Class 12 Chemistry · Chapter 8: Aldehydes, Ketones and Carboxylic Acids

Answer key and marking scheme · 20 marks · about 40 minutes · based on NCERT

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1. Propanoyl chloride, CH_3CH_2COCl, is converted to propanal by [1]

(a) $LiAlH_4$, then H_2O (b) $NaBH_4$ in ethanol

(c) Zn–Hg and conc. HCl (d) H_2 over Pd–$BaSO_4$

Answer: (d) Rosenmund reduction: hydrogen over palladium on barium sulphate reduces an acyl chloride only as far as the aldehyde. $LiAlH_4$ and $NaBH_4$ go on to the alcohol; Zn–Hg/HCl reduces C=O to CH_2.

2. Cyclohexanecarbonyl chloride, $C_6H_{11}COCl$, reacts with dimethylcadmium. The product is [1]

(a) 1-cyclohexylethan-1-one, $C_6H_{11}COCH_3$ (b) cyclohexanecarbaldehyde, $C_6H_{11}CHO$

(c) 1-cyclohexylethan-1-ol, $C_6H_{11}CH(OH)CH_3$ (d) methylcyclohexane, $C_6H_{11}CH_3$

Answer: (a) $2R'COCl + R_2Cd \rightarrow 2R'COR + CdCl_2$: the acyl group joins the methyl group of the cadmium reagent, giving the ketone $C_6H_{11}COCH_3$. Dialkylcadmium stops at the ketone; it does not go on to the tertiary or secondary alcohol.

3. Oxidation of 3-methylbutan-2-ol, $CH_3CH(OH)CH(CH_3)_2$, with acidified $K_2Cr_2O_7$ gives [1]

(a) 3-methylbutanal (b) 3-methylbutan-2-one

(c) 3-methylbutanoic acid (d) 2-methylbut-2-ene

Answer: (b) It is a secondary alcohol (–OH on C-2, which carries one H); secondary alcohols are oxidised to ketones: $CH_3COCH(CH_3)_2$, 3-methylbutan-2-one.

4. Methyl pent-3-enoate, $CH_3–CH=CH–CH_2–COOCH_3$, is treated with DIBAL-H and then with water. [1] The organic product is

(a) $CH_3–CH=CH–CH_2–CH_2OH$ (b) $CH_3CH_2CH_2CH_2CHO$

(c) $CH_3–CH=CH–CH_2–CHO$ (d) $CH_3–CH=CH–CH_2–COOH$

Answer: (c) DIBAL-H reduces an ester to the aldehyde and leaves the C=C untouched, as it does with nitriles: pent-3-enal. It does not hydrogenate the double bond, and hydrolysis to the acid is not a reduction.

5. Toluene can be converted to benzaldehyde, the oxidation stopping at the aldehyde stage, by [1] treating it with

(a) alkaline $KMnO_4$, heat, then H_3O^+ (b) CrO_2Cl_2 in CS_2, then H_3O^+

(c) acidified $K_2Cr_2O_7$, heat (d) Cl_2 and $FeCl_3$ in the dark

Answer: (b) Etard reaction: chromyl chloride turns the methyl group into a chromium complex, $C_6H_5CH(OCrOHCl_2)_2$, which hydrolyses to C_6H_5CHO. Strong oxidants ($KMnO_4$, $K_2Cr_2O_7$) go on to benzoic acid; $Cl_2/FeCl_3$ chlorinates the ring.

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6. The addition of HCN to propanone is very slow with pure HCN but fast when a little base is present. Explain, writing the product formed. [2]

Base removes a proton from HCN to give CN^-, a much stronger nucleophile than HCN; CN^- attacks the electrophilic carbonyl carbon and the alkoxide formed takes a proton. Product: $(CH_3)_2C(OH)CN$, propanone cyanohydrin (2-hydroxy-2-methylpropanenitrile).

- base generates CN^-, the stronger nucleophile, which attacks the carbonyl carbon (1)
- product $(CH_3)_2C(OH)CN$, the cyanohydrin (1)

7. What hydrocarbon is obtained when (a) sodium 2-methylpropanoate is heated with sodalime, (b) an aqueous solution of sodium propanoate is electrolysed? Write the equation for (a). [2]

(a) $(CH_3)_2CH{-}COONa + NaOH \rightarrow (CH_3)_2CH_2 + Na_2CO_3$ (CaO, heat): propane, $CH_3CH_2CH_3$; decarboxylation removes one carbon. (b) Kolbe electrolysis joins two ethyl groups: $CH_3CH_2{-}CH_2CH_3$, butane.

- (a) propane, with the decarboxylation equation (1)
- (b) butane by Kolbe electrolysis (1)

8. A sample of pentane is contaminated with a little pentanal. How can the aldehyde be separated and then recovered? Give the reason the method works. [2]

Shake the mixture with saturated aqueous $NaHSO_3$: pentanal forms the addition compound $CH_3(CH_2)_3CH(OH)SO_3^-Na^+$, which is water soluble and passes into the aqueous layer; pentane does not react. The aqueous layer, treated with dilute mineral acid or alkali, gives back pentanal.

- $NaHSO_3$ adds to the aldehyde to give a water-soluble addition compound, separated from pentane (1)
- dilute acid or alkali regenerates pentanal (1)

9. Butanal is warmed with dilute NaOH. Write the structure and IUPAC name of the aldol formed and of the product it gives on heating. Which hydrogen of butanal makes the reaction possible? [3]

The α-hydrogen, on C-2 next to the C=O, is acidic; its carbanion attacks the carbonyl carbon of a second molecule. Aldol: $CH_3CH_2CH_2{-}CH(OH){-}CH(CH_2CH_3){-}CHO$, 2-ethyl-3-hydroxyhexanal. On heating it loses water: $CH_3CH_2CH_2{-}CH{=}C(CH_2CH_3){-}CHO$, 2-ethylhex-2-enal.

- the α-hydrogen on C-2 is the acidic one (1)
- aldol structure and name, 2-ethyl-3-hydroxyhexanal (1)
- dehydration product 2-ethylhex-2-enal (1)

10. Write, as numbered steps, the mechanism of nucleophilic addition of cyanide ion to ethanal, and state how the hybridisation and shape at the carbonyl carbon change. [3]

1. CN^- approaches the electrophilic carbonyl carbon roughly perpendicular to the plane of its sp^2 orbitals and forms a C–C bond; the π electrons move onto oxygen. 2. A tetrahedral alkoxide intermediate, $CH_3CH(O^-)CN$, forms. 3. The alkoxide takes a proton from the medium (HCN or water): $CH_3CH(OH)CN$, 2-hydroxypropanenitrile. The carbon changes from sp^2, trigonal planar, to sp^3, tetrahedral.

- step 1: CN^- attacks the carbonyl carbon, π electrons to oxygen (1)
- steps 2 and 3: alkoxide intermediate protonated to $CH_3CH(OH)CN$ (1)
- sp^2 trigonal planar becomes sp^3 tetrahedral (1)

11. Show two ways of converting 1-bromopropane into butanoic acid, writing the equations. What do the two routes have in common? [3]

Route 1: $CH_3CH_2CH_2Br + KCN \rightarrow CH_3CH_2CH_2CN$; $CH_3CH_2CH_2CN \rightarrow CH_3CH_2CH_2CONH_2 \rightarrow CH_3CH_2CH_2COOH$ (H_3O^+, heat). Route 2: $CH_3CH_2CH_2Br + Mg \rightarrow CH_3CH_2CH_2MgBr$ (dry ether); + $CO_2 \rightarrow CH_3CH_2CH_2COO^-MgBr^+$; $H_3O^+ \rightarrow CH_3CH_2CH_2COOH$. Both give an acid with one carbon more than the alkyl halide.

- nitrile route with hydrolysis (1)
- Grignard route with CO_2 and acidification (1)
- both add one carbon (ascending the series) (1)