RAFFLES INSTITUTION
YEAR 6 H2 CHEMISTRY 2023
Lecture Notes 16 – Hydroxy Compounds

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A **Content**

- I Alcohols (exemplified by ethanol)
  - (i) formation of halogenoalkanes
  - (ii) reaction with sodium; oxidation; dehydration
  - (iii) the tri-iodomethane test
- II Phenol
  - (i) its acidity; reaction with bases and sodium
  - (ii) nitration of, and bromination of, the aromatic ring

B **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)
- (f) describe the reaction of carboxylic acids in the formation of esters on condensation with alcohols, using ethyl ethanoate as an example
- (g) describe the condensation reactions of acyl chlorides with alcohols and phenols
- (h) describe the formation of esters from the condensation reaction of acyl chlorides, using phenyl benzoate as an example

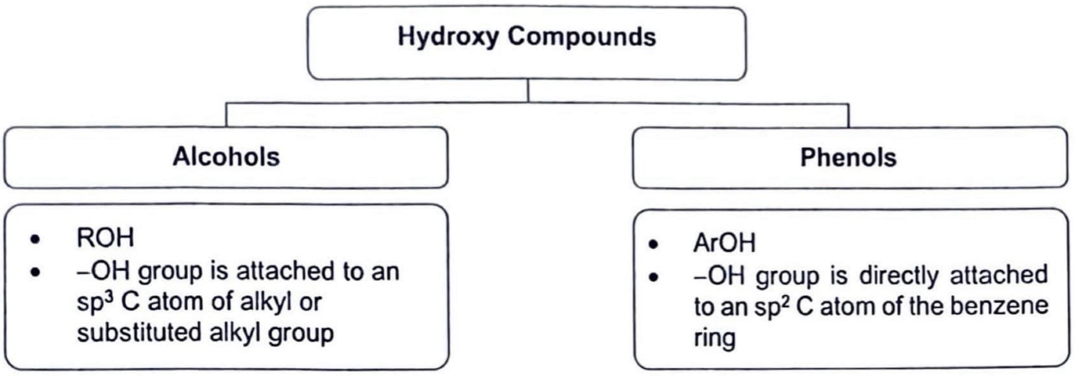
C **Lecture Outline**

D **References & Websites**

1. Organic Chemistry by David Klein
2. Organic Chemistry by John McMurry
3. Chemistry in Context by G C Hill & J S Holman

1 INTRODUCTION

- Hydroxy compounds are compounds containing the **hydroxy (–OH)** functional group.



Hydroxy Compounds

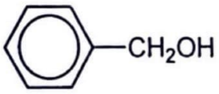
Alcohols

- ROH
- –OH group is attached to an sp^3 C atom of alkyl or substituted alkyl group

Phenols

- ArOH
- –OH group is directly attached to an sp^2 C atom of the benzene ring

eg



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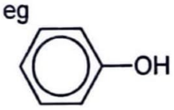
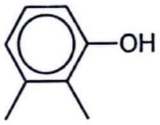




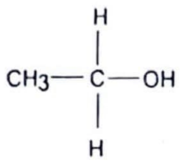
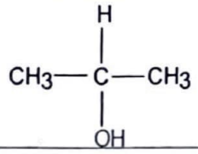
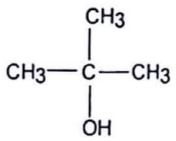
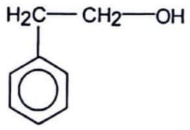
2 ALCOHOLS

2.1 NOMENCLATURE AND CLASSIFICATION

- General formula of $\mathbf{C_nH_{2n+1}OH}$
- Ending '–e' of corresponding alkane is replaced by suffix '**–ol**'
- Alcohols may be classified as a primary, secondary or tertiary alcohol, depending on the number of alkyl groups directly attached to the carbon bearing the hydroxy group.
- Being able to classify alcohols is important because the different classes of alcohols respond differently to some reactions e.g. oxidation.

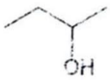
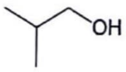
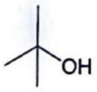
Type of alcohol	Primary (1°)	Secondary (2°)	Tertiary (3°)
Number of R groups on C to which –OH is attached	1	2	3
Structure	$R-\overset{H}{\underset{H}{C}}-OH$	$R-\overset{R}{\underset{H}{C}}-OH$	$R-\overset{R}{\underset{R}{C}}-OH$

- Examples:

Formula	IUPAC Name	Classification
CH_3CH_2OH  $CH_3-\overset{H}{\underset{H}{C}}-OH$	ethanol	primary
$CH_3CH(OH)CH_3$  $CH_3-\overset{H}{\underset{OH}{C}}-CH_3$	propan-2-ol	secondary
$(CH_3)_3COH$  $CH_3-\overset{CH_3}{\underset{OH}{C}}-CH_3$	2-methylpropan-2-ol	tertiary
$C_6H_5CH_2CH_2OH$ 	2-phenylethanol	primary
	cyclopentanol	secondary
$CH_3CH{=}CHCH_2OH$ 	but-2-en-1-ol	primary

■■ Worked Example 1 ■■

Give the structural formulae and the names of all the structural isomers of $C_4H_{10}O$. Classify them into primary, secondary and tertiary alcohols.

isomer				
name	Butan-1-ol	Butan-2-ol	2-methylpropan-1-ol	2-methylpropan-2-ol
classification	Primary	Secondary	Primary	Tertiary

2.2 PHYSICAL PROPERTIES OF ALCOHOLS

(a) Boiling point

- Boiling points of alcohols are much higher than those of alkanes of similar number of electrons.
- Example:

compound	no. of electrons	b.p. / °C	intermolecular interactions
C_2H_5OH	26	78.0	**hydrogen bonding**, pd–pd, id–id
C_3H_8	26	–42	id–id

Since the compounds have a comparable number of electrons per molecule (⇒ similar strength of instantaneous dipole-induced dipole interactions), the alcohol has a much higher boiling point because of its ability to form hydrogen bonds between the molecules.

■■ Worked Example 2 ■■

Draw a labelled diagram illustrating the hydrogen bonding between ethanol molecules.

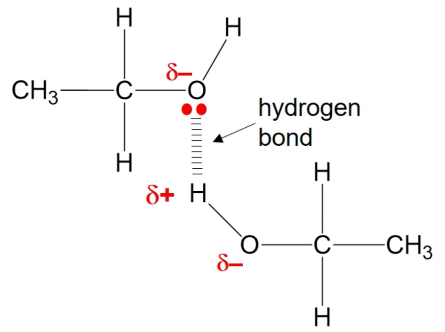


Diagram illustrating hydrogen bonds between molecules must include:

- δ+ and δ– on the H–X bond, where X = F, O or N
- δ– and lone pair of electrons on F, O or N
- dash lines from lone pair of electrons on F, O or N to H
- label "hydrogen bond"

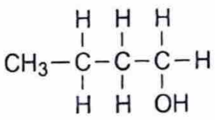
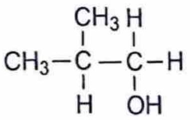
- **Factors Affecting Boiling Points**

① **Length of alkyl chain**: Boiling point increases with increasing length of alkyl chain.

alcohol	methanol	ethanol	propan-1-ol
structural formula	CH_3OH	CH_3CH_2OH	$CH_3(CH_2)_2OH$
boiling point / °C	65	78	97

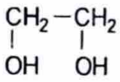
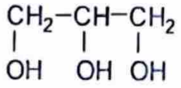
Reason:
More energy is required to break the stronger instantaneous dipole-induced dipole interactions between molecules due to the larger and more polarisable electron cloud.

② **Branching**: Branching of the carbon skeleton lowers boiling point.

alcohol	butan-1-ol	2-methylpropan-1-ol
structural formula	 $CH_3-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-H$	 $CH_3-\underset{H}{\overset{CH_3}{C}}-\underset{OH}{\overset{H}{C}}-H$
boiling point / °C	118	108

Reason:
With branching, molecules become more spherical (more compact). Hence, there is less surface area of contact for instantaneous dipole-induced dipole interaction than in straight-chain isomers.

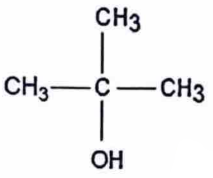
③ **Number of –OH groups**: Boiling point increases with increase in number of –OH groups

alcohol	pentan-1-ol	ethane-1,2-diol	propan-1,2,3-triol
structural formula	$CH_3CH_2CH_2CH_2CH_2OH$	 $\underset{OH}{CH_2}-\underset{OH}{CH_2}$	 $\underset{OH}{CH_2}-\underset{OH}{CH}-\underset{OH}{CH_2}$
boiling point / °C	137	195	290

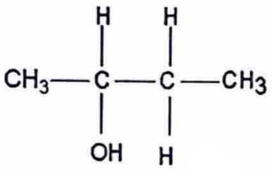
Reason:
An increase in the number of –OH groups leads to more extensive hydrogen bonding. This increases the boiling points of the alcohols.

■■ Worked Example 3 ■■

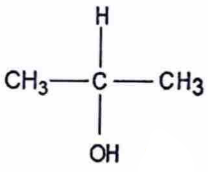
Arrange the following alcohols in order of increasing boiling point.


$CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_3$

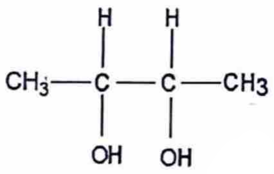
2-methylpropan-2-ol


$CH_3-\underset{OH}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-CH_3$

butan-2-ol


$CH_3-\underset{OH}{\overset{H}{C}}-CH_3$

propan-2-ol


$CH_3-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-CH_3$

2,3-butanediol

Answer: 3<1<2<4

(b) Solubility

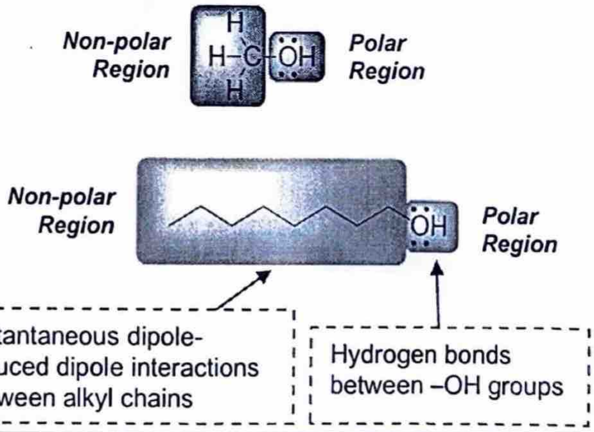
- **Solubility in water**

Alcohols are more soluble in water compared to corresponding alkanes as alcohols are able to form hydrogen bonds with water.

However, as the hydrocarbon chain becomes longer, the respective alcohol shows a marked decrease in solubility. This is because the hydrocarbon portion is non-polar and as the carbon chain increases,

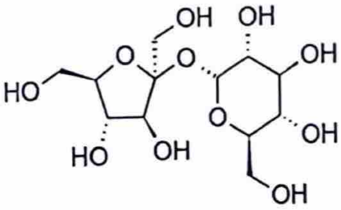
- the instantaneous dipole-induced dipole (id-id) interactions between alcohol molecules becomes predominant.
- In addition, the non-polar hydrocarbon chains get in the way of, and interfere with, the hydrogen bonding between water and alcohol molecules.
- Hence the solvation of long chain alcohol molecules, which would entail breaking the hydrogen bonds between the water molecules and the id-id interactions between the non-polar hydrocarbon chains of alcohol molecules, is too endothermic a process for the positive entropy change of solution to counter.

Name	Structural Formula	Solubility g/100 g H_2O
methanol	CH_3OH	miscible
ethanol	CH_3CH_2OH	miscible
propan-1-ol	$CH_3CH_2CH_2OH$	miscible
butan-1-ol	$CH_3(CH_2)_2CH_2OH$	7.9
pentan-1-ol	$CH_3(CH_2)_3CH_2OH$	2.3
hexan-1-ol	$CH_3(CH_2)_4CH_2OH$	0.6
heptan-1-ol	$CH_3(CH_2)_5CH_2OH$	0.2
octan-1-ol	$CH_3(CH_2)_6CH_2OH$	0.05



An increase in the number of –OH groups <u>increases</u> the number of hydrogen bonds the alcohol can form with water, and hence its solubility in water.

- Example: A molecule of sucrose is large with 12 C atoms and we would expect it to be relatively non-polar. However, the presence of 8 –OH groups allows the molecule to form <u>extensive hydrogen bonding</u> with water. This releases sufficient energy to compensate for the energy needed to break the hydrogen bonds in pure water and in pure sucrose. Hence, sucrose is soluble in water.



sucrose

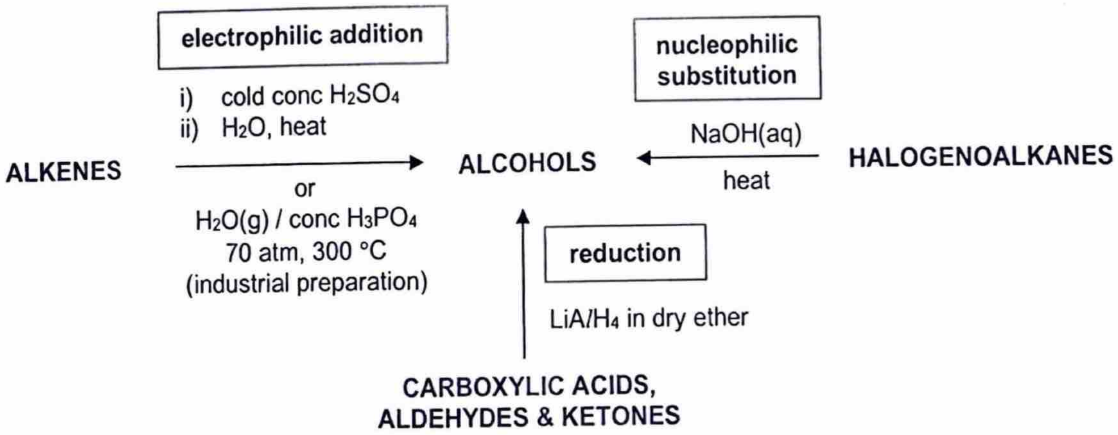
- **Solubility in organic solvents**

- Alcohols are miscible with most organic solvents as the hydrocarbon portions can interact with the hydrocarbon portions of other organic solvents via instantaneous dipole-induced dipole interactions. Some alcohols are useful organic solvents.
- As a result of having a polar –OH group and a non-polar hydrocarbon chain, alcohols can act as solvents to dissolve both water-soluble substances (e.g. KOH, KCN) and organic substances (e.g. alkyl halide).
- E.g. Reaction of RX ⟶ RCN using hot NaCN in aqueous ethanol. The CH_3CH_2– portion of ethanol interacts with the R– of the alkyl halide while the –OH group of ethanol interacts with water and the dissolved ions to improve miscibility between NaCN and RX. *(refer to Halogen Derivatives notes)*

2.3 ACIDITY OF ALCOHOLS

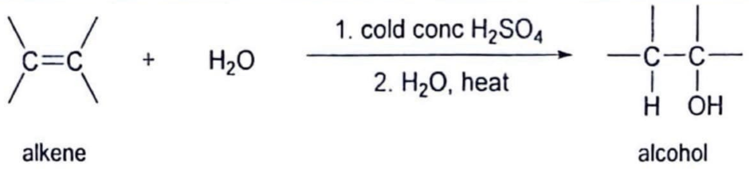
- Alcohols are weaker acids than water and phenols *(refer to Section 4)*.

2.4 PREPARATION OF ALCOHOLS



(a) Hydration of Alkenes *(refer to Alkenes notes)*

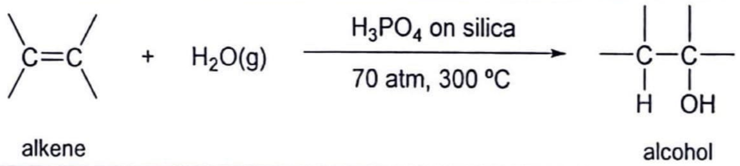
- **Laboratory method**

Electrophilic Addition (hydration of alkene; laboratory method)	
Reagents and conditions	Step 1: cold conc H_2SO_4 Step 2: H_2O, heat

Example: Hydration of ethene to form ethanol

Overall: $CH_2{=}CH_2 + H_2O \longrightarrow CH_3CH_2OH$	
Step (1): $CH_2{=}CH_2 + H_2SO_4 \xrightarrow{\text{cold conc. } H_2SO_4} CH_3CH_2\text{–O–}SO_3H$ ethyl hydrogensulfate(VI)	electrophilic addition
Step (2): $CH_3CH_2\text{–O–}SO_3H + H_2O \xrightarrow{H_2O\text{, heat}} CH_3CH_2\text{–}OH + H_2SO_4$ ethanol	hydrolysis

- **Industrial method** (unsuitable for laboratory use)

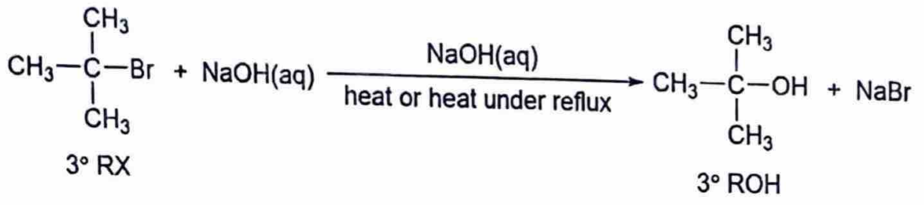
Electrophilic Addition (hydration of alkene; industrial method)	
Reagent	$H_2O(g)$
Conditions	concentrated H_3PO_4 (catalyst) on a silica support, 70 atm, 300 °C
Mechanism	Electrophilic Addition

- For unsymmetrical alkenes, the reaction follows the mechanism-based Markovnikov's rule. During the reaction, the more stable carbocation is formed faster and hence more available to react further to give the major product.

(b) Alkaline Hydrolysis of Halogenoalkanes *(refer to Halogen Derivatives notes)*

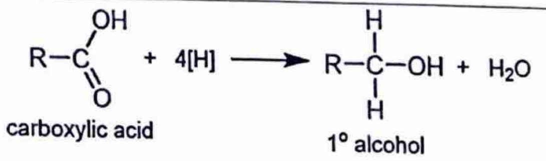
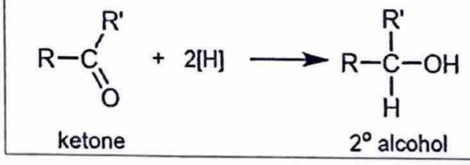
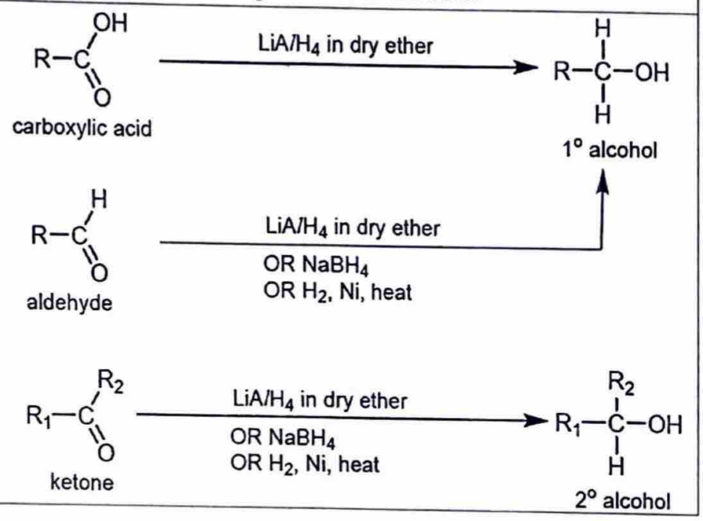
Nucleophilic Substitution (alkaline hydrolysis of halogenoalkanes)	$R\text{-}X + OH^-(aq) \xrightarrow[\text{heat or heat under reflux}]{NaOH(aq) \text{ or } KOH(aq)} R\text{-}OH + X^-(aq)$ halogenoalkane (R-X) where X = C*l*, Br or I alcohol (R-OH)
Reagent	NaOH(aq) or KOH(aq)
Conditions	heat / heat under reflux
Mechanism	Nucleophilic Substitution (S_N1) or (S_N2)

- Examples:

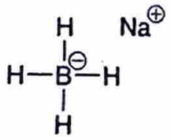
$\underset{1^\circ\ RX}{CH_3CH_2Cl} + KOH(aq) \xrightarrow[\text{heat or heat under reflux}]{KOH(aq)} \underset{1^\circ\ ROH}{CH_3CH_2OH} + KCl$	Nucleophilic Substitution (S_N2)
 $\underset{3^\circ\ RX}{(CH_3)_3C{-}Br} + NaOH(aq) \xrightarrow[\text{heat or heat under reflux}]{NaOH(aq)} \underset{3^\circ\ ROH}{(CH_3)_3C{-}OH} + NaBr$	Nucleophilic Substitution (S_N1)

(c) Reduction of Aldehydes, Ketones and Carboxylic Acids

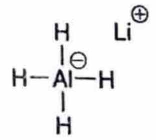
(refer to Carbonyl Compounds & Carboxylic Acids and Derivatives notes)

Equations	Reagents and conditions
  	

- Both $LiAlH_4$ and $NaBH_4$ function as a source of hydride ions (H^-).



sodium borohydride ($NaBH_4$)

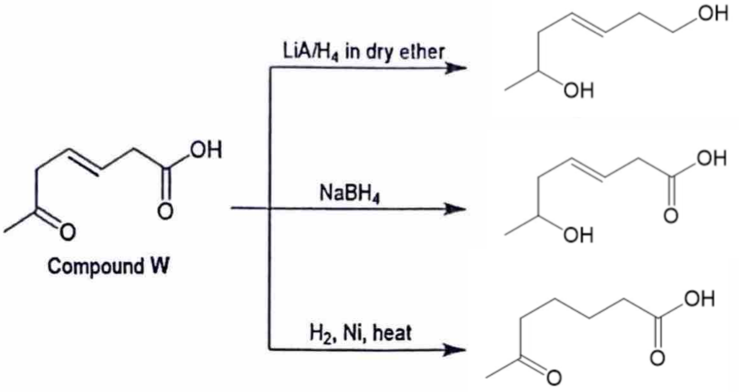


lithium aluminium hydride ($LiAlH_4$)

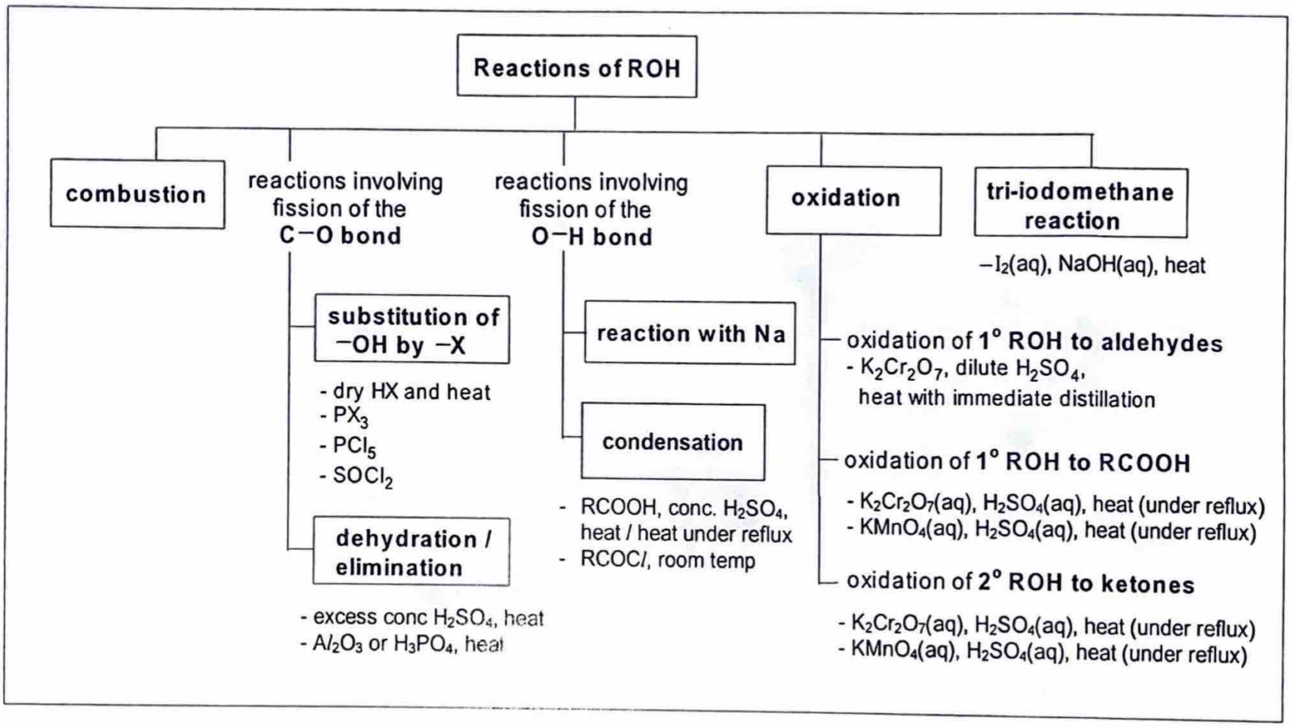
- Note: <u>$NaBH_4$ is a weaker reducing agent</u> and does not reduce carboxylic acid. $LiAlH_4$ is used instead.
- For reduction using $LiAlH_4$, dry ether solvent (i.e. anhydrous condition) is used as $LiAlH_4$ can react with water.

■■ Worked Example 4 ■■

Give the structural formulae of the organic products formed when compound **W** reacts with different reducing agents.



2.5 CHEMICAL PROPERTIES OF ALCOHOLS



(a) Combustion

- Example of combustion of ethanol: $CH_3CH_2OH(l) + 3O_2(g) \xrightarrow{heat} 2CO_2(g) + 3H_2O(l)$
- With a good supply of air, alcohols burn with a pale blue (non-luminous) flame to give carbon dioxide and water.
- With a limited supply of air, alcohols burn with a yellow (luminous) flame and some soot is also formed.

(b) Reactions involving fission of R—OH bond

- **Halogenation** *(Refer to Halogen Derivatives notes)*

Nucleophilic Substitution (halogenation of alcohols)	$R{-}\vdots{-}OH \longrightarrow R{-}X$
Reagents and conditions	• dry HX, heat (X = Cl, Br or I) • PX_3, room temperature (X = Cl, Br or I) • PCl_5, room temperature • $SOCl_2$, room temperature

- Alcohols can undergo nucleophilic substitution reactions in which the –OH group is replaced by a halogen atom X.
- The reaction involves the cleavage of the C–O bond and the formation of the C–X bond.

Using hydrogen halides

Reaction	Reagents and conditions
$R{-}OH + HCl \longrightarrow R{-}Cl + H_2O$	▪ dry HCl, $ZnCl_2$, heat ▪ or conc. HCl, $ZnCl_2$, heat *($ZnCl_2$, a Lewis acid, is sometimes added to promote this reaction.)*
$R{-}OH + HBr \longrightarrow R{-}Br + H_2O$	▪ dry HBr, heat ▪ or KBr, conc. H_2SO_4, heat (Not in syllabus) HBr generated *in situ:* $KBr(s) + H_2SO_4(l) \longrightarrow KHSO_4(s) + HBr(g)$
$R{-}OH + HI \longrightarrow R{-}I + H_2O$	▪ dry HI, heat ▪ or KI, conc. H_3PO_4, heat (Not in syllabus) HI generated *in situ:* $KI(s) + H_3PO_4(l) \longrightarrow KH_2PO_4(s) + HI(g)$ HI(g) <u>cannot</u> be prepared with conc. H_2SO_4 + KI because it would produce I_2 instead of HI. Hence conc. H_3PO_4, a non-oxidising agent, is used in place of conc. H_2SO_4.

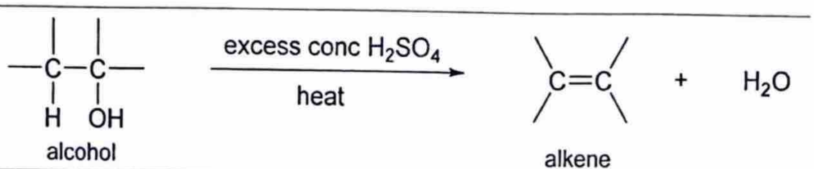
Using phosphorus halides

Reaction	Reagents and conditions
$3R{-}OH + PX_3 \longrightarrow 3R{-}X + H_3PO_3$ phosphorous acid	▪ PX_3, room temperature (X = Cl, Br or I) ▪ red P, I_2 PI_3 is not sufficiently stable to be stored, but it can be generated *in situ:* $2P + 3I_2 \longrightarrow 2PI_3$ **Note:** ▪ <u>Anhydrous</u> condition must be used because PX_3 reacts with water.
$R{-}OH + PCl_5 \rightarrow R{-}Cl + POCl_3 + HCl$ phosphorus oxychloride Observation: Steamy white fumes of HCl produced. (can be used as chemical test for aliphatic –OH group)	▪ PCl_5, room temperature **Note:** ▪ <u>Anhydrous</u> condition must be used because $PCl_5(s)$ reacts with water. *(refer to Periodic Table I notes)*

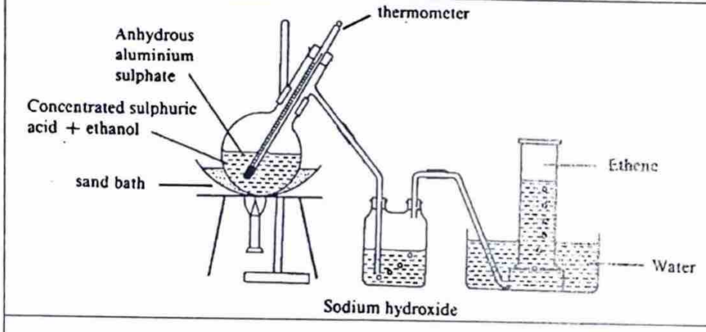
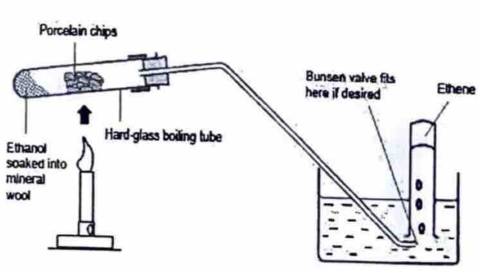
Using thionyl chloride

Reaction	Reagents and conditions
$R{-}OH + SOCl_2 \rightarrow R{-}Cl + SO_2 + HCl$ Observation: Steamy white fumes of HCl produced. (can be used as chemical test for aliphatic –OH group)	▪ $SOCl_2$, room temperature **Note:** ▪ Anhydrous condition must be used because $SOCl_2$ reacts with water. *(refer to Periodic Table I notes)* ▪ This reaction is sometimes preferred than those using PCl_3 or PCl_5 because its side products (i.e. SO_2 and HCl) are gases and can be removed easily.

- **Dehydration** *(refer to Alkenes notes)*

Elimination (dehydration)	
Reagent and conditions	**excess** conc. H_2SO_4, heat or Al_2O_3, heat or H_3PO_4, heat

- Alcohols can undergo dehydration to give alkenes.
- A H atom and the hydroxy group (i.e. –OH) from adjacent carbon atoms in the alcohol molecule are eliminated as a molecule of water.
- Laboratory apparatus for carrying out the reaction:

Using excess concentrated H_2SO_4	**Using hot Al_2O_3**
	

Note:
During the reaction, conc. H_2SO_4 may oxidise some of the ethanol and is itself reduced to SO_2. The acidic SO_2 gas is removed by bubbling the gaseous mixture through sodium hydroxide solution.

(c) Reactions involving fission of RO—H bond

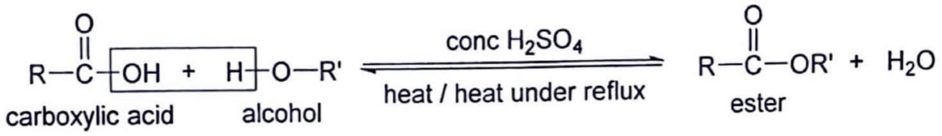
- **Reaction with sodium**

Redox reaction	$\underset{\text{alcohol}}{ROH} + Na \xrightarrow{\text{Na (or K)}} \underset{\text{sodium alkoxide}}{RO^{-}Na^{+}} + \tfrac{1}{2}H_2$
Reagents and conditions	Na or K, room temperature
Observations	Effervescence of H_2 gas that extinguished a lighted splint with a 'pop' sound.

- Alcohols react with reactive metals, such as sodium and potassium, to form alkoxides and hydrogen gas. It involves cleavage of the O–H bond.
- **Note:** Mole ratio of ROH : H_2 = **1 : ½**

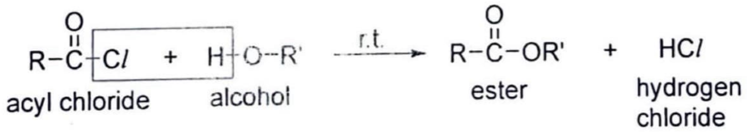
- **Condensation** *(refer to Carboxylic Acids and Derivatives notes)*

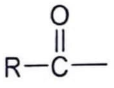
Esterification

Condensation (esterification)	 $\underset{\text{carboxylic acid}}{R-\overset{O}{\overset{\|}{C}}}\boxed{-OH + H}\underset{\text{alcohol}}{-O-R'} \underset{\text{heat / heat under reflux}}{\overset{\text{conc } H_2SO_4}{\rightleftharpoons}} \underset{\text{ester}}{R-\overset{O}{\overset{\|}{C}}-OR'} + H_2O$
Reagents **Conditions**	RCOOH, concentrated H_2SO_4 heat / heat under reflux

- Alcohols react with carboxylic acids in the presence of an acid catalyst (usually conc. H_2SO_4) at an elevated temperature to produce sweet-smelling esters.
- The reaction is slow and reversible. Reaction reaches equilibrium in a few hours.
- Concentrated H_2SO_4 supplies H^+ ions to catalyse the reaction.

Acylation

Condensation (acylation)	 $\underset{\text{acyl chloride}}{R-\overset{O}{\overset{\|}{C}}}\boxed{-Cl + H}\underset{\text{alcohol}}{-O-R'} \xrightarrow{\text{r.t.}} \underset{\text{ester}}{R-\overset{O}{\overset{\|}{C}}-OR'} + \underset{\text{hydrogen chloride}}{HCl}$
Reagents and conditions	RCO*Cl*, room temperature (Note: Anhydrous condition must be used as acyl chlorides hydrolyse readily in water.)
Observations	Steamy white fumes of hydrogen chloride are evolved, which turn damp blue litmus paper red.

- Acylation is the introduction of an acyl group,  $R-\overset{O}{\overset{\|}{C}}-$, into a molecule and the common acylating agent used is acyl chloride.
- Reaction of alcohols with acyl chlorides yield ester.

Comparison between Esterification and Acylation

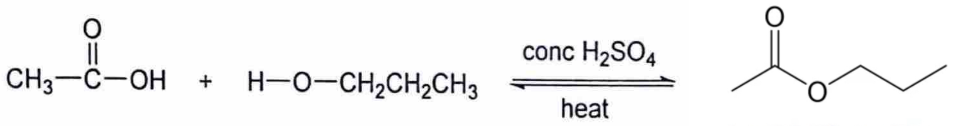
- Acylating agents are more reactive than carboxylic acids.

	Esterification	Acylation
i	Incomplete reaction	Complete reaction
ii	Lower yield	High yield
iii	Heating required	Reaction is held at room temperature
iv	H_2SO_4 catalyst required	H_2SO_4 catalyst is not required

■■ Worked Example 5 ■■

Give the structural formulae and names of the esters formed.

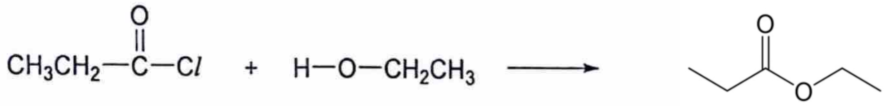
(i)



$CH_3COOH + H{-}O{-}CH_2CH_2CH_3 \xrightleftharpoons[\text{heat}]{\text{conc } H_2SO_4}$

propyl ethanoate

(ii)



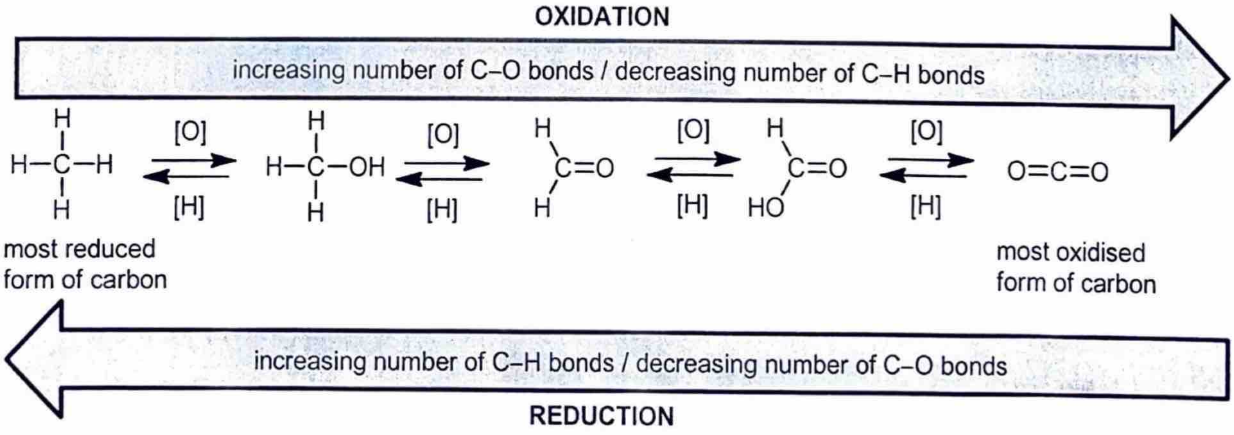
$CH_3CH_2COCl + H{-}O{-}CH_2CH_3 \longrightarrow$

ethyl propanoate

(d) Oxidation

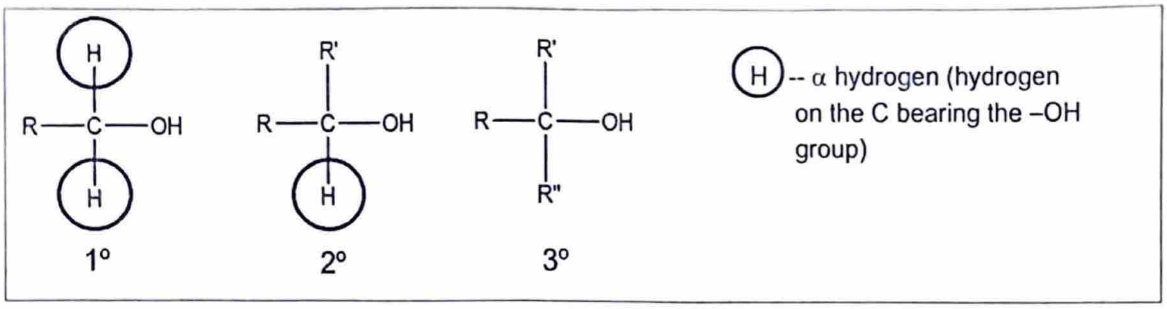
- To determine if an organic compound undergoes oxidation or reduction, we concentrate on the carbon atoms of the starting material and product, and compare the relative number of C–H and C–Z bonds, where Z = an element more electronegative than carbon (usually O, N, or X).

Oxidation results in an increase in the number of C–Z bonds (usually C–O bonds) or a decrease in the number of C–H bonds.
Reduction results in a decrease in the number of C–Z bonds (usually C–O bonds) or an increase in the number of C–H bonds.



$CH_4 \rightleftharpoons CH_3OH \rightleftharpoons HCHO \rightleftharpoons HCOOH \rightleftharpoons O{=}C{=}O$

- The oxidation of an alcohol involves the loss of one or more hydrogens (α-hydrogen) from the carbon bearing the –OH group.



- Common oxidising agents
  - acidified potassium manganate(VII) *(stronger oxidising agent)*
  - acidified potassium dichromate(VI) *(weaker oxidising agent)*

- Product of oxidation is governed by:
  - the type of alcohol (1°, 2° or 3°)
  - the power of the oxidising agent

- Oxidation of alcohols can be employed to **distinguish** between the different classes of alcohols (1°, 2° or 3°).

Primary (1°) Alcohols

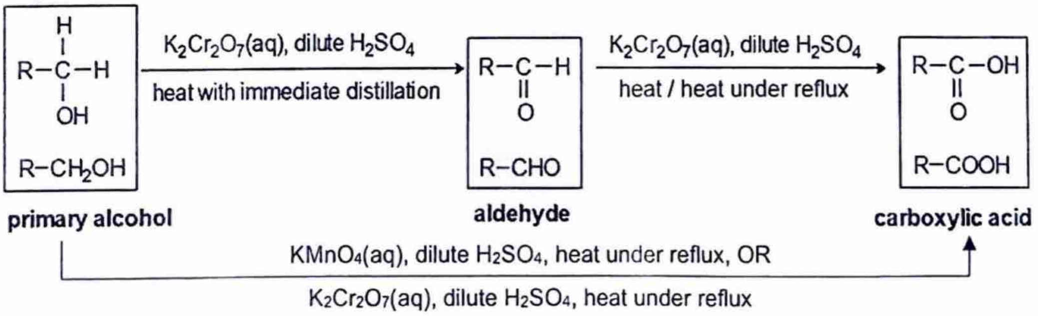
- Primary alcohols are readily oxidised on heating to form aldehydes.

Oxidation (formation of aldehyde)	$R{-}CH_2OH + [O] \xrightarrow[\text{heat with immediate distillation}]{K_2Cr_2O_7(aq),\ \text{dilute } H_2SO_4} R{-}CHO + H_2O$ 1° alcohol aldehyde
Reagents	$K_2Cr_2O_7(aq)$, $H_2SO_4(aq)$
Conditions	heat with **immediate distillation**
Observations	Orange solution turns green.

- In the presence of excess oxidising agent, the reaction proceeds further, yielding the carboxylic acid.

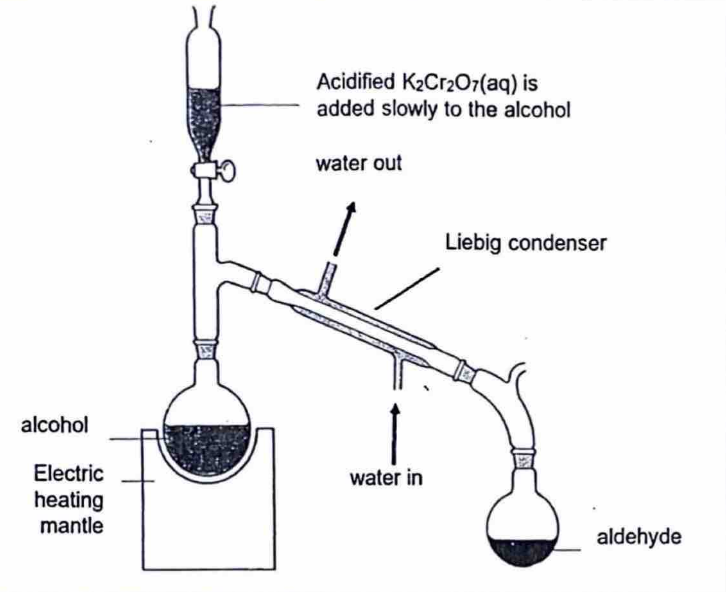
Oxidation (formation of carboxylic acid)	$R{-}CH_2OH + 2[O] \xrightarrow[\text{heat / heat under reflux}]{\substack{K_2Cr_2O_7(aq),\ \text{dilute } H_2SO_4 \\ \text{or } KMnO_4(aq),\ \text{dilute } H_2SO_4}} R{-}COOH + H_2O$ 1° alcohol carboxylic acid
Reagents	$K_2Cr_2O_7(aq)$, $H_2SO_4(aq)$ or $KMnO_4(aq)$, $H_2SO_4(aq)$
Conditions	heat / heat under reflux
Observations	Orange solution turns green (for acidified $K_2Cr_2O_7$) Purple solution decolourises (for acidified $KMnO_4$)

- Summary



- To obtain the aldehyde, i.e. prevent further oxidation of the aldehyde to form the carboxylic acid, we must use acidified $K_2Cr_2O_7$ as the oxidising agent and perform immediate distillation from the alcohol.

- **Laboratory apparatus for the synthesis of aldehyde from primary alcohol:**



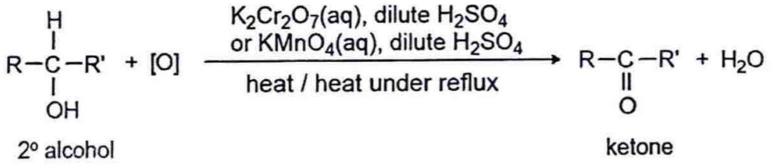
Question:
Why can we isolate the aldehyde by immediate distillation?

Answer:
Aldehydes have generally lower boiling points compared to alcohols (e.g. ethanal has a lower boiling point of 20 °C compared to ethanol's boiling point of 78 °C). This is because aldehydes experience weaker intermolecular interactions (aldehydes only have pd-pd interactions compared to the hydrogen bonding in alcohols).

By keeping the setup at a temperature between the two boiling points, the aldehyde will be distilled off once it is formed.

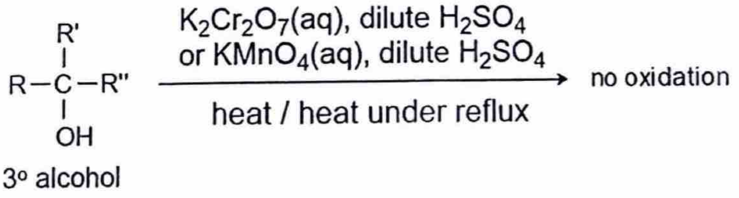
Secondary (2°) Alcohols

- Secondary alcohols are oxidised to the corresponding ketones.

Oxidation (formation of ketones)	 $R-CH(OH)-R' + [O] \xrightarrow[\text{heat / heat under reflux}]{K_2Cr_2O_7(aq),\ dilute\ H_2SO_4\ or\ KMnO_4(aq),\ dilute\ H_2SO_4} R-C(=O)-R' + H_2O$ 2° alcohol → ketone
Reagents	$K_2Cr_2O_7$(aq), H_2SO_4(aq) or $KMnO_4$(aq), H_2SO_4(aq)
Conditions	heat / heat under reflux
Observations	Orange solution turns green (for acidified $K_2Cr_2O_7$) Purple solution decolourises (for acidified $KMnO_4$)

Tertiary (3°) Alcohols

- Tertiary alcohols have no α-hydrogens and hence **cannot** be oxidised under the usual condition.



$$R-C(R')(OH)-R'' \xrightarrow[\text{heat / heat under reflux}]{K_2Cr_2O_7(aq),\ dilute\ H_2SO_4\ or\ KMnO_4(aq),\ dilute\ H_2SO_4} \text{no oxidation}$$

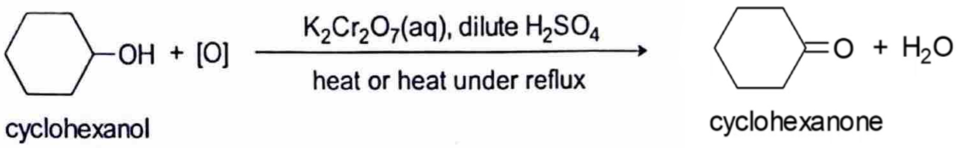
3° alcohol

■■ Worked Example 6 ■■

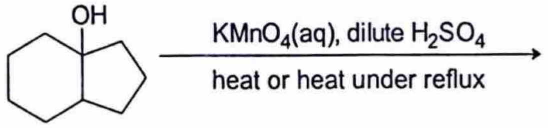
Classify the following alcohols and draw the structure of the oxidation product (if any).

$CH_3CH(OH)CH_3 + [O] \xrightarrow[\text{heat or heat under reflux}]{K_2Cr_2O_7(aq),\ \text{dilute}\ H_2SO_4} CH_3COCH_3 + H_2O$

propan-2-ol propanone



$(CH_3)_3CCH_2OH + 2[O] \xrightarrow[\text{heat or heat under reflux}]{K_2Cr_2O_7(aq),\ \text{dilute}\ H_2SO_4} (CH_3)_3C\text{–}COOH + H_2O$

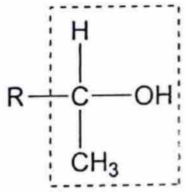


No oxidation

Note: Manganate(VII) ions can be used in a neutral, alkaline or acidic medium, whereas the dichromate(VI) ions functions only in acidic medium.

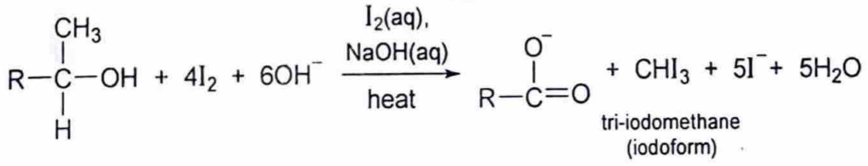
(e) Tri-iodomethane (Iodoform) Test

- The tri-iodomethane (iodoform) test is only positive for an alcohol containing the –CH(OH)CH₃ group.



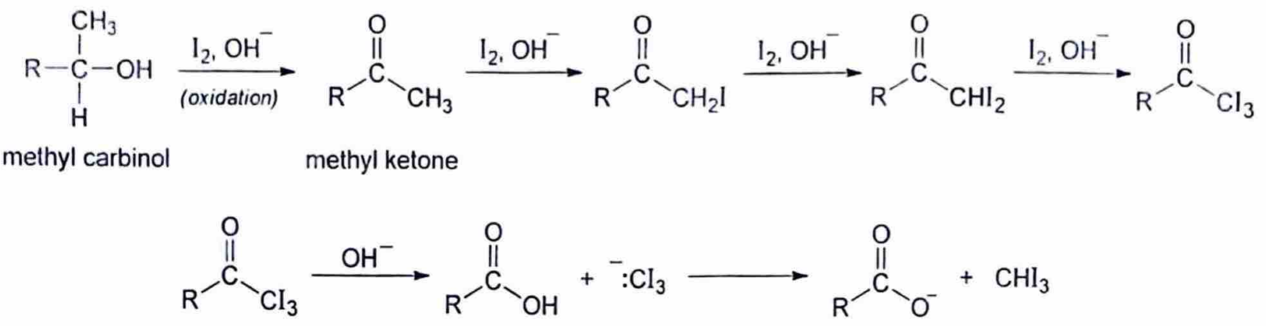
$R\text{–}\overset{\displaystyle H}{\underset{\displaystyle CH_3}{C}}\text{–}OH$

R = H, alkyl or aryl group

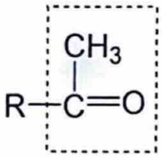
Iodoform Test (oxidation reaction)	 $R\text{–}\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}\text{–}OH + 4I_2 + 6OH^- \xrightarrow[\text{heat}]{I_2(aq),\ NaOH(aq)} R\text{–}\overset{\displaystyle O^-}{C}{=}O + CHI_3 + 5I^- + 5H_2O$ tri-iodomethane (iodoform)
Reagents	$I_2(aq)$, NaOH(aq)
Conditions	heat
Observations	Yellow ppt of CHI_3 formed.

- After reaction, a carboxylate (with one less carbon atom than the starting alcohol) and yellow crystals/ppt of tri-iodomethane (iodoform), CHI_3, are formed.

- Overview of the mechanism



- **Note:** The tri-iodomethane test can also be used to identify ketones with the following structure:

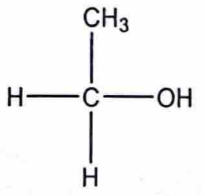

$R-\overset{\displaystyle CH_3}{\overset{|}{C}}=O$

Compounds such as $RCOCH_2I$, $RCOCHI_2$ and $RCOCI_3$ also give a positive tri-iodomethane test *(refer to Carbonyl Compounds notes)*.

■■ Worked Example 7 ■■

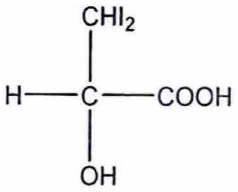
Which of the following compound(s) will give a positive iodoform test?

(a)


$H-\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-OH$

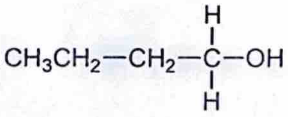
✓

(b)


$H-\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle CHI_2}{\overset{|}{C}}}}-COOH$

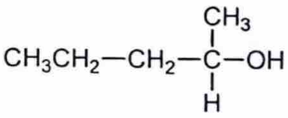
✓

(c)


$CH_3CH_2-CH_2-\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle H}{\overset{|}{C}}}}-OH$

✗

(d)


$CH_3CH_2-CH_2-\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-OH$

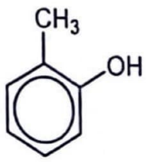
✓

Answer:

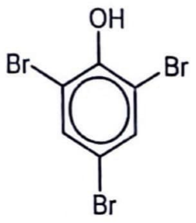
3 PHENOLS

3.1 NOMENCLATURE

- Phenols have an –OH group directly attached to a benzene ring.



2-methylphenol



2,4,6-tribromophenol

4-hydroxybenzoic acid

3.2 PHYSICAL PROPERTIES OF PHENOLS

(a) Appearance

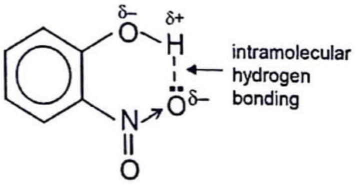
- Phenol is a colourless, hygroscopic, crystalline solid (m.p. 42°C).

(b) Boiling Point

- Phenols have a relatively high boiling point of 181°C compared to other organic compounds of similar electron cloud size due to intermolecular hydrogen bonding.
- Boiling point of substituted phenol depends on the extent of intermolecular hydrogen bonding.

  Example: 2-nitrophenol (217°C) versus 4-nitrophenol (245°C)

  In 2-nitrophenol, intramolecular hydrogen bonding occurs, reducing the sites available to form hydrogen bonding with neighbouring molecules, hence resulting in less extensive intermolecular hydrogen bonding and a lower boiling point. *(refer to Chemical Bonding 1 notes)*



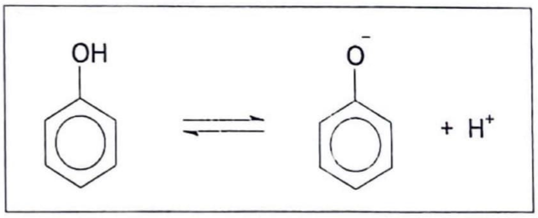
2-nitrophenol

(c) Solubility

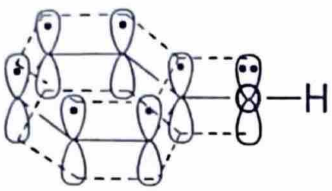
- Phenols are only partially soluble in water at room temperature as its large non-polar benzene ring interferes with the formation of hydrogen bonding between the –OH group and water.
- Solubility is enhanced by heating or by addition of alkali to form a phenoxide salt *(refer to section 4)*.

3.3 ACIDITY OF PHENOLS

- Phenol can behave as an acid by donating a proton, H^+.
- Phenols are stronger acids than alcohols and water. *(refer to Section 4)*
- An aqueous solution of phenol turns blue litmus red.



3.4 CHEMICAL PROPERTIES OF PHENOLS



- A lone pair of electrons on the O atom can interact with the delocalised π electron cloud of the benzene ring and delocalises into the ring.
- This results in the partial double bond character of the C–O bond. This bond is strengthened and hence not easily broken.

Note:

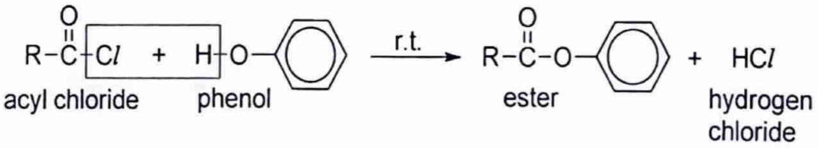
- Phenols differ from alcohols in that they **do not undergo** reactions involving the **cleavage of the C–O bond** due to the **partial double bond character of the C–O bond**.
- Hence, the reactions that phenol undergoes only involve
  - cleavage of the O–H bond in the hydroxy (-OH) group
  - the benzene ring of phenol
  - combustion

(a) Reactions of the hydroxy (–OH) group

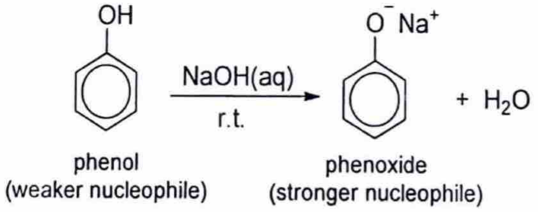
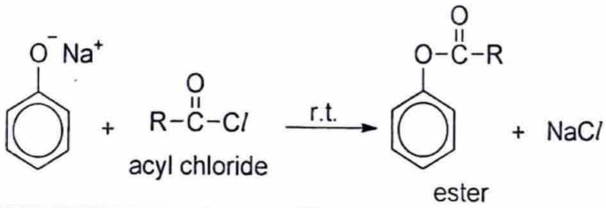
- Unlike alcohols, phenol does **not** react with carboxylic acids but reacts with more powerful acylating agents, e.g. acyl halides, to form phenyl esters.

> **Question**: Why do alcohols react with carboxylic acids to form esters but not phenols?
>
> **Answer**: Phenol is a weaker nucleophile than an alcohol because the lone pair of electrons on the O atom is delocalised into the benzene ring.

- **Reaction with acyl halides to form esters**

(less preferred method)	
Condensation (acylation)	
Reagents and conditions	RCOC*l*, room temperature (Note: Anhydrous condition must be used as acyl chlorides hydrolyse readily in water.)
Observations	Steamy white fumes of hydrogen chloride are evolved, which turn damp blue litmus paper red.

- Acylation is particularly effective when phenol is first reacted with an alkali, e.g. NaOH(aq), to form the phenoxide ion which is a **stronger nucleophile** than phenol.

(more preferred method)	
Step 1: Acid-Base reaction (formation of phenoxide)	
Step 2: Condensation (acylation)	

(b) Reactions involving the benzene ring of phenol

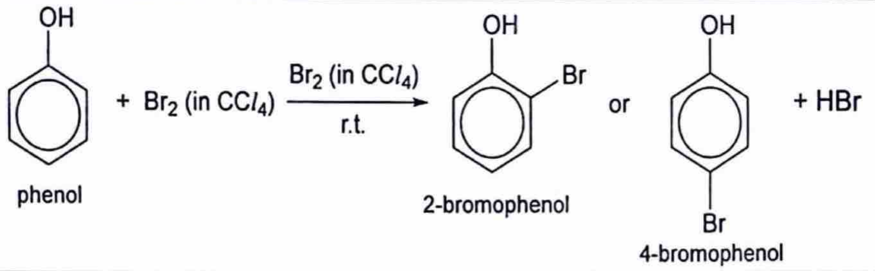
- Reactions involving the benzene ring of phenols are carried out under milder conditions and polysubstitution can occur.

> **Question**: Why does phenol undergo electrophilic substitution under milder conditions compared to benzene?
>
> **Answer**: The hydroxy (–OH) group is electron-donating. The delocalisation of lone pair of electrons on oxygen atom into the benzene ring increases the electron density in the ring. Hence phenol undergoes electrophilic substitution much more readily than benzene. *(refer to Arenes notes)*

- Recall also that the –OH substituent on a benzene ring is 2,4-directing.

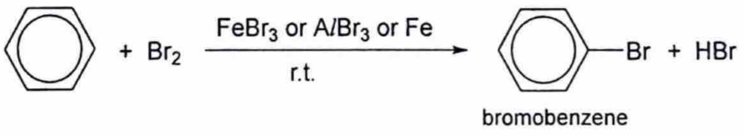
- **Halogenation**

With bromine **in CC*l*₄**

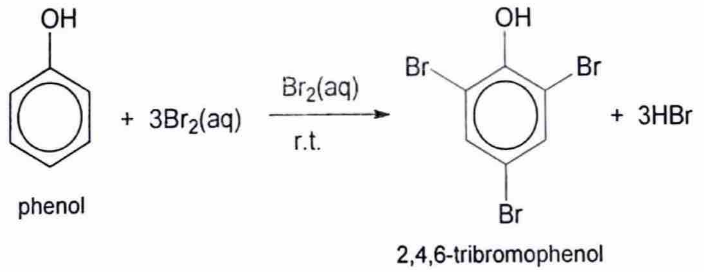
Electrophilic Substitution (halogenation)	
Reagents and conditions	Br_2 **(in CCl_4)**, room temperature
Observations	There is (rapid) decolourisation of the orange-red Br_2.

- Phenol reacts with Br_2 **(in CCl_4)** at room temperature **without** the need of a Lewis acid catalyst to form the **mono-substituted** products, 2-bromophenol or 4-bromophenol.

> Recall from Arenes topic:
>
> Lewis acid catalyst ($FeBr_3$ or $AlBr_3$) or iron filings, Fe, is required for benzene to undergo electrophilic substitution reaction under room temperature and anhydrous condition.



With bromine in **aqueous medium**

Electrophilic Substitution (halogenation)	
Reagents and conditions	Br_2**(aq)**, room temperature
Observations	There is (rapid) decolourisation of the orange Br_2(aq) and a white ppt of 2,4,6-tribromophenol is formed.

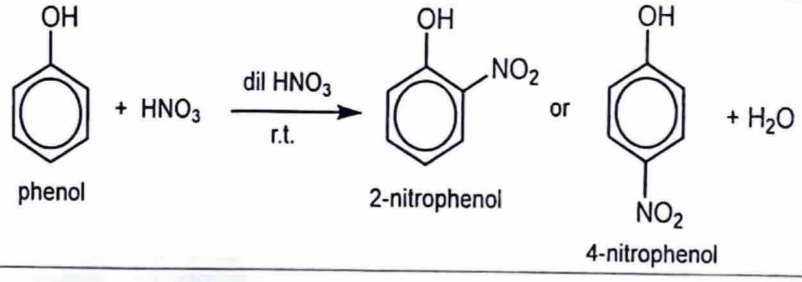
- Phenol reacts with Br_2**(aq)** at room temperature **without** the need of a Lewis acid catalyst and a **tri-substituted** product (2,4,6-tribromophenol) is formed.

Question: Explain why poly-substitution occurs when aqueous Br_2 is used, but mono-substitution occurs when Br_2 (in CCl_4) is used.

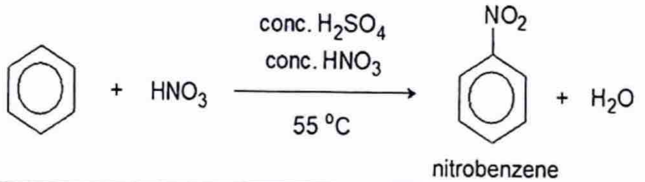
Answer: Phenol undergoes partial ionisation in water to form the phenoxide ion *(refer to Section 4)*. The aromatic ring in the phenoxide ion is more electron-rich and undergoes electrophilic substitution more easily than phenol, hence forming poly-substituted products.

- **Nitration**

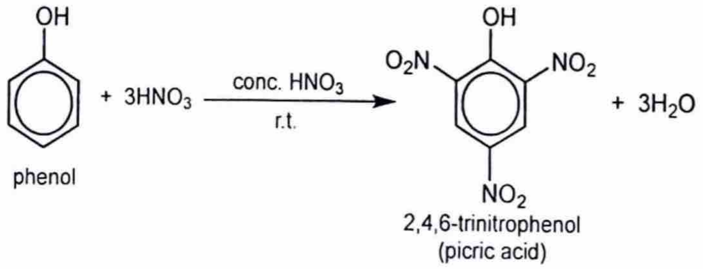
With **dilute** **HNO_3**

Electrophilic Substitution (nitration)	
Reagents and conditions	**dilute** HNO_3 or **HNO_3(aq)**, room temperature

- Phenol reacts with **dilute** HNO_3 at **room temperature** **without** the need of a Bronsted Lowry acid catalyst to form the **mono-substituted** products, 2-nitrophenol or 4-nitrophenol.

> Recall from Arenes topic:
>
> For nitration of benzene, benzene needs to be heated under reflux at 55–60 °C with concentrated HNO_3 and Bronsted Lowry acid catalyst, concentrated H_2SO_4.
>
> 
>
>

With **concentrated** **HNO_3**

Electrophilic Substitution (nitration)	
Reagents and conditions	**conc** HNO_3, room temperature *(note: DO NOT write conc HNO_3(aq))*

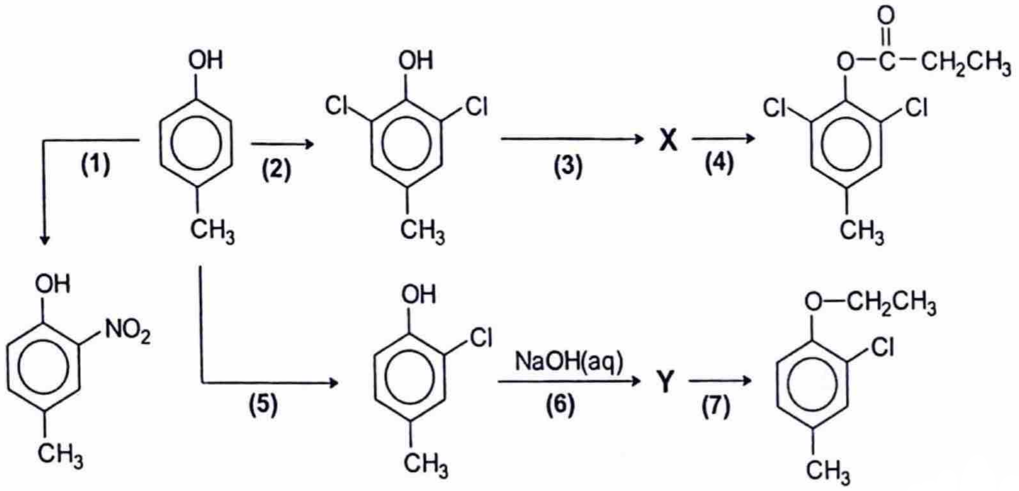
- Phenol reacts with **concentrated** HNO_3 at **room temperature** **without** the need of a Bronsted Lowry acid catalyst to form a **tri-substituted** product (2,4,6-trinitrophenol).

(c) Combustion

- Similar to benzene, phenol burns with a sooty flame because of its high C to H ratio.

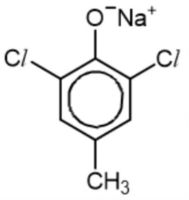
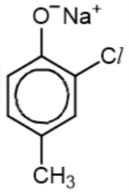
■■ Worked Example 8 ■■

(a) State the reagents and conditions for steps **(1)** to **(5)** and step **(7)** in the reaction scheme shown below.
(b) Give the structural formula for compounds **X** and **Y**.



(a) Step 1: dilute HNO_3, r.t.
Step 2: $Cl_2(aq)$, r.t.
Step 3: NaOH(aq), r.t.
Step 4: CH_3CH_2COCl, r.t
Step 5: Cl_2 in CCl_4, r.t.
Step 7: CH_3CH_2Cl, heat/heat under reflux

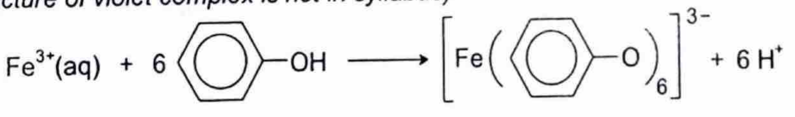
(b)

X	Y
	

3.5 DISTINGUISHING TEST FOR PHENOLS

- Phenol reacts with **neutral $FeCl_3(aq)$** to form a violet compound.

(structure of violet complex is not in syllabus)



violet complex

- This reaction is used to test for the presence of phenol. The colour of the complex may vary if other substituents are bonded to the aromatic ring.

- Other distinguishing tests for phenols:

Use of bromine *(refer to Section 3.4(b) - Halogenation)*

Add Br_2 in CCl_4 drop-wise to the sample in a test-tube at room temperature.

- For phenol, there is (rapid) decolourisation of the orange-red Br_2.
  (Note: Alkenes also give the same observation for this test.)

Add aqueous Br_2 drop-wise to the sample in a test-tube at room temperature.

- For phenol, there is (rapid) decolourisation of the orange $Br_2(aq)$ and a white ppt of 2,4,6-tribromophenol is formed.
  (Note: Alkenes also decolourises orange $Br_2(aq)$ but no white ppt is formed.)

Use of aqueous NaOH *(refer to Section 4.2 – Reaction of phenol with sodium hydroxide)*

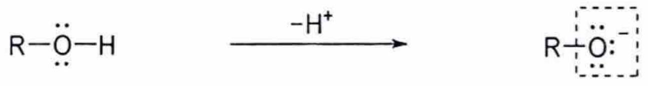
Add aqueous NaOH dropwise to the sample in a test-tube at room temperature.

- Phenol dissolves to give a colourless solution.
  (For other liquid compounds which are insoluble in water and does not react with NaOH(aq), e.g. cyclohexanol, two immiscible layers will be formed.)

4 ACIDITY OF ALCOHOL, PHENOL AND WATER

Recall from Acid-Base Equilibria topic: • A Bronsted-Lowry base is a proton acceptor. • A Bronsted-Lowry acid is a proton donor. • The **larger** the K_a value, the **stronger** the acid. • The **smaller** the pK_a value, the **stronger** the acid.	For a weak acid, $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$ $K_a = \frac{[H^+][A^-]}{[HA]}$ units: mol dm^{-3} $pK_a = -\lg K_a$

To compare the acidity of alcohols and (substituted) phenols, we need to compare the stability of their conjugate bases:



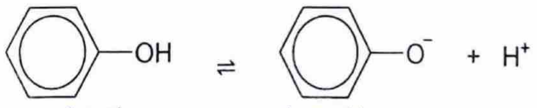
R = H, alkyl
or aryl group

to evaluate the acidity of this compound ... ... deprotonate... ... and assess the stability of the conjugate base

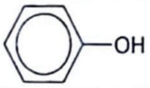
The more stable the conjugate base, the stronger the acid.

4.1 COMPARING ACIDITY OF PHENOL, ALCOHOL AND WATER

- Equations showing the partial dissociation of alcohol, water and phenol in aqueous medium:

$ROH \rightleftharpoons RO^- + H^+$ alcohol alkoxide $HOH \rightleftharpoons HO^- + H^+$ water hydroxide  phenol phenoxide	The **more stable** the conjugate base, • the equilibrium position for the acid dissociation lies more to the right, • the **stronger** the acid

- Comparison of K_a values:

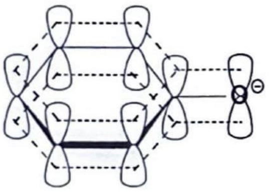
Compound	Formula	K_a / mol dm^{-3}	Remarks
ethanol	CH_3CH_2OH	1.3×10^{-16}	K_a increases from ethanol < water < phenol
water	H_2O	1.0×10^{-14}	
phenol		1.3×10^{-10}	

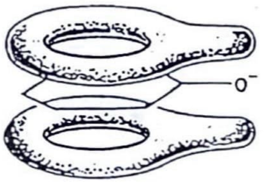
Relative acidity: Phenol > Water > Alcohol

- To explain the relative acidity of the three compounds (phenol, alcohol and water), we must compare the relative stability of their conjugate bases.

Stability of phenoxide ion (PhO^-) vs hydroxide ion (OH^-)

- Compared to OH^-, the phenoxide ion is more stable due to **resonance stabilisation.**
- The p-orbital of the oxygen atom overlaps with the π electron cloud of the benzene ring.
- This results in the delocalisation of **negative charge** on oxygen into the ring, i.e. dispersal of the negative charge over the ring.
- Hence, the phenoxide ion is said to be resonance stabilised.





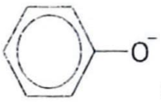
Stability of alkoxide ion (RO^-) vs hydroxide ion (OH^-)

- Compared to OH^-, the alkoxide ion, RO^-, is less stable due to the electron-donating effect of the alkyl group which increases the electron density and intensifies the negative charge on the oxygen atom.

$R \rightarrow \ddot{\underset{\cdot\cdot}{O}}{:}^-$

- Hence, the anion is destabilised.

In conclusion

Since relative stability of conjugate bases:  > OH^- > RO^-

Relative acidity: Phenol > Water > Alcohol

■■ Worked Example 9 ■■

Predict and explain if an aqueous solution of an alcohol will turn damp blue litmus red.

Solution:

- Alcohols have Lower acidity than water. An aqueous solution of an alcohol is effectively Neutral and will Not turn damp blue litmus paper red.

$$ROH \rightleftharpoons RO^- + H^+ \quad \text{-- (1)}$$
$$HOH \rightleftharpoons HO^- + H^+ \quad \text{-- (2)}$$

- The Electron donating alkyl group Increase the electron density on the oxygen atom in the alkoxide ion, RO^-, and Intensifies the negative charge.
- This causes the alkoxide ion to be Unstable and makes it more ready to accept protons.
- The equilibrium position in equation (1) above lies comparatively Less to the right than in (2), indicating that alcohol is a weaker acid than water.
- Hence alcohol does not dissociate in water to give a significant $[H^+]$ which is required to turn damp blue litmus red.

4.2 REACTIONS WITH SODIUM, SODIUM HYDROXIDE AND SODIUM CARBONATE

- **Reaction of alcohol with sodium, sodium hydroxide and sodium carbonate**

- Alcohols being weak acids, react **only** with **reactive metals** such as sodium.

$ROH + Na(s) \longrightarrow RO^-Na^+ + ½ H_2(g)$ E.g. $CH_3CH_2OH(l) + Na(s) \longrightarrow CH_3CH_2O^-Na^+(s) + ½ H_2(g)$	**Observations:** Effervescence of H_2 gas that extinguished a lighted splint with a 'pop' sound. **Note:** Mole ratio of ROH : H_2 = **1 : ½**

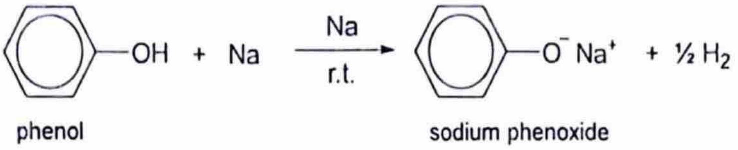
- Alcohols do **not** react with hydroxides or carbonates or hydrogen carbonates.

  Alcohol is too weak an acid to react with NaOH(aq), Na_2CO_3(aq) or $NaHCO_3$(aq).

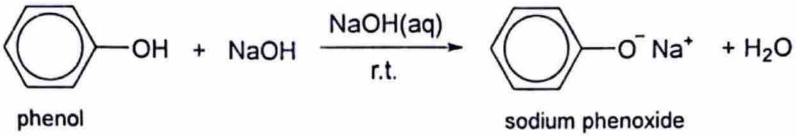
  $CH_3CH_2OH + NaOH(aq) \longrightarrow$ no reaction
  $CH_3CH_2OH + Na_2CO_3(aq) \longrightarrow$ no reaction
  $CH_3CH_2OH + NaHCO_3(aq) \longrightarrow$ no reaction

- **Reaction of phenol with sodium, sodium hydroxide and sodium carbonate**

Reaction with **Sodium**

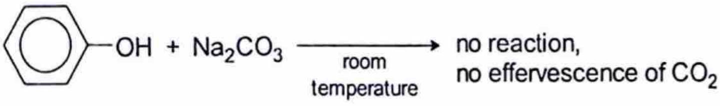
Redox reaction	
Reagents and conditions	Na, room temperature
Observations	Effervescence of H_2 gas that extinguished a lighted splint with a 'pop' sound.

Reaction with **Sodium Hydroxide**

Acid-Base reaction	
Reagents and conditions	NaOH(aq), room temperature
Observations	Phenol dissolves in NaOH(aq) to give a colourless solution.

- Phenols do <u>not</u> react with carbonates or hydrogen carbonates.

  Phenol is too weak an acid to react with Na_2CO_3(aq) or $NaHCO_3$(aq).



- **Summary**

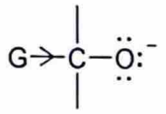
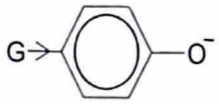
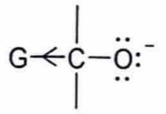
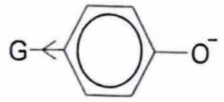
Compound	Reaction with		
	Na(s)	NaOH(aq)	Na_2CO_3(aq) (or $NaHCO_3$(aq))
alcohol	√	no rxn	no rxn
phenol	√	√	no rxn
carboxylic acid *(refer to Carboxylic Acids and Derivatives notes)*	√	√	√

Note: The above three reagents (Na, NaOH and Na_2CO_3) can be used to **<u>distinguish</u>** between the three classes of organic compounds (alcohols, phenols and carboxylic acids).

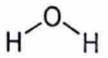
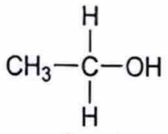
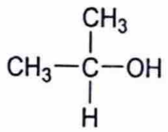
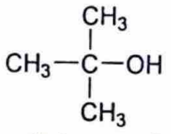
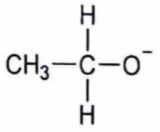
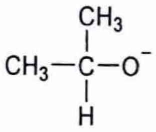
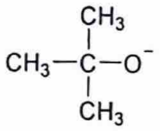
4.3 EFFECT OF SUBSTITUENTS ON ACIDITY OF ALCOHOLS AND PHENOLS

(a) Electron-donating vs electron-withdrawing group

- In general,

An **electron-donating** substituent	An **electron-withdrawing** substituent
▪ increases the electron density and intensifies the negative charge on the oxygen atom of the alkoxide ion (RO^-) or phenoxide ion (PhO^-) ▪ which causes the alkoxide ion (RO^-) or phenoxide ion (PhO^-) to be less stable ▪ resulting in **lower** acidity of the alcohol or phenol	▪ decreases the electron density and disperses the negative charge on the oxygen atom of the alkoxide ion (RO^-) or phenoxide ion (PhO^-). ▪ which causes the alkoxide ion (RO^-) or phenoxide ion (PhO^-) to be more stable ▪ resulting in **higher** acidity of the alcohol or phenol
 	 

(b) Effect of substituents on acidity of alcohols

alcohol *(with water for comparison)*	 water	CH_3-CH_2-OH ethanol	$CH_3-CH(CH_3)-OH$ propan-2-ol	$CH_3-C(CH_3)_2-OH$ 2-methyl-propan-2-ol
p*K*a	14.0	15.9	18	19
conjugate base	H–O⁻	$CH_3-CH_2-O^-$	$CH_3-CH(CH_3)-O^-$	$CH_3-C(CH_3)_2-O^-$

From the above data, we can observe that

- the more electron-donating alkyl groups present,
- the more intensified the negative charge on the oxygen atom,
- the less stable the alkoxide ion,
- the **lower** the acidity of the alcohols.

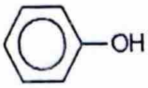
(c) Effect of substituents on acidity of phenols

Compound	p*K*a	Explanation
4–methylphenol	10.26	• Presence of electron-donating groups (e.g. $-CH_3$) in the ring **decreases** the acidity of the substituted phenol. • The electron-donating group intensifies the negative charge on the oxygen atom, thus making the respective phenoxide ion less stable.
phenol	10.00	--
4–chlorophenol	9.38	• Presence of electron-withdrawing groups (e.g. $-NO_2$ and $-Cl$) in the ring **increases** the acidity of the substituted phenol. • The electron-withdrawing group further disperses the negative charge on the oxygen atom, thus making the respective phenoxide ion more stable.
4–nitrophenol	7.15	
2,4,6–trinitrophenol	0.42	

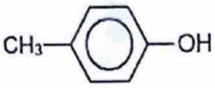
For a list of substituents which are electron-donating (activating groups) and electron-withdrawing (deactivating groups), refer to the *Data Booklet* section 8 on 'The orientating effect of groups in aromatic substitution reactions'.

■■ Worked Example 10 ■■

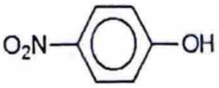
Arrange the following compounds in order of increasing acidity.



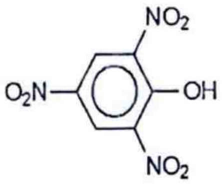
(1)



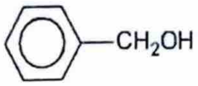
(2)



(3)



(4)



(5)

Answer:

5<2<1<3<4

5 SUMMARY OF DIFFERENCES BETWEEN ALCOHOLS AND PHENOLS

Property / Reagent	Ethanol, C_2H_5OH	Phenol, C_6H_5OH
Physical state at rtp	Liquid	Solid
Solubility in H_2O at rtp & acidity of solution	Completely soluble, forms a neutral solution	Slightly soluble (but soluble in hot water), forms a weakly acidic solution
Combustion	Burns with a clean smokeless flame	Burns with a sooty flame because of its high C to H ratio
Na(s), r.t.	Forms $CH_3CH_2O^-Na^+(aq)$ and $H_2(g)$	Forms $C_6H_5O^-Na^+(aq)$ and $H_2(g)$
NaOH(aq), r.t.	No reaction	Forms $C_6H_5O^-Na^+(aq)$ and $H_2O(l)$
Condensation	Reacts with carboxylic acids as well as acyl halides to form esters $CH_3CH_2OH + R'COOH \overset{\text{conc } H_2SO_4\text{, heat}}{\rightleftharpoons} R'COOCH_2CH_3 + H_2O$ $CH_3CH_2OH + R'COCl \longrightarrow R'COOCH_2CH_3 + HCl$	Reacts **only** with acyl halides to form esters. Preferable to react phenol with an alkali first to form phenoxide ion (stronger nucleophile). $C_6H_5OH + R'COCl \xrightarrow{NaOH} R'COOC_6H_5 + HCl$
Substitution of –OH by halogen	$CH_3CH_2OH(l) + PCl_5(s) \rightarrow CH_3CH_2Cl(l) + POCl_3(l) + HCl(g)$ $CH_3CH_2OH(l) + SOCl_2(l) \rightarrow CH_3CH_2Cl(l) + SO_2(g) + HCl(g)$ (HCl seen as white fumes) $CH_3CH_2OH \xrightarrow{\text{dry HBr, heat}} CH_3CH_2Br$	No reaction
Elimination: excess conc. H_2SO_4, heat	$\underset{\text{ethanol}}{CH_3CH_2OH} \longrightarrow \underset{\text{ethene}}{CH_2{=}CH_2} + H_2O$	No reaction
Oxidation: $K_2Cr_2O_7(aq)$ or $KMnO_4(aq)$, dil H_2SO_4, heat (with *immediate distillation to obtain aldehyde when using* $K_2Cr_2O_7(aq)$)	ethanol, $CH_3CH_2OH \xrightarrow{[O]}$ ethanal, $CH_3CHO \xrightarrow{[O]}$ ethanoic acid, CH_3COOH Observations: acidified $K_2Cr_2O_7(aq)$ (orange → green) OR acidified $KMnO_4(aq)$ (purple → colourless)	No reaction
dilute HNO_3	No reaction	Forms 2-nitrophenol and 4-nitrophenol
aq Br_2 only	No reaction	Forms 2,4,6-tribromophenol and HBr. Observations: (Rapid) decolourisation of orange bromine and white ppt of 2,4,6-tribromophenol.
Iodoform test (I_2, NaOH(aq), heat)	Yellow ppt of CHI_3 formed. $CH_3CH_2OH + 4I_2 + 6NaOH \longrightarrow CHI_3 + HCOO^-Na^+ + 5NaI + 5H_2O$	No yellow ppt produced
neutral $FeCl_3(aq)$	No violet colouration	Violet colouration observed

RAFFLES INSTITUTION
YEAR 6 H2 CHEMISTRY 2023
Tutorial 16 – Hydroxy Compounds

Self-Check Questions

1 **(a)** Draw the displayed formulae for all the eight alcohols with the molecular formulae $C_5H_{12}O$ and classify them into primary, secondary and tertiary alcohols. Indicate any chiral centre(s) with an asterisk (*).

(b) Name the alcohol(s) in **(a)** which will produce only one possible product upon dehydration.

(c) Name the alcohol(s) in **(a)** that cannot undergo dehydration.

(d) Name the alcohol(s) in **(a)** that produces a yellow ppt when heated with alkaline aqueous I_2. Write equations for the reactions that occur.

(e) Name the alcohol(s) in **(a)**, which upon heating under reflux with acidified $K_2Cr_2O_7$,

(i) gives no visible reaction

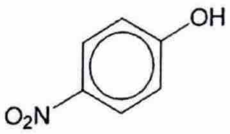
(ii) produces a compound that gives effervescence with aqueous Na_2CO_3. The gas evolved gives a white ppt when bubbled into limewater/$Ca(OH)_2(aq)$.

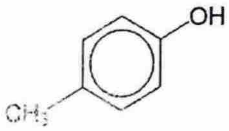
2 Suggest how the following conversions can be carried out in two stages. Indicate the reagents and conditions required for each stage, and give the structural formulae of all intermediates.

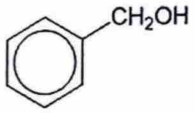
(a) $CH_3CH_2OH \longrightarrow CH_3CH_2NH_2$

(b) $CH_3CH(OH)CH_3 \longrightarrow CH_3CHBrCH_2Br$

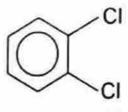
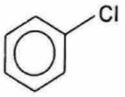
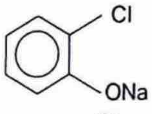
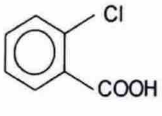
3 Arrange the following compounds in order of increasing K_a values, and explain your answer.







4 Which of the following shows the correct product formed when 2-chlorophenol is reacted with the respective reagent indicated in the table below?

	Reagent	Product
A	chlorine	
B	concentrated sulfuric acid	
C	aqueous sodium hydroxide	
D	hot acidified potassium manganate (VII)	

5 The molecular formula of a sugar is $C_6H_{12}O_6$. Its structure consists of an unbranched chain of carbon atoms, each of which has an oxygen atom bonded to it. It does not contain any carbon–carbon double bonds.

How many moles of sodium react with 1 mol of the sugar and how many moles of gaseous hydrogen are formed?

	moles of sodium	moles of gaseous hydrogen
A	5	2.5
B	5	5
C	6	3
D	6	6

6 The compound hex-3-en-1-ol, **P**, has a strong 'leafy' smell of newly cut grass and is used in perfumery.

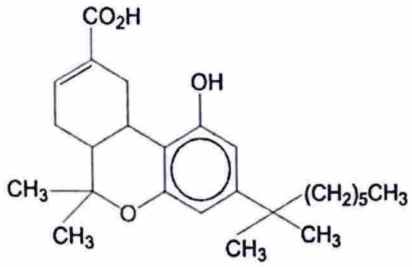
$CH_3CH_2CH{=}CHCH_2CH_2OH$

P

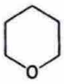
What is produced when **P** is treated with an excess of hot concentrated acidic $KMnO_4$?

A $CH_3CH_2CH(OH)CH(OH)CH_2CH_2OH$
B $CH_3CH_2CH{=}CHCH_2CO_2H$
C CH_3CH_2CHO and $OCHCH_2CH_2OH$
D $CH_3CH_2CO_2H$ and $HO_2CCH_2CO_2H$

7 Ajulemic acid is a derivative of cannabis which does not have any hallucinogenic properties. It is being developed as a pain killer.



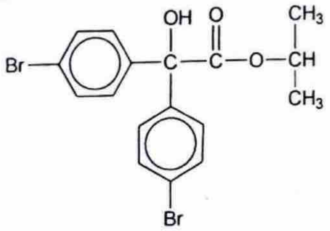
Ajulemic acid

In the following reactions, the  ring remains unaltered.

Which reaction will Ajulemic acid undergo?

A It reacts with dilute nitric acid to form an addition product.
B It will form a diester on heating with ethanol under reflux in the presence of a catalytic amount of concentrated sulfuric acid.
C It will turn a heated acidified solution of potassium dichromate(VI) from orange to green.
D It reacts with $Br_2(aq)$ to incorporate up to 4 atoms of bromine in each molecule.

8 *Acarol* is sold as an insecticide for use on fruit and vegetables.



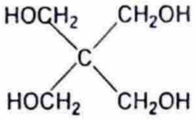
Acarol

The final stage in its manufacture is an esterification.

Which alcohol is used to form the ester?

A di(4-bromophenyl)methanol
B methanol
C propan-1-ol
D propan-2-ol

9 Pentaerythritol is an intermediate in the manufacture of paint.

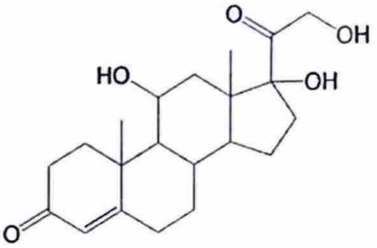


pentaerythritol

Which of the following statements about pentaerythritol are correct?

1 It decolourises acidified potassium manganate(VII) on warming.
2 It reacts with metallic sodium.
3 Its empirical formula is CH_3O.

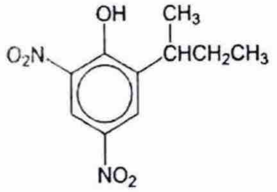
10 Hydrocortisone is the active ingredient in some anti-inflammatory skin creams.



Which statements are correct?

1 The hydrocortisone molecule has 7 chiral centres.
2 When treated with an excess of hot concentrated acidified $KMnO_4$, hydrocortisone will produce a compound with 2 carboxylic acid groups.
3 When treated with an excess of hot acidified $K_2Cr_2O_7$, hydrocortisone will produce a compound with 4 carbonyl groups.

11 Dinoseb is an herbicide.



Which statements about Dinoseb are correct?

1 Its aqueous solution is acidic.
2 It can exist in optically active forms.
3 It reacts with ethanol in the presence of concentrated sulfuric acid to give an ester.

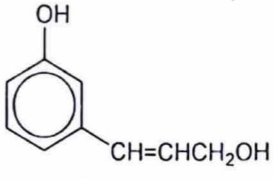
Practice Questions

1 Arrange the following in order of increasing acidity and explain your answer.

phenol, 2-nitrophenol, ethanol, methylpropan-2-ol, water, 2-methylphenol

2 Under what conditions does each of the following reagents react (if any) with compound **A**?

For the reactions that occur, draw the structural formula of the organic product(s) formed and state the type(s) of reaction involved.



A

Reagent	Condition	Structure	Type of reaction
(a) sodium			
(b) sodium hydroxide			
(c) sodium carbonate			
(d) phosphorus (V) chloride			
(e) hydrogen bromide			
(f) ethanoic acid			

Reagent	Condition	Structure	Type of reaction
(g) ethanoyl chloride			
(h) aqueous bromine			
(i) bromine in CCl_4			
(j) potassium manganate (VII)			

3 For each of the following pairs of compounds, describe one simple chemical test which would enable you to distinguish between them. State clearly how **each** compound behaves in the test and write balanced equations for the reactions involved.

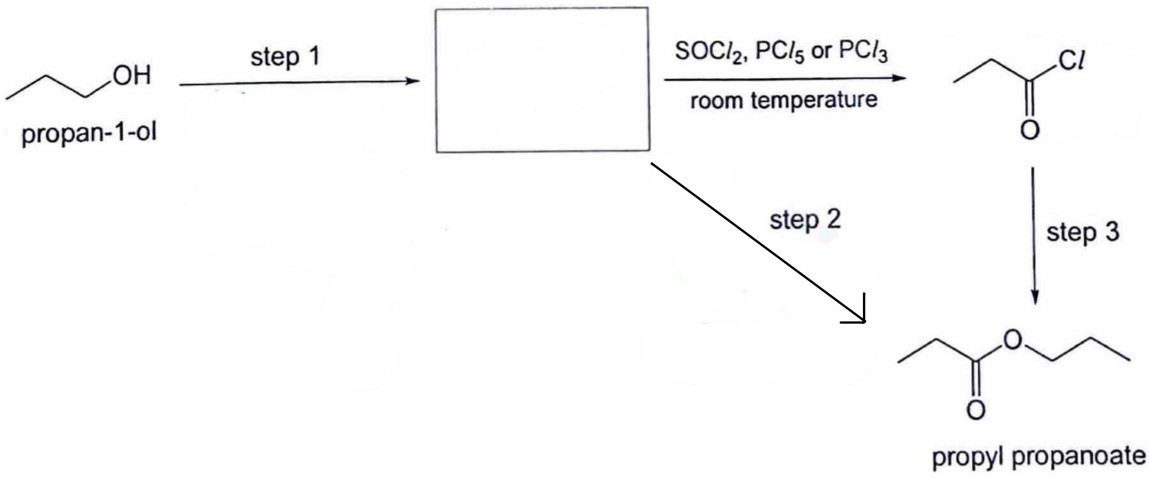
(a) $C_6H_5CH_2{=}CH_2$ and $C_6H_5CH_2CH_2OH$

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

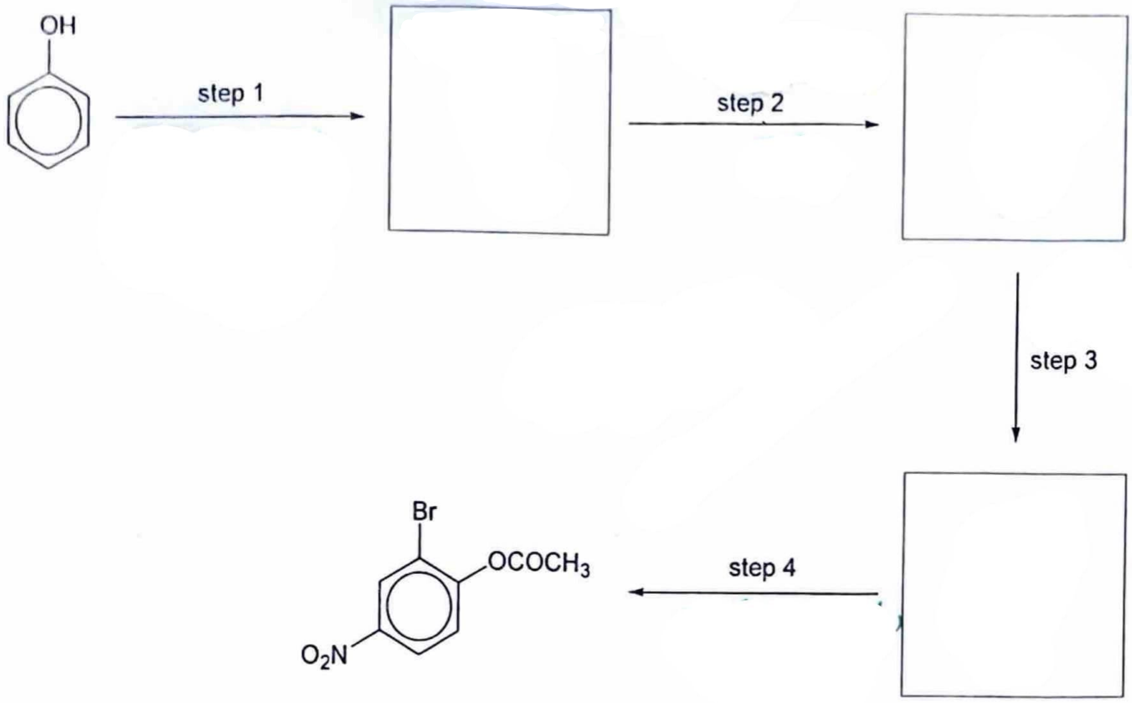
(c) cyclohexanol and phenol

4 Suggest suitable reagents and conditions to carry out the conversions given below. Give the structural formulae of all intermediates formed.

(a)



(b)



[N2010/III/3(d)]

5 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 293 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 293 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 293 K).

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

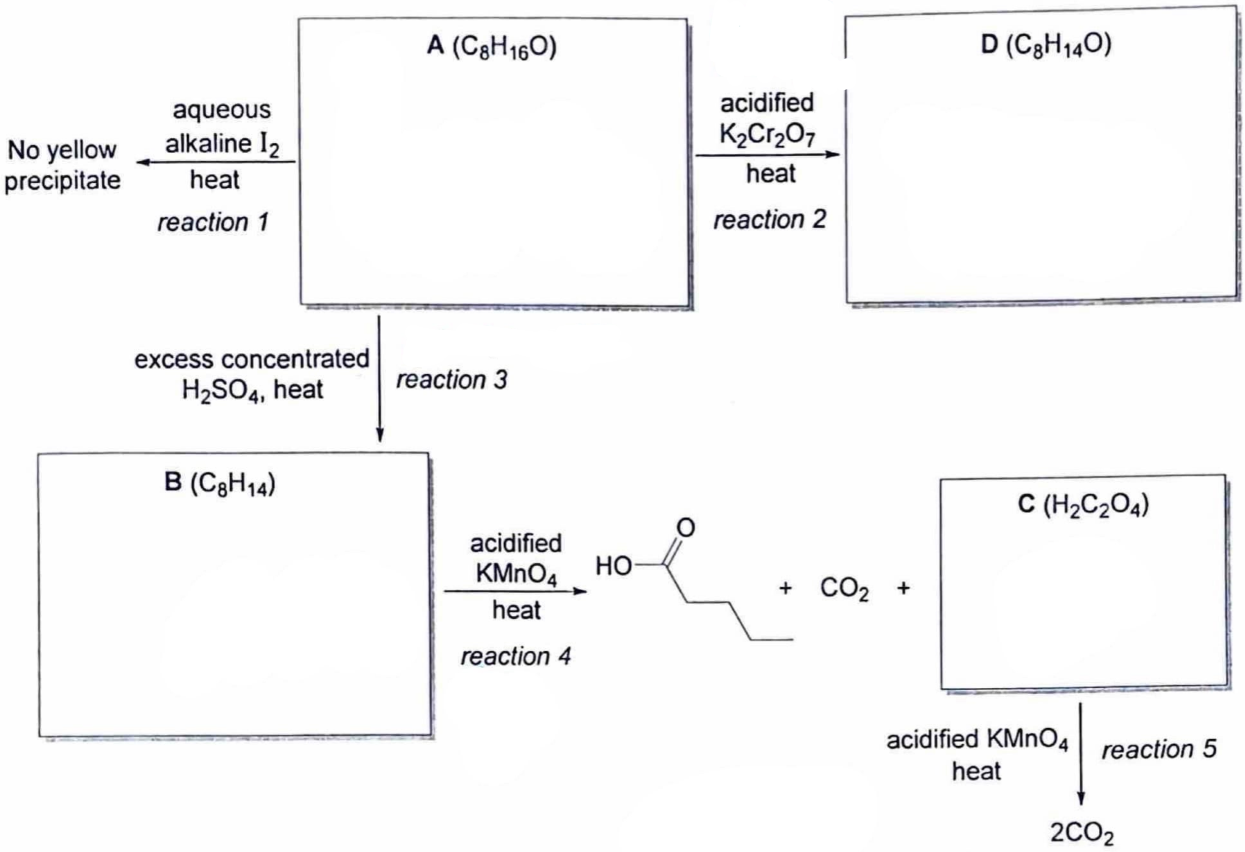
(c) Suggest suitable reagents and conditions for the conversion of **J** into **K**.

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

[RI2017CT1/B2(c)]

6 The fermentation of starch and sugars in fruits, barley and rice produces ethanol that is found in alcoholic drinks such as gin.

Alcohol **A** is obtained from the fermentation of mushrooms. Its chemistry was studied through a series of reactions as shown in the following reaction scheme.



It was also found that 1 mol of **A** reacts with 1 mol of Br_2 in the dark. In *reaction 3*, **B** was obtained as the **only** product, ignoring stereoisomers.

(a) State the deductions which can be made from the information that

- no yellow precipitate was observed when **A** was heated with aqueous alkaline iodine in *reaction 1*.
- 1 mol of **A** reacts with 1 mol of Br_2 in the dark.

(b) By considering your answers to **(a)** and the information from the above reaction scheme, draw the structures of compounds **A** to **D** in the boxes provided.

(c) State the type of reaction for the conversion of

- **A** to **B** in *reaction 3*.
- **A** to **D** in *reaction 2*.

(d) Using the symbol [O] to represent the oxidising agent, write the balanced equation for the reaction between **B** and acidified $KMnO_4$ in *reaction 4*.
You may use the molecular formulae of the compounds in the equation.