

4.5.6 Carbonyl properties, synthesis and combined analytical transfer

Name: _____ Class: _____ Date: _____

Total: 50 marks

KEY WORDS nucleophilic addition • chromatography

Objective

Test physical-property explanations, select organic methods and combine unfamiliar analytical evidence. All questions, data models and marking guidance are original.

1 Key knowledge and worked examples

A carbonyl oxygen can accept a hydrogen bond from water. Simple aldehydes/ketones cannot donate the O–H hydrogen needed for hydrogen bonding between their own molecules. Carboxylic acids can both donate and accept. Compare substances of similar size before attributing a boiling-point difference to hydrogen bonding; increasing a non-polar chain can reduce water solubility.

■ Worked chain accounting

Hydrolysing $\text{CH}_3\text{CH}_2\text{CN}$ retains the nitrile carbon, giving a three-carbon acid or carboxylate. In acid, $\text{CH}_3\text{CH}_2\text{CN} + 2\text{H}_2\text{O} + \text{H}^+ \rightarrow \text{CH}_3\text{CH}_2\text{COOH} + \text{NH}_4^+$. In alkali, $\text{CH}_3\text{CH}_2\text{CN} + \text{H}_2\text{O} + \text{OH}^- \rightarrow \text{CH}_3\text{CH}_2\text{COO}^- + \text{NH}_3$. Both need heating with aqueous reagent; acidifying the carboxylate afterwards gives the free acid.

A positive DNPH test establishes a carbonyl candidate, not its identity. Use a purified derivative's melting range against supplied reference data and combine it with other tests. Accurate mass tests molecular formula; NMR shifts, integration and splitting test connectivity; chromatography separates by interactions with two phases. None is automatically unique proof alone.

2 Practice

2.1 Explain why propanal and propanone can hydrogen-bond with water but do not form hydrogen bonds between their own molecules. Explain why propanoic acid has a higher boiling temperature than a similar-sized aldehyde, and why increasing the hydrocarbon chain can reduce water solubility in either class. Identify the intermolecular interaction and its role in each explanation. [6]

2.2 Write balanced equations for propanenitrile hydrolysis in (a) aqueous acid and (b) aqueous alkali; state the condition and how to obtain free acid after (b). Write equations for propanoic acid (c) reduced to propan-1-ol, using [H], and (d) with PCl_5 . Include the organic product and all by-products. State the reduction conditions. [8]

2.3 Unknown U gives orange DNPH precipitate, no Tollens' silver and yellow iodoform. Its purified DNPH derivative melts at 125–127°C. Use the supplied illustrative reference data to select a candidate, explain which test excludes A and why iodoform alone cannot distinguish B/C. Explain the role of a sharp melting range and one remaining identification limit. No derivative equation is required. ^[6]

Candidate	Structure	Supplied derivative melting point / °C
A	Propanal	146
B	Propanone	126
C	Butan-2-one	116

2.4 An enantiopure chiral halogenoalkane is converted to an alcohol. Independent structural analysis confirms the alcohol still has a single chiral centre, but its solution has zero optical rotation. Under the simple achiral-reaction models, explain which substitution mechanism is supported. Contrast with the expected configuration after S_N2 and state why zero rotation alone would be inadequate without the structural result. ^[4]

3 Exam-style questions

3.1 C₃H₈O and C₂H₄O₂ both have nominal mass 60. Use C = 12.0000, H = 1.0078 and O = 15.9949 to calculate their accurate relative molecular masses to four decimal places. U has measured mass 60.0210, a very broad acid O–H band plus C=O in IR, and two carbon-13 signals. Select the formula, suggest a simple structure and explain why nominal mass alone is inadequate. ^[6]

3.2 Predict low-resolution proton-NMR sets and integrated areas, then high-resolution splitting for CH₃COCH₂CH₃. Assign approximate chemical-shift regions using only the supplied data. Predict the number and types of carbon-13 environments. Explain why equivalent H in one methyl group do not split one another. Use the simple n+1 model and neglect long-range coupling. ^[8]

Supplied shift data	Range / ppm
H on alkyl carbon away from C=O	0.8–1.5
H on carbon next to C=O	2.0–2.7
C in alkyl region	8–50
Aldehyde/ketone carbonyl C	190–220

3.3 A TLC sample gives spots 1.8 and 4.2 cm above baseline with solvent front 6.0 cm above baseline. Calculate both R_f values and explain the separation using stationary/mobile phase interactions. A separate GC drug screen has one peak at the reference drug's retention time. Explain why this does not prove identity or purity, and how GC-MS and one suitable control strengthen the conclusion. [6]

3.4 Draw the complete two-stage CN^- -catalysed addition of HCN to propanal. Show the carbonyl dipole, relevant lone pairs, both first-stage curly arrows, the intermediate's charge and both proton-transfer curly arrows using HCN as donor. Give the product and explain the optical result in achiral conditions. [6]

Solutions

Original marking guidance: B1 for each specified correct feature unless M1/A1 is stated.

2.1 Carbonyl oxygen has a lone pair that accepts a hydrogen bond from water's O–H hydrogen; aldehydes/ketones lack an O–H/N–H/F–H donor for hydrogen bonding between their own molecules. An acid has O–H donor and carbonyl acceptor, permitting intermolecular hydrogen-bonded associations; more energy is needed to overcome these attractions when boiling, at comparable molecular size. A longer hydrocarbon region is non-polar and interacts less favourably with water; the polar group becomes a smaller part of the molecule, reducing solubility rather than eliminating its ability to hydrogen-bond. Boiling separates molecules, not covalent C=O bonds.

2.2 (a) $\text{CH}_3\text{CH}_2\text{CN} + 2\text{H}_2\text{O} + \text{H}^+ \rightarrow \text{CH}_3\text{CH}_2\text{COOH} + \text{NH}_4^+$. (b) $\text{CH}_3\text{CH}_2\text{CN} + \text{H}_2\text{O} + \text{OH}^- \rightarrow \text{CH}_3\text{CH}_2\text{COO}^- + \text{NH}_3$. Heat under reflux with the appropriate aqueous acid/alkali; acidify carboxylate to obtain propanoic acid. (c) $\text{CH}_3\text{CH}_2\text{COOH} + 4[\text{H}] \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{H}_2\text{O}$; LiAlH_4 in dry ether then suitable work-up. (d) $\text{CH}_3\text{CH}_2\text{COOH} + \text{PCl}_5 \rightarrow \text{CH}_3\text{CH}_2\text{COCl} + \text{POCl}_3 + \text{HCl}$. The three-carbon skeleton is retained in each conversion.

2.3 B, propanone, whose derivative reference lies in 125–127°C. A is an aldehyde expected to give Tollens' silver under the stated conditions. Both B/C have CH_3CO – and can give iodoform, so that test does not distinguish them. A sharp range supports a reasonably pure derivative, but coincident/overlapping reference ranges or another unlisted compound can defeat unique identification; use independent spectral evidence/reference agreement. Impurities commonly broaden/lower a melting range. These reference values are supplied illustrative data.

2.4 The structurally chiral product with zero rotation supports equal enantiomers/racemate. A planar carbocation in the ideal $\text{S}_{\text{N}}1$ model allows equal attack from either face. $\text{S}_{\text{N}}2$ instead gives inversion at the reacting chiral centre, retaining an enantiopure product in the simple model. Without structural evidence, zero could also indicate an achiral product, so rotation alone is not a unique mechanism proof. Real deviations from the simple models need further evidence.

3.1 $M_r(\text{C}_3\text{H}_8\text{O}) = 3(12.0000) + 8(1.0078) + 15.9949 = 60.0573$. $M_r(\text{C}_2\text{H}_4\text{O}_2) = 2(12.0000) + 4(1.0078) + 2(15.9949) = 60.0210$. Choose $\text{C}_2\text{H}_4\text{O}_2$. Ethanoic acid CH_3COOH fits acid O–H/C=O and two distinct carbon environments. Integer mass 60 fits both formulae and does not resolve the 0.0363 mass difference; structural assignment also needs the other evidence.

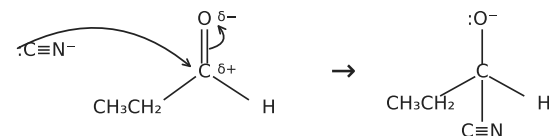
3.2 Three proton sets, integrated 3:2:3 for acyl CH_3 , CH_2 and terminal CH_3 . Acyl CH_3 is a singlet because the adjacent carbonyl carbon has no H; CH_2 is a quartet split by three neighbouring methyl H; terminal CH_3 is a triplet split by two CH_2 H. Acyl CH_3/CH_2 fall in the supplied 2.0–2.7 ppm region and terminal CH_3 in 0.8–1.5 ppm. Four distinct carbon environments: three alkyl-region signals and one carbonyl at 190–220 ppm. Equivalent H within a methyl set do not split one another in this simple first-order model. Neither proton nor carbon signal count equals total atom count automatically.

3.3 $R_f = 1.8/6.0 = 0.30$ and $4.2/6.0 = 0.70$, no units. Different relative affinities/interactions with stationary and mobile phases cause different migration; the lower- R_f component is relatively more retained by the stationary phase under these conditions. Retention times

are not unique and one peak can conceal co-elution. MS adds molecular/fragment evidence for separated material; a matched reference standard, blank or documented contamination control tests whether the match is reliable. One peak alone proves neither identity nor purity.

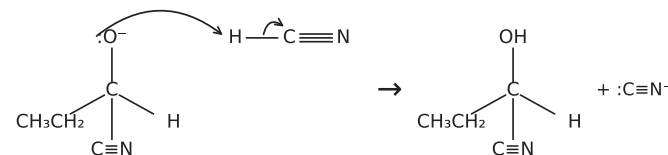
3.4 Complete mechanism and product:

1 Carbon attack and movement of the C=O π pair



The negative charge is on oxygen; the new C–C bond retains the nitrile carbon.

2 Proton transfer from HCN regenerates CN^-



O lone pair $\rightarrow$ H; H–C bond pair $\rightarrow$ C. Product: $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CN}$.

B1 CN carbon lone pair $\rightarrow$ carbonyl carbon with $\text{C}\delta^+/\text{O}\delta^-$; B1 π pair $\rightarrow$ O; B1 correctly connected O^- intermediate; B1 oxygen lone pair $\rightarrow$ H of HCN; B1 H–C bond pair $\rightarrow$ cyanide carbon, regenerating CN^- and forming $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CN}$. B1 equal attack on the two faces of planar propanal in achiral conditions gives equal enantiomers/racemate. HCN's carbon becomes the nitrile carbon, making a four-carbon product; no C–C bond is lost.