

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 $\text{C}_3\text{H}_8\text{O}$ and $\text{C}_2\text{H}_4\text{O}_2$ both have nominal mass 60. Use $\text{C} = 12.0000$, $\text{H} = 1.0078$ and $\text{O} = 15.9949$ 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 $\text{C}=\text{O}$ 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 $\text{CH}_3\text{COCH}_2\text{CH}_3$. 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 $\text{C}=\text{O}$	0.8–1.5
H on carbon next to $\text{C}=\text{O}$	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]