

Tutorial 18 – Hydroxy Compounds (Suggested Solutions)

Practice Questions

- 1 Relative acidity: methylpropan-2-ol < ethanol < water < 2-methylphenol < phenol < 2-nitrophenol

Methylpropan-2-ol and ethanol are alcohols while 2-methylphenol and 2-nitrophenol are substituted phenols.

The more stable the conjugate base, the more acidic the compound.

Alcohols are less acidic than water.

- Alkoxide ion, RO^- , is less stable than hydroxide ion, OH^- , due to the electron-donating alkyl group which intensifies the negative charge on the oxygen atom.

Methylpropan-2-ol is less acidic than ethanol.

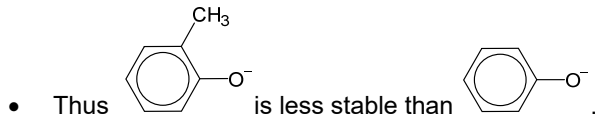
- $(\text{CH}_3)_3\text{CO}^-$ has more electron-donating alkyl groups than $\text{CH}_3\text{CH}_2\text{O}^-$ that further intensifies the negative charge on the oxygen atom.
- Thus $(\text{CH}_3)_3\text{CO}^-$ is less stable than $\text{CH}_3\text{CH}_2\text{O}^-$.

Phenols are more acidic than water.

- The p-orbital containing the lone pair of electrons on the oxygen atom of the phenoxide ions overlaps with the π electron cloud of the benzene ring and the lone pair of electrons is delocalised into the ring.
- This results in the delocalisation of negative charge on oxygen into the ring, i.e. dispersal of the negative charge over the ring.
- Thus, the phenoxide ion is resonance-stabilised and more stable than hydroxide ion.

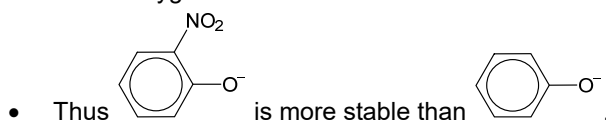
2-methylphenol is less acidic than phenol.

- Presence of electron-donating group, $-\text{CH}_3$, on the benzene ring intensifies the negative charge on the oxygen atom.

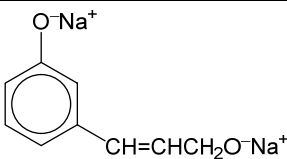
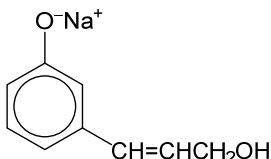


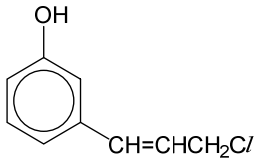
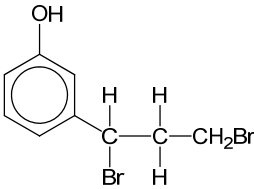
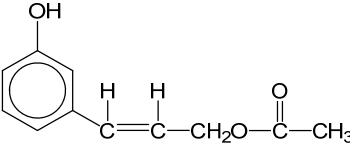
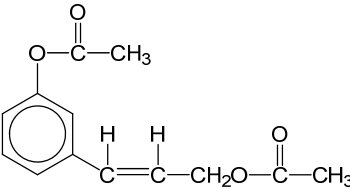
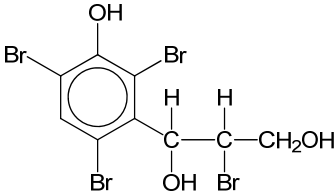
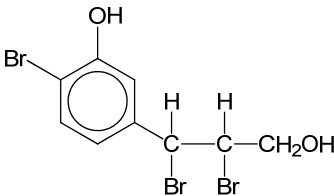
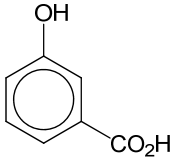
2-nitrophenol is more acidic than phenol.

- Presence of electron-withdrawing group, $-\text{NO}_2$, on the benzene ring disperses the negative charge on the oxygen atom.



2

Reagents	Condition	Structure	Type of reaction
(a) sodium	room temp		Redox
(b) sodium hydroxide	room temp		Acid-Base
(c) sodium carbonate	NA	NO REACTION	NA

(d)	phosphorus (V) chloride	room temp, (anhydrous)		Nucleophilic Substitution
(e)	hydrogen bromide	dry HBr, heat		Nucleophilic substitution and Electrophilic Addition Note: • Benzylic carbocation intermediate is more stable. • Without heating, only electrophilic addition of C=C occurs.
(f)	ethanoic acid	conc. H ₂ SO ₄ , heat		Condensation (esterification)
(g)	ethanoyl chloride	room temp.		Condensation (acylation)
(h)	aqueous bromine	room temp.		Electrophilic Substitution and Electrophilic Addition Note: • Benzylic carbocation intermediate is more stable.
(i)	bromine in CCl ₄	room temp.	 (or 2- or 4-substituted product)	Electrophilic Substitution and Electrophilic Addition
(j)	potassium manganate (VII)	KMnO ₄ (aq), H ₂ SO ₄ (aq), heat		Vigorous oxidation (Oxidative cleavage of the C=C)

3 (a)

Test

Add Br₂ (in CCl₄) dropwise to each sample in a test-tube at room temperature, in the absence of uv light.

Observations

- For C₆H₅CH=CH₂, there is (rapid) decolourisation of orange-red Br₂.

$$\text{C}_6\text{H}_5\text{CH}=\text{CH}_2 + \text{Br}_2 \longrightarrow \text{C}_6\text{H}_5\text{CHBrCH}_2\text{Br}$$
- For C₆H₅CH₂CH₂OH, there is no decolourisation of orange-red Br₂.

OR

Test

Add two drops of K₂Cr₂O₇(aq) acidified with dilute H₂SO₄(aq) to each sample in a test-tube, and heat the mixture in a hot water bath. (Note: DO NOT heat under reflux)

Observations

- For C₆H₅CH=CH₂, the solution remains orange.
- For C₆H₅CH₂CH₂OH, orange acidified K₂Cr₂O₇(aq) turns green.

$$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{OH} + 2[\text{O}] \longrightarrow \text{C}_6\text{H}_5\text{CH}_2\text{COOH} + \text{H}_2\text{O}$$

(b) Test

Add I₂(aq), followed by NaOH(aq) to each sample in a test-tube and heat each mixture in a hot water bath. (Note: DO NOT heat under reflux)

Observation

- For butan-1-ol, no yellow ppt is formed.
- For butan-2-ol, yellow ppt of CHI₃ is formed.

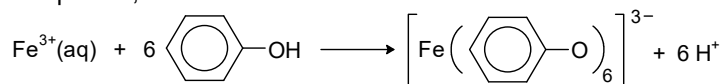
$$\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3 + 4\text{I}_2 + 6\text{NaOH} \longrightarrow \text{CHI}_3 + \text{CH}_3\text{CH}_2\text{COO}^-\text{Na}^+ + 5\text{NaI} + 5\text{H}_2\text{O}$$

(c) Test

Add neutral FeCl₃(aq) to each sample in a test-tube at room temperature.

Observation

- For cyclohexanol, no violet colouration is observed.
- For phenol, violet colouration is observed.



(structure of violet complex is not in syllabus)

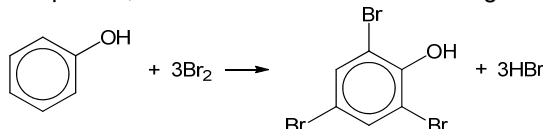
OR

Test

Add Br₂(aq) dropwise to each sample in a test-tube at room temperature, in the absence of uv light.

Observation

- For cyclohexanol, there is no decolourisation of orange Br₂ and no white ppt is formed.
- For phenol, there is decolourisation of orange Br₂ and a white ppt is formed.



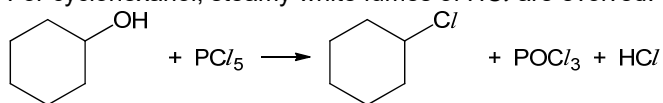
OR

Test

Add PCl₅(s) to each sample in a test-tube at room temperature.

Observation

- For cyclohexanol, steamy white fumes of HCl are evolved.



- For phenol, no steamy white fumes are evolved.

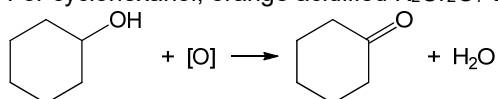
OR

Test

Add two drops of $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$ acidified with dilute $\text{H}_2\text{SO}_4(\text{aq})$ to each sample in a test-tube, and heat the mixture in a hot water bath. (Note: DO NOT heat under reflux)

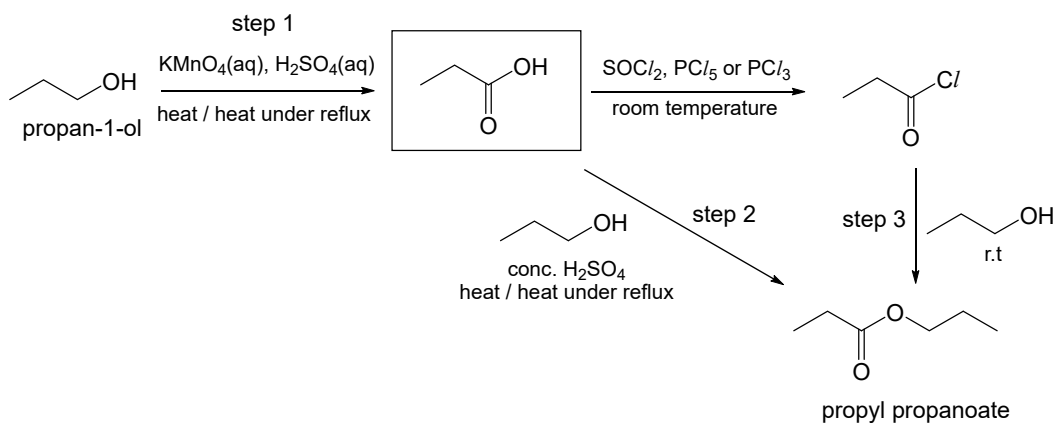
Observation

- For cyclohexanol, orange acidified $\text{K}_2\text{Cr}_2\text{O}_7$ turns green.

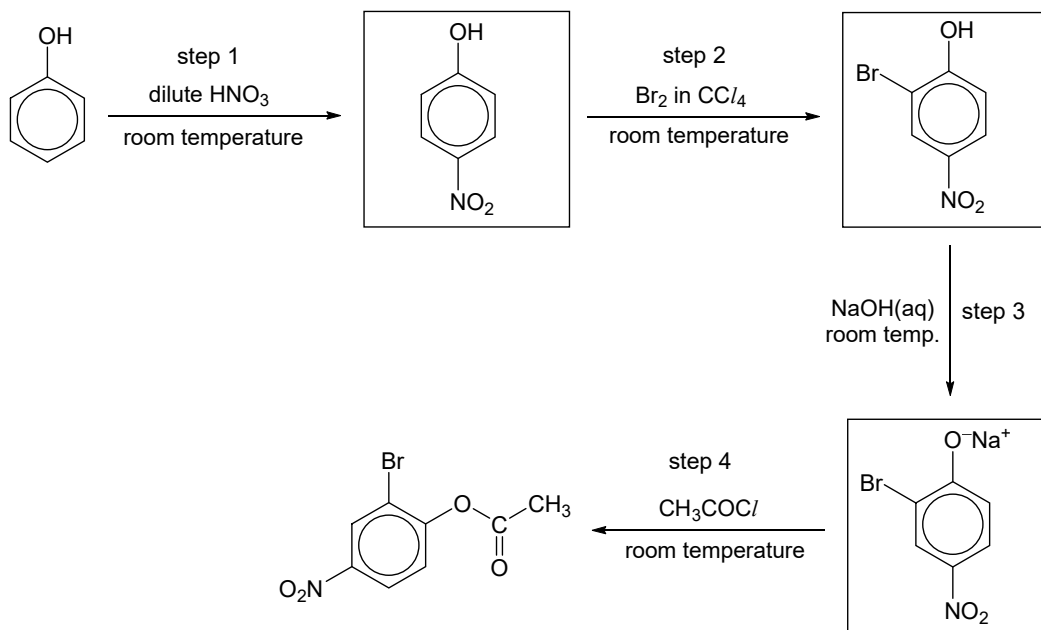


- For phenol, solution remains orange.

4 (a)

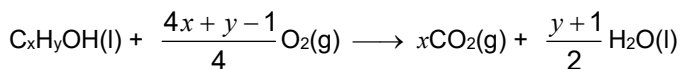


(b)



- 5 (a) Method 1 (using volume of gases only and Avogadro's law)
 $C_xH_yOH(l) + Na(s) \rightarrow \frac{1}{2}H_2(g) + C_xH_yO^-Na^+(l)$

$$\text{Vol of } H_2 = 10.9 \text{ cm}^3$$



Change in volume = Final volume of gases – Initial volume of gases

$$-54.4 = (\text{Vol. of } O_2 \text{ left} + \text{Vol. of } CO_2 \text{ produced}) - \text{Initial vol. of } O_2$$

$$54.4 = \text{Initial vol. of } O_2 - (\text{Vol. of } O_2 \text{ left} + \text{Vol. of } CO_2 \text{ produced})$$

$$54.4 = (\text{Initial vol. of } O_2 - \text{Vol. of } O_2 \text{ left}) - \text{Vol. of } CO_2 \text{ produced}$$

$$54.4 = \text{Vol. of } O_2 \text{ reacted} - \text{Vol. of } CO_2 \text{ produced}$$

$$\text{Vol. of } O_2 \text{ reacted} = 54.4 + \text{Vol. of } CO_2 \text{ produced}$$

$$= 54.4 + 109$$

$$= 163.4 \text{ cm}^3$$

Since the same amount of $C_xH_yOH(l)$ is used in both experiments,

$$\frac{1}{2}H_2(g) \equiv \frac{4x+y-1}{4}O_2(g) \equiv xCO_2(g)$$

(to find x)

$$\frac{\text{Vol of } CO_2}{\text{Vol of } H_2} = \frac{x}{0.5}$$

$$\frac{109}{10.9} = \frac{x}{0.5}$$

$$x = 5$$

(to find y)

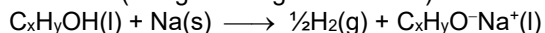
$$\frac{\text{Vol of } O_2}{\text{Vol of } H_2} = \frac{\frac{4x+y-1}{4}}{0.5}$$

$$\frac{163.4}{10.9} = \frac{\frac{4x+y-1}{4}}{0.5} \text{ where } x = 5$$

$$y = 11$$

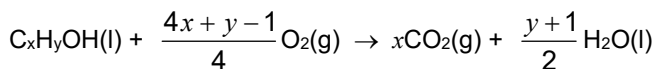
$\therefore J$ is $C_5H_{11}OH$

Method 2 (using amt of gases formed)



$$\text{Amount of } H_2(g) = \frac{10.9}{24000} = 4.54 \times 10^{-4} \text{ mol}$$

$$\text{Amount of } C_xH_yOH = 2 \times 4.54 \times 10^{-4} = 9.08 \times 10^{-4} \text{ mol}$$



$$\text{Amount of } O_2(g) = \frac{163.4}{24000} = 6.81 \times 10^{-3} \text{ mol}$$

$$\text{Amount of } CO_2(g) = \frac{109}{24000} = 4.54 \times 10^{-3} \text{ mol}$$

Amount of J : Amount of CO₂(g) : Amount of O₂(g)

$$9.08 \times 10^{-4} : 4.54 \times 10^{-3} : 6.81 \times 10^{-3}$$

$$1 : 5.00 : 7.50$$

$$1 : x : \frac{4x + y - 1}{4}$$

$$\therefore x = 5 \text{ and } \frac{4x + y - 1}{4} = 7.5$$

$$y = 11$$

$\therefore$ J is C₅H₁₁OH

Evidence / Information	Deduction and explanation
J reacts with acidified K ₂ Cr ₂ O ₇ .	<u>Oxidation</u> of alcohol occurred. J is either a <u>primary or secondary alcohol</u> .
$J \xrightarrow{-H_2O} K$	Molecular formula of K is <u>C₅H₁₀</u> .
$K, C_5H_{10} \xrightarrow{\text{excess of hot acidified conc } KMnO_4} \begin{array}{c} OH \\ \\ CH_3-C=O \\ + \\ CH_3 \\ \\ O=C-CH_3 \end{array}$	<u>Vigorous oxidation</u> (oxidative cleavage of C=C) occurred. K is $\begin{array}{c} H & CH_3 \\ & \backslash & / \\ & C=C \\ & / & \backslash \\ CH_3 & & CH_3 \end{array}$ and J is $\begin{array}{c} H & CH_3 \\ & \\ CH_3-C & -C-CH_3 \\ & \\ OH & H \end{array}$

(c) excess concentrated H₂SO₄, heat

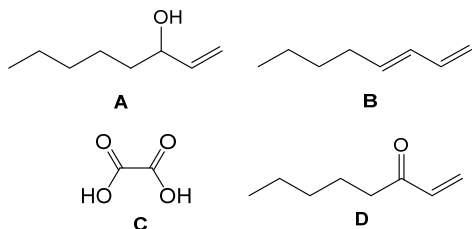
(d) K cannot exhibit cis-trans isomerism as there are two identical –CH₃ groups bonded to one of the carbon atoms of the C=C bond.

- 6 (a)
- The –CH(OH)CH₃ group is absent in A.
 - A contains one C=C bond.

Examiner Comments

- Students **should not** describe the –CH(OH)CH₃ group as “methyl alcohol” as it is ambiguous. No credit will be given for ambiguous descriptions.
- It is important to state that there is **ONE C=C bond** given that **ONE mole of Br₂** reacts with **ONE mole of A**.
- Answers that just stated A has a double bond or a doubly bonded carbon was not given credit as this could also imply a C=O group.
- 1 degree of unsaturation was also not accepted as C=O is also unsaturated.

(b)



Examiner Comments

- Many students did not realise that C and subsequently B can be obtained independently without having to obtain the structures of A and B.

- The thought process for deducing the structures is as follows:

Molecular formula ($C_8H_{16}O$) and 1 mol of **A** reacts with 1 mol of Br_2 in the dark.

⇒ **A** undergoes electrophilic addition with Br_2

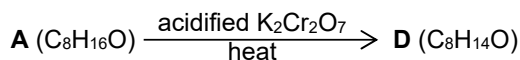
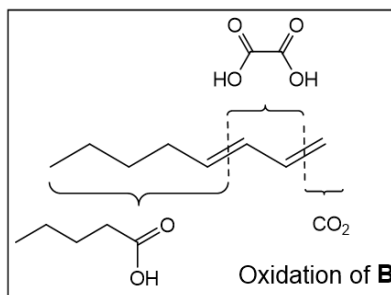
⇒ **A** contains 1 $C=C$

From molecular formula, **C** is $HOOC-COOH$.

B (C_8H_{16}) undergoes vigorous oxidation to form $CH_3(CH_2)_3COOH$, CO_2 & $HOOC-COOH$.

⇒ Oxidative cleavage of $C=C$ bonds occurred.

⇒ **B** contains 2 $C=C$ (CO_2 formed from terminal alkene, while $HOOC-COOH$ formed from $-C=C-C=C-$)



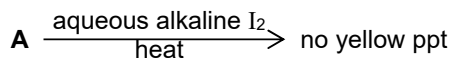
⇒ oxidation of alcohol in **A** occurred.

⇒ **A** does not contain a 1° alcohol since **D** does not contain a $-COOH$, which has 2 O atoms.

⇒ **A** does not contain a 3° alcohol since **A** undergoes oxidation. (3° alcohols do not undergo oxidation)

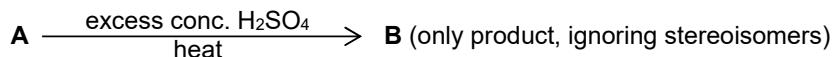
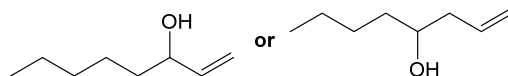
⇒ **A** contains a 2° alcohol

⇒ **A** could be

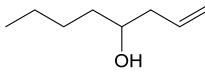


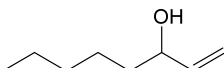
⇒ $-CH(OH)CH_3$ group is absent

⇒ **A** could be



⇒ elimination of water occurred i.e. $C=C$ formed in **B**.

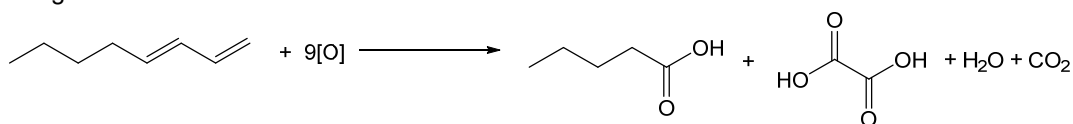
⇒ **A** cannot be  since it gives 2 possible alkenes.

⇒ **A** is 

- (c) **A to B** : elimination
A to D: oxidation

- (d) $\text{C}_8\text{H}_{14} + 9[\text{O}] \longrightarrow \text{CO}_2 + \text{H}_2\text{C}_2\text{O}_4 + \text{C}_4\text{H}_9\text{COOH} + \text{H}_2\text{O}$

Note: If the question did not state 'may use molecular formulae', then the above equation will be ambiguous. A more appropriate chemical equation will be to represent the organic molecules using skeletal / structural formulae.



Examiner Comments

- Many students used 8[O] to balance the equation and ignored the fact that H_2O has to be added to the RHS to balance the hydrogen atoms on the left.