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.

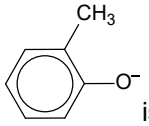
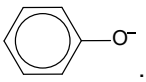
Methylpropan-2-ol is less acidic than ethanol.

- $(CH_3)_3CO^-$ has more electron-donating alkyl groups than $CH_3CH_2O^-$ that further intensifies the negative charge on the oxygen atom.
- Thus $(CH_3)_3CO^-$ is less stable than $CH_3CH_2O^-$

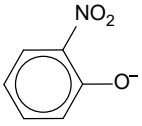
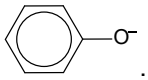
Phenols are more acidic than water.

- 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, $-CH_3$, on the benzene ring intensifies the negative charge on the oxygen atom.
- Thus  is less stable than  .

2-nitrophenol is more acidic than phenol.

- Presence of electron-withdrawing group, $-NO_2$, on the benzene ring disperses the negative charge on the oxygen atom.
- Thus  is more stable than  .

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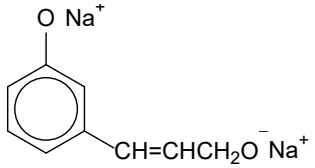
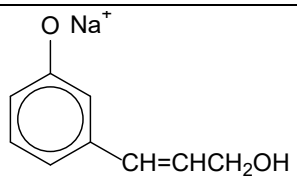
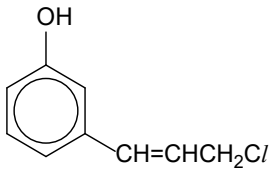
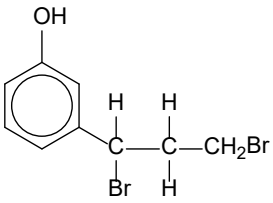
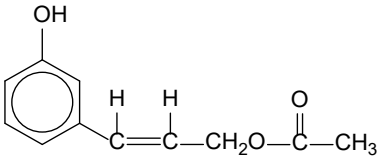
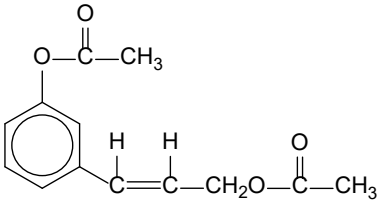
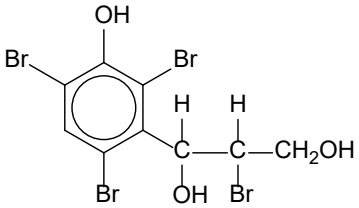
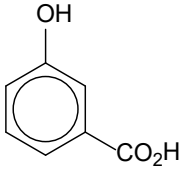
Reagents	Condition	Structure	Type of reaction
(a) sodium	room temp		Redox
(b) sodium hydroxide	room temp		Acid-Base
(c) sodium carbonate	NA	NO REACTION	NA

(d)	phosphorus (V) chloride	room temp, (anhydrous)		Nucleophilic Substitution
(e)	hydrogen bromide	dry HBr		Nucleophilic substitution and Electrophilic Addition **Note:** • Benzylic carbocation intermediate is more stable.
(f)	ethanoic acid	conc. H_2SO_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)	potassium manganate (VII)	$KMnO_4$(aq), H_2SO_4(aq), heat		Vigorous oxidation (Oxidative cleavage of the C=C)

3 (a)

Test
Add Br_2 (in CCl_4) dropwise to each sample in a test-tube at room temperature, in the absence of uv light.

Observations
- For $C_6H_5CH=CH_2$, there is (rapid) decolourisation of orange-red Br_2.
  $C_6H_5CH=CH_2 + Br_2 \longrightarrow C_6H_5CHBrCH_2Br$
- For $C_6H_5CH_2CH_2OH$, there is no decolourisation of orange-red Br_2.

OR

Test
Add two drops of acidified $K_2Cr_2O_7$(aq) to each sample in a test-tube, and heat the mixture in a hot water bath. (Note: DO NOT heat under reflux)

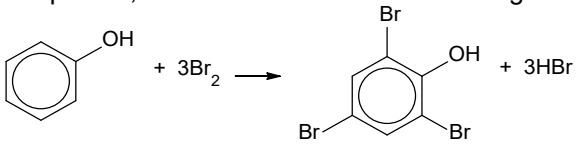
Observations
- For $C_6H_5CH=CH_2$, the solution remains orange.
- For $C_6H_5CH_2CH_2OH$, orange acidified $K_2Cr_2O_7$(aq) turns green.
  $C_6H_5CH_2CH_2OH + 2[O] \longrightarrow C_6H_5CH_2COOH + H_2O$

(b) Test
Add I_2(aq), followed by NaOH(aq) to each sample in a test-tube and warm 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 CHI_3 is formed.
  $CH_3CH_2CH(OH)CH_3 + 4I_2 + 6NaOH \longrightarrow CHI_3 + CH_3CH_2COO^-Na^+ + 5NaI + 5H_2O$

(c) Test
Add Br_2(aq) dropwise to each sample in a test-tube at room temperature, in the absence of uv light.

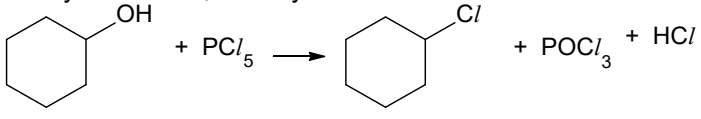
Observation
- For cyclohexanol, there is no decolourisation of orange Br_2 and no white ppt is formed.
- For phenol, there is decolourisation of orange Br_2 and a white ppt is formed.



OR

Test
Add PCl_5(s) to each sample in a test-tube at room temperature.

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



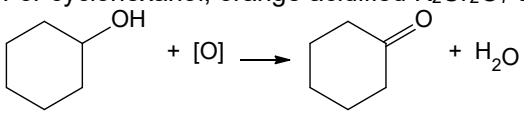
- For phenol, no steamy white fumes are evolved.

OR

Test
Add two drops of $K_2Cr_2O_7$(aq), acidified with H_2SO_4(aq), to each sample in a test-tube, and heat the mixture in a hot water bath. (Note: DO NOT heat under reflux)

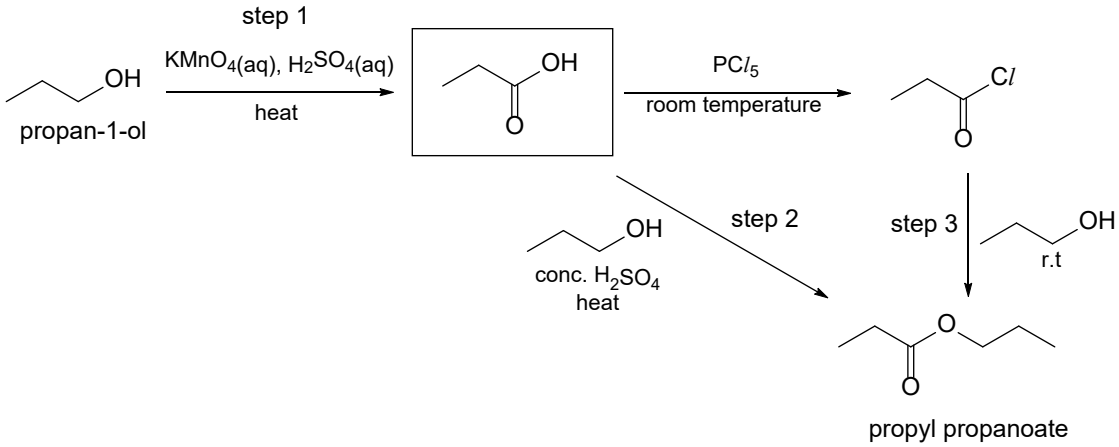
Observation

- For cyclohexanol, orange acidified $K_2Cr_2O_7$ turns green.

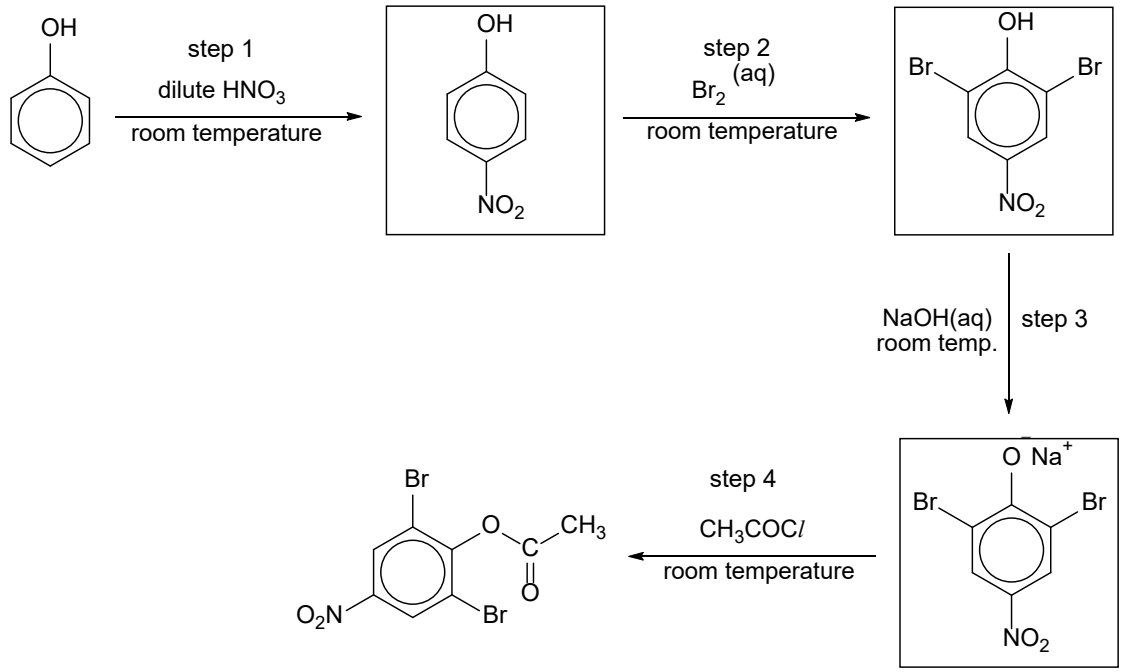


- For phenol, solution remains orange.

4 (a)



(b)



5 (a) Method 1 (using volume of gases only and Avogadro's law)

$C_xH_yOH(l) + Na(s) \rightarrow ½H_2(g) + C_xH_yO^-Na^+(l)$

Vol of H_2 = 10.9 cm^3

$$C_xH_yOH(l) + \frac{4x + y - 1}{4}O_2(g) \longrightarrow xCO_2(g) + \frac{y+1}{2}H_2O(l)$$

$$\text{Change in volume} = \text{Final volume of gases} - \text{Initial volume of gases}$$
$$-54.4 = (\text{Vol. of } O_2 \text{ left} + \text{Vol. of } CO_2 \text{ produced}) - \text{Initial vol. of } O_2$$
$$54.4 = \text{Initial vol. of } O_2 - (\text{Vol. of } O_2 \text{ left} + \text{Vol. of } CO_2 \text{ produced})$$
$$54.4 = (\text{Initial vol. of } O_2 - \text{Vol. of } O_2 \text{ left}) - \text{Vol. of } CO_2 \text{ produced}$$
$$54.4 = \text{Vol. of } O_2 \text{ reacted} - \text{Vol. of } CO_2 \text{ produced}$$
$$\text{Vol. of } O_2 \text{ reacted} = 54.4 + \text{Vol. of } CO_2 \text{ produced}$$
$$= 54.4 + 109$$
$$= 163.4 \text{ cm}^3$$

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

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

(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

∴ **J** is $\underline{C_5H_{11}OH}$

Method 2 (using amt of gases formed)

$C_xH_yOH(l) + Na(s) \longrightarrow \tfrac{1}{2}H_2(g) + C_xH_yO^-Na^+(l)$

$$\text{Amount of } H_2(g) = \frac{10.9}{24000} = 4.54 \times 10^{-4} \text{ mol}$$
$$\text{Amount of } C_xH_yOH = 2 \times 4.54 \times 10^{-4} = 9.08 \times 10^{-4} \text{ mol}$$

$$C_xH_yOH(l) + \frac{4x+y-1}{4}O_2(g) \rightarrow xCO_2(g) + \frac{y+1}{2}H_2O(l)$$

$$\text{Amount of } O_2(g) = \frac{163.4}{24000} = 6.81 \times 10^{-3} \text{ mol}$$
$$\text{Amount of } CO_2(g) = \frac{109}{24000} = 4.54 \times 10^{-3} \text{ mol}$$

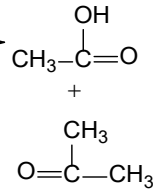
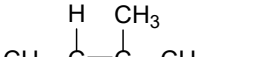
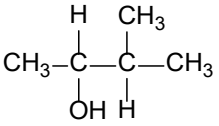
Amount of J	:	Amount of $CO_2(g)$	:	Amount of $O_2(g)$
9.08×10^{-4}	:	4.54×10^{-3}	:	6.81×10^{-3}
1	:	5.00	:	7.50
1	:	x	:	$\frac{4x+y-1}{4}$

∴ x = 5 and $\frac{4x+y-1}{4} = 7.5$

$y = 11$

∴ **J** is $\underline{C_5H_{11}OH}$

(b)

Evidence / Information	Deduction and explanation
J reacts with acidified $K_2Cr_2O_7$.	Oxidation of alcohol occurred. **J** is either a primary or secondary alcohol.
J $\xrightarrow{[O]}$ **K**	Molecular formula of **K** is C_5H_{10}.
K, C_5H_{10} $\xrightarrow{\text{excess of hot acidified conc } KMnO_4}$ 	Vigorous oxidation (oxidative cleavage of C=C) occurred. **K** is  and **J** is 

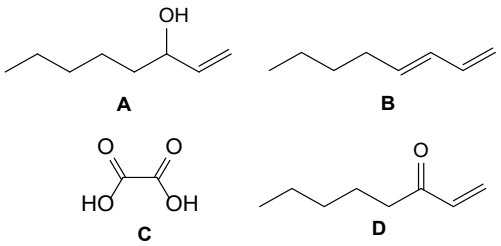
(c) concentrated H_3PO_4, heat

(d) **K** cannot exhibit cis-trans isomerism as there are two identical $–CH_3$ groups bonded to one of the carbon atoms of the C=C bond.

6 **(a)**
- The $–CH(OH)CH_3$ group is absent in **A**.
- **A** contains **one** C=C bond.

Examiner Comments
- Students **should not** describe the $–CH(OH)CH_3$ 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 Br_2** 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)



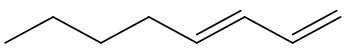
Examiner Comments
- Many students did not realise that **C** and subsequently **B** can be obtained independently without having to obtain the structures of **A** and **B**.
- The thought process for deducing the structures is as follows:

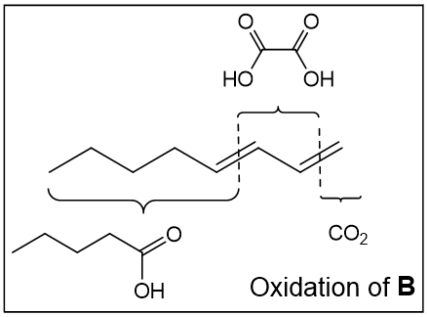
  Molecular formula ($C_8H_{16}O$) and 1 mol of **A** reacts with 1 mol of Br_2 in the dark.
  ⇒ **A** undergoes electrophilic addition with Br_2
  ⇒ **A** contains 1 C=C

  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–)

B is 



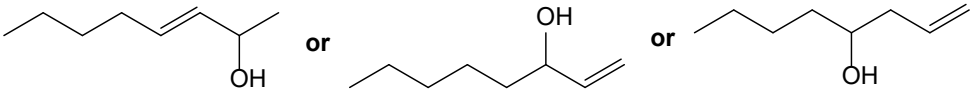
A ($C_8H_{16}O$) $\xrightarrow[\text{heat}]{\text{acidified } K_2Cr_2O_7}$ **D** ($C_8H_{14}O$)

⇒ 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.

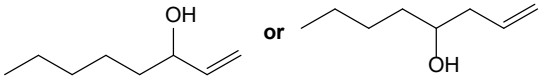
⇒ **A** does not contain a 3° alcohol since **A** undergoes oxidation. (3° alcohols do not undergo oxidation)

⇒ **A** contains a 2° alcohol

⇒ **A** could be 

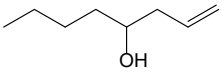
A $\xrightarrow[\text{warm}]{\text{aqueous alkaline } I_2}$ no yellow ppt

⇒ -$CH(OH)CH_3$ group is absent

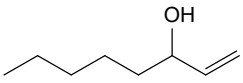
⇒ **A** could be 

A $\xrightarrow[\text{heat}]{\text{conc. } H_3PO_4}$ **B** (only product, ignoring stereoisomers)

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

⇒ **A** cannot be 

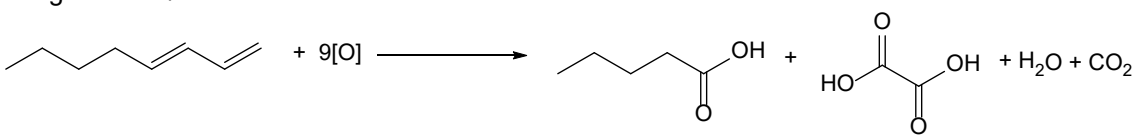
since it gives 2 possible alkenes.

⇒ **A** is 

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

(d) $C_8H_{14} + 9[O] \longrightarrow CO_2 + H_2C_2O_4 + C_4H_9COOH + H_2O$

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.