent an attempt at an elimination mechanism, cannot score **M2** or **M3***

(b) **M1** Amount 1-bromo-2-methylpropane
(= (2 × 1.26) / 136.9 = 2.52/136.9) = 0.0184 mol

Correct answer scores 3 marks; answer to at least 2sf and any individual marks for M1/2 should be at least 2sf; answers that are a factor of 10^x out score 2;

1

M2 mass of 2-methylpropan-1-ol expected
(= 0.0184 × 74.0) = 1.36 g

Allow ECF through the question

1

M3 % yield = 100 × (0.895/1.36) = 65.7% (65-67%)

1

Alternative method:

***M2** amount of 2-methylpropan-1-ol produced*
= 0.895/74.0 = 0.0121 mol
***M3** % yield = 100 × (0.0121/0.0184) = 65.7% (65-67%)*

Allow 2 marks for 82.7-83% (comes from starting with 2 g not 2.52 g), with answers that are a factor of 10^x out from this scoring 1

(c) **M1** methylpropene

***M1** Do not allow any names with numbers for the position of the double bond. Allow 2-methylpropene but no other answer*
Ignore any drawn mechanism

1

M2 elimination

***M2** allow base (or basic) elimination but no other answer*

1

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7. (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

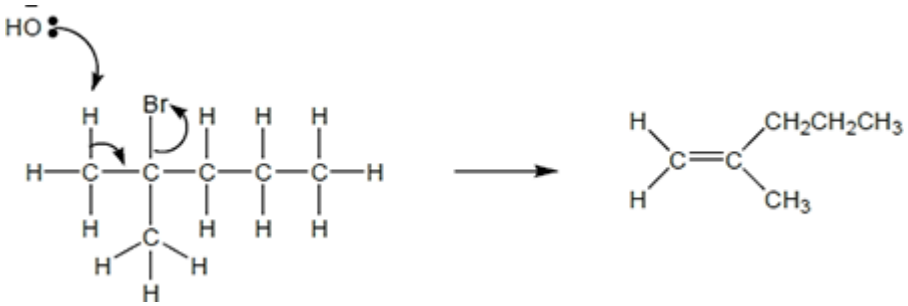
1

Correct arrow from C–Br bond to Br

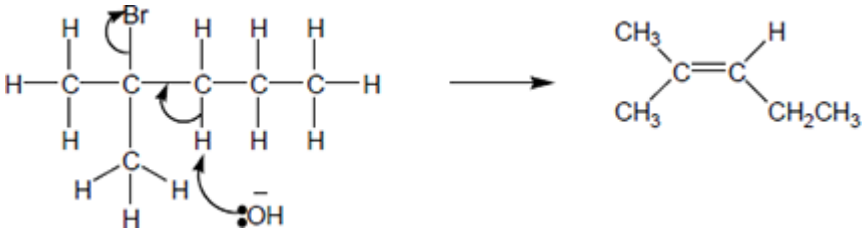
1

Structure of chosen product

1



OR



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