HL Paper 2

Urea, $(H_2N)_2CO$, is excreted by mammals and can be used as a fertilizer.

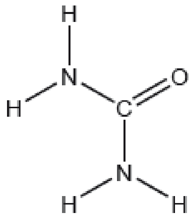
Urea can also be made by the direct combination of ammonia and carbon dioxide gases.

$$2NH_3(g) + CO_2(g) \rightleftharpoons (H_2N)_2CO(g) + H_2O(g) \quad \Delta H < 0$$

a.i. Calculate the percentage by mass of nitrogen in urea to two decimal places using section 6 of the data booklet. [2]

a.ii. Suggest how the percentage of nitrogen affects the cost of transport of fertilizers giving a reason. [1]

b. The structural formula of urea is shown. [3]



Predict the electron domain and molecular geometries at the nitrogen and carbon atoms, applying the VSEPR theory.

	Electron domain geometry	Molecular geometry
Nitrogen	....	....
Carbon	....	trigonal planar

c. Urea can be made by reacting potassium cyanate, KNCO, with ammonium chloride, NH_4Cl. [2]

$$KNCO(aq) + NH_4Cl(aq) \rightarrow (H_2N)_2CO(aq) + KCl(aq)$$

Determine the maximum mass of urea that could be formed from $50.0\ cm^3$ of $0.100\ mol\ dm^{-3}$ potassium cyanate solution.

d.i. State the equilibrium constant expression, K_c. [1]

d.ii. Predict, with a reason, the effect on the equilibrium constant, K_c, when the temperature is increased. [1]

d.iii. Determine an approximate order of magnitude for K_c, using sections 1 and 2 of the data booklet. Assume $\Delta G^\ominus$ for the forward reaction is approximately +50 kJ at 298 K. [2]

e.i. Suggest one reason why urea is a solid and ammonia a gas at room temperature. [1]

e.ii. Sketch two different hydrogen bonding interactions between ammonia and water. [2]

f. The combustion of urea produces water, carbon dioxide and nitrogen. [2]

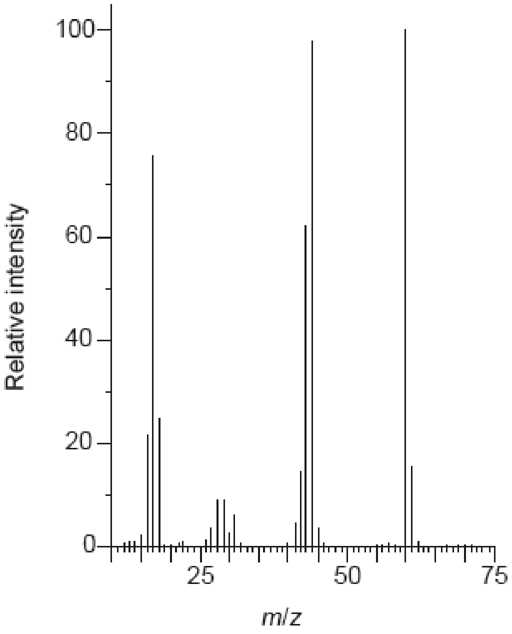
Formulate a balanced equation for the reaction.

g. Calculate the maximum volume of CO_2, in cm^3, produced at STP by the combustion of 0.600 g of urea, using sections 2 and 6 of the data booklet. [1]

h. Describe the bond formation when urea acts as a ligand in a transition metal complex ion. [2]

i. The C–N bonds in urea are shorter than might be expected for a single C–N bond. Suggest, in terms of electrons, how this could occur. [1]

j. The mass spectrum of urea is shown below. [2]



[Source: http://sdbs.db.aist.go.jp]

Identify the species responsible for the peaks at *m/z* = 60 and 44.

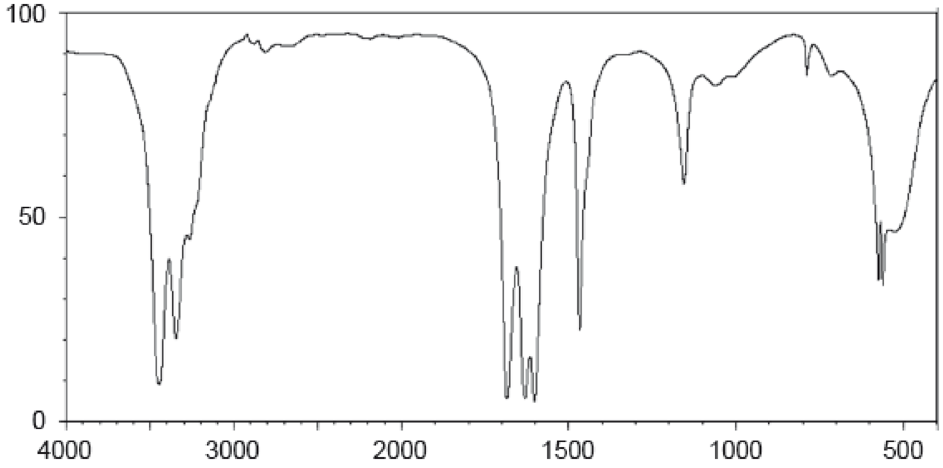
60:

- -

44:

- -

k. The IR spectrum of urea is shown below. [2]



[Source: sdbs.db.aist.go.jp]

Identify the bonds causing the absorptions at 3450 cm^{-1} and 1700 cm^{-1} using section 26 of the data booklet.

3450 cm^{-1}:

. . . .

1700 cm^{-1}:

. . . .

I.i. Predict the number of signals in the ^{1}H NMR spectrum of urea. [1]

I.ii. Predict the splitting pattern of the ^{1}H NMR spectrum of urea. [1]

I.iii. Outline why TMS (tetramethylsilane) may be added to the sample to carry out ^{1}H NMR spectroscopy and why it is particularly suited to this role. [2]

Markscheme

a.i. molar mass of urea «4 × 1.01 + 2 × 14.01 + 12.01 + 16.00» = 60.07 «g mol^{-1}»

«% nitrogen = $\frac{2 \times 14.01}{60.07}$ × 100 =» 46.65 «%»

*Award **[2]** for correct final answer.*

*Award **[1 max]** for final answer not to two decimal places.*

[2 marks]

a.ii. «cost» increases ***AND*** lower N% «means higher cost of transportation per unit of nitrogen»

OR

«cost» increases ***AND*** inefficient/too much/about half mass not nitrogen

Accept other reasonable explanations.

*Do **not** accept answers referring to safety/explosions.*

[1 mark]

b.

	Electron geometry	Molecular geometry
Nitrogen	tetrahedral ✓	trigonal pyramidal ✓
Carbon	trigonal planar ✓	trigonal planar

Note: Urea’s structure is more complex than that predicted from VSEPR theory.

[3 marks]

c. *n*(KNCO) «= 0.0500 dm^3 × 0.100 mol dm^{-3}» = 5.00 × 10^{-3} «mol»

«mass of urea = 5.00 × 10^{-3} mol × 60.07 g mol^{-1}» = 0.300 «g»

*Award **[2]** for correct final answer.*

[2 marks]

d.i. $K_c = \frac{[(H_2N)_2CO] \times [H_2O]}{[NH_3]^2 \times [CO_2]}$

[1 mark]

d.ii. «K_c» decreases ***AND*** reaction is exothermic

OR

«K_c» decreases ***AND*** Δ*H* is negative

OR

«K_c» decreases ***AND*** reverse/endothermic reaction is favoured

[1 mark]

d.iii. ln *K* «= $\frac{-\Delta G^{\ominus}}{RT} = \frac{-50 \times 10^3 \text{ J}}{8.31 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}$» = –20

«K_c =» 2 × 10^{-9}

OR

1.69 × 10^{-9}

OR

10^{-9}

Accept range of 20-20.2 for M1.

*Award **[2]** for correct final answer.*

[2 marks]

e.i. *Any one of:*

urea has greater molar mass

urea has greater electron density/greater London/dispersion

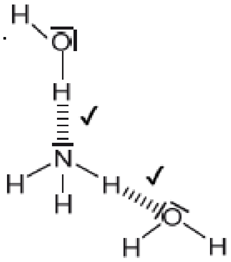
urea has more hydrogen bonding

urea is more polar/has greater dipole moment

Accept “urea has larger size/greater van der Waals forces”.

*Do **not** accept "urea has greater intermolecular forces/IMF".*

[1 mark]

e.ii. 

*Award **[1]** for each correct interaction.*

*If lone pairs are shown on N or O, then the lone pair on N or one of the lone pairs on O **MUST** be involved in the H-bond.*

Penalize solid line to represent H-bonding only once.

[2 marks]

f. $2(H_2N)_2CO(s) + 3O_2(g) \rightarrow 4H_2O(l) + 2CO_2(g) + 2N_2(g)$

correct coefficients on LHS

correct coefficients on RHS

Accept $(H_2N)_2CO(s) + \frac{3}{2}O_2(g) \rightarrow 2H_2O(l) + CO_2(g) + N_2(g)$.

Accept any correct ratio.

[2 marks]

g. «$V = \frac{0.600 \text{ g}}{60.07 \text{ g mol}^{-1}} \times 22700 \text{ cm}^3 \text{ mol}^{-1}$ =» 227 «cm^3»

[1 mark]

h. lone/non-bonding electron pairs «on nitrogen/oxygen/ligand» given to/shared with metal ion

co-ordinate/dative/covalent bonds

[2 marks]

i. lone pairs on nitrogen atoms can be donated to/shared with C–N bond

OR

C–N bond partial double bond character

OR

delocalization «of electrons occurs across molecule»

OR

slight positive charge on C due to C=O polarity reduces C–N bond length

[1 mark]

j. *60*: $CON_2H_4^+$

44: $CONH_2^+$

Accept "molecular ion".

[2 marks]

k. *3450 cm^{-1}:* N–H

1700 cm^{-1}: C=O

*Do **not** accept “O–H” for 3450 cm^{-1}.*

[2 marks]

l.i. 1

[2 marks]

l.ii. singlet

Accept “no splitting”.

[1 mark]

l.iii. acts as internal standard

OR

acts as reference point

one strong signal

OR

12 H atoms in same environment

OR

signal is well away from other absorptions

Accept “inert” or “readily removed” or “non-toxic” for M1.

[2 marks]

Examiners report

a.i. [N/A]
a.ii. [N/A]
b. [N/A]
c. [N/A]
d.i. [N/A]
d.ii. [N/A]
d.iii. [N/A]
e.i. [N/A]
e.ii. [N/A]
f. [N/A]
g. [N/A]
h. [N/A]
i. [N/A]
j. [N/A]
k. [N/A]
l.i. [N/A]
[N/A]

I.iii. [N/A]

This question is about carbon and chlorine compounds.

a. Ethane, C_2H_6, reacts with chlorine in sunlight. State the type of this reaction and the name of the mechanism by which it occurs. [1]

Type of reaction:

. . . .

Mechanism:

. . . .

b.i. Formulate equations for the two propagation steps and one termination step in the formation of chloroethane from ethane. [3]

Two propagation steps:

. . . .
. . . .
. . . .
. . . .

One termination step:

. . . .
. . . .

b.ii. Deduce the splitting patterns in the ^1H NMR spectrum of C_2H_5Cl. [1]

b.iii. Explain why tetramethylsilane (TMS) is often used as a reference standard in ^1H NMR. [2]

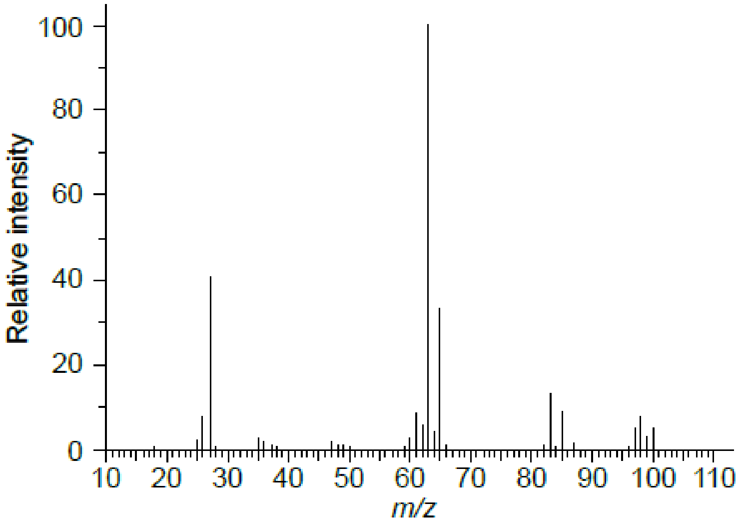
c.i. One possible product, **X**, of the reaction of ethane with chlorine has the following composition by mass: [2]

carbon: 24.27%, hydrogen: 4.08%, chlorine: 71.65%

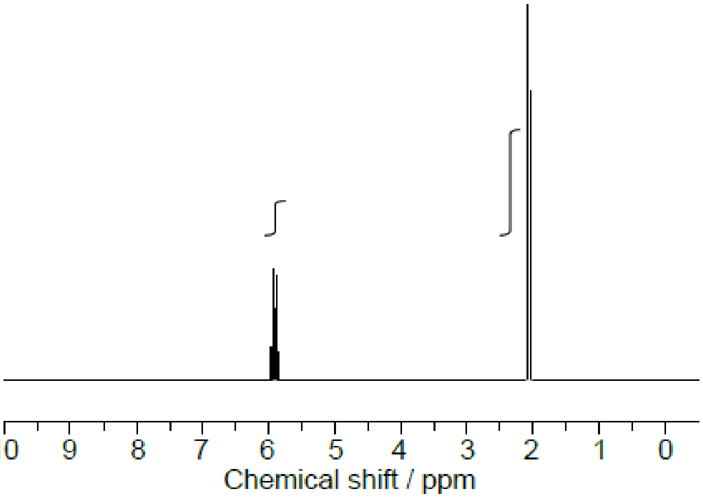
Determine the empirical formula of the product.

c.ii. The mass and ^1H NMR spectra of product **X** are shown below. Deduce, giving your reasons, its structural formula and hence the name of the compound. [3]

Mass spectrum:



^{1}H NMR spectrum:



[Source: http://sdbs.db.aist.go.jp]

c.iii When the product **X** is reacted with NaOH in a hot alcoholic solution, C_2H_3Cl is formed. State the role of the reactant NaOH other than as a nucleophile. [1]

d. Chloroethene, C_2H_3Cl, can undergo polymerization. Draw a section of the polymer with three repeating units. [1]

Markscheme

a. substitution ***AND*** «free-»radical

OR

substitution ***AND*** chain

Award [1] for "«free-»radical substitution" or "S_R" written anywhere in the answer.

[1 mark]

b.i. *Two propagation steps:*

$C_2H_6 + \bullet Cl \rightarrow C_2H_5\bullet + HCl$

$C_2H_5\bullet + Cl_2 \rightarrow C_2H_5Cl + \bullet Cl$

One termination step:

$C_2H_5 \bullet + C_2H_5 \bullet \rightarrow C_4H_{10}$

OR

$C_2H_5 \bullet + \bullet\, Cl \rightarrow C_2H_5Cl$

OR

$\bullet Cl + \bullet Cl \rightarrow Cl_2$

Accept radical without ● if consistent throughout.

Allow ECF for incorrect radicals produced in propagation step for M3.

[3 marks]

b.ii. triplet ***AND*** quartet

[1 mark]

b.iii. chemical shift/signal outside range of common chemical shift/signal

strong signal/12/all H atoms in same environment
OR
singlet/no splitting of the signal

volatile/easily separated/easily removed
OR
inert/stabl

contains three common NMR nuclei/^1H and ^{13}C and ^{29}Si

*Do **not** accept chemical shift = 0.*

[2 marks]

c.i. $C = \frac{24.27}{12.01} = 2.021$ ***AND*** $H = \frac{4.08}{1.01} = 4.04$ ***AND*** $Cl = \frac{71.65}{35.45} = 2.021$

«hence» CH_2Cl

Accept $\frac{24.27}{12.01} : \frac{4.08}{1.01} : \frac{71.65}{35.45}$.

*Do **not** accept $C_2H_4Cl_2$.*

Award [2] for correct final answer.

[2 marks]

c.ii. molecular ion peak(s) «about» *m/z* 100 ***AND*** «so» $C_2H_4Cl_2$ «isotopes of Cl»

two signals «in ^1H NMR spectrum» ***AND*** «so» CH_3CHCl_2
OR
«signals in» 3:1 ratio «in ^1H NMR spectrum» ***AND*** «so» CH_3CHCl_2
OR
one doublet and one quartet «in ^1H NMR spectrum» ***AND*** «so» CH_3CHCl_2

1,1-dichloroethane

Accept “peaks” for “signals”.

Allow ECF for a correct name for M3 if an incorrect chlorohydrocarbon is identified.

[3 marks]

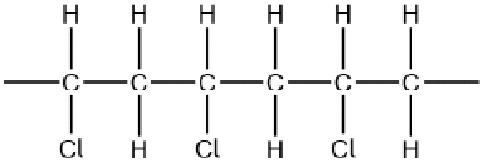
c.iii base

OR

proton acceptor

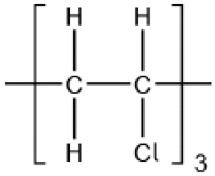
[1 mark]

d.



Continuation bonds must be shown.

Ignore square brackets and "n".

Accept  .

Accept other versions of the polymer, such as head to head and head to tail.

Accept condensed structure provided all C to C bonds are shown (as single).

[1 mark]

Examiners report

a. [N/A]
b.i. [N/A]
b.ii. [N/A]
b.iii. [N/A]
c.i. [N/A]
c.ii. [N/A]
c.iii. [N/A]
d. [N/A]

Ethane-1,2-diol, $HOCH_2CH_2OH$, has a wide variety of uses including the removal of ice from aircraft and heat transfer in a solar cell.

b. (i) Calculate ΔH^{θ}, in kJ, for this similar reaction below using ΔH_f^{θ} data from section 12 of the data booklet. ΔH_f^{θ} of $HOCH_2CH_2OH(l)$ is –454.8kJmol^{-1}. [6]

$$2CO\ (g) + 3H_2\ (g) \rightleftharpoons HOCH_2CH_2OH\ (l)$$

(ii) Deduce why the answers to (a)(iii) and (b)(i) differ.

(iii) ΔS^{θ} for the reaction in (b)(i) is –620.1JK^{-1}. Comment on the decrease in entropy.

(iv) Calculate the value of ΔG^{θ}, in kJ, for this reaction at 298 K using your answer to (b)(i). (If you did not obtain an answer to (b)(i), use –244.0 kJ, but this is not the correct value.)

(v) Comment on the statement that the reaction becomes less spontaneous as temperature is increased.

f. Predict the ^{1}HNMR data for ethanedioic acid and ethane-1,2-diol by completing the table. [2]

	Number of signals	Splitting pattern
Ethanedioic acid:	. . . .	. . . .
Ethane-1,2-diol:	. . . .	Not required

Markscheme

b. i

«$\Delta H = \Sigma\ \Delta H_f$ products – $\Sigma \Delta H_f$ reactants = –454.8 kJ mol^{-1} – 2(–110.5 kJ mol^{-1}) =» –233.8 «kJ»

ii

in (a)(iii) gas is formed and in (b)(i) liquid is formed

OR

products are in different states

OR

conversion of gas to liquid is exothermic

OR

conversion of liquid to gas is endothermic

OR

enthalpy of vapourisation needs to be taken into account

Accept product is «now» a liquid.
Accept answers referring to bond enthalpies being means/averages.

iii

«ΔS is negative because five mols of» gases becomes «one mol of» liquid

OR

increase in complexity of product «compared to reactants»

OR

product more ordered «than reactants»

Accept "fewer moles of gas" but not "fewer molecules".

iv

$\Delta S = \left(\frac{-620.1}{1000}\right)$ «kJ K^{-1}»

ΔG = –233.8 kJ – (298 K $\left(\frac{-620.1}{1000}\right)$ kJ K^{-1}) = –49.0 «kJ»

*Award **[2]** for correct final answer.*
*Award **[1 max]** for «+»185 × 10^3.*

If –244.0 kJ used, answer is:

ΔG = –244.0 kJ – (298 K $\left(\frac{-620.1}{1000}\right)$ kJ K^{-1}) = –59.2 «kJ»

*Award **[2]** for correct final answer.*

v

increasing T makes ΔG larger/more positive/less negative

OR

$-T\Delta S$ will increase

f.

	Number of signals	Splitting pattern
Ethanedioic acid:	1 ***AND***	singlet ✓
Ethane-1,2-diol:	2 ✓	Not required

Accept “none/no splitting” for singlet.

Examiners report

b. [N/A]
f. [N/A]

Organic compounds often have isomers.

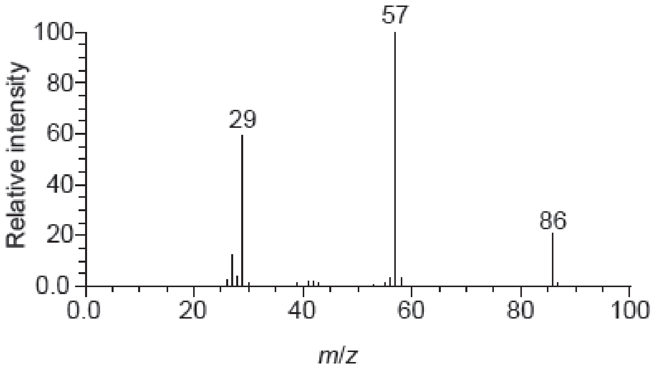
A straight chain molecule of formula $C_5H_{10}O$ contains a carbonyl group. The compound cannot be oxidized by acidified potassium dichromate(VI) solution.

A tertiary halogenoalkane with three different alkyl groups, $(R_1R_2R_3)C{-}X$, undergoes a S_N1 reaction and forms two isomers.

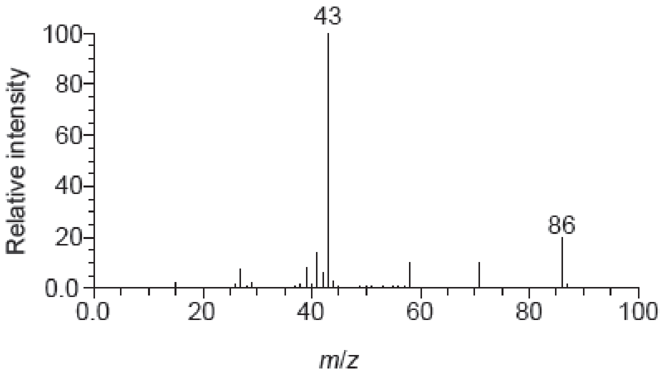
a.i. Deduce the structural formulas of the two possible isomers. [2]

a.ii. Mass spectra **A** and **B** of the two isomers are given. [2]

A



B



[Source: NIST Mass Spec Data Center, S.E. Stein, director, "Mass Spectra" in *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, Eds. P.J. Linstrom and W.G. Mallard, National Institute of Standards and Technology, Gaithersburg MD, 20899, doi:10.18434/T4D303, (retrieved May 31, 2018).]

Explain which spectrum is produced by each compound using section 28 of the data booklet.

A:

B:

b.i. State the type of bond fission that takes place in a S_N1 reaction. [1]

b.ii. State the type of solvent most suitable for the reaction. [1]

b.iii. Draw the structure of the intermediate formed stating its shape. [2]

Shape:

b.iv. Suggest, giving a reason, the percentage of each isomer from the S_N1 reaction. [2]

c. Nitrobenzene, $C_6H_5NO_2$, can be converted to phenylamine via a two-stage reaction. [2]

In the first stage, nitrobenzene is reduced with tin in an acidic solution to form an intermediate ion and tin(II) ions. In the second stage, the intermediate ion is converted to phenylamine in the presence of hydroxide ions.

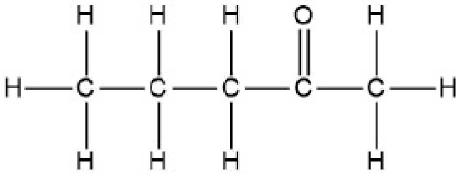
Formulate the equation for each stage of the reaction.

Stage one:

Stage two:

Markscheme

a.i.



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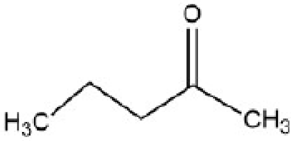

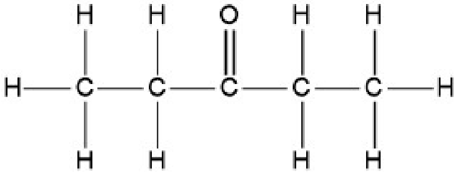

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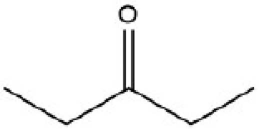


Accept condensed formulas.

[2 marks]

a.ii **A:**

$CH_3CH_2COCH_2CH_3$ ***AND*** «peak at» 29 due to

$(CH_3CH_2)^+$/$(C_2H_5)^+$/$(M - CH_3CH_2CO)^+$

OR

$CH_3CH_2COCH_2CH_3$ ***AND*** «peak at» 57 due to

$(CH_3CH_2CO)^+$/$(M - CH_3CH_2)^+$/$(M - C_2H_5)^+$

B:

$CH_3COCH_2CH_2CH_3$ ***AND*** «peak at» 43 due to

$(CH_3CH_2CH_2)^+$/$(CH_3CO)^+$/$(C_2H_3O)^+$/$(M - CH_3CO)^+$

Penalize missing "+" sign once only.

Accept "$CH_3COCH_2CH_2CH_3$ by elimination since fragment CH_3CO is not listed" for M2.

[2 marks]

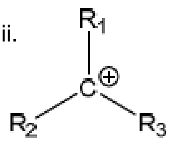
b.i. heterolytic/heterolysis

[1 mark]

b.ii. polar protic

[1 mark]

b.iii.



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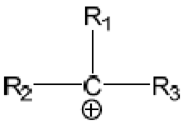


Shape: triangular/trigonal planar

[2 marks]

b.iv. «around» 50% «each»

OR

similar/equal percentages

nucleophile can attack from either side «of the planar carbocation»

Accept "racemic mixture/racemate" for M1.

[2 marks]

c. *Stage one:*

$C_6H_5NO_2(l) + 3Sn(s) + 7H^+(aq) \rightarrow C_6H_5NH_3^+(aq) + 3Sn^{2+}(aq) + 2H_2O(l)$

Stage two:

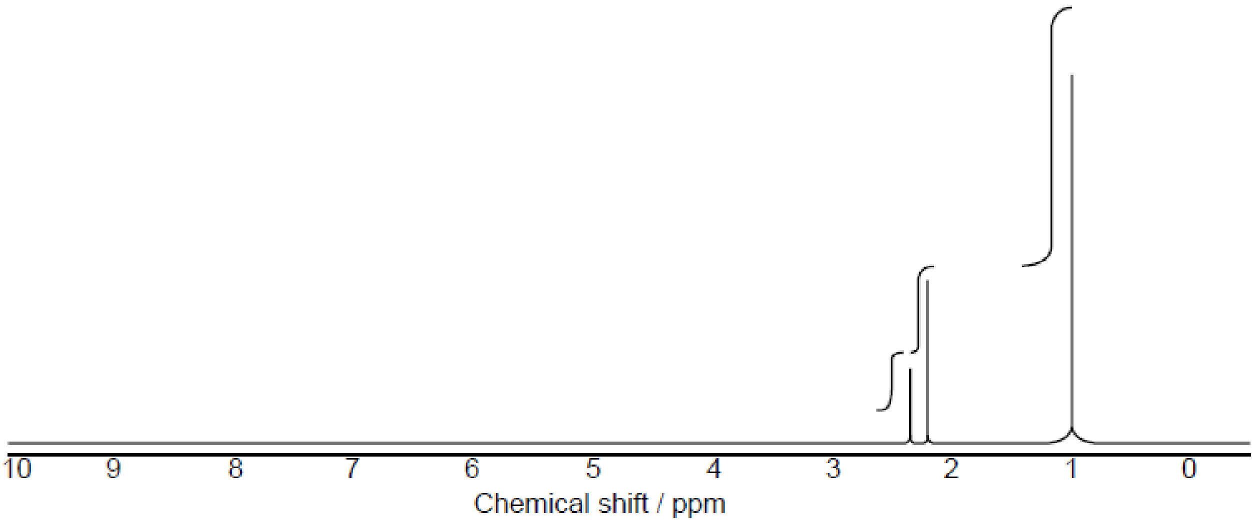
$C_6H_5NH_3^+(aq) + OH^-(aq) \rightarrow C_6H_5NH_2(l) + H_2O(l)$

[2 marks]

Examiners report

a.i. [N/A]
a.ii. [N/A]
b.i. [N/A]
b.ii. [N/A]
b.iii. [N/A]
b.iv. [N/A]
c. [N/A]

A compound with a molecular formula $C_7H_{14}O$ produced the following high resolution ^1H NMR spectrum.



a.i. Deduce what information can be obtained from the ^1H NMR spectrum. [3]

Number of hydrogen environments:

. . . .

Ratio of hydrogen environments:

. . . .

Splitting patterns:

. . . .

a.ii. Identify the functional group that shows stretching at 1710 cm^{-1} in the infrared spectrum of this compound using section 26 of the data booklet and the ^1H NMR. [1]

a.iii. Suggest the structural formula of this compound. [2]

b.i. Bromine was added to hexane, hex-1-ene and benzene. Identify the compound(s) which will react with bromine in a well-lit laboratory. [1]

b.ii. Deduce the structural formula of the main organic product when hex-1-ene reacts with hydrogen bromide. [1]

c.i. State the reagents and the name of the mechanism for the nitration of benzene. [2]

Reagents:

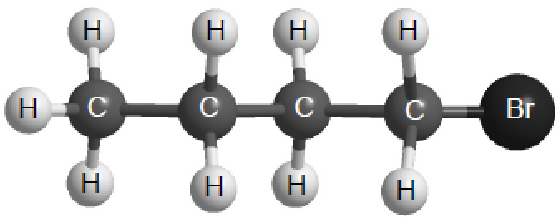
. . . .

Name of mechanism:

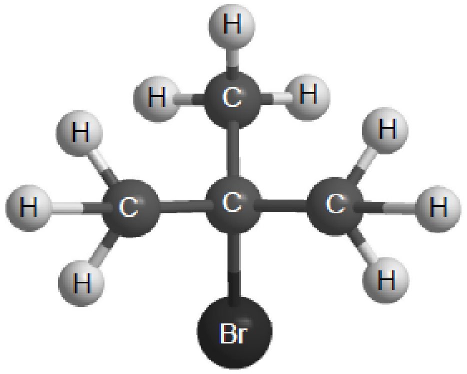
. . . .

c.ii. Outline, in terms of the bonding present, why the reaction conditions of halogenation are different for alkanes and benzene. [1]

d. Below are two isomers, A and B, with the molecular formula C_4H_9Br. [3]



A



B

Explain the mechanism of the nucleophilic substitution reaction with NaOH(aq) for the isomer that reacts almost exclusively by an S_N2 mechanism using curly arrows to represent the movement of electron pairs.

Markscheme

a.i. *Number of hydrogen environments:* 3

Ratio of hydrogen environments: 2:3:9

Splitting patterns: «all» singlets

Accept any equivalent ratios such as 9:3:2.

Accept "no splitting".

[3 marks]

a.ii. carbonyl

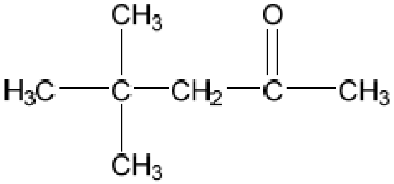
OR

C=O

Accept "ketone" but not "aldehyde".

[1 mark]

a.iii.



Accept $(CH_3)_3CCH_2COCH_3$.

Award ***[1]*** *for any aldehyde or ketone with $C_7H_{14}O$ structural formula.*

[2 marks]

b.i. hexane ***AND*** hex-1-ene

Accept "benzene ***AND*** *hexane* ***AND*** *hex-1-ene".*

[1 mark]

b.ii. $CH_3CH_2CH_2CH_2CHBrCH_3$

Accept displayed formula but ***not*** *molecular formula.*

[1 mark]

c.i. *Reagents:* «concentrated» sulfuric acid ***AND*** «concentrated» nitric acid

Name of mechanism: electrophilic substitution

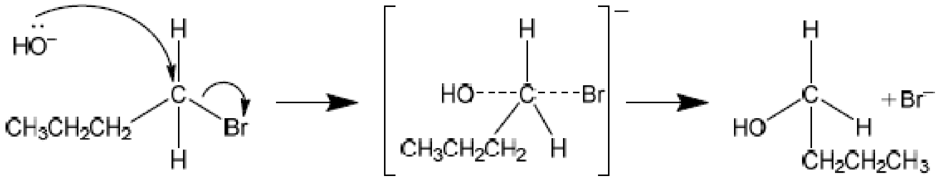
[2 marks]

c.ii. benzene has «delocalized» π bonds «that are susceptible to electrophile attack» ***AND*** alkanes do not

Do ***not*** *accept "benzene has single and double bonds".*

[1 mark]

d.



curly arrow going from lone pair/negative charge on O in ^{-}OH to C

curly arrow showing Br leaving

representation of transition state showing negative charge, square brackets and partial bonds

Accept OH^{-} with or without the lone pair.

Do not allow curly arrows originating on H in OH^{-}.

Accept curly arrows in the transition state.

Do not penalize if HO and Br are not at 180°.

Do not award M3 if OH–C bond is represented.

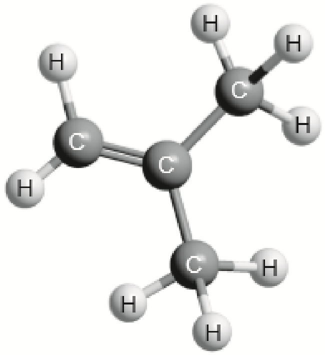
*Award **[2 max]** if wrong isomer is used.*

[3 marks]

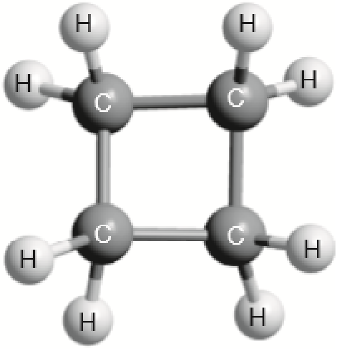
Examiners report

a.i. [N/A]
a.ii. [N/A]
a.iii. [N/A]
b.i. [N/A]
b.ii. [N/A]
c.i. [N/A]
c.ii. [N/A]
d. [N/A]

Compound **A** and compound **B** are hydrocarbons.



A



B

a. (i) State the term that is used to describe molecules that are related to each other in the same way as compound **A** and compound **B**. [3]

(ii) Suggest a chemical test to distinguish between compound **A** and compound **B**, giving the observation you would expect for each.

Test:

Observation with **A**:

Observation with **B**:

b. Outline how you could use the IR spectra of compounds **A** and **B** and section 26 of the data booklet to identify them. [1]

c. Two signals occur in the ^{1}H NMR spectrum of compound **A**. Deduce their expected chemical shift and their splitting pattern, using section 27 of the data booklet. [2]

Signal	**1**	**2**
Chemical shift / ppm	. . . .	. . . .
Splitting pattern	. . . .	. . . .

Markscheme

a. (i)

«structural/functional» isomer«s»

(ii)
Test:
«react with» bromine/Br_2 «in the dark»
OR
«react with» bromine water/Br_2 (aq) «in the dark»

A: from yellow/orange/brown to colourless ***AND*** *B*: colour remains/slowly decolourized

Accept other correct reagents, such as manganate(VII) or iodine solutions, and descriptions of the corresponding changes observed.

Accept "decolourized" for A and "not decolourized/unchanged" for B.
*Do **not** accept "clear/transparent" instead of "colourless".*

b. compound **A** would absorb at 1620–1680«cm^{-1}»

Accept any value in range 1620 – 1680 cm^{-1}.

c.

Signal	1/2		2/1
Chemical shift/ ppm	0.9 - 1.0	***AND***	4.5 - 6.0
Splitting pattern	singlet	***AND***	singlet

Accept 0.9 to 2.0 for the first signal as the C=C affects the CH_3 shift (actually 1.7).

Accept "none/no splitting" for both splitting patterns

*Award **[1 max]** for the correct deduction (both shift and splitting) of signal 1 or 2.*

Examiners report

a. [N/A]
b. [N/A]
c. [N/A]