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ANSWER BOOK

Aldehydes and ketones: nucleophilic addition and the tests that tell them apart

Carbonyls and carboxylic acids · Unit C20

AQA 3.3.8 · OCR A 6.1.2

17 questions · 56 marks

NAVY EDITION

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SECTION A · Short, 1 to 2 marks

A1 AK-Q4

B1 an aldehyde has a hydrogen atom on its carbonyl carbon, which is replaced by OH to give a carboxylic acid. **B1** a ketone has no such hydrogen, and oxidising it would need a C–C bond to break, which a mild oxidising agent cannot do. [2]

A2 AK-Q19

B1 impurities lower the melting point and make the solid melt over a range of temperatures. **B1** so only a pure derivative gives a sharp melting point that can be matched to the data table. [2]

A3 AK-Q21

B1 $LiAlH_4$ is a more powerful source of hydride ions and reacts violently with water, releasing hydrogen. **B1** so it must be kept dry until the reduction is complete, and dilute acid is added only afterwards. [2]

SECTION B · Standard, 3 to 5 marks

B1 AK-Q7

B1 curly arrow from the lone pair on the carbon of CN^- to the carbonyl carbon. **B1** curly arrow from the C=O double bond to the oxygen atom. **B1** intermediate $(CH_3)_2C(CN)O^-$ with the negative charge on oxygen. **B1** curly arrow from a lone pair on O^- to H^+. **B1** the product is 2-hydroxy-2-methylpropanenitrile. [5]

B2 AK-Q6

B1 curly arrow from the lone pair on H^- to the carbonyl carbon. **B1** curly arrow from the C=O double bond to the oxygen atom. **B1** intermediate $CH_3CH_2CH_2O^-$ drawn with the negative charge on oxygen. **B1** curly arrow from a lone pair on O^- to an H of H_2O, with an arrow from the O–H bond to the water's oxygen, giving propan-1-ol. [4]

B3 AK-Q16

B1 propene reacts by electrophilic addition, propanal by nucleophilic addition. **B1** in propene the electron-rich C=C bond attacks the δ+ hydrogen of HBr, the electrophile. **B1** in propanal the CN^- nucleophile attacks the δ+ carbonyl carbon, using the lone pair on its carbon. **B1** the alkene gives a carbocation intermediate, whereas the carbonyl compound gives an alkoxide ion with a negative charge on oxygen. [4]

B4 AK-Q18

B1 a few drops of the liquid are added to 2,4-DNP solution, and a yellow or orange precipitate shows an aldehyde or ketone. **B1** the precipitate is filtered off and recrystallised from the minimum volume of hot ethanol. **B1** the dried crystals' melting point is measured. **B1** the melting point is compared with a data table of the melting points of 2,4-DNP derivatives to identify the compound. [4]

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B5 AK-Q5 **B1** oxygen is more electronegative than carbon, so the C=O bond is polar. **B1** the carbonyl carbon carries a δ+ charge, which attracts the lone pair of a nucleophile. **B1** the C=C bond is non-polar and a region of high electron density, so it repels nucleophiles and attracts electrophiles instead. [3]

B6 AK-Q8 **B1** HCN is a weak acid, so its solution contains few CN^- ions and the reaction is slow. **B1** KCN is fully ionised and supplies the CN^- nucleophile directly. **B1** cyanide with acid releases HCN, a highly toxic gas, so the reaction is done in a fume cupboard. [3]

B7 AK-Q9 **B1** the product, 2-hydroxypentanenitrile, has a chiral centre bonded to H, OH, CN and C_3H_7. **B1** the carbonyl group of butanal is planar, so the cyanide ion attacks from either side with equal probability. **B1** the two enantiomers are therefore formed in equal amounts. [3]

B8 AK-Q10 **B1** butanal gives butan-1-ol, a primary alcohol. **B1** butanone gives butan-2-ol, a secondary alcohol. **B1** $CH_3COCH_2CH_3 + 2[H] \rightarrow CH_3CH(OH)CH_2CH_3$; allow molecular formulae if the structure is clear. [3]

B9 AK-Q12 **M1** amount of ethanal = $0.220 \div 44.0 = 5.00 \times 10^{-3}$ mol. **M1** each ethanal releases two electrons, so the amount of silver = $2 \times 5.00 \times 10^{-3} = 1.00 \times 10^{-2}$ mol. **A1** mass of silver = $1.00 \times 10^{-2} \times 107.9 = 1.08$ g, to 3 significant figures. [3]

B10 AK-Q14 **B1** $NaBH_4$ gives prop-2-en-1-ol, $CH_2{=}CHCH_2OH$. **B1** hydrogen and nickel gives propan-1-ol, $CH_3CH_2CH_2OH$. **B1** the hydride ion is a nucleophile, which attacks the δ+ carbonyl carbon but is repelled by the electron-rich C=C bond, whereas H_2 with nickel adds across both double bonds. [3]

B11 AK-Q15 **B1** no silver mirror means Y is not an aldehyde, and its reduction by $NaBH_4$ shows a C=O group, so Y is a ketone. **B1** the only ketone with formula C_4H_8O is butanone, $CH_3COCH_2CH_3$. **B1** its reduction product, butan-2-ol, has carbon 2 bonded to H, OH, CH_3 and C_2H_5, so it is chiral. [3]

B12 AK-Q17 **B1** a negative Fehling's test shows only that the liquid is not an aldehyde. **B1** alcohols, esters, carboxylic acids and many other compounds also leave Fehling's solution blue, so the conclusion is not justified. **B1** a test showing a carbonyl group is needed as well, such as a C=O absorption near 1700 cm^{-1} in the infrared spectrum, with no broad O–H absorption. [3]

B13 AK-Q20 **B1** butanone and butan-2-ol give the precipitate of triiodomethane, CHI_3. **B1** butanone contains the $CH_3CO–$ group, and butan-2-ol contains $CH_3CH(OH)–$, which alkaline iodine oxidises to $CH_3CO–$. **B1** butanal and butan-1-ol have neither group, so they give no precipitate. [3]

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SECTION C · Long, 6 marks or more

C1 AK-Q22

Indicative content [6]

B1 each compound is warmed in a water bath with freshly made Tollens' reagent, which contains the $[Ag(NH_3)_2]^+$ ion. **B1** propanal gives a silver mirror on the inside of the tube, while propanone gives no change and the solution stays colourless. **B1** the silver complex is reduced: $[Ag(NH_3)_2]^+ + e^- \rightarrow Ag + 2NH_3$; allow $Ag^+ + e^- \rightarrow Ag$. **B1** warmed with Fehling's solution, propanal gives a brick-red precipitate while propanone leaves the solution blue; allow red or orange-red precipitate. **B1** the copper(II) is reduced, $Cu^{2+} + e^- \rightarrow Cu^+$, and copper(I) oxide, Cu_2O, precipitates in the alkaline solution. **B1** propanal is oxidised, $CH_3CH_2CHO + H_2O \rightarrow CH_3CH_2COOH + 2H^+ + 2e^-$ or with [O]; propanone has no H on its carbonyl carbon and is not oxidised.

Levels

Level 3 (5–6 marks) both tests are described with their observations for both compounds, the half-equations for the reduction of silver and of copper(II) are given, the oxidation of propanal is written, and the answer explains why propanone does not react.

Level 2 (3–4 marks) both tests give the silver mirror and the brick-red precipitate for propanal and no change for propanone; only one equation is right, or the answer does not say why propanone resists oxidation.

Level 1 (1–2 marks) one test is described with its positive result, often with the observations of the two tests swapped; no equations and no reason propanone does not react.

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