A-Level Chemistry

Addition Reactions of Alkenes

Mark Scheme

Time available: 66 minutes
Marks available: 62 marks

1.

(a) **M1** electrophilic addition

*All arrows are double-headed. Penalise one mark from the total for **M2-5** if half headed arrows are used.*

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

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

1

M2 must show an arrow from the double bond towards a Br atom in a Br–Br molecule

***M2** ignore partial negative charges on the double bond*

1

M3 must show the breaking of the Br–Br bond

***M3** penalise incorrect partial charges on the Br–Br bond and penalise formal charges*

*Penalise **M4** if there is a bond drawn to the positive charge*

1

M4 is for the structure of the correct carbocation

1

M5 must show an arrow from the lone pair of electrons on the Br^- towards the positively charged atom of <u>their</u> carbocation

***Max 3 of 4 marks (M2-5)** for wrong organic reactant or wrong carbocation (ignore structure of product)*

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

1

(b) **M1** C=C electron rich / area of high electron density

***M1** ignore idea that C=C is negative or highly electronegative*

1

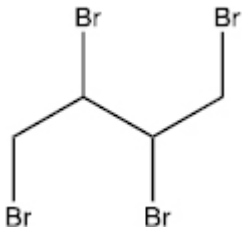
M2 Br-Br becomes polarised

1

M3 δ+ Br attracted to C=C

1

(c)

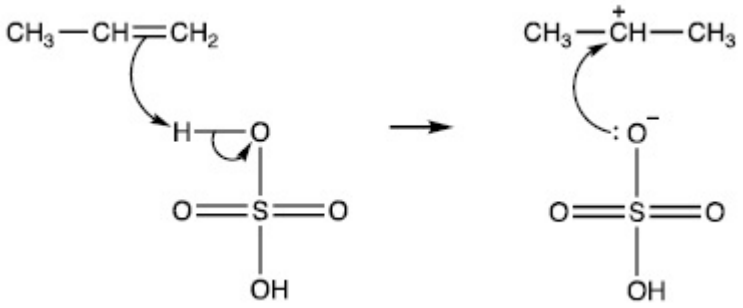


Must be skeletal structure

1

[9]

2. (a) **M1** <u>electrophilic addition</u>



*All arrows are double-headed. Penalise one mark from the total for **M2-5** if half headed arrows are used.*

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

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

1

M2 must show an arrow from the double bond towards the H atom of the H_2SO_4 molecule

*For **M2/3**, the full structure of H_2SO_4 does not need to be shown, but the key features for the mechanism should be shown and the formula must be correct. Penalise only once in **M2/3** an incorrect but genuine attempt at the structure of sulfuric acid*

***M2** ignore partial negative charges on the double bond*

1

M3 must show the breaking of the H-O bond in H_2SO_4

***M3** penalise incorrect partial charges on the H–O bond and penalise formal charges*

1

M4 is for the structure of the correct carbocation

*Penalise **M4** if there is a bond drawn to the positive charge*

1

M5 must show an arrow from the lone pair of electrons on the negatively charged oxygen of HSO_4^- towards the positively charged atom of <u>their</u> carbocation drawn

***Max 3 of 4 marks** (**M2-5**) for wrong organic reactant or wrong carbocation (ignore structure of product)*

1

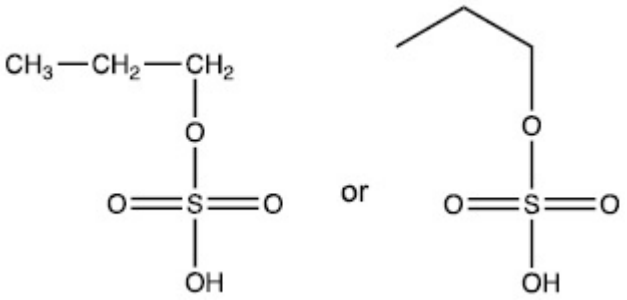
*If attack is shown from C=C to H^+ rather than H_2SO_4, then allow **M2** but not **M3***

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

*For **M5**, the full structure of HSO_4^- is not essential, but attack must come from a lone pair on an individual oxygen on HSO_4^-, but the – sign could*

by anywhere on the ion (e.g.: OSO_3H^-)

(b)



Any correct structural formula, including OSO_3H bonded through O to correct C

1

(c) **M1** idea that **E** is formed from/via more stable carbocation

***M1-2** Allow carbonium ion in place of carbocation*

1

M2 idea that 2^y carbocation is more stable than 1^y carbocation

***M2** Allow descriptions in terms of number of alkyl groups attached to positive C atom*

1

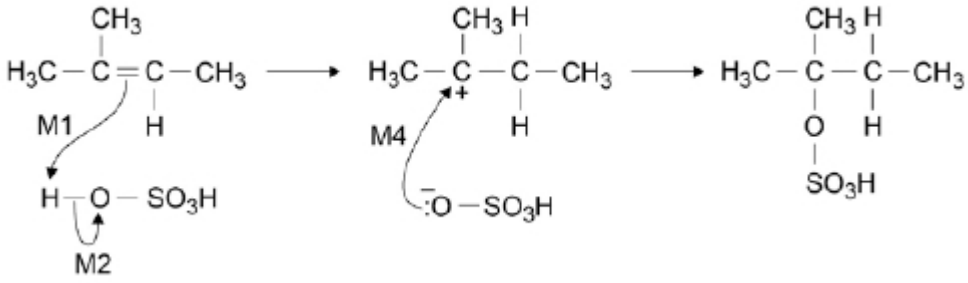
Ignore reference to inductive effect

*Penalise **M1** if answer suggests that the products are carbocations (but could score **M2**)*

*In order to access **M1** and/or **M2** there must be some reference to carbocations (carbonium ions) by name or structure or description*

[8]

3. (a)

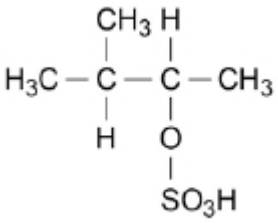


M1, M2 and M4 are awarded for the three curly arrows shown on the mechanism (1 mark for each correct)

M3 is for the structure of the carbocation intermediate

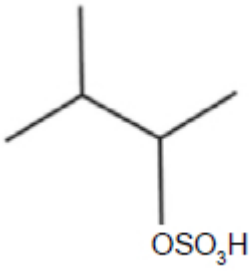
4

(b)



Correct answers include:

- *the displayed formula*
- *structural formulae such as $CH_3CH(CH_3)CH(OSO_3H)CH_3$*
- *skeletal formulae such as*



1

(c) The major product is formed via a tertiary carbocation intermediate and the minor product is formed via a secondary carbocation intermediate

1

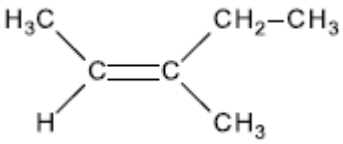
The tertiary carbocation is more stable than the secondary carbocation

1

[7]

4.

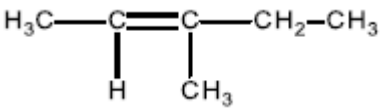
(a)



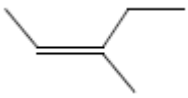
Must show all 4 groups bonded to C=C

Allow CH_3– for methyl group; allow C_2H_5 for ethyl group

Allow correct structure of the style

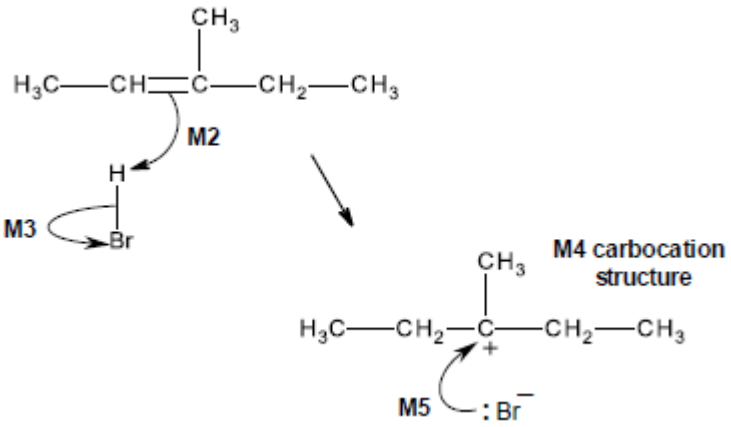


Allow correct skeletal structure



1

(b) M1 electrophilic addition



NB the arrows here are double-headed

1

M2 must show an arrow from the double bond towards the H atom of the H-Br molecule

1

M3 must show the breaking of the H-Br bond

1

M4 is for the structure of the tertiary carbocation

1

M5 must show an arrow from the lone pair of electrons on the negatively charged bromide ion towards the positively charged atom (of either a secondary or) of a tertiary carbocation

1

M6 3-bromo-3-methylpentane is formed from 3^{y} carbocation
OR
2-bromo-3-methylpentane is formed from 2^{y} carbocation

1

M7 3^{y} carbocation more stable than 2^{y}

1

M2-M5 *Penalise one mark from their total if half-headed arrows are used*

M2 *Ignore partial negative charge on the double bond*

M3 *Penalise incorrect partial charges on H-Br bond and penalise formal charges*

Penalise ***M4*** *if there is a bond drawn to the positive charge*

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

Max 3 of any 4 marks (M2-5) *for wrong organic reactant or wrong organic product (if shown) or secondary carbocation*

Max 2 of any 4 marks in the mechanism *for use of bromine*

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

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

M6 is high demand and must refer to product being formed from/via correct class of carbocation

M7 is high demand and must be clear answer refers to stability of carbocations (intermediates) not products

Candidate that states that products are carbocations would lose M6 and M7

***M6,7** allow carbonium ion in place of carbocation; or a description of carbocation in terms of alkyl groups/ number of carbon atoms joined to a positive C*

*When asked to outline a mechanism, candidates are **expected** to draw a mechanism with curly arrows (specification 3.3.1.2). On this occasion only we would allow a detailed description as shown.*

***M2** must describe the movement of a pair of electrons / curly arrow from the C=C towards the H atom of the H-Br molecule*

***M3** must describe the breaking of the H-Br bond with the bonding pair of electrons moving to the Br / curly arrow from H-Br bond to Br*

***M4** is for the structure of the tertiary carbocation (i.e. positive C bonded to one methyl and two ethyl groups)*

***M5** must describe the movement of a pair of electrons from the Br^- ion to the positive C atom of the carbocation / curly arrow from the lone pair of electrons on the negatively charged bromide ion towards the positively charged C atom (of either a secondary or) of a tertiary carbocation*

[8]

5. (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

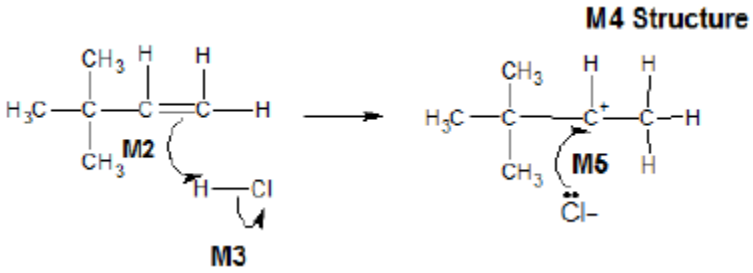
OR

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"

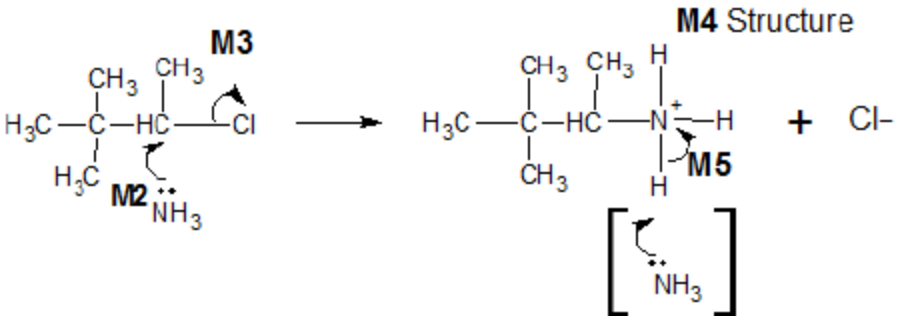
For ***M5****, credit attack on a partially positively charged carbocation structure, but penalise* ***M4***

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 78°C 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

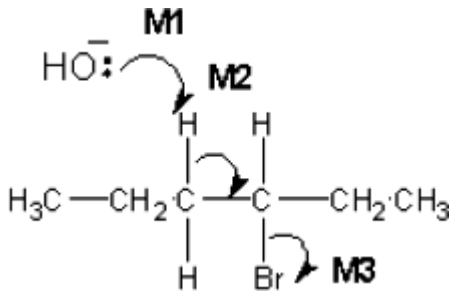
*In **M2** and **M3** the two gases need to be identified. If equations are used using sulfuric acid and the toxic gases are not identified clearly, allow one mark for the formulas of SO_2 and Br_2*

- *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]

6. (a) (i)



Penalise one mark from their total if half-headed arrows are used

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

Ignore other partial charges

M1 must show an arrow from the lone pair on oxygen of a negatively charged hydroxide ion <u>to the correct</u> H atom

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

M2 must show an arrow from the correct C–H bond to the correct C–C bond. Only award if an arrow is shown <u>attacking</u> the H atom of the correct C–H bond in **M1**

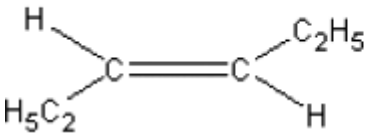
M3 is independent but **CE=0 if nucleophilic substitution**

N.B these are double-headed arrows

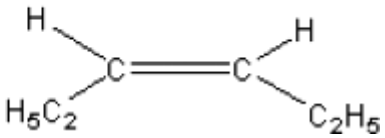
3

(ii)

M1 E isomer



M2 Z isomer



Award 1 mark if both correct stereoisomers but in the wrong places

Accept no other alkenes.

Be reasonably lenient on the bonds to ethyl (or to CH_2CH_3) since the question is about E and Z positions but penalise once only if connection is clearly to the CH_3 of CH_2CH_3

Accept linear structures

2

(iii) **M1** (Compounds / molecules with) the <u>same structural formula</u>

*Penalise **M1** if "same structure"*

M2 with <u>atoms/bonds/groups</u> arranged <u>differently in space</u>

Ignore references to "same molecular formula" or "same empirical formula" or any reference to "displayed formula"

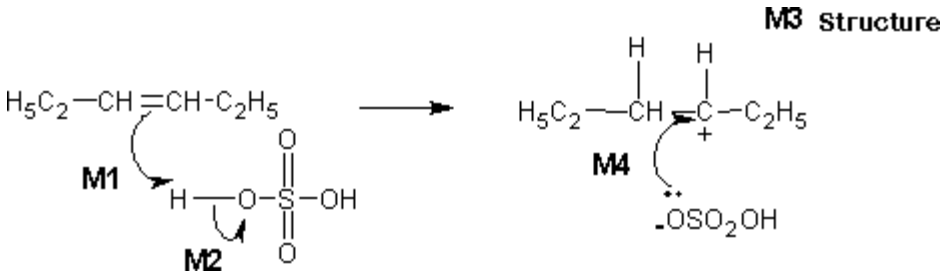
OR

<u>atoms/bonds/groups</u> that have <u>different spatial arrangements / different orientation</u>.

Mark independently

2

(b)



M1must show an arrow from the double bond towards the H atom of the H – O bond OR HO on a compound with molecular formula for H_2SO_4

M1 could be to an H+ ion and M2 an independent O – H bond break on a compound with molecular formula for H_2SO_4

M1 *Ignore partial negative charge on the double bond.*

M2 must show the breaking of the O – H bond.

M2 *Penalise partial charges on O – H bond if wrong way and penalise formal charges*

In M2 do not penalise incorrect structures for H_2SO_4

M3 is for the structure of the carbocation.

M4 must show an arrow from the lone pair of electrons on the correct oxygen of the negatively charged ion towards a correct (positively charged) carbon atom.

M4 *NOT* HSO_4^-

*For **M4**, credit <u>as shown</u> or* $^{-}\!:\!OSO_3H$ *<u>ONLY</u> with the negative charge anywhere on this ion*

OR <u>correctly</u> drawn out with the negative charge placed correctly on oxygen

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

NB The arrows here are double-headed

<u>Max 3 of any 4 marks</u> for wrong organic reactant or wrong organic product (if shown)

Accept the correct use of "sticks"

4

[11]