Questions

Q1.

This question is about some carbonyl compounds with the molecular formula C₅H₁₀O.

An aldehyde with molecular formula $C_5H_{10}O$ has a ^{13}C NMR spectrum with three peaks.

The high resolution ¹H NMR spectrum of this aldehyde has two peaks and neither of them is split.

Deduce the **displayed** formula of this aldehyde. Justify your answer by referring to both NMR spectra.

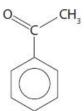
| (4) |
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(Total for question = 4 marks)

Edexcel Chemistry A-level - Ketones & Aldehydes

Q2.

Phenylethanone is an ingredient in many types of chewing gum.



One method for the production of phenylethanone involves the reaction of benzene with ethanoyl chloride, CH₃COCI.

Phenylethanone can be distinguished from its structural isomer, phenylethanal, in a number of different ways.

| (i) | Whic | ch would react with phenylethanone but not with phenylethanal? | () |
|-----|------|---|-----|
| * | Α | acidified sodium dichromate(VI) | (1) |
| 1 | В | alkaline iodine solution | |
| | С | Fehling's solution | |
| 13 | D | Tollens' reagent | |
| | | e the steps to show how 2,4-dinitrophenylhydrazine could be used to distinguish phenylethanone and phenylethanal. | (4) |
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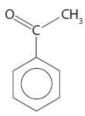
* (iii) Compare and contrast the high resolution proton NMR spectra of phenylethanone and phenylethanal.

You should use the Data Booklet.

(Total for question = 11 marks)

Q3.

Phenylethanone is an ingredient in many types of chewing gum.



One method for the production of phenylethanone involves the reaction of benzene with ethanoyl chloride, CH_3COCl .

The compound 1-phenylethanol can be formed from phenylethanone.

| Give the reagent and conditions that would be used to form 1- | phenylethanol. |
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| | Total for augstion - 2 marks |

Q4.

The table contains data on propanone and ethanoic acid.

| Substance | Molar mass / g mol ⁻¹ | Boiling temperature / °C | Solubility in water |
|---------------|----------------------------------|--------------------------|---------------------|
| Propanone | 58 | 56 | completely miscible |
| Ethanoic acid | 60 | 118 | completely miscible |

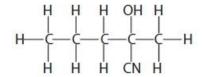
| (i) Explain, by reference to the data and any intermolecular forces involved, the difference in the boiling temperatures. | 1 |
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| (ii) Explain, with the aid of a diagram, why propanone is completely miscible with water. | |
| (2 | ?) |
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| (Total for question = 6 marks | ;) |

| This question is about some carbonyl compounds with the molecular formula $C_5H_{10}O$. |
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| Describe a chemical test, and its result, to distinguish between pentan-2-one, CH ₃ CH ₂ COCH ₃ , and pentan-3-one, CH ₃ CH ₂ COCH ₂ CH ₃ . |
| (2 |
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| (Total for question = 2 marks |

Q6.

This question is about some carbonyl compounds with the molecular formula C₅H₁₀O.

Pentan-2-one reacts with hydrogen cyanide in the presence of cyanide ions to form 2-hydroxy-2-methylpentanenitrile.



2-hydroxy-2-methylpentanenitrile

(i) Draw the mechanism for the reaction between pentan-2-one and hydrogen cyanide in the presence of cyanide ions.

Include curly arrows and any relevant lone pairs.

(4)

| (ii) The product of this reaction, 2-hydroxy-2-methylpentanenitrile, has a chiral centre. Explain why a racemic mixture of 2-hydroxy-2-methylpentanenitrile is formed in this reaction. | |
|---|-----|
| | (2) |
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(Total for question = 6 marks)

Q7.

This question is about some carbonyl compounds with the molecular formula C₅H₁₀O.

* Describe the oxidation and reduction reactions of pentanal and pentan-3-one.

Include the reagents and the structures of the organic products formed in any reactions that take place.

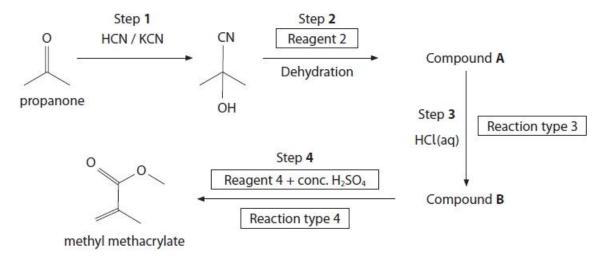
(6)

(Total for question = 6 marks)

Q8.

This question is about some reactions of carbonyl compounds.

Methyl methacrylate is the monomer used to make the polymer perspex. It can be synthesised from propanone using the reaction scheme shown.



(i) Draw the mechanism for the reaction in Step 1.

Include curly arrows and any relevant lone pairs and dipoles.

(4)

(ii) Complete the table to show the information missing from the reaction scheme.

Reagent 2

Structure of compound A

Reaction type 3

Structure of compound B

Reagent 4

Reaction type 4

(iii) Complete the equation for the formation of the polymer from methyl methacrylate.

(Total for question = 12 marks)

Q9.

Sodium tetrahydridoborate(III), NaBH₄, is used in organic chemistry. It is an alternative reagent to lithium tetrahydridoaluminate(III) for the reduction of carbonyl compounds.

(i) Draw a dot-and-cross diagram of the BH_4^- ion.

Use crosses (x) for the boron electrons, dots (•) for the hydrogen electrons and triangles (Δ) for the additional electron forming the negative ion.

(1)

(ii) The $\ensuremath{BH_4^-}\xspace$ ions reduce carbonyl compounds to alcohols in aqueous solution.

Complete the mechanism for the reduction of propanone to propan-2-ol by adding curly arrows, and any relevant lone pairs and dipoles.

(4)

(Total for question = 5 marks)

Mark Scheme

Q1.

| Question Number | Answer | Additional Guidance | Mark |
|--------------------|---|--|------|
| 2000 | An answer that makes reference to the following points: | Example of displayed formula: | (4) |
| | displayed formula of aldehyde | | |
| | | Allow CH ₃ groups but aldehyde group must be displayed | |
| | three different carbon environments indicated | Example of three carbon environments: | |
| | | | |
| | two different proton environments indicated | Example of two proton environments: | |
| | | (1) 2 0 0 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 | |
| | no splitting as there are no hydrogens on the adjacent carbon atom(s) | Stand alone mark | |

Q2.

| Question Number | Answer | Mark |
|--------------------|--|------|
| (i) | The only correct answer is B (alkaline iodine solution) | (1) |
| | A is not correct because this oxidising agent would react with phenylethanal and not with phenylethanone which is the wrong way round | |
| | C is not correct because test is for aldehydes and so would react with phenylethanal and not with phenylethanone which is the wrong way round | |
| | D is not correct because test is for aldehydes and so would react with phenylethanal and not with phenylethanone which is the wrong way round | |

| Question Number | Answer | Additional Guidance | Mark |
|--------------------|--|---|------|
| (ii) | An answer that makes reference to the following points: • formation of yellow/orange/red (crystalline) precipitate (1) | Colour and state are both required Allow solid for ppt Ignore any conditions given with the use of 2,4-DNPH | (4) |
| | (Filter then) recrystallisation of products (1) | | |
| | determination of melting temperature (1) | Penalise M3 if any reference to boiling temperature | |
| | comparison (and hence identification) from use of database/known values (1) | Award only in the context of melting temperature of the hydrazones or as a TE of boiling temperature | |
| | | Max 3 out of 4 if test is only carried out with one of the carbonyls | |

| Question Number | Ansv | wer | Additional Guidance | Mark |
|--------------------|--|---|---|------|
| * (iii) | This question assess ability to show a constructured answer wifully sustained reason Marks are awarded for content and for how structured and shows. The following table simarks should be awardent. | erent and logically th linkages and ning. or indicative the answer is lines of reasoning. | Guidance on how the mark scheme should be applied: The mark for indicative content should be added to the mark for lines of reasoning. For example, a response with four indicative marking points that is partially structured with some linkages and lines of reasoning scores 4 marks (3 | (6) |
| | Number of indicative marking points seen in answer 6 5-4 3-2 1 0 | Number of marks awarded for indicative marking points 4 3 2 1 0 | marks for indicative content and 1 mark for partial structure and some linkages and lines of reasoning). If there were no linkages between the points, then the same indicative marking points would yield and overall score of 3 marks (3 | |
| | The following table s marks should be awa and lines of reasonin | rded for structure | marks for indicative content and zero marks for linkages). In general it would be expected that 5 or 6 indicative points would get 2 reasoning marks, and 3 or 4 indicative points would get 1 mark for | |
| | Answer shows a coherent logical structure with linkages and fully sustained lines of reasoning demonstrated throughout Answer is partially | 2 | reasoning, and 0, 1 or 2 indicative points would score zero marks for reasoning. If there is any incorrect chemistry, deduct mark(s) from the reasoning. If no reasoning mark(s) awarded do not deduct mark(s). | |
| | structured with some linkages and lines of reasoning Answer has no linkages between points and is unstructured | 0 | If there is no mention of protons/hydrogens in the response then deduct one structure and reasoning mark | |

Indicative content

Ignore references to C¹³ nmr Accept annotations on a structure towards crediting the following IPs Allow either a single chemical shift value or a range within the stated values Penalise incorrect chemical shifts

Similarities

 IP1: aromatic hydrogens will give similar/same peaks Both have peaks in the range 6.5-8.4 (ppm) Ignore any splitting description

 IP2: both have a peak in the range 1.7-3.0 (ppm) (due to the hydrogen of the H-C-C=O type) Ignore any splitting pattern given for this peak to award this mark

Differences

 IP3 (Hydrogen environments): Phenylethanone has one less peak/hydrogen environment than phenylethanal Allow any difference of one in the number of peaks stated

 IP4 (Splitting patterns): a singlet for phenylethanone but a doublet and a triplet in phenylethanal All these splitting patterns required for this IP

 IP5 (Peak area ratios): relative peak (area) ratio in phenylethanone is 3 but in phenylethanal the peak (area) ratio is 2 to 1 Ignore the splitting pattern for this IP and ignore any peak areas given for the aryl hydrogens

IP6 (Chemical shifts): (Only)
 phenylethanal has an aldehyde
 (hydrogen) peak in the range 9 –
 10.1 (ppm)

Ignore the splitting pattern for this IP

Q3.

| Question Number | Answer | Additional Guidance | Mark |
|--------------------|---|---|------|
| | Reagent: lithium tetrahydridoaluminate((III)) /LiAlH4 (1) | Allow lithium aluminium hydride Accept sodium tetrahydridoborate /sodium borohydride/ NaBH4 In water/alcohol for 2 marks | (2) |
| | | Ignore reference to addition of acid after use of LiAlH ₄ in dry ether | |
| | | Do not award with additional reagents | |
| | Conditions: (dry) ether/ethoxyethane | Ignore heat | |
| | (1) | The mark for conditions is dependent on correct reagent or near miss such as incorrect formula LiAlH ₃ /LiAlH/LiAl | |

Q4.

| Question Number | Answer | Additional Guidance | Mark |
|--------------------|---|---|------|
| (i) | An explanation that makes reference to the following points: | | (4) |
| | similar molar masses so the number of electrons is similar/same resulting in similar London forces (1) | Allow van der Waals' forces / dispersion forces / instantaneous dipole- induced dipole forces | |
| | | Ignore reference to ethanoic acid having greater London forces | |
| | propanone (and ethanoic acid) form permanent dipole(-dipole) forces (1) | Ignore reference to hydrogen bonding to water by propanone Penalise abbreviation pd-d once only | |
| | (only) ethanoic acid forms (intermolecular) hydrogen bonding (1) | Ignore references to ethanoic acid dimerization | |
| | which is stronger so requires more energy to break (giving a higher boiling temperature) (1) | Reference to energy must be linked to the breaking of hydrogen bonds | |

| Question Number | Answer | Additional Guidance | Mark |
|--------------------|---|---|------|
| (ii) | An explanation that makes reference to the following points: • forms hydrogen bonds with water (1) • diagram of hydrogen bond (1) | Allow H bonds for hydrogen bonds H ₃ C H ₃ C Ignore bond angle and missing dipoles and missing lone pair Do not award incorrect dipoles Do not award incorrect propanone and/or water structure Do not award if second hydrogen bond drawn to the hydrogen of the CH ₃ | (2) |

Q5.

| Question Number | Answer | Additional Guidance | Mark |
|--------------------|---|---|------|
| | A description that makes reference to the following points: • (add a solution of) iodine and alkali / sodium hydroxide / potassium hydroxide / hydroxide ions (and warm) or (add a solution of) potassium iodide | (1) Allow names or formulae but if both are given, both must be correct | (2) |
| | in sodium chlorate(I) (and warm) • (only) pentan-2-one give a (pale) yellow precipitate / ppt(e) / solid | (1) Stand alone mark Allow antiseptic smell Ignore observation for pentan-3- one unless also stated that it gives a yellow precipitate | |

Q6.

| Question Number | Answer | Additional Guidance | Mark |
|--------------------|---|--|------|
| (i) | An answer that makes reference to the following points: | Example of mechanism: | (4) |
| | • curly arrow from lone pair on C of CN⁻ to C of ketone group | (1) | |
| | curly arrow from C=O to, or just beyond, O | Allow C ₃ H ₇ and CH ₃ for propyl and methyl groups Allow CN bond displayed | |
| | 87 | Ignore correct dipoles, penalise an incorrect dipole once only Do not award M3 if C ⁺ is shown on intermediate For M4, allow curly arrow from lone pair on O ⁻ to H ⁺ ion | |
| | from H-CN bond to anywhere on CN | / H ₂ O molecule Penalise incorrect ketone once only in M3 intermediate Penalise curly arrow from -ve charge instead of lone pair once only | |

| Question Number | Answer | | Additional Guidance | Mark |
|--------------------|--|-----|---|------|
| (ii) | An explanation that makes reference to the following points: | | | (2) |
| | pentan-2-one / ketone is planar about the carbonyl carbon | (1) | Allow bonds about C=O are (trigonal) planar or the carbonyl carbon is (trigonal) planar | |
| | so the CN ⁻ / nucleophile attacks (equally) from above and below / either side (of the plane) | (1) | Do not award planar molecule / reference to planar intermediate / ion Do not award multiple | |
| | | | directions | |

Q7.

| uestion umber | | Acceptable Answe | ers | Additional Guidance | Mar |
|------------------|---|--|---|--|-----|
| * | and logically struc sustained reasonin Marks are awarded answer is structure | d for indicative conter ed and shows lines of le shows how the mar | kages and fully- nt and for how the | Guidance on how the mark scheme should be applied: The mark for indicative content should be added to the mark for lines of reasoning. For example, an answer with five indicative marking | (6) |
| | Number of indicative marking points seen in answer 6 5-4 3-2 | Number of marks awarded for indicative marking points 4 3 | | points that is partially structured with some linkages and lines of reasoning scores 4 marks (3 marks for indicative content and 1 mark for partial structure and some linkages and lines of reasoning). | |
| | The following tabl | | ks should be awarded | If there are no linkages between points, the same five indicative marking points would yield an overall score of 3 marks | |
| | 0 The following table | 0 le shows how the mar | Number of marks awarded for structure of answer and sustained line of reasoning | If there are no linkages between points, the same five indicative marking points would yield an | |
| | The following tabl | le shows how the mar ines of reasoning. | Number of marks awarded for structure of answer and sustained line of | If there are no linkages between points, the same five indicative marking points would yield an overall score of 3 marks (3 marks for indicative content and no marks for | |
| | Answer shows a structure with lin sustained lines of demonstrated three Answer is partial | le shows how the mar ines of reasoning. | Number of marks awarded for structure of answer and sustained line of reasoning | If there are no linkages between points, the same five indicative marking points would yield an overall score of 3 marks (3 marks for indicative content and no marks for | |

In general it would be

expected that 5 or 6 indicative points would get 2 reasoning marks,

and 3 or 4 indicative points would get 1 mark for reasoning, and 0, 1

or 2 indicative points would score zero marks for reasoning.

Indicative content

IP1 Reagents and conditions for oxidation –
 acidified potassium dichromate((VI)) / K₂Cr₂O₇ and
 H⁺/H₂SO₄
 or acidified sodium dichromate((VI)) / Na₂Cr₂O₇ and
 H⁺/H₂SO₄
 or Fehling's solution / Benedict's solution
 or Tollens' reagent / ammoniacal silver nitrate /
 Ag(NH₃)²⁺

 IP2 Oxidation of aldehyde – structure of pentanoic acid

- IP3 Oxidation of ketone—pentan-3-one / ketone is not (easily) oxidised
- IP4 Reagents and conditions for reduction —
 lithium tetrahydridoaluminate((III)) / lithium aluminium
 hydride and dry ether /ethoxyethane (followed by a dilute
 acid)
 or sodium tetrahydridoborate((III)) / sodium borohydride
 and aqueous / methanol solution (followed by a dilute
- IP5 Reduction of aldehyde structure of pentan-1-ol
- IP6 Reduction of ketone structure of pentan-3-ol

Reagents - Allow names or formulae but if both are given, both must be correct

Products - Allow any combination of displayed and structural formulae / skeletal formulae Allow C₄H₉ / C₃H₇ for the alkyl groups

Allow acidified dichromate((VI)) ions / $Cr_2O_7^{2-}$ and H^+/H_2SO_4 Allow acidified manganate((VII)) ions / MnO_4^- and H^+/H_2SO_4 Ignore reference to heat Do not award just Cu^{2+} for Fehling's / Benedict's

CH3CH2CH2CH2COOH

| | Allow lithal Ignore hydrogen and platinum (catalyst) Ignore reference to heat |
|--|--|
| | CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ OH |
| | CH ₃ CH ₂ CH(OH)CH ₂ CH ₃ |

Q8.

| Question Number | Answer | Additional Guidance | Mark |
|--------------------|---|--|------|
| (i) | curly arrow from lone pair on C of CN⁻ ion to C of C=O (1) dipole on C=O and curly arrow from C=O bond to or just beyond O (1) intermediate structure (1) | Penalise omission of lone pair once in M1 and M4 Penalise use of single-headed arrows only once Penalise use of incorrect nucleophile once only in M1 e.g. OH ⁻ Allow skeletal, displayed or structural formulae Allow CN ⁻ to attack from any angle Allow CN triple bond displayed Do not award curly arrow from lone pair on N Do not award CN ⁵⁻ Ignore missing lone pair on O Ignore connectivity for vertical CN group if M1 awarded Do not award O ⁿ⁻ | (4) |
| | curly arrow from lone pair on O to H of HCN and curly arrow from H-C bond to anywhere on CN (1) | Allow curly arrow from lone pair on O ⁻ to H ⁺ Ignore dipole on HCN Ignore products, even if incorrect | |

Allow straight arrows

Curly arrows in M1 and M4 must start from, or close to, at least 1 of the electrons in the lone pair, but penalise this once only

If candidate shows dipole on C=O and curly arrow first, allow M2 but if CN- then attacks C+, do not allow M1. M3 can score for the correct intermediate and M4 as per MS

| uestion umber | | Answer | Additional Guidance | Mark |
|------------------|----------------------------------|--|---|------|
| ii) | Reagent 2 | (conc) phosphoric acid / H ₃ PO ₄ (conc) sulfuric acid/ H ₂ SO ₄ aluminium oxide/ Al ₂ O ₃ (1) | Ignore connectivity of groups All marks are stand alone Allow 'alumina' | (6) |
| | Structure | | Do not award steam / water Do not award dilute for either acid | |
| | of compound A | (1) H C=C CN CH ₃ | Allow structural, displayed or any combination of structural, displayed or skeletal for Compounds | |
| | Reaction type 3 | (acid) Hydrolysis (1) | A and B Do not award hydration halogenation for M3 | (|
| 8 | Structure of compound B | он (1) H ССН3 | Allow TE for M4 based on incorrect M2 structure provided the nitrile group has been hydrolysed correctly and no other changes | |
| | Reagent 4 | CH ₃ OH / methanol (1) | Allow additionelimination for | |
| | Reaction type 4 | Esterification / condensation (1) | condensation in M6 | |

| Question Number | Answer | Additional Guidance | Mark |
|--------------------|---|--|------|
| (iii) | correct • repeat unit shown • (1) equation balanced (1) | Allow displayed or structural formulae or a combination of these e.g. H COOCH ₃ C C C H CH ₃ n Do not award 2 as the balancing number | (2) |

Q9.

| Question Number | Acceptable Answers | Additional Guidance | Mark |
|--------------------|-------------------------|---|------|
| (i) | • dot-and-cross diagram | Example of diagram H B H H H H H H H H H H H | (1) |
| | | Electrons must have the correct symbols i.e. 3 bonds with • and x and 1 bond with • and Δ Circles do not need to be shown Allow missing brackets but charge needs to be shown Allow charge anywhere on or close to diagram Ignore lines representing covalent bonds e.g. X • Ignore missing atom labels / inner shell of 2 electrons on B | |

| Question Number | Acceptable Answers | Additional Guidance | Mark |
|--------------------|---|--|------|
| (ii) | | Example of mechanism | (4) |
| | curly arrow from (1) B-H bond to C of C=O Allow curly arrow from B-H bond to H and curly arrow from H to C dipole on C=O (1) and curly arrow from C=O bond to or just beyond O | H ₃ C—C—CH ₃ + BH ₃ H ₃ C—CH ₃ + BH ₃ | |
| | lone pair on O⁻ (1) and curly arrow from lone pair to H of H₂O curly arrow from (1) | H ₂ C—C—CH ₃ — H ₃ C—C—CH ₃ + OH— | |
| | O-H bond to O and dipole on H-O bond | Allow curly arrow from any B-H bond Ignore lone pair on O in H ₂ O Penalise half-headed curly arrow once only | |