VICTORIA JUNIOR COLLEGE
CHEMISTRY DEPARTMENT

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JC2 H2 CHEMISTRY
HYDROXY COMPOUNDS (ALCOHOLS & PHENOLS)

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3 Summary

REFERENCES

1 Modern Organic Chemistry by R.O.C. Norman and D.J.Waddington
2 Principles of Organic Chemistry by Peter R.S. Murray
3 A-Level Chemistry by E.N. Ramsden
4 Chemistry in Context by Hill and Holman

LEARNING OUTCOMES

Candidates should be able to:

(a) recall the chemistry of alcohols, exemplified by ethanol:
  (i) combustion
  (ii) nucleophilic substitution to give halogenoalkanes
  (iii) reaction with sodium
  (iv) oxidation to carbonyl compounds and carboxylic acids
  (v) dehydration to alkenes

(b) suggest characteristic distinguishing reactions for the different classes of alcohols (primary, secondary and tertiary alcohols), e.g. mild oxidation

(c) deduce the presence of a $CH_3CH(OH)$– group in an alcohol from its reaction with alkaline aqueous iodine to form tri-iodomethane

(d) recall the chemistry of phenol, as exemplified by the following reactions:
  (i) with bases
  (ii) with sodium
  (iii) nitration of, and bromination of, the benzene ring

(e) explain the relative acidities of water, phenol and ethanol in aqueous medium (interpret as Brønsted-Lowry acids)

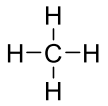
1 Alcohols

1.1 Introduction (Nomenclature/Structure)

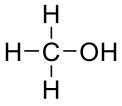
Nomenclature

☑ General formula of $C_nH_{2n+1}OH$ or $\mathbf{C_nH_{2n+2}O}$.

☑ Ending *'–e'* of corresponding alkane is replaced by the suffix *'–ol'*.



methan**e**



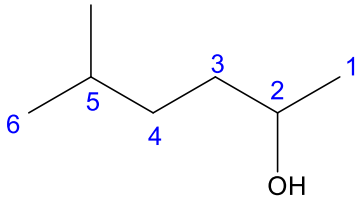
methan**ol**

☑ Position of –OH group in carbon chain is specified by inserting the appropriate *number* between the stem of the name and the '–ol'.

☑ When choosing the parent of an alcohol, identify the longest chain that includes the carbon atom connected to the –OH group.

☑ When numbering the parent chain of an alcohol, the C atom to which the –OH group is attached to should receive the lowest number possible.

Example:

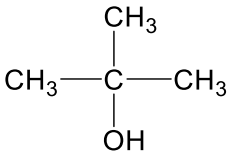


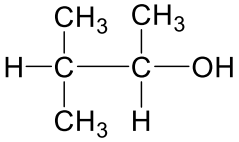
- Longest carbon chain bearing the -OH group is 6 carbons. The -OH group is attached to carbon 2 (not carbon 5) of this chain. Thus, the parent compound is **hexan-2-ol**.
- There is a methyl group ($-CH_3$) attached to carbon 5 of the chain. Thus, the full name of this compound is **5-methylhexan-2-ol**.

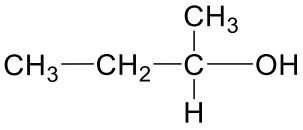
Exercise 1

Name the following alcohols.

CH_3CH_2OH



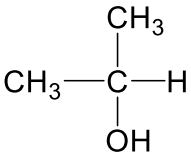




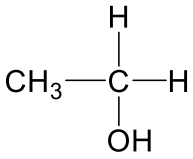
☑ Primary, secondary and tertiary alcohols

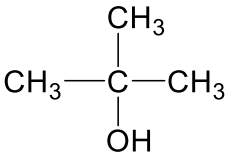
type of alcohol	*number of alkyl groups on C to which OH is attached to*
primary (1°)	1
secondary (2°)	2
tertiary (3°)	3

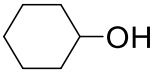
Exercise 2
Classify the following alcohols as primary, secondary or tertiary.

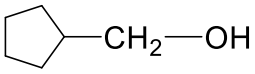


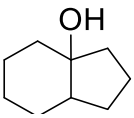
secondary







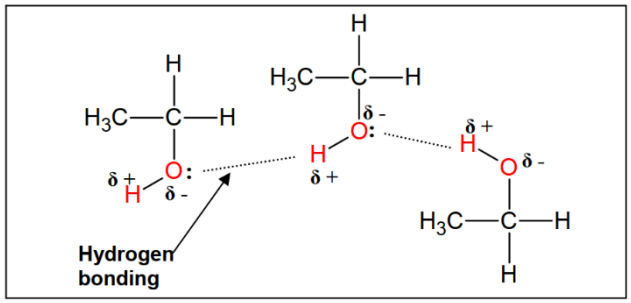




1.2 Physical Properties

1.2.1 Boiling Point

☑ Compared to alkanes of similar M_r, alcohols have **higher boiling points**. This is because there are **intermolecular hydrogen bonds** between alcohol molecules, which are stronger than **instantaneous dipole – induced dipole interactions between alkane molecules**, and require more energy to overcome.



compound	*molecular formula*	*boiling point/ °C*
methane	CH_4	-161.5
methanol	CH_3OH	64.5

☑ *Factors affecting boiling points:*

(i) Number of electrons in the molecule:
Boiling point of alcohol increases with number of electrons as more energy is required to overcome the **stronger instantaneous dipole-induced dipole interactions.**

alcohol	*molecular formula*	*boiling point/ ^oC*
methanol	CH_3OH	64.5
ethanol	CH_3CH_2OH	78.4
propan-1-ol	$CH_3(CH_2)_2OH$	97.0

(ii) Degree of branching:
For constitutional isomers, boiling point of alcohol decreases with greater degree of branching as molecule becomes **more spherical** and **less energy** is required to overcome the **weaker instantaneous dipole-induced dipole interactions** due to **lower surface area for electron interactions**.

alcohol	*molecular formula*	*boiling point/ ^oC*
butan-1-ol	$CH_3(CH_2)_3OH$	118
2-methylpropan-1-ol	$(CH_3)_2CHCH_2OH$	108

1.2.2 Solubility

☑ Shorter chain alcohols (C_1 to C_3) are **miscible with** (are able to mix with) water due to their ability to form **hydrogen bonds** with water molecules.

☑ As the hydrocarbon chain length of the alcohol increases, the **miscibility decreases** because the energy released from forming hydrogen bonds with water molecules is insufficient to overcome the **increasingly stronger instantaneous dipole-induced dipole interactions between the alkyl chains,** and existing hydrogen bonds between water molecules.

1.2.3 Acidity

☑ Alcohols can behave as an acid by donating protons:

$$ROH \rightleftharpoons RO^- + H^+ \qquad (1)$$

☑ Alcohols are **weaker acids** than water; an aqueous solution of alcohol is **neutral**.

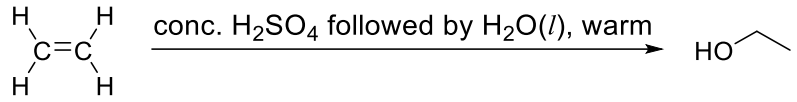
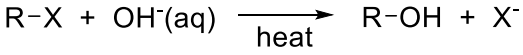
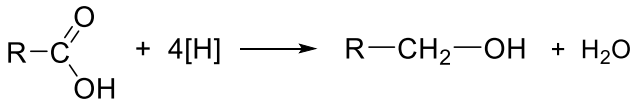
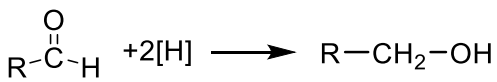
☑ The *lower* acidity of alcohol is due to the *destabilisation* of alkoxide anion (RO^-) by *charge intensification*.

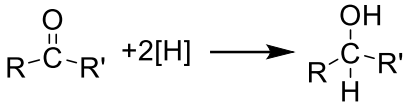
- The alkyl group (–R) exerts a stronger **electron-donating inductive effect** than the H atom.
- This **intensifies** the **negative charge on the oxygen atom** in alkoxide ion and causes alkoxide ion to be **less stable** than hydroxide ion.
- Alkoxide ion is formed less readily and position of equilibrium (1) lies to the left.

1.3 Laboratory Preparation

Alcohols can be synthesised from **alkenes, halogenoalkanes, carboxylic acids or carbonyl compounds (aldehydes or ketones)**.

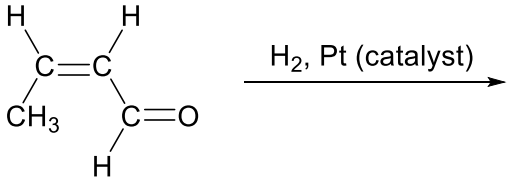
<table>
<tr><th>reagent</th><th>condition</th><th>type of reaction</th><th>remarks</th></tr>
<tr><td>alkenes</td><td>concentrated H_2SO_4 followed by H_2O (l), warm

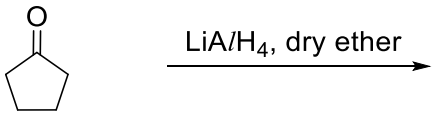
Industrial synthesis of alcohols from alkenes: steam, H_3PO_4 catalyst, high temperature and pressure</td><td>electrophilic addition</td><td>Remember to use Markovnikov's rule to predict the major product formed when steam adds to alkenes.</td></tr>
<tr><td colspan="4">example:
  </td></tr>
<tr><td>halogenoalkanes</td><td>aqueous NaOH, heat</td><td>nucleophilic substitution</td><td></td></tr>
<tr><td colspan="4">example:
  </td></tr>
<tr><td>carboxylic acids</td><td>lithium aluminium hydride (LiAlH$_4$) in dry ether</td><td>reduction</td><td>Forms primary alcohols as a product.</td></tr>
<tr><td colspan="4">example:
  </td></tr>
<tr><td>aldehydes</td><td>• lithium aluminium hydride (LiAlH$_4$) in dry ether, or
• sodium borohydride ($NaBH_4$) in methanol, or
• H_2 gas, Pt catalyst/Ni catalyst with heat</td><td>reduction</td><td>Forms primary alcohols as a product.</td></tr>
<tr><td colspan="4">example:
  </td></tr>
</table>

ketones	• lithium aluminium hydride ($LiAlH_4$) in dry ether, or • sodium borohydride ($NaBH_4$) in methanol, or • H_2 gas, Pt catalyst/Ni catalyst with heat	reduction	Forms **secondary alcohols** as a product.
example: 			

Exercise 3

Draw the structure of the compound formed by the reduction of the following carbonyl compounds.





Exercise 4

What is the structural formula of the compound formed when CH_2CHCH_2CHO reacts with $NaBH_4$?

A $CH_2CHCH_2CO_2H$

B $CH_2CHCH_2CH_2OH$

C $CH_3CH_2CH_2CHO$

D $CH_3CH_2CH_2CH_2OH$

N15/I/23

1.4 Reactions

Candidates should be able to:
(a) recall the chemistry of alcohols, exemplified by ethanol:
  (i) combustion
  (ii) nucleophilic substitution to give halogenoalkanes
  (iii) reaction with sodium
  (iv) oxidation to carbonyl compounds and carboxylic acids
  (v) dehydration to alkenes
(b) suggest characteristic distinguishing reactions for the different classes of alcohols (primary, secondary and tertiary alcohols), e.g. mild oxidation

1.4.1 Complete Combustion

☑ Complete combustion produces **CO_2 and H_2O**. The complete combustion of alcohols can be expressed with a general equation:

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

1.4.2 Nucleophilic Substitution – Formation of Halogenoalkanes

☑ Substitution involves replacement of the hydroxy functional group with a halide.

- Using **hydrogen halides, HX** (X = C*l*, Br or I)

  reagent and condition: HX, heat. For HC*l*, ZnCl_2 catalyst is also required.

$$ROH + HX \xrightarrow[\text{heat}]{} RX + H_2O \text{ (where X = C}l\text{ or Br or I)}$$

- Using **phosphorus trihalides, PX_3** (X = C*l* or Br)

  reagent and condition: PX_3, heat.

$$3ROH + PX_3 \xrightarrow[\text{heat}]{} 3RX + H_3PO_3 \text{ (where X = C}l\text{ or Br)}$$

  *PI_3 is unstable. Thus, to synthesise iodoalkanes in this way, PI_3 is generated *in-situ* by heating the red phosphorus (P) with iodine (I_2). The PI_3 formed will react with the alcohol directly, before it breaks down.

- Using **phosphorus pentachloride, PCl_5** or **thionyl chloride, SOCl_2** (synthesis of chloroalkanes only)

  reagent and condition: PCl_5, room temperature or SOCl_2, heat

equation when PCl_5 is used:

$$ROH + PCl_5 \longrightarrow RCl + POCl_3 + HCl$$

equation when $SOCl_2$ is used:

$$ROH + SOCl_2 \xrightarrow[\text{heat}]{} RCl + SO_2 + HCl$$

Think!

The use of thionyl chloride to synthesise chloroalkanes from alcohols is generally preferred over the use of phosphorus pentachloride. By looking at the equations for both reactions, can you suggest why this is so?

- The reaction between alcohols and PCl_5/$SOCl_2$ can be used to **identify -OH groups in alcohols and carboxylic acids** (but not phenols, which do not react with both compounds)

Identification Test: test for **-OH group in alcohols or carboxylic acids**

⇨ test: **add $SOCl_2$ or PCl_5** to the unknown organic compound.
⇨ observation:
- if alcohol or carboxylic acid present, **steamy white fumes (of HCl) are evolved**
- if alcohol or carboxylic acid absent, no visible reaction.

Exercise 5
Which pair of reagents **cannot** be used to prepare CH_3CH_2Cl?

A $CH_2=CHCl + H_2$

B $CH_3CH_2OH + HCl$

C $CH_3CH_2OH + PCl_5$

D $CH_3CH_2OH + Cl_2$

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1.4.3 Redox (Acid-Metal) Reaction with Sodium

☑ Alcohols react rapidly with **sodium to form alkoxides (RO^-)** . This is a redox reaction where Na is oxidised (oxidation state increases from 0 to +1), while H is reduced (oxidation state decreases from +1 to 0).

Reagents and conditions: Na(s)

$$ROH + Na \longrightarrow RO^-Na^+ + \tfrac{1}{2} H_2$$

Identification Test: test for **organic compounds with -OH group** (alcohol, phenol or carboxylic acid)

⇨ test: **add Na metal** to the unknown organic compound.
⇨ observation:
- if the compound contains an -OH group, effervescence observed. Gas extinguishes lighted splint with 'pop' sound.
- if -OH group is absent from the compound: no visible reaction

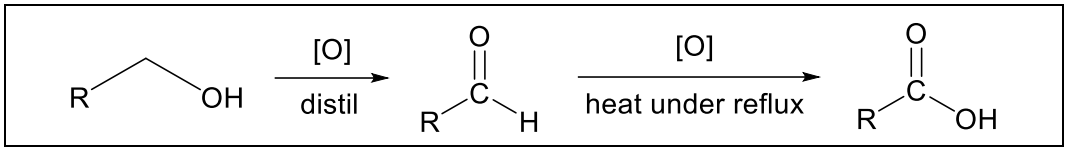
1.4.4 Oxidation to Carbonyl Compounds and Carboxylic Acids

☑ Primary alcohols can be oxidised to either aldehydes or carboxylic acids, depending on the condition, with **$K_2Cr_2O_7$ in the presence of dilute H_2SO_4**.

➔ to obtain the aldehyde: **heat the alcohol with aqueous $K_2Cr_2O_7$ and dilute H_2SO_4 with immediate distillation**.

➔ to obtain the carboxylic acid: **heat the alcohol under reflux with aqueous $K_2Cr_2O_7$ and dilute H_2SO_4**.

Note that acidified $KMnO_4$, being a much stronger oxidizing agent, **oxidises the primary alcohol directly to a carboxylic acid** (it is not possible to obtain the aldehyde).

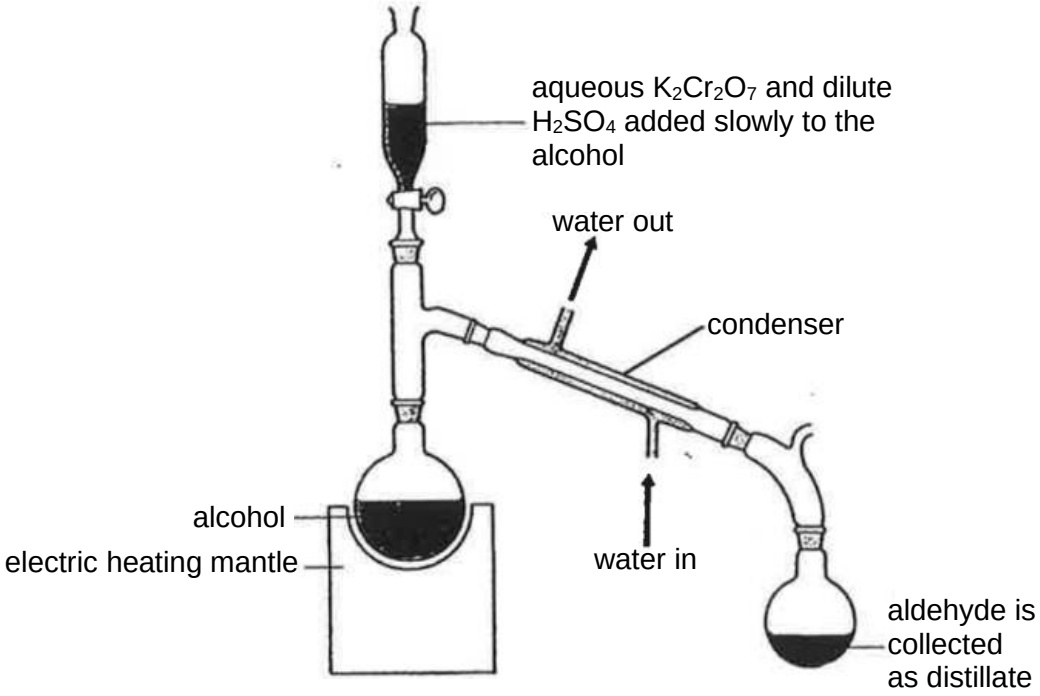


E.g. First, $RCH_2OH + [O] \longrightarrow RCHO + H_2O$

Then, $RCHO + [O] \longrightarrow RCO_2H$

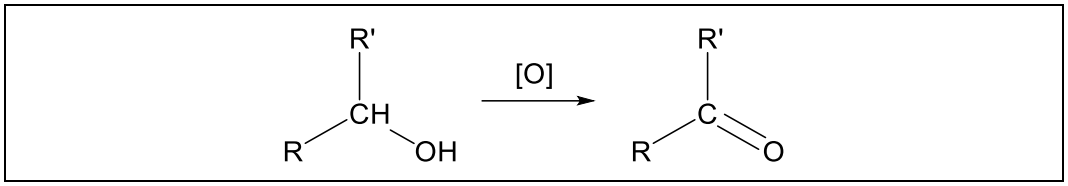
Overall, $RCH_2OH + 2[O] \longrightarrow RCO_2H + H_2O$

setup for reflux with distillation:



☑ Secondary alcohols are oxidised to the corresponding **ketones** by heating with **acidified $K_2Cr_2O_7$.** Ketones are not oxidised further by acidified $K_2Cr_2O_7$.

Reagents and conditions: $K_2Cr_2O_7$(aq), dilute H_2SO_4(aq), heat

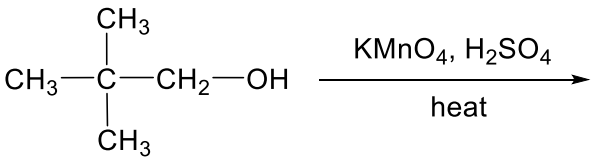


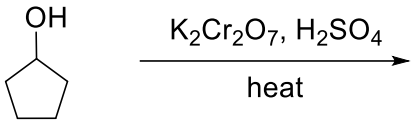
E.g. $RCH(OH)R' + [O] \longrightarrow RCOR' + H_2O$

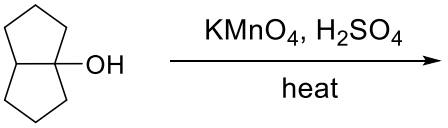
☑ Tertiary alcohols, e.g. $(CH_3)_3COH$, and phenols (compounds where an -OH group is directly bonded to a benzene ring) have **no hydrogen atoms** on the carbon with –OH group (alpha carbon) and cannot be oxidised.

Exercise 6

Give the structural formula of the organic products (if any) when the following alcohols are oxidised under the conditions given.







Identification Test: test for **primary, secondary and tertiary alcohol**

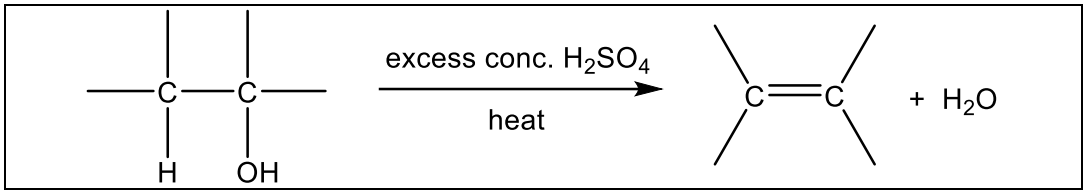
- ⇨ test: warm the alcohol with **$K_2Cr_2O_7$ and dilute H_2SO_4**
- ⇨ observation:
  - if acidified **$K_2Cr_2O_7$** changes from orange to green, primary or secondary alcohol is present.
  - if acidified **$K_2Cr_2O_7$** remains orange, tertiary alcohol is present.

Note that there is no straightforward way to distinguish primary and secondary alcohols (oxidise and test for ketones – more in the next topic on *Carbonyl Compounds*)

1.4.5 Dehydration to Alkenes

☑ Elimination of water from alcohol gives the corresponding *alkene.*

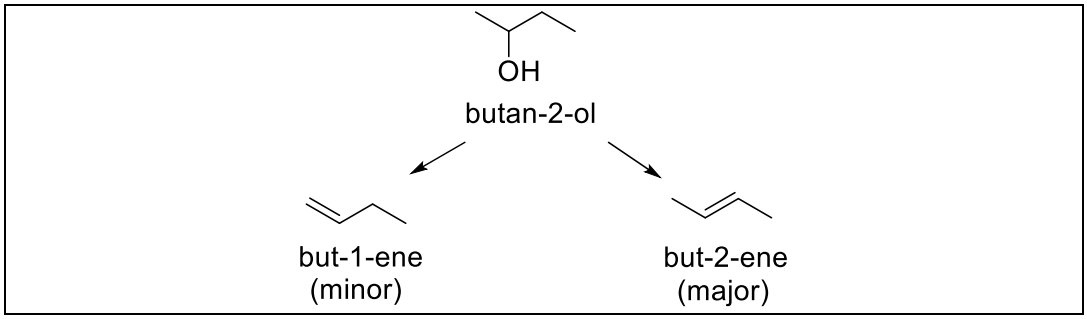
Reagents and conditions: excess concentrated H_2SO_4, heat



☑ *Saytzeff's rule*

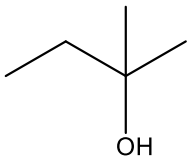
Dehydration of secondary and tertiary alcohols containing *four or more* carbon atoms (e.g. butan-2-ol) yields a mixture of 2 structural alkenes as products.

Alkene produced in *greater abundance* is predicted by Saytzeff's rule which states that the **more substituted alkene will be predominantly formed**, i.e. the one containing the *higher* number of alkyl groups.

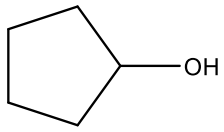


Exercise 7
Give the structural formula of the possible alkenes that are formed when the following alcohols are dehydrated with excess concentrated H_2SO_4. Indicate the major and minor products.

(i)

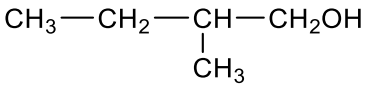


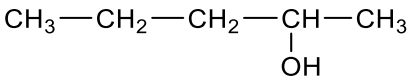
(ii)

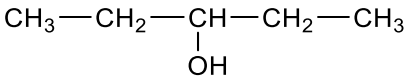


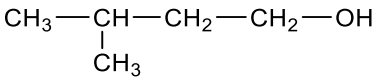
Exercise 8

Which of the following isomers of $C_5H_{11}OH$ gives, on dehydration, the greatest number of different alkenes?

A 

B 

C 

D 

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You are now ready to attempt Tutorial Questions 1 to 3.

1.4.6 Condensation to Esters

☑ In a condensation reaction, two molecules combine to form a larger single molecule with the loss of a small molecule.

☑ Alcohols undergo condensation with **carboxylic acids, or acyl chlorides, (RCOC*l*) to form esters.**

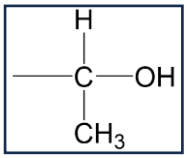
	reaction between alcohols and ***carboxylic acids***	*reaction between alcohols and* ***acyl chlorides***
equation	alcohol + carboxylic acid ⇌ ester + water	alcohol + acyl chloride → ester + hydrogen chloride gas
example	**CH_3CH_2O**H + CH_3COOH ⇌ CH_3CO**OCH_2CH_3** + H_2O	**CH_3CH_2O**H + CH_3COC*l* → CH_3CO**OCH_2CH_3** + HC*l*
reagent & condition	heat the alcohol with carboxylic acid, with **concentrated H_2SO_4 catalyst** 1. The catalyst provides H^+ ions which catalyse the reaction. 2. The catalyst serves as a dehydrating agent, removing water from the equilibrium reaction, shifting position of equilibrium to the right by Le Chatelier's Principle.	add acyl chloride to the alcohol
evaluation	Using acyl chlorides to form esters from alcohols is the greatly preferred method of synthesising esters. As acyl chlorides are more reactive, the reaction goes to completion.	

We will revisit this reaction in *Carboxylic Acids and Derivatives.*

1.4.7 Tri-Iodomethane (Iodoform) Formation

Candidates should be able to:
(c) deduce the presence of a $CH_3CH(OH)$– group in an alcohol from its reaction with alkaline aqueous iodine to form tri-iodomethane

☑ This reaction is positive for an alcohol **containing a methyl group and a hydrogen atom attached to the carbon atom at which the hydroxy group is also attached**, i.e.



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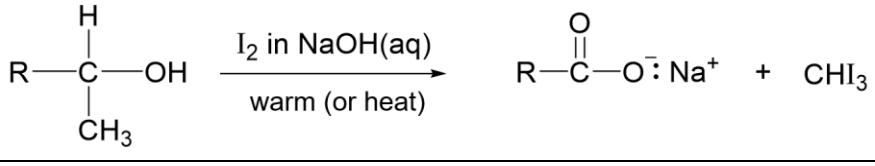
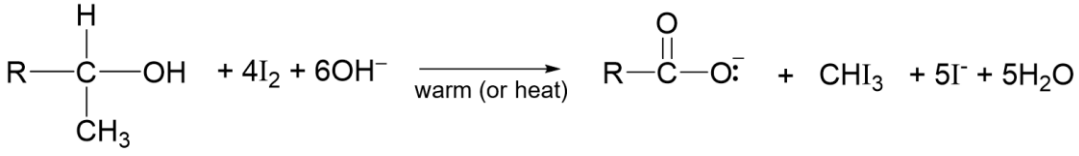
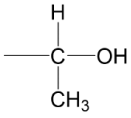
☑ When such an alcohol is **warmed with iodine and aqueous sodium hydroxide, a pale yellow precipitate of tri-iodomethane (iodoform) is formed**. This is considered an **oxidation** reaction.

☑ Reagents and conditions: I_2 in NaOH(aq), warm (or heat)



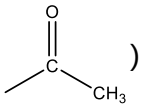
☑ Overall equation:



Identification Test: test for alcohols which contain a  group.

test: warm the alcohol with **iodine and aqueous sodium hydroxide**

⇨ observation:
- if the alcohol contains a $-CH(OH)CH_3$ group, a **yellow precipitate (of CHI_3) is formed**.
- if $-CH(OH)CH_3$ group is absent, no visible reaction is observed.

Note that carbonyl compounds containing a **methyl carbonyl group** () also give a positive iodoform test. We will revisit this reaction in *Carbonyl Compounds.*

Exercise 10
Which of the alcohols show positive iodoform test?

(i) ethanol

(ii) 2-methylpropan-1-ol

(iii) butan-1-ol

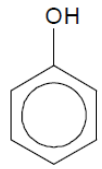
(iv) butan-2-ol

You are now ready to attempt Tutorial Questions 4, 6 and 7.

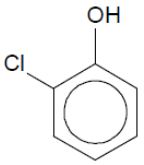
2 Phenols

2.1 Introduction

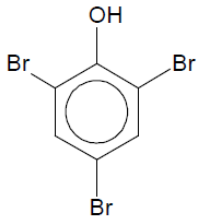
☑ Phenols are compounds containing a hydroxy group attached **directly** to an aromatic ring.



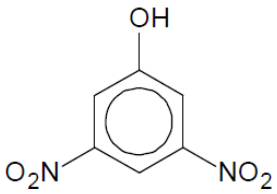
phenol



2-chlorophenol



2,4,6-tribromophenol



3,5-dinitrophenol

2.2 Physical Properties

2.2.1 Appearance

☑ Phenol is a colourless, hygroscopic and crystalline solid (m.p. 42 °C).

2.2.2 Boiling point

☑ Compared to hydrocarbons with similar M_r, phenol has higher boiling point due to the presence of **intermolecular hydrogen bonding** between molecules, which are stronger than instantaneous dipole – induced dipole interactions between alkane molecules, and require more energy to overcome.

2.2.3 Solubility

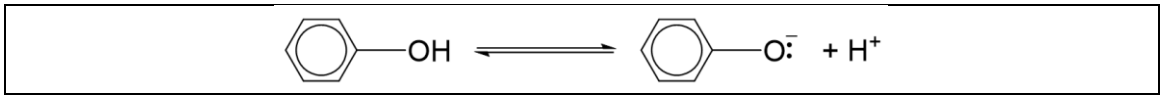
☑ **Partially soluble** in water. The -OH group can engage in hydrogen bonding with water, but the large non-polar aryl group cannot. The solubility of phenol in water increases with temperature.

2.2.4 Acidity

Candidates should be able to:
(e) explain the relative acidities of water, phenol and ethanol in aqueous medium (interpret as Brønsted-Lowry acids)

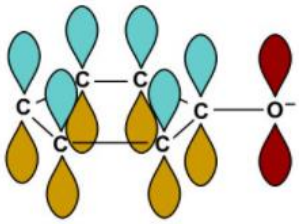
☑ *Relative acidity:* **phenol > water > alcohol**

☑ Phenol can behave as an acid by donating protons.

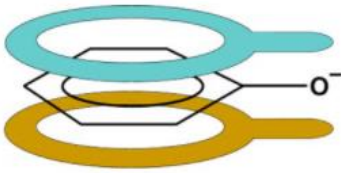


☑ The greater acidity of phenol is due to the stabilisation of **phenoxide anion ($C_6H_5O^-$)** by charge dispersal.

- The p-orbital of oxygen overlaps with the π–cloud of the benzene ring.
- This results in **delocalisation** of negative charge on the oxygen into the **benzene ring**.
- The phenoxide anion is thus stabilised by **charge dispersal**.
- Phenol is thus **more acidic** than water since such delocalisation effect is not found in water.



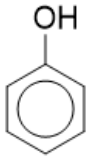
p orbitals in the system

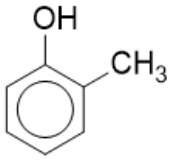


the p orbital on the O overlaps with the p orbitals in the ring

☑ The acidity of phenols is also affected by the presence of different substituents on the benzene ring:

- **electron-donating substituents** (such as $-CH_3$) **decrease the acidity of phenol:**



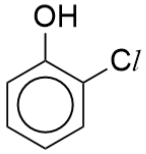


phenol: $pK_a = 10.0$ 2-methylphenol: $pK_a = 10.3$

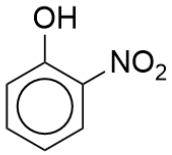
This is because electron-donating groups **increase the electron density** on the O atom in the phenoxide ion, thus making the phenoxide ion less stable. This decreases the acidity of 2-methylphenol compared to phenol.

- **electron-withdrawing substituents** (such as -C*l* or -NO_2) **increase the acidity of phenol**:

phenol: pK_a = 10.0



2-chlorophenol: pK_a = 8.48



2-nitrophenol: pK_a = 7.20

This is because electron-withdrawing groups **decrease the electron density** on the O atom in the phenoxide ion, thus making the phenoxide ion more stable. This increases the acidity of 2-chlorophenol and 2-nitrophenol compared to phenol.

2.3 Reactions

Candidates should be able to:
(d) recall the chemistry of phenol, as exemplified by the following reactions:
(i) with bases
(ii) with sodium
(iii) nitration of, and bromination of, the benzene ring

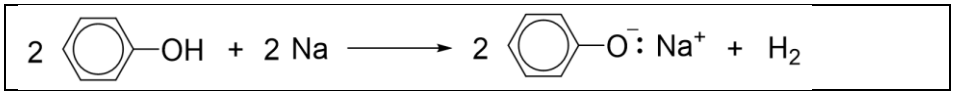
The reactions of phenol are of *two* types:

☑ Redox (acid-metal) and acid-base reactions of the hydroxy group
☑ Electrophilic substitution at the benzene ring

2.3.1 Reactions of the Hydroxy Group

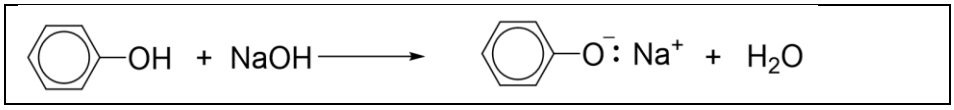
(i) Redox (Acid – Metal) Reaction with Sodium

Regents and conditions: Na(s)



(ii) Acid-Base Reaction (Neutralisation) with Sodium Hydroxide

Reagents and conditions: NaOH(aq)



(iii) Acid-Base Reaction with Sodium Carbonate

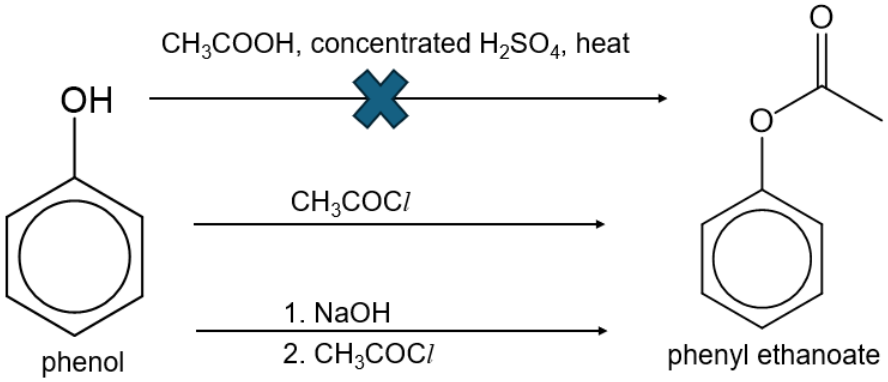
✎ Phenol **does not** react with Na_2CO_3.
✎ Since phenol is a weaker acid than carbonic acid, it is not acidic enough to release CO_2.

Differences in Reactions between Phenol and Alcohol

☑ The hydroxy group of phenol is attached **directly** to the benzene ring. The lone pair of electrons on oxygen is **delocalised** into the benzene ring, giving the C -O bond partial double bond character. This changes the chemistry of phenols compared to alcohols:

alcohols	*phenols*
undergo nucleophilic substitution with reagents such as PCl_5 and $SOCl_2$	do not undergo nucleophilic substitution
weaker acid the presence of **alkyl group**, which exerts an **electron-donating inducting effect**, bonded to the O atom in the conjugate base of alcohol, **intensifies the negative charge on the O atom, destabilising the conjugate base.**	stronger acid the **negative charge** on the O atom in the conjugate base of phenol is **delocalised into the adjacent benzene ring**. This **disperses the negative charge, stabilising the conjugate base**.
stronger nucleophile	weaker nucleophile lone pair on O atom is **delocalised into the adjacent benzene ring** and is **less available to be donated to an electrophile** compared to the lone pair on O atom in an alcohol.

☑ For example, alcohols react with carboxylic acids in the presence of concentrated sulfuric acid to form esters. However, **phenols, being weaker nucleophiles than alcohols, cannot react with carboxylic acids to form esters**. Only **acyl chlorides** react with phenols to form esters. The reaction is even more effective if phenol is converted to phenoxide ion first (by reacting it with NaOH); this is because phenoxide ion is a stronger nucleophile than phenol.



2.3.2 Electrophilic Substitution at the Benzene Ring

☑ The hydroxy group is *strongly activating*. The **delocalisation** of lone pair of electrons on oxygen into the benzene ring **enhances the electron density in the ring** so that phenol is **more susceptible to electrophilic attack**.

☑ Phenol undergoes electrophilic substitution much more readily than benzene, often under much milder conditions.

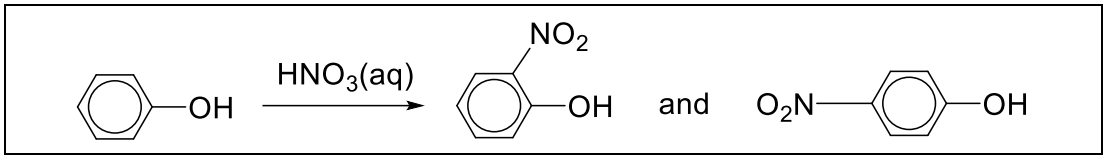
☑ The –OH group is 2,4–directing and strongly activating, often resulting in **polysubstitution.**

(i) Nitration

✎ With **dilute** nitric acid

Phenol reacts with **dilute HNO_3** to form 2-nitrophenol and 4-nitrophenol (a mixture of both isomers is formed)

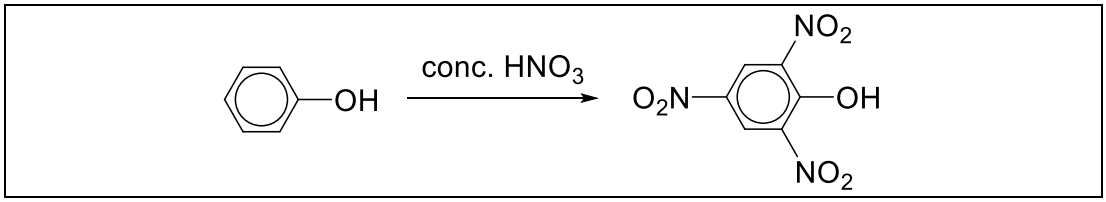
Reagents and conditions: dilute HNO_3, or HNO_3(aq)



✎ With **concentrated** nitric acid

Phenol reacts with concentrated HNO_3 to form 2,4,6-trinitrophenol.

Reagents and conditions: concentrated HNO_3



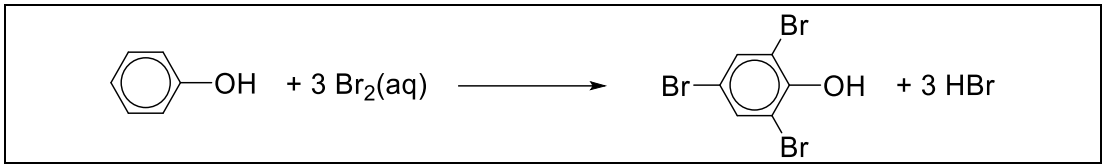
(ii) Halogenation

✎ With **aqueous bromine or aqueous chlorine**

Phenol undergoes **polysubstitution** with $Br_2(aq)$ at room temperature **without** halogen carrier.

Orange $Br_2(aq)$ is **decolourised** and a **white precipitate** of 2,4,6-tribromophenol is formed.

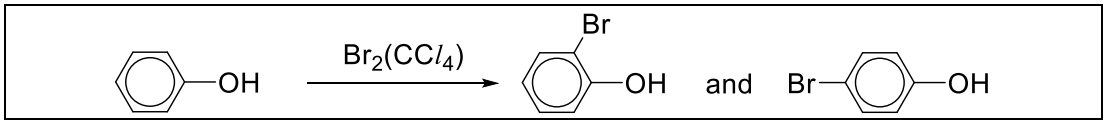
Reagents and conditions: $Br_2(aq)$



✎ With bromine or chlorine in **organic solvent**

Phenol undergoes monosubstitution with Br_2 or CIl_2 in *organic* solvent.

Reagents and conditions: Br_2 (or CIl_2) in $CCIl_4$



Identification Test: test for **highly activated benzene rings** (such as in phenol, but also phenylamine, $C_6H_5NH_2$)

test: add **aqueous bromine** to the compound

⇨ observation:
- if a phenol or phenylamine is present, **aqueous bromine is decolourised and a white precipitate is formed**.
- if a phenol or phenylamine is absent, no visible reaction is observed, if C=C double bond is absent (if C=C double bond is present, aqueous bromine is decolourised but no precipitate is formed)

We will learn more about phenylamine and its other reactions in *Nitrogen Compounds.*

You are now ready to attempt Tutorial Question 5.

2.3.3 Reaction with Neutral $FeCl_3$(aq) – Test for Phenol

☑ Phenol reacts with neutral aqueous iron(III) chloride to form a ***purple*** or ***violet**** *colouration*.
[* the colour of the complex may vary if other substances are attached to the ring.]

☑ This reaction is a useful distinguishing test for phenols in unknown organic compounds. A purple or violet colouration observed on reaction with neutral $FeCl_3$(aq) confirms the presence of phenol.

Identification Test: test for **phenol** (highly specific)**

test: add **neutral $FeCl_3$** to the compound**.**

⇨ observation:
- if a phenol is present, **violet colouration is observed.**
- if a phenol is absent, no visible reaction is observed.

Think!

How do the reactions of aromatic alcohols, e.g. phenylmethanol (benzyl alcohol) or phenylethanol compare with those of primary aliphatic alcohols and phenol?

3 Summary

(a) Complete the following table.

starting compound	reaction type	reagents and conditions	organic product(s) [if any]
$(CH_3)_2CHCH(OH)CH_3$	redox or acid-metal		
		NaOH	
		Na_2CO_3	
		HBr or PBr_3 heat	
		$SOCl_2$, heat or PCl_5	

		$K_2Cr_2O_7$, H_2SO_4(aq) heat	
	elimination		
		CH_3COOH, conc. H_2SO_4, heat	
		CH_3COCl	
		I_2, NaOH (aq) warm	

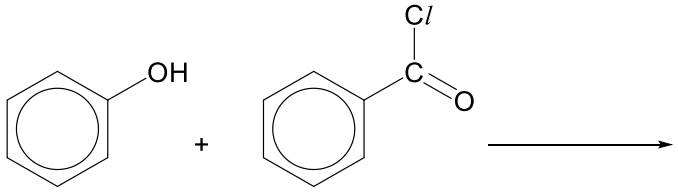
(b) Give the products of the following reactions and balance the equations.

(i) $CH_3CH_2OH + 4I_2 + 6OH^- \xrightarrow{\text{warm}}$

(ii) $CH_3CO_2H + CH_3OH \xrightarrow[\text{heat}]{\text{conc. } H_2SO_4}$

(iii) $CH_3CH_2OH + HCO_2H \xrightarrow[\text{heat}]{\text{conc. } H_2SO_4}$

(iv)



Victoria Junior College
JC2 H2 Chemistry

Hydroxy Compounds Tutorial

Preparation and Reactions of Alcohols

1 Give the skeletal formulae of the possible alkenes formed when pentan-2-ol undergoes dehydration. State which is the major product formed.

2 Suggest synthetic routes to form the following dicarboxylic acids.

(a) $BrCH_2CH_2Br \rightarrow HO_2C{-}CO_2H$

.....

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(b) $HOCH_2CH_2OH \rightarrow HO_2C{-}(CH_2)_2{-}CO_2H$

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N11/III/2(d)

3 **(a)** Calculate the oxidation state of carbon in methanol, CH_3OH.

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(b) Using only the elements C, H and O, draw the structural formulae of three compounds **A**, **B** and **C**, each containing a single carbon atom with oxidation number of zero, +2 and +4 respectively. (Your compound may not contain all three elements.)

A	**B**	**C**

(c) Suggest reagents and conditions for converting methanol into each of the three compounds **A**, **B** and **C**.

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N09/III/2(a)

4 All the isomeric alcohols with the molecular formula $C_5H_{12}O$ are added separately to warm alkaline aqueous iodine.

How many of the isomers will give a pale yellow precipitate (ignore stereoisomers)?

A 0 **B** 1 **C** 2 **D** 3

Properties and Reactions of Phenol

5 **(a)** The strength of an acid is measured by its K_a value. The table below shows pK_a values for phenol, C_6H_5OH, and phenylmethanol, $C_6H_5CH_2OH$.

acid	pK_a at 25 ^oC
C_6H_5OH	10.0
$C_6H_5CH_2OH$	15.4

Explain the relative acidities of phenol and phenylmethanol in aqueous solutions.

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(b) Suggest the structural formula for the organic product formed when phenylmethanol is reacted with hot acidified potassium dichromate(VI).

(c) Suggest why phenol does not undergo a similar reaction with that in **(b)**.

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(d) Describe the chemical test you would carry out in the laboratory to distinguish between phenol and phenylmethanol by giving the reagents, conditions and observations for each compound. Do not use the same type of reaction given in **(b)**. Write an equation for the reaction that occurs.

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Integrated Questions

6 Alcohol **B** forms esters which are responsible for the flavours of various fruits and has the molecular formula $C_5H_{12}O$. Reaction of **B** with acidified potassium dichromate(VI) produces a compound **C**, $C_5H_{10}O_2$. Heating **B** with concentrated sulfuric acid produces **D**, C_5H_{10}. Vigorous oxidation of **D** forms 2-methylpropanoic acid as one of the products.

E, a structural isomer of **B**, decolourises purple potassium manganate(VII) to produce a compound **F**, $C_5H_{10}O$. **E** forms a yellow precipitate **G**, when warmed with alkaline aqueous iodine. When **E** is heated with concentrated sulfuric acid, it produces $CH_3CH_2CH{=}CHCH_3$ as one of the products.

H, a structural isomer of **B**, produces an effervescence with sodium but does not decolourise acidified potassium manganate(VII) upon heating.

Suggest structures for **B**, **C**, **D**, **E**, **F**, **G** and **H** and explain the reactions involved.
[Remark: Explanation should include reaction type and functional group.]

observation	deductions

B	**C**	**D**	**E**
F	**G**	**H**	

J94/I/10

7 Alcohol **J**, C_xH_yOH, is a volatile fungal metabolite whose presence when detected in air can indicate hidden fungal attack on the timbers of a house.

When 0.10 cm^3 of liquid **J** was dissolved in an inert solvent and an excess of sodium metal added, 10.9 cm^3 of gas (measured at 298 K) was produced.

When 0.10 cm^3 of liquid **J** was combusted in an excess of oxygen in an enclosed vessel, the volume of gas (measured at 298 K) was reduced by 54.4 cm^3. The addition of an excess of NaOH(aq) caused a further reduction in gas volume of 109 cm^3 (measured at 298 K).

(a) Use these data to calculate values for x and y in the molecular formula C_xH_yOH for **J**.

Hints!

- Consider the reaction of **J** with Na(s), what functional group can react with Na(s) to give a gas? What is the gas that is associated with Na(s) reaction in organic chemistry?
- After combustion, there was a reduction of 54.4 cm^3. This reduction is due to two processes: the consumption of $O_2(g)$ and the production of $CO_2(g)$.
- The reduction in gas volume after reaction with NaOH gives the volume of $CO_2(g)$. Use this information to determine the number of moles of carbon atoms per mole of **J**.

Alcohol **J** reacts with acidified $K_2Cr_2O_7$, and can be dehydrated to alkene **K**. On treating **K** with an excess of hot acidified concentrated $KMnO_4$, an equimolar mixture of ethanoic acid and propanone is produced.

(b) Use this information to deduce the structural formulae for **J** and **K**, explaining your reasoning.

[Remark: Explanation should include reaction type and functional group.]

observation	**deductions**

J	**K**

(c) Suggest suitable reagents and conditions for the conversion of **J** into **K**.

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(d) Explain whether **K** can show *cis-trans* isomerism.

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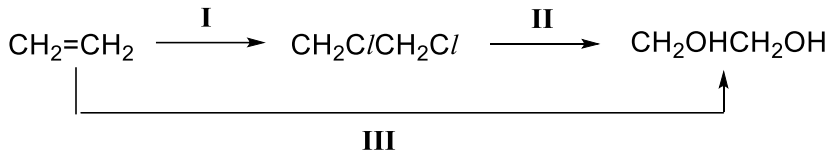
N10/III/3(d)

Victoria Junior College
Hydroxy Compounds Supplementary Questions

Preparation and Reactions of Alcohols

1 There are two ways to attain ethane-1,2-diol from ethane as shown in the reaction scheme below.



Which are the correct reagents and conditions for the reactions **I** to **III** above?

	I	**II**	**III**
A	Cl_2 in CCl_4	aqueous NaOH, heat	cold $KMnO_4$, OH^-
B	PCl_5	aqueous NaOH, heat	cold $KMnO_4$, OH^-
C	PCl_5	alcoholic NaOH, heat	aqueous KOH
D	Cl_2 in CCl_4	alcoholic NaOH, heat	$KMnO_4$, OH^-, heat

2 Bacteria have been suggested as a possible means of cleaning up oil spillages. Some bacteria contain enzymes that can insert one or more oxygen atoms into any carbon-hydrogen bond in an alkane. This converts a water-insoluble alkane into a water-soluble alcohol, e.g.

$$CH_3CH_3 \rightarrow CH_3CH_2OH$$

Which of the following alcohols could be obtained by this process from $(CH_3)_2CHCH_2CH_3$?

1 $(CH_3)_2C(OH)CH(OH)CH_3$
2 $CH_3CH(OH)CH(CH_3)_2$
3 $CH_3CH_2CH(CH_2OH)_2$

A 1, 2 and 3
B 1 and 2 only
C 1 and 3 only
D 1 only

3 Which compound reacts with its own oxidation product (an oxidation which involves no loss of carbon) to give a sweet smelling liquid?

A propanal
B propanoic acid
C propanone
D propan-1-ol

4 In its reaction with sodium, 1 mol of a compound **X** gives 1 mol of $H_2(g)$.

Which compound might **X** be?

1 $(CH_3)_3COH$
2 $CH_3CH(OH)CH_2CHO$
3 $CH_3CH(OH)CH_2OH$

A 1 and 2 only
B 2 and 3 only
C 1 only
D 3 only

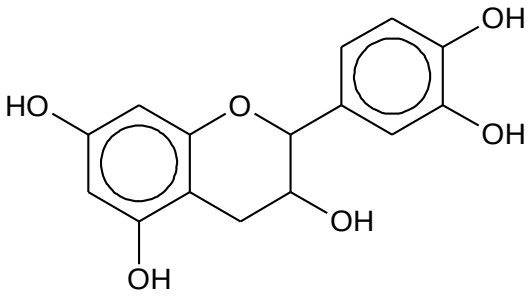
5 Describe the chemical tests you would carry out in the laboratory to distinguish between the following compounds by giving the reagents, conditions and observations for each compound.

(a) phenylmethanol and methylbenzene

(b) propan-1-ol and propan-2-ol

Reactions of Phenol

6 Catechin is an antioxidant found in tea leaves, chocolates and red wine. It is often studied for its function as an inhibitor to the growth of cancer cells, amongst other health benefits.



catechin

The

ring is not involved in any of the following reactions.

Which statement about catechin is correct?

A It can undergo electrophilic addition with $Br_2(aq)$.
B It can undergo oxidation with hot acidified $K_2Cr_2O_7$.
C 1 mol of catechin reacts with 5 mol of NaOH.
D 1 mol of catechin reacts with 4 mol of Na_2CO_3.