Anderson Serangoon Junior College
JC2 H2 Chemistry
HYDROXY COMPOUNDS

Contents/Outline

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 aromatic ring
(e) explain the relative acidities of water, phenol and ethanol in aqueous medium (interpret as Bronsted–Lowry acids)

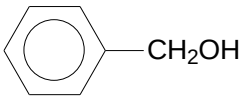
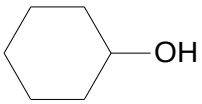
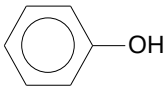
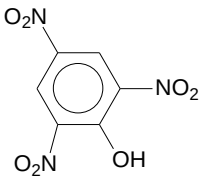
References

1. Organic Chemistry (Sixth Edition), McMurry, Brooks/Cole
2. Chemistry for Advanced Level, Cann and Hughes, Murray

1 INTRODUCTION

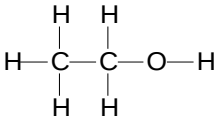
Hydroxy compounds are organic compounds containing the functional group –OH.

There are two types of hydroxy compounds:

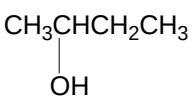
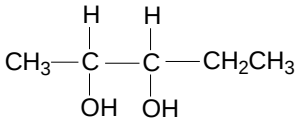
Alcohols	**Phenols**
–OH group bonded to a saturated C (sp^3 hybridised) of an alkyl group	–OH group bonded directly to a C (sp^2 hybridised) in the benzene ring
<u>Examples:</u> CH_3CH_2OH ethanol  phenylmethanol  cyclohexanol	<u>Examples:</u>  phenol  4–methylphenol  2,4,6-trinitrophenol

2 NOMENCLATURE AND STRUCTURE

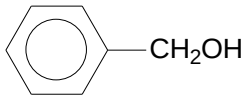
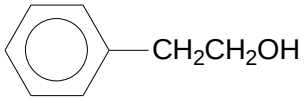
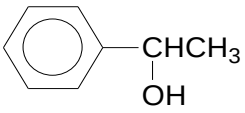
- Alcohols are named with the suffix, ***–ol***, added to the corresponding alkane.

CH_3OH	
methanol	ethanol

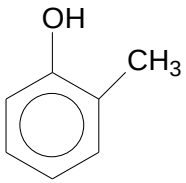
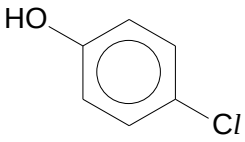
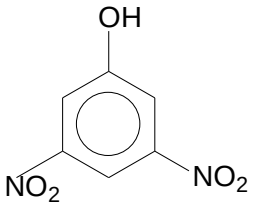
- A number is used to indicate the position of the –OH group if there is more than one possible position on the parent chain.

$CH_3CH_2CH_2CH_2OH$		
butan–1–ol	butan–2–ol	penta–2,3–diol

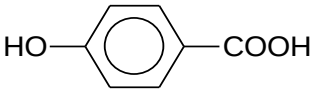
- The benzene ring is named as a 'phenyl' group when it is considered as a substituent.

		
phenylmethanol	2–phenylethanol	1–phenylethanol

- Compounds that have a hydroxyl group directly attached to a benzene ring are called phenols. The carbon bearing the –OH group is numbered 1, other substituents are numbered relative to it.

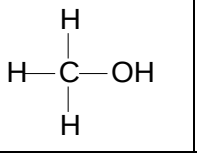
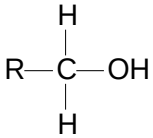
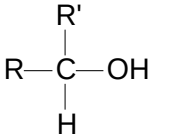
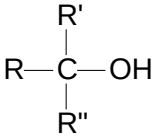
		
2–methylphenol	4–chlorophenol	3,5–dinitrophenol

- In cases where there are higher priority substituent groups such as the carboxyl group, the –OH group is named as ***hydroxy*** in the prefix.



4–hydroxybenzoic acid

- Alcohols are classified according to the number of carbon atoms attached to the carbon bonded to the –OH group. They can be primary, secondary or tertiary.

Primary (1°)		**Secondary (2°)**	**Tertiary (3°)**
methanol	1 R group	2 R groups	3 R groups
			

Note: the groups R, R' and R'' may or may not be the same.

3 PHYSICAL PROPERTIES OF ALCOHOLS AND PHENOLS (SDL)

Study this part of the topic on your own by recalling and applying Chemical Bonding concepts here.

3.1 Boiling points

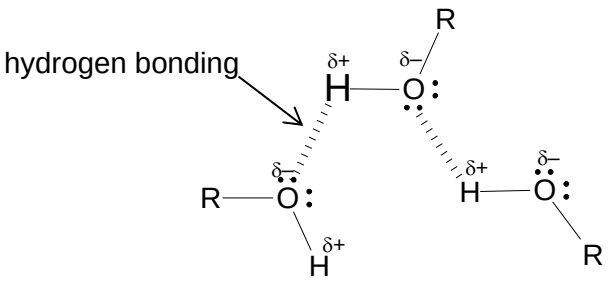
1. Alcohols have considerably higher boiling points than the alkanes of comparable molecular masses.

Example

Compound	M_r	Boiling point / ^oC
CH_3CH_2OH	46.0	78.5
$CH_3CH_2CH_3$	44.0	–42.1

Chemical bonding concept: relative strength of hydrogen bonding vs id–id

More energy is required to overcome the **stronger hydrogen bonding between CH_3CH_2OH molecules** as compared to the **weaker instantaneous dipole–induced dipole attractions between $CH_3CH_2CH_3$ molecules**.



2. Boiling point of alcohols increases with increasing length of alkyl chain.

Example

Compound	CH_3OH	CH_3CH_2OH	$CH_3CH_2CH_2OH$
Boiling point / ^oC	65	78	97

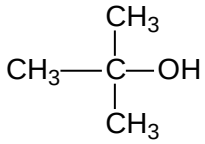
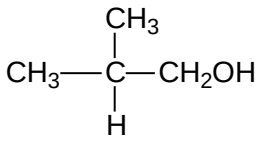
Chemical bonding concept: Factors affecting strength of id-id: no of e^-

As the length of the alkyl chain increases, the **number of electrons / electron cloud size increases**, which results in a **greater ease of distortion of the electron cloud**. More energy is required to overcome the **stronger instantaneous dipole–induced dipole attractions between the alcohol molecules**.

3. Alcohols with branched carbon chains generally have lower boiling points than their unbranched chain isomers.

   Chemical bonding concept: Factors affecting strength of id-id: surface area

   Example

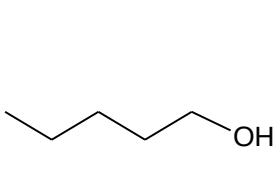
		$CH_3CH_2CH_2CH_2OH$
83 °C	108 °C	118 °C

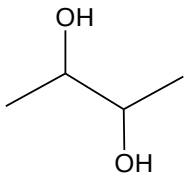
   Among the three alcohols, butan-1-ol is the most **elongated** molecule which provides the **greatest surface area** of contact. **More energy** is required to overcome the **stronger instantaneous dipole–induced dipole attractions between butan-1-ol molecules**.

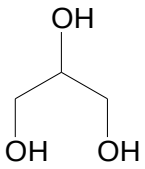
4. Boiling point of alcohols increases with increasing number of hydroxyl groups.

   Chemical bonding concept: Average number of hydrogen bonding per molecule (extensiveness)

   Example





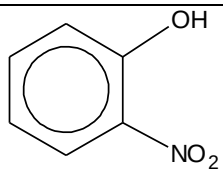
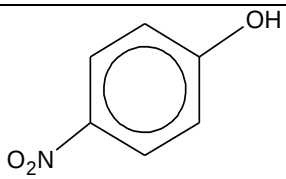


Boiling point	137°C	195°C	290°C
M_r	88.0	90.0	92.0

   As the number of OH groups increases, the average no. of hydrogen bonds per molecule increases. More energy is required to overcome the more extensive hydrogen bonding between molecules and hence **boiling point increases**.

5. Phenols exist as **crystalline solids** with a **low melting point** of 40.5 °C. As a liquid, phenol has relatively **high boiling point** as compared to other organic compounds of the same molecular masses. This is because a **larger amount** of **energy** is needed to overcome the **stronger hydrogen bonds between phenol molecules.**

6. 2-nitrophenol has a lower boiling point than 4-nitrophenol.

	
217 °C	245 °C

   There is **intramolecular hydrogen bonding** due to the close proximity of the –OH group and the $-NO_2$ group. This **reduces** the number of sites available for **intermolecular hydrogen bonding**. **Less energy** is needed to overcome the **less extensive intermolecular hydrogen bonding** in 2-nitrophenol during boiling.

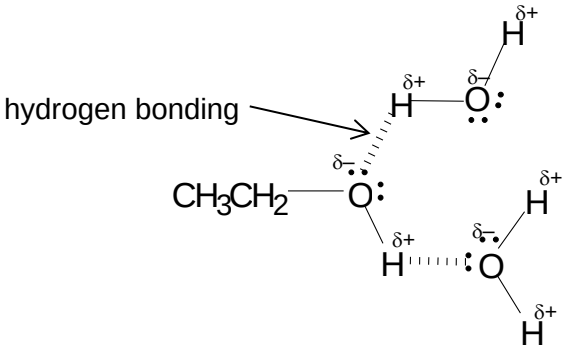
3.2 Solubility

1. The <u>lower alcohols</u> (methanol, ethanol, and propanol) are <u>completely miscible</u> with water.

   The energy released during the formation of hydrogen bonding between alcohol molecules and water molecules is able to compensate for the energy taken in to break the hydrogen bonding between alcohol molecules and the hydrogen bonding between water molecules.

   Example

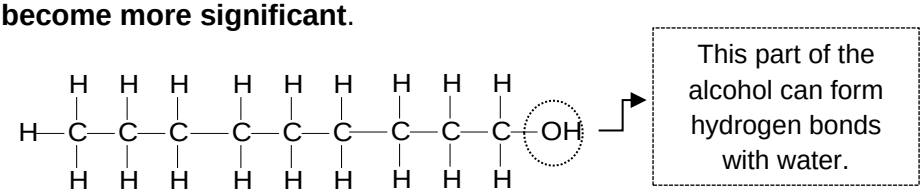
   Hydrogen bonding between ethanol and water



2. The **solubility of alcohols in water decreases as the number of carbon atoms in the molecule increases**.

   Alcohols with more than 4 carbons are partially or immiscible with water *(you may well end up with two layers in your test tube)*.

   As the length of the non–polar alkyl chain increases, **id–id attractions between the alcohol molecules become more significant**.



   Hence, the energy evolved during the formation of hydrogen bonding between the water molecules and the alcohol molecules is not enough to compensate for the energy required to break the hydrogen bonding and the stronger id-id attractions between alcohol molecules and the hydrogen bonding between water molecules.

3. Alcohols are completely miscible with organic solvents.

4. Phenols are not very soluble in water.

   This is due to the non-polar benzene ring that causes the id-id attraction between phenol molecules to become significant. Hence, the energy evolved during the formation of hydrogen bonding between the water molecules and the phenol molecules is not enough to compensate for the energy required break the hydrogen bonding and the more extensive id-id attractions between phenol molecules and the hydrogen bonding between water molecules.

4 PREPARATION OF ALCOHOLS

How are alcohols synthesised?

Alcohols can be obtained from four main groups of organic compounds, namely, alkenes, halogenoalkanes, carbonyl compounds and carboxylic acids.

4.1 Electrophilic addition from alkenes
(Refer to Alkene Lecture Notes for more details)

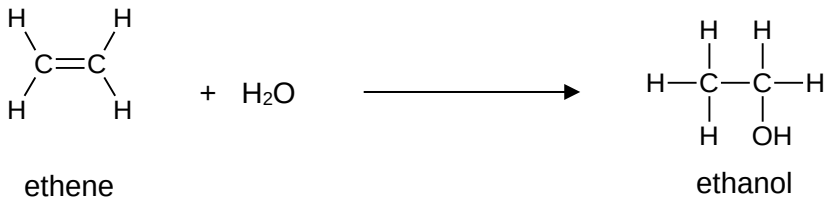
Type of reaction	Electrophilic addition

Industrial method

Reagents	steam, with concentrated phosphoric acid, H_3PO_4, as catalyst
Conditions	heat under reflux at high pressure

Laboratory method

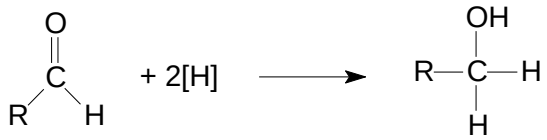
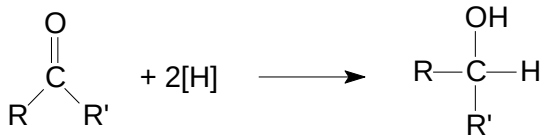
Stage 1	**Reagents and conditions**	concentrated H_2SO_4, cold
Stage 2	**Reagents and conditions**	water, warm

Example	 ethene + H_2O ethanol

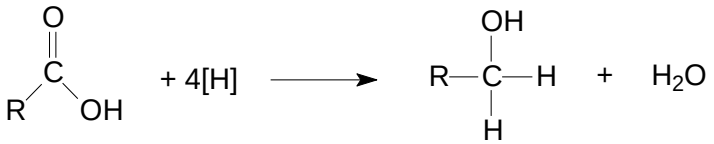
4.2 Nucleophilic substitution from halogenoalkane
(Refer to Halogenoalkane Lecture Notes for more details)

Type of reaction	Nucleophilic substitution
Reagents & conditions	NaOH (aq) or KOH (aq), heat under reflux
Example	$CH_3CH_2Br + NaOH \longrightarrow CH_3CH_2OH + NaBr$

4.3 Reduction from carbonyl compounds

Type of reaction	Reduction
Reagents & conditions	<u>Reducing agent</u> • Lithium aluminium hydride ($LiAlH_4$) in dry ether, or • Sodium borohydride ($NaBH_4$) in methanol, or • H_2, Pt or Pd catalyst, room temperature and pressure or H_2, Ni catalyst, heat
Example	(a) Reduction of aldehydes  aldehyde 1° alcohol
	(b) Reduction of ketones  ketone 2° alcohol

4.4 Reduction from carboxylic acid

Type of reaction	Reduction
Reagents & conditions	<u>Reducing agent</u> • Lithium aluminium hydride ($LiAlH_4$) in dry ether
Example	 carboxylic acid 1° alcohol
<u>Note</u> $LiAlH_4$ reacts violently with water. Hence, it has to be handled with care and so, dry ether is often used as a solvent for $LiAlH_4$.	

4.5 Summary of reducing agents

- Both $NaBH_4$ and $LiAlH_4$ only affect polar bonds (i.e. C=O), hence they cannot reduce both C=C and C≡C.

- $NaBH_4$ is usually used to reduce aldehydes and ketones, due to its safety and ease of handling. $NaBH_4$ <u>does not</u> reduce RCOOH and its derivatives.

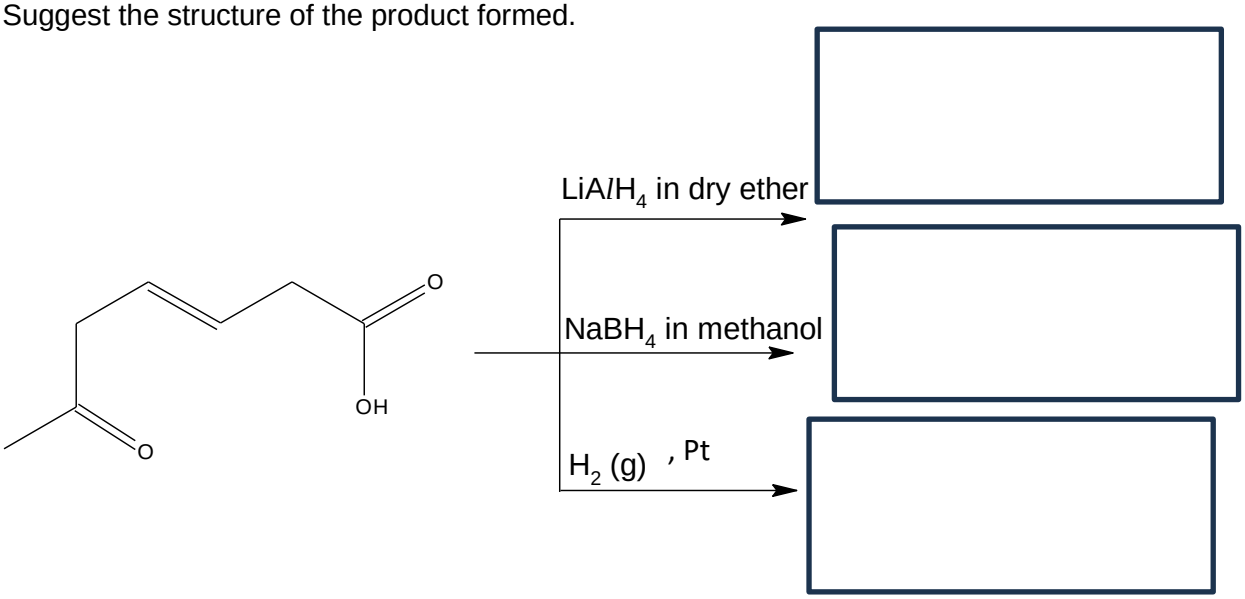
- $LiAlH_4$ is a **<u>stronger reducing agent</u>** than $NaBH_4$. $LiAlH_4$ can reduce all carbonyl groups including acids, esters, ketones and aldehydes rapidly.

- H_2/Pt cannot reduce RCOOH to RCH_2OH. Hence it can be used to selectively reduce C=C in compounds with both alkene and carboxylic acid functional groups present.

In summary, functional groups that the various reducing agents can reduce are:

Reducing Agent / **Functional Grp**	**$LiAlH_4$ in dry ether**	**$NaBH_4$ in methanol**	**H_2, Ni, heat / H_2, Pt/Pd, r.t.p.**
Alkene	x	x	✓
Aldehyde	✓	✓	✓
Ketone	✓	✓	✓
Carboxylic acid	✓	x	x
Ester	✓	x	x
Nitrile	✓	x	✓

<u>Exercise 1</u>
Suggest the structure of the product formed.

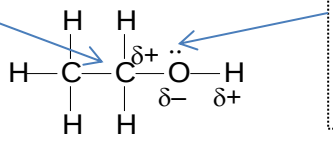


5 CHEMICAL PROPERTIES AND REACTIONS OF ALCOHOLS

Which classes of reagents do alcohols react with and why?
What types of reactions do alcohols undergo and why?

Alcohols are polar molecules with two polar bonds (the C–O bond and the O–H bond) due to the presence of the electronegative O atom.

Nucleophiles will be attracted to the electron deficient C atom on ROH (electrophile).



Lone pair of electrons on the O atom allows ROH to act as a nucleophile / Lewis base

Hence, reactions of alcohols involve the breaking of the C–O bond and O–H bond. In addition, alcohols undergo combustion and oxidation reactions.

5.1 Combustion

Alcohols burn in excess oxygen to give carbon dioxide and water.

E.g. Complete combustion of ethanol

$$CH_3CH_2OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O$$

5.2 Breaking of the O-H bond

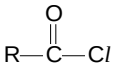
5.2.1 Reaction with sodium metal

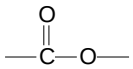
Alcohols react rapidly with sodium metal to form alkoxides.

$ROH + Na \rightarrow RO^-Na^+ + ½\ H_2$

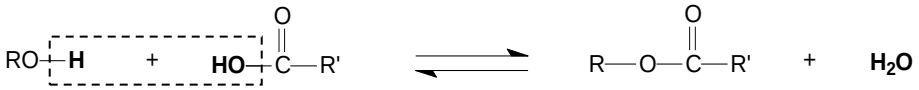
Type of reaction	
Reagents & conditions	
Example	$CH_3CH_2O–\mathbf{H} + \mathbf{Na} \rightarrow CH_3CH_2O^-\mathbf{Na^+} + ½\ \mathbf{H_2}$ ethanol sodium ethoxide
Observations	Effervescence (of H_2) is observed.
Note: This reaction can be used to generate the alkoxide, which is a stronger nucleophile for subsequent reactions.	

5.2.2 Formation of ester

Alcohols react with carboxylic acids or acyl chlorides () to form esters.

Esters are compounds that contain the functional group  .

(i) Reaction with carboxylic acid



alcohol carboxylic acid ester

Type of reaction	
Reagents & conditions	
Example	Reaction of propanol with ethanoic acid to form propyl ethanoate: $CH_3CH_2CH_2O\mathbf{H} + CH_3CO\mathbf{OH} \rightleftharpoons CH_3CO_2CH_2CH_2CH_3 + \mathbf{H_2O}$
Observations	Sweet smell of ester. Immiscible layer with water. *(Note that this reaction cannot be used as a distinguishing test.)*

Note:
Reaction is slow and reversible. This is usually a less preferred method of preparing the ester. A better method is to react the acyl chloride with alcohol.

Concentrated H_2SO_4 acts as both a catalyst and a drying agent.

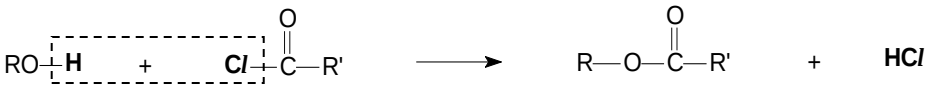
i) as a drying agent
It removes water produced in the reaction and shifts the position of equilibrium to the right, increasing the yield of the ester.

ii) as a catalyst
It speeds up the forward and backward reaction by the same extent so that the equilibrium can be achieved faster.

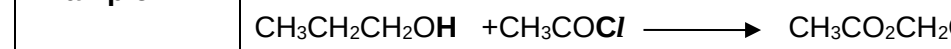
Note:

Condensation – occurs when two reactants react to form a single product, with the elimination of a small molecule (such as water or HC*l*).

(ii) Reaction with acid chlorides (acyl chlorides)



alcohol acid chloride ester

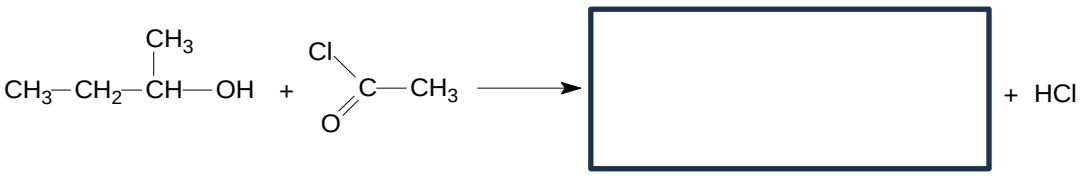
Type of reaction	
Reagents & conditions	
Example	Reaction of propanol with ethanoyl chloride to form propyl ethanoate: 
Observations	White fumes (of HC*l*) evolved. Sweet smell of ester.
Note: This is a more effective method to obtain an ester because this is an irreversible reaction and it proceeds to completion. A high yield of ester can be easily obtained. This reaction occurs rapidly at room temperature and does not require a catalyst or heat.	

Exercise 2

Name the class of the compound formed when butan-2-ol, $CH_3CH(OH)CH_2CH_3$, reacts with ethanoyl chloride, and draw its structural formula.

Answer:

Class: _____



5.3 Breaking of the C–O bond

5.3.1 Nucleophilic substitution to form halogenoalkane

(This part is also covered in Halogenoalkane lecture)

(i) Reaction with HX

$ROH + HX \longrightarrow RX + H_2O$

Type of reaction	
Reagents and conditions	To form RC*l*: conc. HC*l* and $ZnCl_2$, heat under reflux To form RBr: NaBr, conc H_2SO_4, heat under reflux
Example	To form RC*l*: $CH_3CH_2OH + HCl \rightarrow CH_3CH_2Cl + H_2O$ To form RBr: $NaBr + H_2SO_4 \rightarrow HBr + NaHSO_4$ $CH_3CH_2OH + HBr \rightarrow CH_3CH_2Br + H_2O$
Note: Concentrated H_2SO_4 cannot be used to prepare HI because H_2SO_4 oxidises HI to I_2. Phosphoric acid is used instead to produce HI. $3NaI + H_3PO_4 \rightarrow 3HI + Na_3PO_4$ $CH_3CH_2OH + HI \rightarrow CH_3CH_2I + H_2O$	

(ii) Reaction with phosphorous halide (PX_3 or PX_5)

$3ROH + PX_3 \longrightarrow 3RX + H_3PO_3$

$ROH + PX_5 \longrightarrow RX + POX_3 + HX$

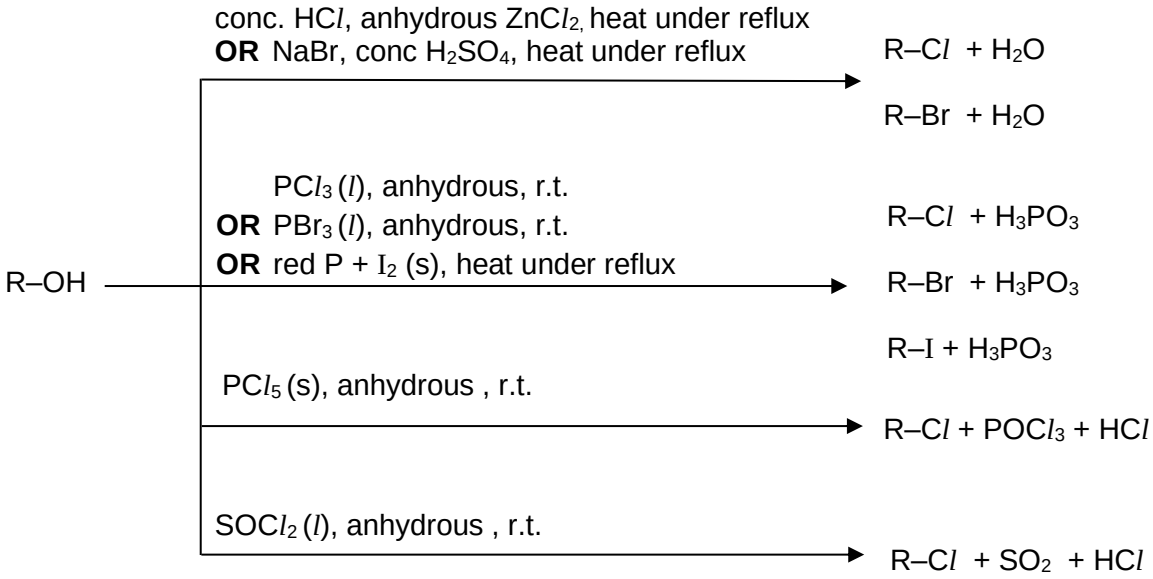
Type of reaction	Nucleophilic substitution
Reagents and conditions	PCl_3 (*l*) , PBr_3 (*l*) , PCl_5 (s), anhydrous, room temperature red P + I_2 (s), heat under reflux
Example	$3CH_3CH_2OH + PI_3 \longrightarrow 3CH_3CH_2I + H_3PO_3$ $3CH_3CH_2OH + PBr_3 \longrightarrow$ $CH_3CH_2OH + PCl_5 \longrightarrow$
Observation	Only when PCl_5 is used: White fumes (of HC*l*) evolved

(iii) Reaction with thionyl chloride ($SOCl_2$)

$ROH + SOCl_2 \longrightarrow RCl + SO_2 + HCl$

Type of reaction	Nucleophilic substitution
Reagents and conditions	$SOCl_2$, anhydrous, room temperature
Example	$CH_3CH_2OH + SOCl_2 \longrightarrow$
Observation	White fumes (of HCl) evolved.

Summary



Note:

- When using PCl_3, PCl_5 and $SOCl_2$, anhydrous condition is required to ensure that there is absence of water. This is to prevent these compounds from reacting with water to give other products.

$PCl_3(l) + 3H_2O(l) \rightarrow H_3PO_3(aq) + 3HCl(aq)$

$PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(aq)$

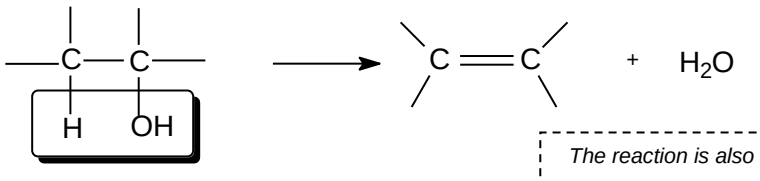
$SOCl_2(l) + H_2O(l) \rightarrow SO_2(g) + 2HCl(aq)$

For reaction of alcohols with PCl_5 and $SOCl_2$, **steamy white fumes of HCl** are produced, which turn **damp blue litmus paper red.** This is useful in determining the presence of hydroxyl groups. However, the same observations will be seen if tested on **carboxylic acids** *(will be covered in the carboxylic acid topic).*

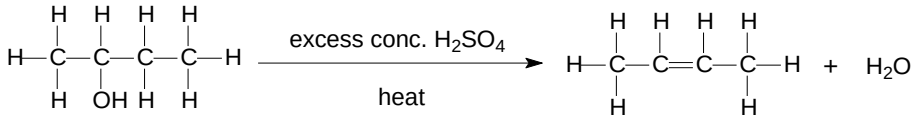
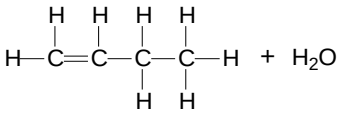
5.3.2 Elimination of H_2O to form alkene

(This part is also covered in Alkene lecture)

A hydrogen atom and the hydroxyl group, –OH from **adjacent** carbon atoms on an alcohol molecule are eliminated as a molecule of water.



The reaction is also known as dehydration.

Type of reaction	Elimination (of H_2O)
Reagents & conditions	• excess concentrated H_2SO_4, heat under reflux, or • concentrated H_3PO_4, heat under reflux, or • Al_2O_3, heat under reflux (industrial process)
Example	 major product *Recall the Saytzeff's rule to identify the major product obtained for the dehydration of unsymmetrical alcohols. (Refer to Alkenes notes).*  minor product

Note:

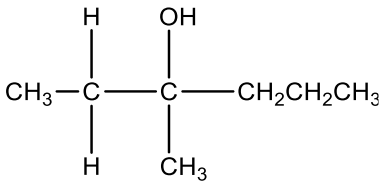
- Concentrated H_2SO_4 must be used in excess for dehydration to occur in order for alkenes to be obtained as the product. Other side reactions such as ether (R–O–R') formation may occur if concentrated H_2SO_4 is not used in excess.

Remember also that if any of the major/minor products can exhibit cis–trans isomerism, both the cis and trans isomers will be formed.

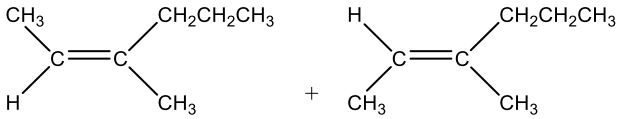
Exercise 3

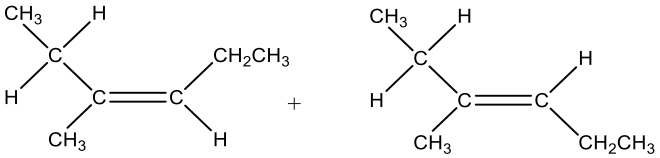
State the number of possible products (including stereoisomers) when 3–methylhexan–3–ol is subjected to reaction with excess concentrated H_2SO_4 at 180 ^oC.

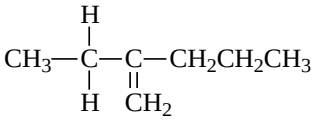
Give the structural formulae of all the possible products of the following reactions and identify the major product(s) (if any):



(3–methylhexan–3–ol)





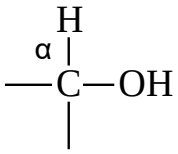


Number of possible products: 5

5.4 Oxidation

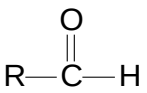
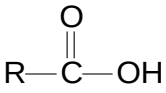
$KMnO_4$ and $K_2Cr_2O_7$ are common oxidising agents that are used to oxidise alcohols. $K_2Cr_2O_7$ is a weaker oxidising agent than $KMnO_4$. The products obtained and observations made will depend on the type of alcohol and the oxidising agent used.

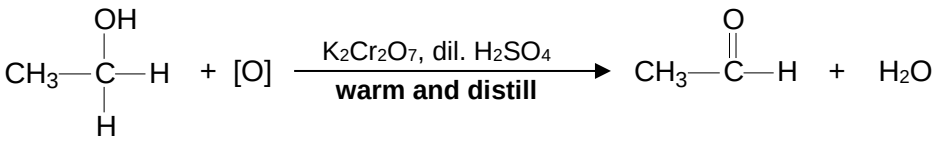
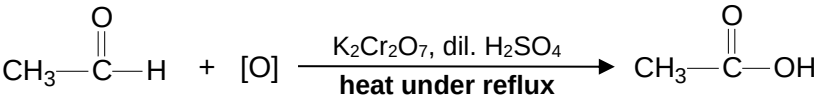
Oxidation of an alcohol involves cleavage of the α C–H bond. Hence, tertiary alcohols cannot undergo oxidation.



5.4.1 Oxidation of primary alcohols

(i) Using $K_2Cr_2O_7$

Reagents & conditions	Oxidation product	Observations
$K_2Cr_2O_7$, in dilute H_2SO_4 **warm** <u>and</u> **distill**	 aldehyde <u>Note:</u> The aldehyde formed can be isolated by distilling it from the hot reaction mixture once it is formed, to prevent further oxidation to carboxylic acid. (Refer to Fig 5.1)	<u>Orange</u> $K_2Cr_2O_7$ solution turns <u>green</u>
$K_2Cr_2O_7$, in dilute H_2SO_4 heat under reflux	 carboxylic acid	<u>Orange</u> $K_2Cr_2O_7$ solution turns <u>green</u>

Example	 Upon further oxidation, 

Note:

What is the difference between distillation and heat under reflux?

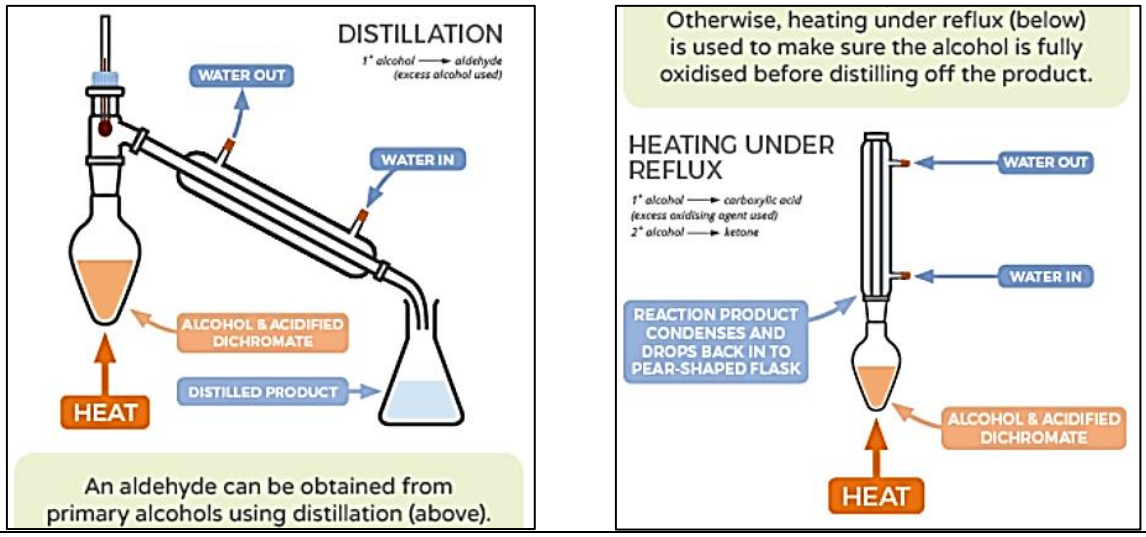
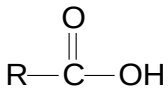
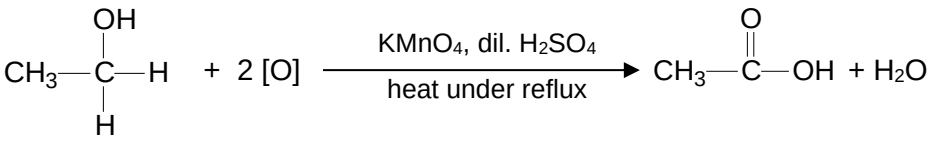


Fig. 5.1

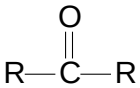
(i) Using $KMnO_4$

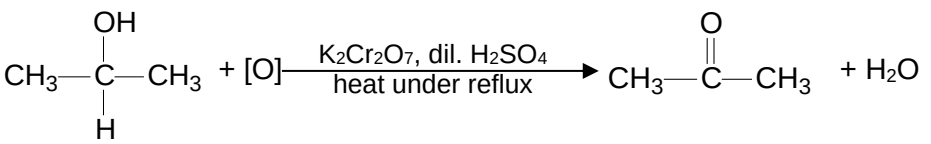
Reagents & conditions	Oxidation product	Observations
$KMnO_4$, in dilute H_2SO_4 heat under reflux	 carboxylic acid	Purple $KMnO_4$ solution turns colourless

Note: Unlike $K_2Cr_2O_7$, warming and distilling primary alcohols with $KMnO_4$ will NOT form aldehydes as the alcohol will be oxidised directly to a carboxylic acid.

Example	

5.4.2 Oxidation of secondary alcohols

Reagents & Conditions	Oxidation product	Observations
$KMnO_4$ in dilute H_2SO_4 heat under reflux	 ketone	Purple $KMnO_4$ solution turns colourless or Orange $K_2Cr_2O_7$ solution turns green
$K_2Cr_2O_7$ in dilute H_2SO_4 heat under reflux		

Example	

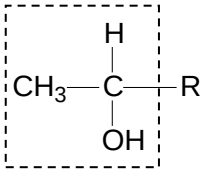
5.4.3 Tertiary alcohols

Do not undergo oxidation.

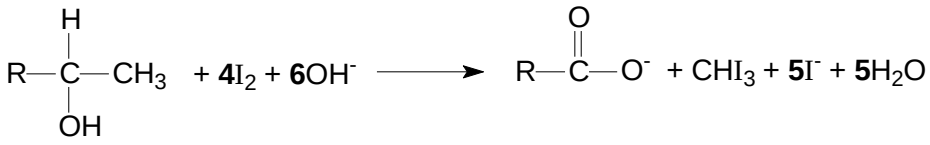
Since oxidation of different classes of alcohols gives different products, it can be used to distinguish between primary, secondary and tertiary alcohols.

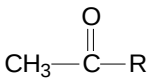
5.4.4 Tri-iodomethane / Iodoform reaction

Only alcohols with the following structure can undergo this reaction.

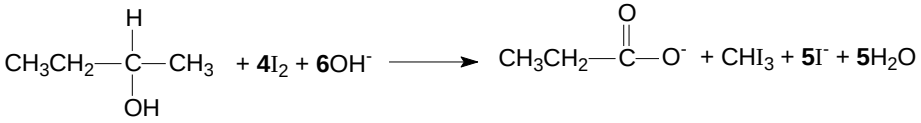


R = H or alkyl or aryl group



Such alcohols are first oxidised by alkaline aqueous iodine into the carbonyl compound,  , which undergoes further substitution and bond cleavage to produce a salt of a carboxylic acid and **tri–iodomethane, CHI_3,** which is a **yellow precipitate**. Due to the distinct formation of the yellow precipitate, CHI_3, this reaction is a useful chemical test for identifying alcohols with the above structure.

Tri–iodomethane reaction is a **step–down** reaction since the **carbon chain length of the organic compound is decreased by 1**.

Type of reaction	Oxidation
Reagents & conditions	
Example	 *Note:* *This redox equation can be obtained from balanced half–equations in alkaline condition.*
Observation	Yellow ppt of CHI_3 with antiseptic smell is formed.

FYI: Mechanism for the formation of tri–iodomethane

Stage 1: Addition of alkaline aq. I_2 oxidises the hydroxyl group to a ketone.

$2NaOH + I_2 + CH_3CH(OH)CH_3 \rightarrow 2NaI + CH_3COCH_3 + 2H_2O$

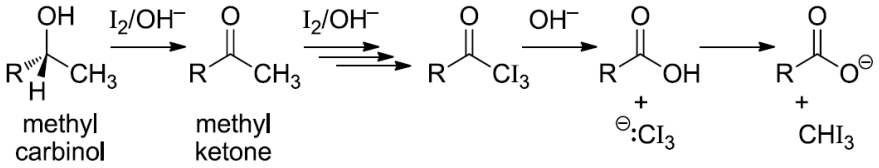
Stage 2: The ketone formed reacts with I_2 in a series of electrophilic substitution reaction to produce a tri–iodoketone.

$CH_3COCH_3 + 3I_2 \rightarrow CH_3COCI_3 + 3HI$

tri–iodoketone

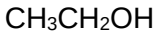
Stage 3/4: Finally, OH^- reacts with the tri–iodoketone in a series of nucleophilic acyl substitution and acid–base reaction to form the yellow tri–iodomethane.

$CH_3COCI_3 + OH^- \rightarrow \mathbf{CHI_3} + CH_3COO^-$

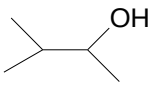


Exercise 4

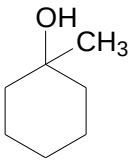
Which of the following will give positive tri–iodomethane reaction when warm alkaline aqueous iodine is added? If there is any reaction, draw the structure of the organic product(s) formed.



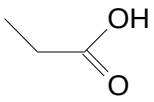
A



B



C

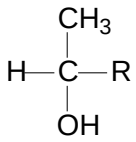


D

For **A**:

For **B**:

5.5 Chemical Identification of alcohols

Test	Observation for positive test	Remarks
PCl_5, anhydrous, room temperature	white fumes of HCl	Test for presence of alcohols. *Note:* *Carboxylic acids also give the same observation.*
$KMnO_4$, in dilute H_2SO_4 heat	purple $KMnO_4$ solution turns colourless	1^o and 2^o alcohols will give observable colour changes, while 3^o alcohols will not.
$K_2Cr_2O_7$, in dilute H_2SO_4, heat	orange $K_2Cr_2O_7$ solution turns green	1^o and 2^o alcohols will give observable colour changes, while 3^o alcohols will not.
I_2(aq) with NaOH, warm	yellow precipitate of CHI_3 with antiseptic smell	Test for alcohols with the following structure:  R = H or alkyl or aryl group

Exercise 5

$CH_3CH(OH)CH_2CH_3$ **A** $(CH_3)_3COH$ **B**

Alcohols **A** and **B** are isomers.
Describe the reaction (reagent and observation) by which **A** could be distinguished from **B**.

Answer:

_____ in separate test-tubes with _____
A will give a _____ of CHI_3 _____.

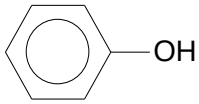
Or

To the separate test tubes containing each alcohol, add _____ followed by a _____ and _____. **A** will turn _____ while _____.

6 PHENOLS

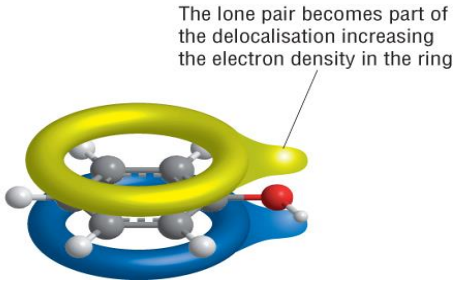
6.1 Structure of phenol

Phenol has the following structure, where the –OH group is bonded directly to the benzene ring.



Recall from Arenes: Benzene ring has a delocalised cloud of π electrons due to the overlapping of p–orbitals of the carbon atoms.

In phenol, the lone pair of electrons on oxygen is delocalised into the benzene ring as the p–orbital of the oxygen overlaps with the π electron cloud of the benzene ring, forming a cloud of delocalised π electron. This introduces some partial double bond character in the C–O bond.



As a result, the C–O bond is strengthened while the O–H bond is weakened. This makes phenol slightly acidic.

6.2 Acidity of phenol, water and ethanol

Order of acid strength: phenol > water > ethanol

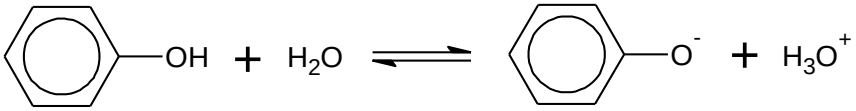
K_a / mol dm^{-3} : 1×10^{-10} > 1.8×10^{-16} > 1×10^{-16}

Recall: K_a is the acid dissociation constant for a weak acid. The value of K_a is a quantitative measure of the strength of a weak acid. The larger the value of K_a, the stronger is the acid.

Alcohols and phenols are Brønsted–Lowry acids (proton donors) in the presence of a suitable base.

$RO{-}H + H_2O \rightleftharpoons RO^- + H_3O^+$

acid (**alcohol**) — conjugate base (**alkoxide ion**)



acid (**phenol**) — conjugate base (**phenoxide ion**)

Water itself reacts similarly but to a very small extent:

$$H{-}OH + H_2O \rightleftharpoons H{-}O^- + H_3O^+$$

Since at any one time, only a small number of water molecules donate H^+ ions to other water molecules, water behaves as a **weak acid**.

A similar reaction occurs with ethanol, but to a lesser extent. The position of equilibrium lies further to the left, and **ethanol is a weaker acid than water**.

With phenol, the position of equilibrium lies further to the right than in water: **phenol is slightly more acidic than water**.

THE BIG IDEA

It is the **STABILITY** of the **anion (conjugate base) formed from the acid** which determines how strong the acid is, i.e. where the position of equilibrium lies.

The more stable the anion, the stronger the acid.

6.2.1 Acidity of ethanol

Ethanol is a weaker acid than water. It loses a proton in water to form the ethoxide ion, $CH_3CH_2O^-$.

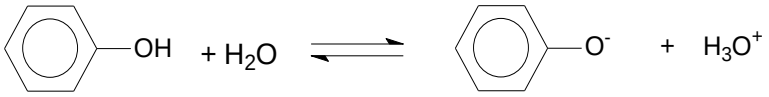
$$CH_3CH_2OH + H_2O \rightleftharpoons \mathbf{CH_3CH_2O^-} + H_3O^+$$

The **ethyl** group is **electron–donating**. This **intensifies** the **negative charge** on the anion, thus, **destabilising** the ethoxide ion. Hence, the dissociation of ethanol to release H^+ is less favoured.

Therefore, alcohols in general do **NOT** react with hydroxides and carbonates.

6.2.2 Acidity of phenol

Phenol is a stronger acid than water and alcohols. It loses a proton in water to form the phenoxide ion.



The **lone pair of electrons** on **oxygen** in the phenoxide anion is **delocalised into the π electron cloud** of the benzene ring, thus, **dispersing** the **negative charge**.

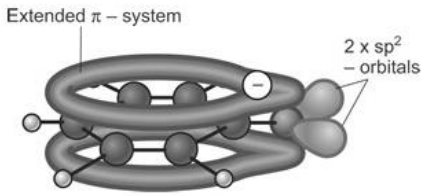
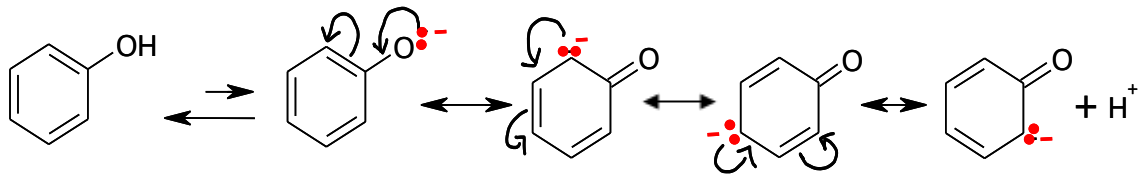


Figure 5 Delocalisation in the phenoxide ion
Source: http://www.presentingscience.com/chemcupboard/dettol/figure2iii.jpg

Since the phenoxide ion is **resonance–stabilised**, the dissociation of phenol to release H^+ is favoured.

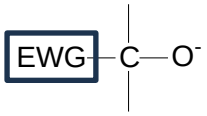
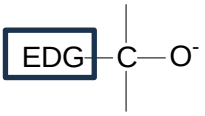
Note: (F.Y.I.)
Resonance stabilisation in phenol:



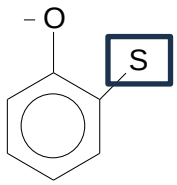
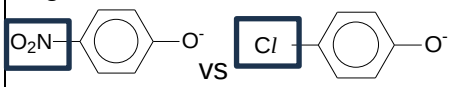
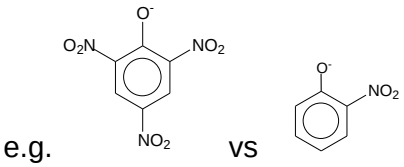
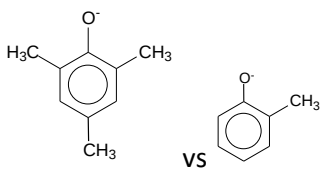
However, phenols are only slightly acidic (less acidic as compared to carboxylic acids).
While it can react with hydroxides, it is **NOT** acidic enough to react with carbonates or hydrogencarbonates *(which are weak bases)* and also has no effect on litmus paper.

6.2.3 Factors affecting acidity of alcohols and phenols

In ***alcohols***,

Factor	Effect	
Type of substituents	 **E**lectron–**W**ithdrawing **G**roup ➢ disperses the negative charge ➢ **<u>stabilises</u>** anion ➢ **<u>increases</u>** acid strength e.g. –F, –C*l*, –Br, –I, –NO_2	 **E**lectron–**D**onating **G**roup ➢ intensifies the negative charge ➢ **<u>destabilises</u>** anion ➢ **<u>decreases</u>** acid strength e.g. alkyl groups –CH_3
Strength of electron-withdrawing effect	**<u>More electronegative</u> <u>atom</u>** ➢ **<u>stronger</u>** electron-withdrawing effect ➢ disperses the negative charge to a greater extent ➢ stabilises anion to a greater extent ➢ increases acid strength e.g. CH_3CH_2CH**C*l***CH_2OH vs CH_3CH_2CH**F**CH_2OH	
No. of electron-withdrawing groups	**<u>Greater</u> <u>number</u>** of electron–withdrawing groups ➢ **<u>stronger</u>** electron-withdrawing effect ➢ disperses the negative charge to a greater extent ➢ stabilises anion to a greater extent ➢ increases acid strength e.g. CH_3CH_2CH**C*l***CH_2OH vs CH_3CH_2C**C*l*$_2$**CH_2OH	
Position of electron-withdrawing group	**<u>Closer distance</u>** between the electron–withdrawing group and the ($–O^–$) ➢ disperses the negative charge to a greater extent ➢ stabilises anion to a greater extent ➢ increases acid strength e.g. CH_3CH_2CH**C*l***CH_2OH vs CH_3CH**C*l***CH_2CH_2OH	

In ***phenols***,

Factor	Effect	
Type of substituent (S) 	**E**lectron–**W**ithdrawing **G**roup ➢ increases the extent of delocalisation of lone pair of e^- on O^- ➢ disperses the negative charge to a greater extent ➢ **<u>stabilises</u>** anion to a greater extent ➢ **<u>increases</u>** acid strength e.g.–NO_2, –F, –C*l*, –Br, –I, $-COCH_3$, –CN, –COOH, –COOR	**E**lectron–**D**onating **G**roup ➢ decreases the extent of delocalisation of lone pair of e^- on O^- ➢ disperses the negative charge to a smaller extent ➢ **<u>stabilises</u>** anion to a smaller extent ➢ **<u>decreases</u>** acid strength e.g. $-CH_3$, $-NH_2$, –OH, $-OCH_3$
Strength of electron-donating or electron withdrawing effect	**<u>Stronger</u>** electron-withdrawing effect ➢ increases the extent of delocalisation of lone pair of e^- on O^- ➢ disperses the negative charge to a greater extent ➢ **<u>stabilises</u>** anion to a greater extent ➢ **<u>increases</u>** acid strength e.g.  (more stable)	**<u>Stronger</u>** the electron donating effect ➢ decreases the extent of delocalisation of lone pair of e^- on O^- ➢ disperses the negative charge to a smaller extent ➢ **<u>stabilises</u>** anion to a smaller extent ➢ **<u>decreases</u>** acid strength e.g.  (less stable)
No. of substituent	**<u>Greater</u>** **<u>number</u>** of electron–withdrawing groups ➢ **<u>stronger</u>** electron-withdrawing effect ➢ increases the extent of delocalisation of lone pair of e^- on O^- ➢ disperses the negative charge to a greater extent ➢ **<u>stabilises</u>** anion to a greater extent ➢ **<u>increases</u>** acid strength  e.g. (more stable)	**<u>Greater</u>** **<u>number</u>** of electron–donating groups ➢ **<u>stronger</u>** electron-donating effect ➢ decreases the extent of delocalisation of lone pair of e^- on O^- ➢ disperses the negative charge to a smaller extent ➢ **<u>stabilises</u>** anion to a smaller extent ➢ **<u>decreases</u>** acid strength  e.g. (less stable)

7 CHEMICAL PROPERTIES AND REACTIONS OF PHENOLS

Which classes of reagents do phenols react with and why?
What types of reactions do phenols undergo and why?
How does the reactivity of phenol compare to that of benzene towards electrophiles?

Phenols have two reactive groups: the –OH group and the benzene ring.

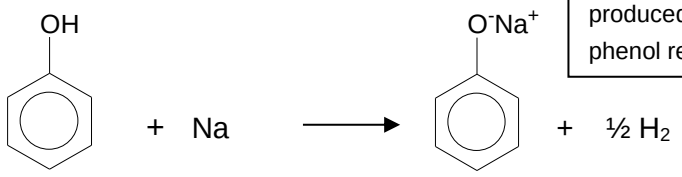
Phenols can undergo reactions involving the breaking of the O–H bond and electrophilic substitution reactions at the benzene ring.

Unlike alcohols, phenols do not undergo reactions involving the breaking of the C–O bond due to the stronger C–O bond in phenol. This is because the lone pair of electrons on oxygen is delocalised into the benzene ring as the p–orbital of the oxygen overlaps with the π electron cloud of the benzene ring, forming a delocalised electron cloud. This introduces some partial double bond character in the C–O bond.

7.1 Breaking of the O–H bond in phenols

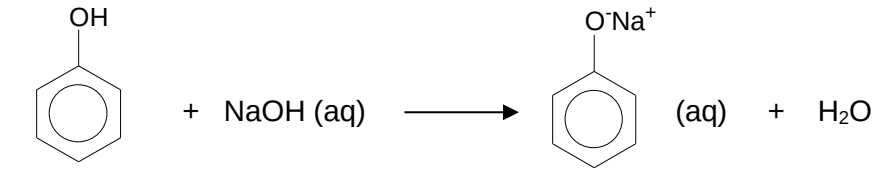
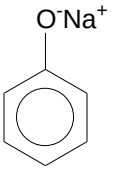
7.1.1 Reaction with sodium metal

Phenol reacts with sodium metal to form sodium phenoxide. Hydrogen gas is evolved.

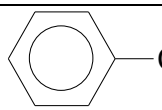
Type of reaction	Redox
Reagents & conditions	Na metal, room temperature
Example	 Only ½ mole of H_2 is produced per mole of phenol reacted.
Observations	Effervescence (of H_2) observed

7.1.2 Reaction with strong bases

Phenol is a weak acid; hence it can react with strong bases like sodium hydroxide. A salt, sodium phenoxide is formed from the reaction.

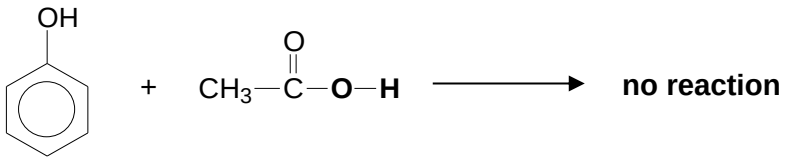
Type of reaction	Acid–base reaction / Neutralisation
Reagents & conditions	NaOH (aq), room temperature
Example	 ***Sodium phenoxide is miscible with water to form a homogeneous solution. Why?*** *Hint: What kind of interaction exists in solution?* *Ans:* _____ Evaporation  (s) white crystalline solid
<u>Note:</u> *Using this reaction, phenols can be converted to phenoxide ions (which are stronger nucleophiles) for subsequent reactions.*	

<u>Summary</u>

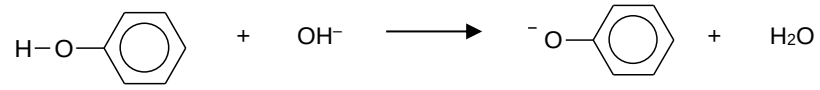
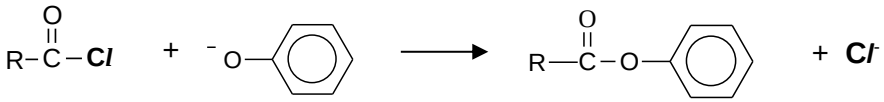
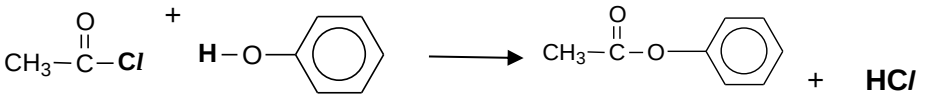
Organic compound	**Na**	**NaOH**	**Na_2CO_3**
ROH			
			
RCOOH			

7.1.3 Reaction with acid chlorides

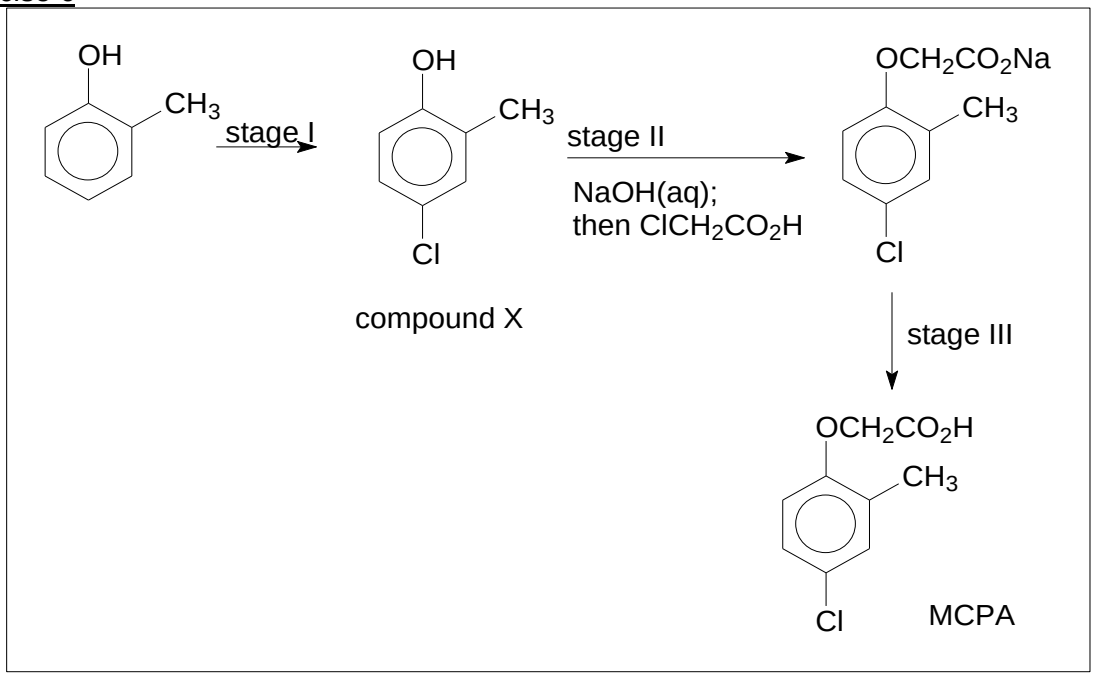
Unlike alcohols, phenols are not nucleophilic enough to undergo esterification by heating with a carboxylic acid and a trace amount of concentrated H_2SO_4. This is as a result of the delocalisation of the lone pair of electrons on the oxygen into the benzene ring.



Hence, phenols react with acid chlorides to form esters instead.

Type of reaction	Nucleophilic (acyl) substitution / Condensation
Reagents & conditions	Stage 1: phenol and NaOH Stage 2: sodium phenoxide formed in stage 1 and acid chloride
Example	Stage 1:  Stage 2:  phenylcarboxylate ester **Overall equation:**  ethanoyl chloride phenylethanoate
Note: *NaOH(aq) is added to phenol to form the phenoxide ion, which is a stronger nucleophile than phenol, before adding the acid chloride to the mixture. This will result in higher yield of the ester.*	

Exercise 6

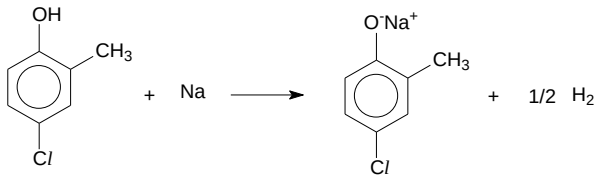


(i) Suggest why NaOH(aq) is added to compound **X** in stage II before C*l*CH_2CO_2H is added.

NaOH reacts with phenol (compound X) to form phenoxide ion. The resulting phenoxide ion is a _____ than the phenol.

(ii) Suggest another reagent that can be used in excess in stage II in place of NaOH(aq). Write an equation for the reaction of **X** with the reagent and state what would be observed.

_____



Effervescence observed. Gas evolved (hydrogen gas) _____ _____.

7.2 Electrophilic substitution reactions at the benzene ring

Due to the delocalisation of the lone pair of electrons on oxygen into the π electron cloud of the benzene ring, the benzene ring in phenol is more electron rich, making phenol more susceptible to react with electrophiles.

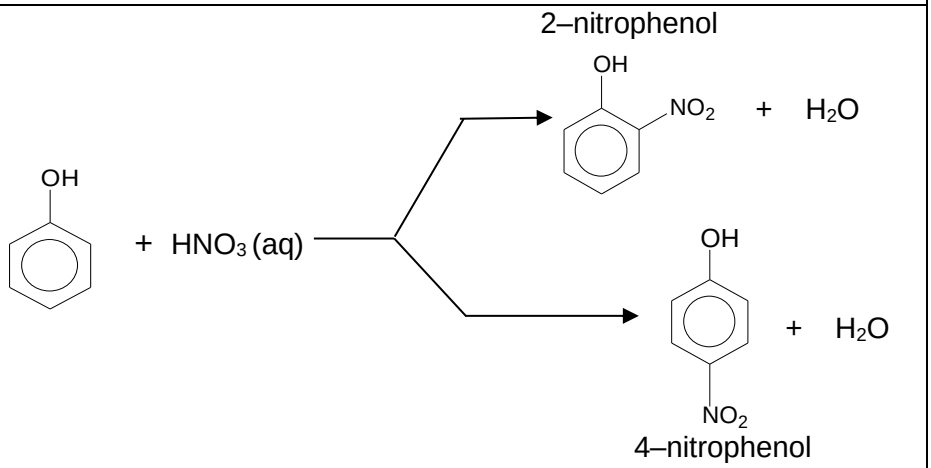
Since the –OH group is a strongly activating group, electrophilic substitution of phenol can occur under **milder** conditions, and multiple substitutions can occur readily.

7.2.1 Nitration

Conc. H_2SO_4 is **not required** to generate the strong electrophile NO_2^+ unlike reaction with benzene. Weak electrophile HNO_3 is sufficient to react with the benzene ring in phenol.

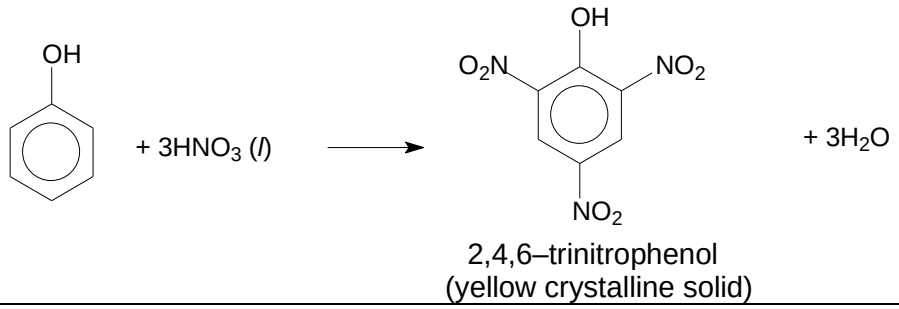
(a) Mono-substitution

Phenol reacts with **<u>dilute</u>** nitric acid to produce a mixture of 2–nitrophenol and 4–nitrophenol.

Type of reaction	
Reagents & conditions	
Example	

(b) Tri-substitution

Phenol reacts with **<u>concentrated</u>** nitric acid to form a **tri–substituted** product, 2,4,6–trinitrophenol.

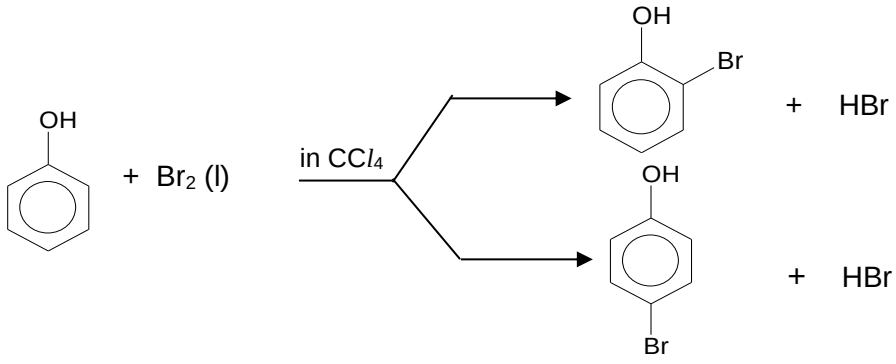
Type of reaction	Electrophilic substitution
Reagents & conditions	
Example	 2,4,6–trinitrophenol (yellow crystalline solid)

7.2.2 Bromination

Similar to nitration**,** a Lewis acid ($AlBr_3$ or $FeBr_3$) is **not required** to generate the strong electrophile Br^+ unlike reaction with benzene.

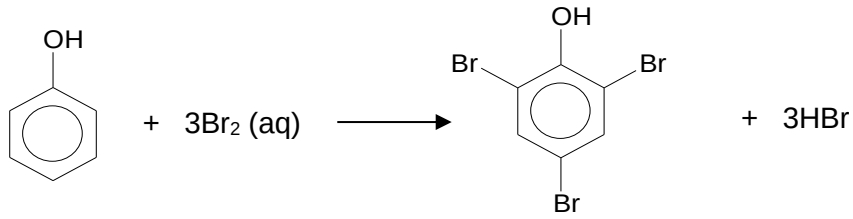
(a) Mono-substitution

Phenol reacts with bromine liquid in **<u>CCl_4</u>** to give a mixture of mono–substituted products.

Type of reaction	Electrophilic substitution
Reagents & conditions	
Example	
Observations	Reddish brown bromine in CCl_4 decolourised. White fumes (of HBr) observed.

(b) Tri-substitution

Phenol reacts with **<u>aqueous</u>** bromine to produce a tri-substituted product, 2,4,6–tribromophenol.

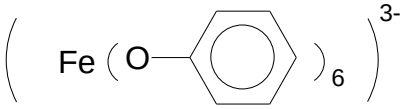
Type of reaction	Electrophilic substitution
Reagents & conditions	
Example	
Observations	Orange aqueous bromine is decolourised. A white precipitate (of 2,4,6–tribromophenol) is formed.

<u>Note:</u>
Poly–substitution occurs when Br_2(aq) is used but only mono–substitution occurs when liquid Br_2 or Br_2(g) in CCl_4.

In aqueous solution, phenol ionises to form phenoxide ion. As a result of the presence of negative charge, the oxygen of phenoxide ion donates electrons to the benzene ring causing it to be highly activated, hence tri–substitution occurs.

On the other hand, in non–polar solvents such as CCl_4, the ionisation of phenols is greatly suppressed. As a result, less electrons are donated into the benzene ring, consequently the ring is only slightly activated, resulting in mono–substitution.

7.3 Chemical identification of phenol

Test	Observation for positive test
aqueous bromine	orange aqueous bromine turns colourless white precipitate observed <u>*Note:*</u> *Phenylamine ($C_6H_5NH_2$) also gives the same observation.*
neutral aqueous solution of $FeCl_3$	purple colouration observed <u>*Note:*</u> *Phenol reacts with <u>neutral</u> aqueous iron(III) chloride to form a purple complex.*  *Under basic condition: $Fe(OH)_3$ is precipitated* *Under acidic condition: Phenoxide ions will not be generated, and hence the purple complex will not form.*

Exercise 7

Which inorganic reagent may be used to distinguish between phenol and methanol?

A alkaline aqueous I_2

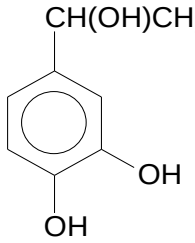
B aqueous $NaHCO_3$

C $K_2Cr_2O_7$ in dilute H_2SO_4

D sodium metal

Exercise 8

Noradrenaline is a hormone which is released in the body when we become stressed.



noradrenaline

Draw the structural formula of each of the organic products formed when noradrenaline is treated with the following reagents.

(i) An excess of bromine dissolved in a suitable solvent.
(ii) An excess of aqueous sodium hydroxide.
(iii) Acidified potassium dichromate(VI) when heated under reflux.

N2008/II/1(c),(d)(i)–(iii)

(i)

(ii)

(iii)