

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 S_N1 model allows equal attack from either face. S_N2 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.

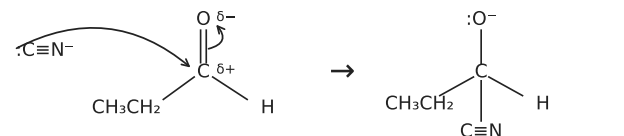
3.2 Three proton sets, integrated 3:2:3 for acyl CH_3 , CH_2 and terminal CH_3 . Acyl CH_3 is a singlet because the adjacent carbonyl carbon has no H; CH_2 is a quartet split by three neighbouring methyl H; terminal CH_3 is a triplet split by two CH_2 H. Acyl CH_3/CH_2 fall in the supplied 2.0–2.7 ppm 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.

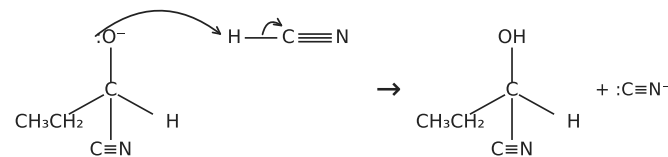
3.4 Complete mechanism and product:

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.