Class 12 Chemistry · Chapter 7: Alcohols, Phenols and Ethers

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

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1. 2-Methylpropene, $(CH_3)_2C{=}CH_2$, is treated with diborane and the product is oxidised with H_2O_2 in aqueous NaOH. The alcohol formed is [1]

(a) 2-methylpropan-2-ol
(b) 2-methylpropan-1-ol
(c) butan-1-ol
(d) butan-2-ol

Answer: (b) In hydroboration boron adds to the sp^2 carbon carrying more hydrogens, the $=CH_2$ end; oxidation replaces boron by $-OH$: $(CH_3)_2CH{-}CH_2OH$, 2-methylpropan-1-ol. This looks like anti-Markovnikov addition of water. (a) is the acid-catalysed hydration product; (c) and (d) have a different carbon skeleton.

2. Resorcinol is [1]

(a) benzene-1,2-diol
(b) benzene-1,4-diol
(c) benzene-1,3-diol
(d) 3-methylphenol

Answer: (c) Catechol is benzene-1,2-diol, resorcinol benzene-1,3-diol, and hydroquinone (quinol) benzene-1,4-diol. 3-Methylphenol is m-cresol.

3. The IUPAC name of $HO{-}CH_2{-}CH(OH){-}CH_2{-}CH_3$ is [1]

(a) butan-1,2-diol
(b) butane-1,2-diol
(c) butane-3,4-diol
(d) 1,2-dihydroxybutane

Answer: (b) For a polyhydric alcohol the 'e' of the alkane is kept and 'di' goes before 'ol'; the chain is numbered to give the $-OH$ groups the lowest locants: butane-1,2-diol. (a) drops the 'e'; (c) numbers from the wrong end; (d) treats $-OH$ as a prefix.

4. 4-Methylphenol is heated with chloroform and aqueous sodium hydroxide, and the mixture is then acidified. The main organic product is [1]

(a) 4-methylbenzaldehyde
(b) 2-hydroxy-5-methylbenzoic acid
(c) 2-hydroxy-5-methylbenzaldehyde
(d) 2-hydroxy-4-methylbenzaldehyde

Answer: (c) This is the Reimer–Tiemann reaction: $-CHCl_2$ enters ortho to the $-O^-$ group and the substituted benzal chloride is hydrolysed by the alkali to $-CHO$. The para position is already held by CH_3, so $-CHO$ goes ortho to $-OH$. Numbering from the CHO carbon: CHO at C-1, OH at C-2, and CH_3 (para to OH) at C-5. (b) is the Kolbe product (CO_2, not $CHCl_3$); (a) loses the $-OH$; (d) puts CH_3 meta to OH.

5. Which of the following is a tertiary alcohol? [1]

(a) $(CH_3)_2CH{-}CH_2{-}OH$
(b) $CH_3{-}CH_2{-}C(CH_3)(OH){-}CH_2{-}CH_3$
(c) $CH_3{-}CH(OH){-}CH(CH_3)_2$
(d) $C_6H_5{-}CH_2{-}CH_2{-}OH$

Answer: (b) In $CH_3CH_2C(CH_3)(OH)CH_2CH_3$ the $-OH$ is on a carbon bonded to three other carbons: tertiary. (a) and (d) have $-OH$ on a $-CH_2-$ carbon (primary); in (c) the $-OH$ carbon carries one hydrogen and two carbons (secondary).

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6. A person has drunk spirit contaminated with methanol. (i) Name the two compounds into which the body oxidises methanol. (ii) Why is diluted ethanol given to the patient intravenously? [2]

(i) Methanol is oxidised first to methanal and then to methanoic acid, which may cause blindness and death. (ii) Ethanol competes for the enzyme that oxidises the aldehyde to the acid and swamps it, so less methanoic acid forms and the kidneys have time to excrete the methanol.

- methanal, then methanoic acid (1)
- ethanol swamps the enzyme; methanol excreted by kidneys (1)

7. Phenol does not give bromobenzene with HBr, yet it loses its oxygen when heated with zinc dust. Write the equation for the zinc dust reaction, and explain why HBr cannot replace the −OH of phenol. [2]

$C_6H_5OH + Zn \rightarrow C_6H_6 + ZnO$. In phenol the C–O bond has partial double bond character (the lone pair on oxygen is conjugated with the ring) and the carbon is sp^2 hybridised; such a carbon cannot undergo the nucleophilic substitution by Br^- that cleavage would need. C–O cleavage of this kind belongs to alcohols.

- $C_6H_5OH + Zn \rightarrow C_6H_6 + ZnO$ (1)
- partial double bond, sp^2 carbon resists nucleophilic substitution (1)

8. To make picric acid today, phenol is first treated with concentrated sulphuric acid and only then with concentrated nitric acid. (i) Name the compound formed in the first step. (ii) Why is picric acid a strong acid although phenol is not? [2]

(i) Phenol-2,4-disulphonic acid; with concentrated nitric acid it gives 2,4,6-trinitrophenol (direct nitration of phenol gives a poor yield). (ii) The three $-NO_2$ groups withdraw electrons from the ring and the oxygen, which makes release of the hydrogen ion easy.

- phenol-2,4-disulphonic acid (1)
- three electron withdrawing $-NO_2$ groups ease release of H^+ (1)

9. 2-Methylpropan-2-ol is dehydrated by 20% H_3PO_4 at 358 K, whereas ethanol needs concentrated H_2SO_4 at 443 K. Write, as numbered steps, the mechanism of dehydration of 2-methylpropan-2-ol, and use it to explain the difference. [3]

1. The alcohol is protonated: $(CH_3)_3C–OH + H^+ \rightarrow (CH_3)_3C–OH_2^+$. 2. Water leaves, giving the carbocation $(CH_3)_3C^+$; this is the slowest, rate-determining step. 3. A proton is lost from a CH_3 group: $(CH_3)_2C=CH_2 + H^+$, and the acid is regenerated. Because step 2 decides the rate and the tertiary carbocation is the most stable, it forms easily; ethanol would have to form a much less stable primary carbocation, so it needs harsher conditions.

- step 1: protonation of the alcohol (1)
- step 2: $(CH_3)_3C^+$ formed, rate determining (1)
- step 3: loss of H^+ to 2-methylpropene; tertiary carbocation most stable, so easier (1)

10. 2-Phenylbutan-2-ol, $C_6H_5–C(CH_3)(OH)–CH_2CH_3$, is to be made by a Grignard reaction. Give two different combinations of a carbonyl compound and a Grignard reagent that give it, and write the equations for one, showing the adduct. [3]

Any two of: $C_6H_5COCH_3 + C_2H_5MgBr$; $C_6H_5COCH_2CH_3 + CH_3MgBr$; $CH_3COCH_2CH_3 + C_6H_5MgBr$. For example: $C_6H_5COCH_3 + C_2H_5MgBr \rightarrow C_6H_5–C(CH_3)(C_2H_5)–OMgBr$; then $+ H_2O \rightarrow C_6H_5–C(CH_3)(OH)–CH_2CH_3 + Mg(OH)Br$. A ketone is needed because the product is a tertiary alcohol.

- first correct ketone + Grignard pair (1)
- second correct pair (1)
- equation with adduct and hydrolysis (1)

11. Show, with one equation each, that ethanol behaves (i) as a Brønsted acid and (ii) as a Brønsted base. (iii) Explain why sodium ethoxide is a stronger base than sodium hydroxide. [3]

(i) $2C_2H_5OH + 2Na \rightarrow 2C_2H_5ONa + H_2$: ethanol gives up the proton of its O–H. (ii) $C_2H_5OH + H^+ \rightarrow C_2H_5OH_2^+$ (with a strong acid such as H_2SO_4): the unshared pairs on oxygen accept a proton. (iii) Ethanol is a poorer proton donor than water, so its conjugate base, the ethoxide ion, is a better proton acceptor than hydroxide.

- acid behaviour, with sodium (1)
- base behaviour, protonation to $C_2H_5OH_2^+$ (1)
- ethanol poorer proton donor than water, so ethoxide stronger base (1)