Nanyang Junior College
Chemistry (9729)

Lecture Notes 14
Hydroxy Compounds

H2

Lecturer: Mrs Judy Tan **JC2/2025**

Content

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

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)

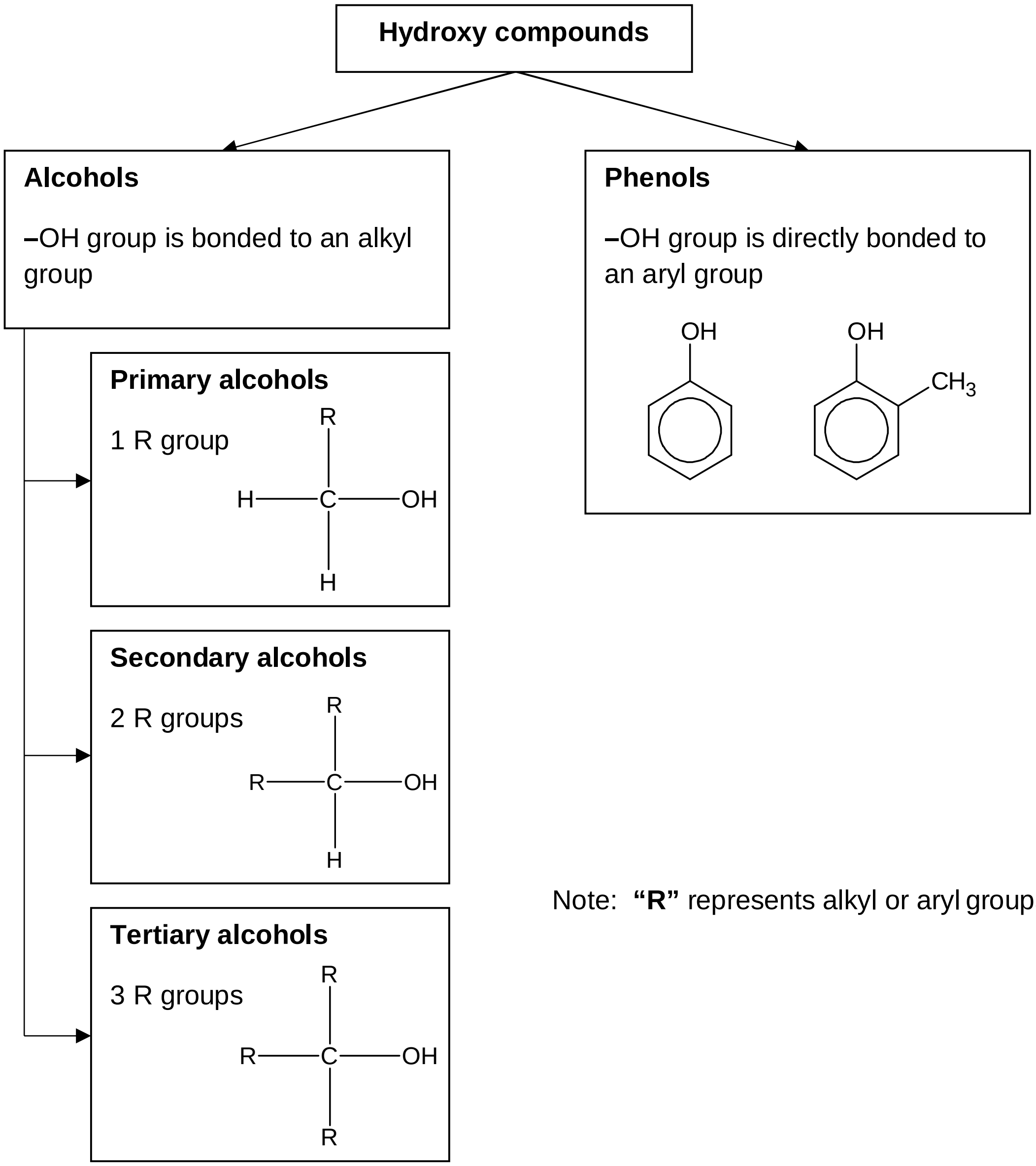
Textbooks and References

1. Chemistry for advanced level; Peter Cann, Peter Hughes, John Murray (Publishers) Ltd Page 477- 493
2. Chemistry in Focus; John Andrew, Paul Rispoli; 2nd edition Hodder & Stoughton Page 276-299
3. Organic Chemistry; John McMurry; 5th edition Brooks/Cole

1. INTRODUCTION

- Hydroxy compounds contain the **–OH functional group**.

- They can be classified as aliphatic compounds called **alcohols** or aromatic compounds, **phenols**.



Hydroxy compounds

Alcohols

–OH group is bonded to an alkyl group

Primary alcohols

1 R group

Secondary alcohols

2 R groups

Tertiary alcohols

3 R groups

Phenols

–OH group is directly bonded to an aryl group

Note: **"R"** represents alkyl or aryl groups**.**

2. ALCOHOLS

- General formula for alcohols: **$C_nH_{2n+1}OH$** or **$C_nH_{2n+2}O$** where n = 1, 2, 3, …

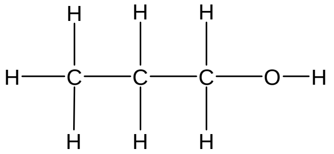
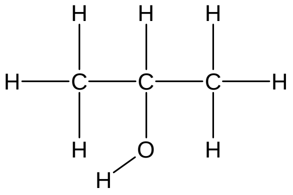
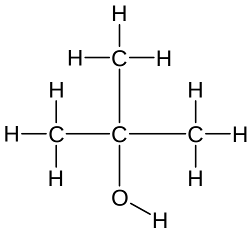
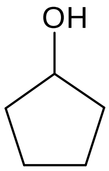
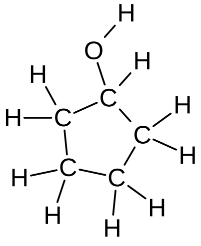
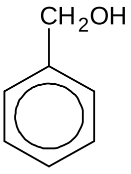
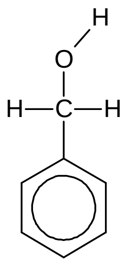
- All alcohols (except methanol) are constitutional isomers (functional group isomers) of ethers.

Ethers (C–O–C), have the same general formula as alcohols but its reactions are not required in the H2 syllabus.

2.1 Nomenclature and Classification of Alcohols

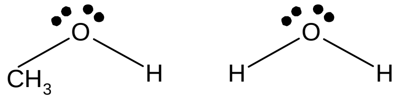
- Alcohols have names ending with ***–ol***
  e.g. Methan**ol**, Ethan**ol**, Propan**ol**

- Examples:

IUPAC Name	**Molecular Formula**	**Structural Formula**	**Displayed formula (Full Structural Formula)**	**Classification**
propan-1-ol	C_3H_7OH	$CH_3CH_2CH_2OH$		primary
propan-2-ol	C_3H_7OH	$CH_3CH(OH)CH_3$		secondary
2-methylpropan-2-ol	C_4H_9OH	$(CH_3)_3COH$		tertiary
cyclopentanol	C_5H_9OH			secondary
phenylmethanol	C_7H_7OH			primary

3 Physical Properties

- Alcohols have the same geometry as water. There are 2 lone pairs and 2 bond pairs of electrons *with respect to the O atom.*

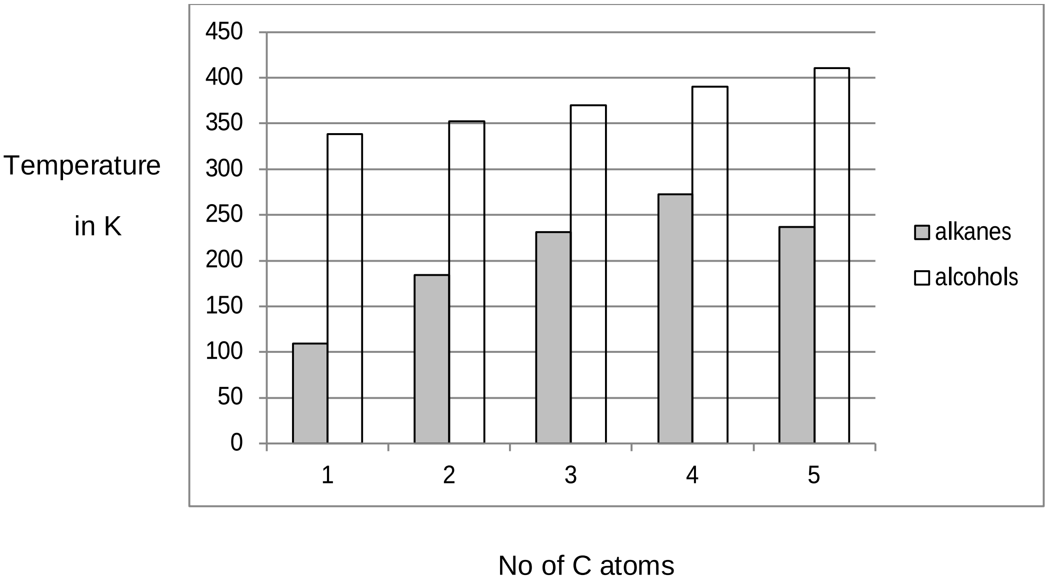


Bent wrt O atom

3.1 Boiling Point

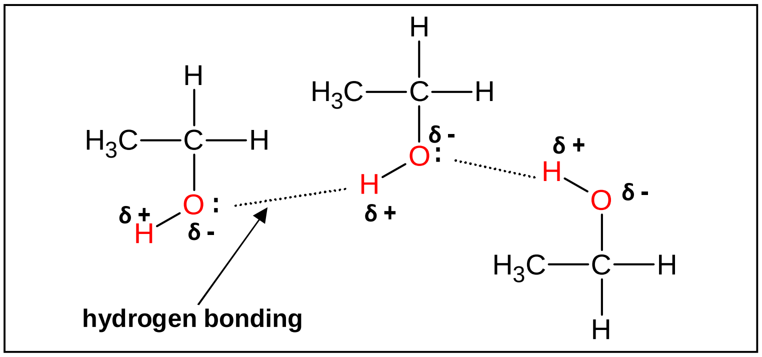
3.1.1 Alcohols vs Alkanes

Alcohols have much higher boiling points compared to alkanes of similar M_r.



Reason:

Both alcohols and alkanes have simple molecular structure. Alcohols are able to form **stronger** intermolecular **hydrogen bonds**, which require **more energy** to overcome than the **weaker** intermolecular **instantaneous dipole-induced dipole interactions** found between alkanes of similar M_r.



3.1.2 Length of Alkyl Chain

Boiling point increases with increasing molecular mass in the alcohol homologous series.

compound	M_r	b.p. / °C
CH_3OH	32.0	65
CH_3CH_2OH	46.0	78
$CH_3CH_2CH_2OH$	60.0	97

Reason:

Alcohols have simple molecular structure. As M_r increases with increasing length of alkyl chain, the **size of electron cloud increases** and **becomes more polarisable**. Hence **more energy** is required to overcome the **stronger instantaneous dipole-induced dipole interactions** between the alcohol molecules.

3.1.3 Straight-chain vs Branched-chain

Branched alcohols have lower boiling points than their straight-chain isomers.

compound	M_r	b.p. / °C
$(CH_3)_3COH$	74.0	82
$CH_3CH_2CH_2CH_2OH$	74.0	117

Reason:

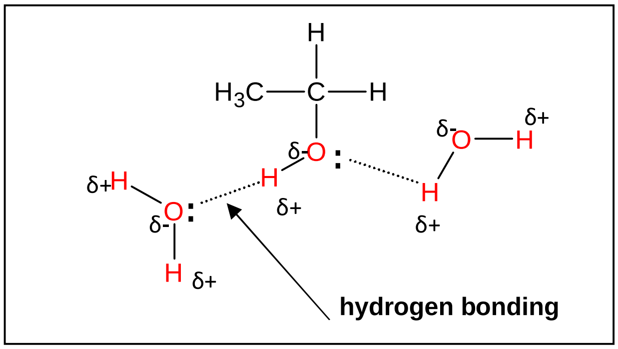
Alcohols have simple molecular structure. The branched isomers are more **spherical** in shape, with **smaller surface area** of contact between molecules. Hence, the strength of intermolecular **instantaneous dipole-induced dipole interactions** is **weaker**, and **less energy** is required to overcome them.

3.2 Solubility

- All alcohols are soluble in organic solvents.
- The first three alcohols (C_1 to C_3) are completely **miscible** with water.

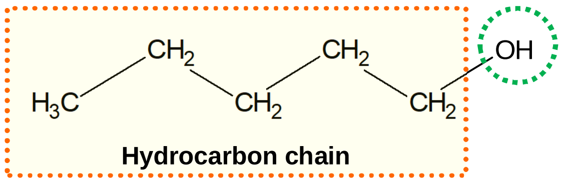
  Reason:

  This is due to the **hydrogen bonding** between the alcohol and the water molecules.



- Alcohols with more than 4 carbons are partially miscible or **immiscible** with water.

  Reason:
  As the **length of the carbon chain increases**, **the instantaneous dipole-induced dipole (id-id) interactions** between the hydrocarbon chains in the alcohol become more significant. Amount of energy evolved during formation of id-id interactions between water and alcohol molecules is **insufficient** to overcome the id-id interactions between alcohol molecules and hydrogen bonding between water molecules.



Alcohols forms hydrogen bonding, making this part *hydrophilic*.

Hydrocarbon chain

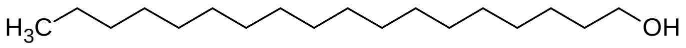
forms instantaneous dipole-induced dipole interactions, making this part *hydrophobic*.

3.2.1 Solubility of alcohol and its applications

Alcohols are good solvents and are used in perfumes and flavourings to dissolve fats and oils. Heavier alcohols with long chains of hydrocarbons act as emulsifiers and surfactants, bringing oil and water together.

Applications:

- Ethanol is used as a fast-drying (due to its low b.p.) solvent in cosmetics and hairsprays.
- Stearyl alcohol (1-octadecanol) is a non-ionic surfactant used as a hair coating in shampoos and conditioners. As water and oil do not dissolve in each other, a surfactant has to be added to the mixture to keep it from separating into layers. Stearyl alcohol can be used as a surfactant as it has both hydrophobic and hydrophilic ends.



Stearyl alcohol $C_{18}H_{38}O$

(1-octadecanol)

4 Chemical Reactions of Alcohols

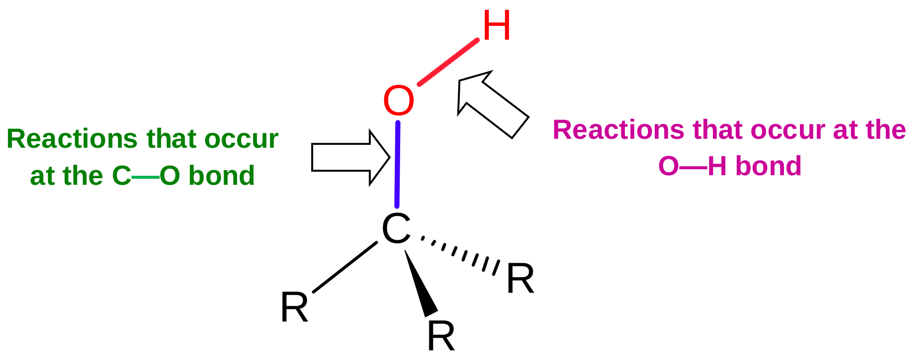
4.1 *Combustion*

Alcohols burn to give carbon dioxide and water.
e.g. ethanol burns with a pale-blue flame

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

4.2 *Other reactions of alcohols*

- Other reactions of alcohols can be divided into two groups: those that occur at the C–O bond and those that occur at the O–H bond.



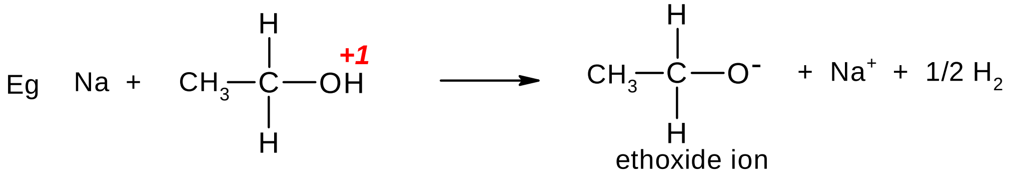
- Overview of the reactions of alcohols

		Type of reaction	Conversion
Reaction at O-H bond	Reaction with Na	reduction	$ROH + Na \rightarrow RO^{-}Na^{+} + \frac{1}{2}\ H_2$
	Esterification	condensation (nucleophilic acyl substitution)	$ROH + R'COOH \rightleftharpoons R'COOR + H_2O$ $ROH + R'COX \rightarrow R'COOR + HX$
	Oxidation	oxidation	ROH → aldehyde / carboxylic acid / ketone (depending on the classification of alcohol)
	Reaction with very strong bases (e.g. NaH, $NaNH_2$, CH_3MgBr)	**Refer to Appendix	
Reaction at C-O bond	Dehydration	elimination	$ROH \rightarrow$ alkene $+ H_2O$
	Halogenation	nucleophilic substitution	$ROH \rightarrow RX + HX$

4.2.1 Reaction with sodium

Type of Reaction	Reduction
Reagents & Conditions	Na(s), room temperature
Equation	CH_3CH_2OH + Na → 2 $CH_3CH_2O^- Na^+$ + ½ H_2
Observation	Effervescence. H_2 (g) evolved gives a 'pop' sound with a lighted splint.
Remarks	• <u>Purpose</u> Reaction can be used to generate a stronger nucleophile RO^- (than ROH) for subsequent reactions. (Refer to appendix Pg 30) • <u>Distinguishing test</u> To test for the presence of –OH group (in alcohols, phenols and carboxylic acids). Test: Add a small piece of Na(s) Observation: Strong effervescence, gas evolved gives a 'pop' sound with lighted splint. H_2(g) is formed. Therefore, –OH group is present.

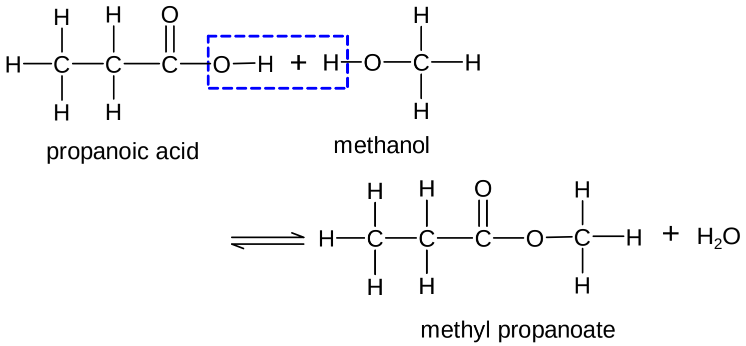
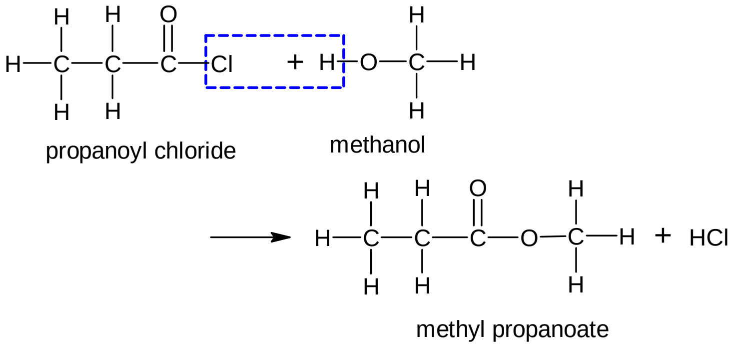
Understanding the reaction in terms of oxidation numbers



$$Na + CH_3CH_2OH \longrightarrow CH_3CH_2O^- + Na^+ + 1/2\,H_2$$

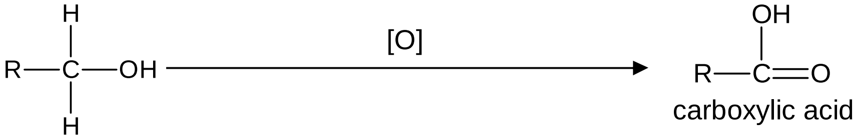
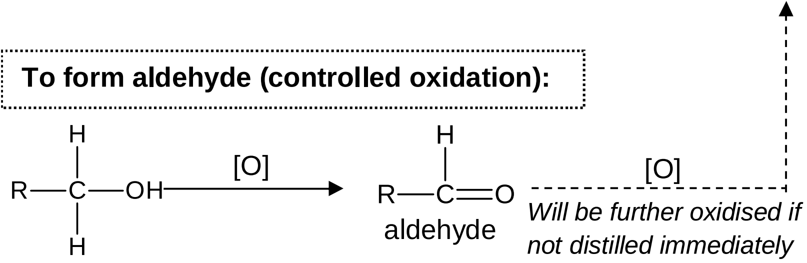
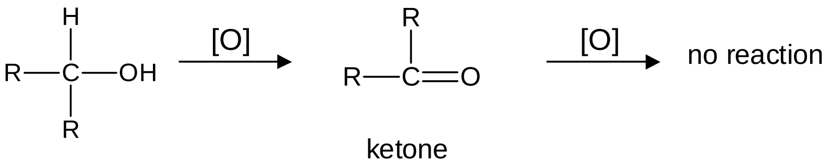
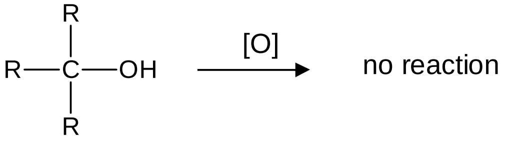
The oxidation no of H decreases from +1 in the OH group to 0 in H_2. Hence ethanol is reduced.

4.2.2 Ester Formation

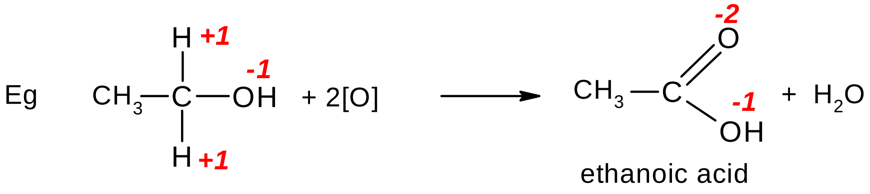
	alcohol + carboxylic acid $\rightleftharpoons$ ester + H_2O	**alcohol + acyl chloride → ester + HC*l***
Equation	$CH_3CH_2COOH + CH_3OH \rightleftharpoons CH_3CH_2COOCH_3 + H_2O$  	$CH_3CH_2COCl + CH_3OH \rightarrow CH_3CH_2COOCH_3 + HCl$ 
Type of Reaction	Condensation (nucleophilic acyl substitution)	Condensation (nucleophilic acyl substitution)
Reagents and Conditions	Carboxylic acid, conc. H_2SO_4, heat under reflux <u>Role of conc. H_2SO_4</u> 1. Catalyst – catalyses the reaction 2. Dehydrating agent – removes the H_2O formed in the reaction, causing the POE to shift to the right to form more products.	Anhydrous acyl chloride at room temperature
Observation	Sweet smell of ester detected, immiscible layer with water (ester is immiscible with water).	Sweet smell of ester detected, Steamy white fumes of HC*l* formed
Remarks	<u>Comparing the two reactions</u> • The reaction between alcohol and carboxylic acid is slow and reversible. Reaction reaches equilibrium in a few hours. • Acyl chlorides are more reactive than carboxylic acids. Hence, using acyl chloride to form the ester is the preferred method since the reaction is <u>complete</u> and takes place rapidly at <u>room temperature</u>.	

4.2.3 Oxidation

Overview:

Type of Reaction	Oxidation
Primary Alcohol	A primary alcohol can be oxidised to either aldehydes or carboxylic acids depending on the conditions. **To form carboxylic acid (oxidation):**  **To form aldehyde (controlled oxidation):**  Aldehydes can be obtained by <u>controlled</u> oxidation of a primary alcohol. The aldehydes formed are immediately removed by distillation, preventing it from further oxidation to give carboxylic acids.
Secondary Alcohol	
Tertiary Alcohol	

Understanding the reaction in terms of oxidation numbers



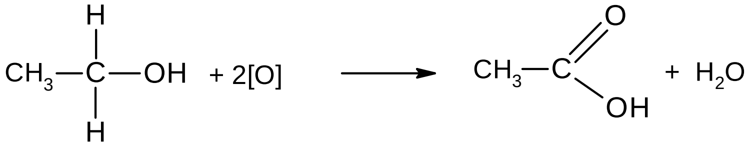
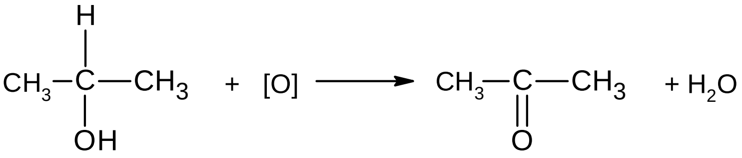
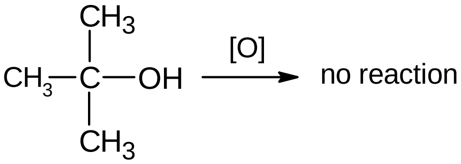
$x + 2(+1) - 1 = 0$

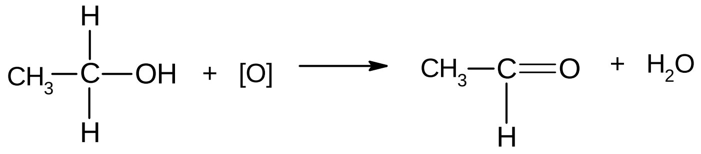
$x = -1$

$y - 2 - 1 = 0$

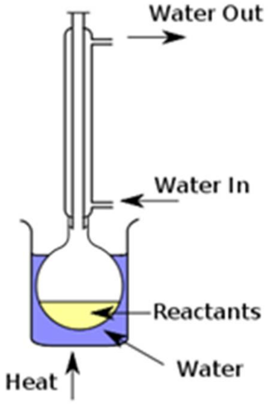
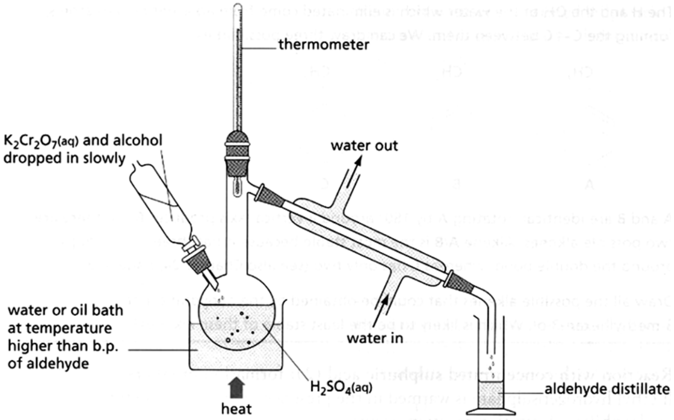
$y = +3$

The oxidation no of C increases from -1 in ethanol to +3 in ethanoic acid. Hence ethanol is oxidised.

Type of Reaction	Oxidation
Reagents & Conditions	(a) $K_2Cr_2O_7$, H_2SO_4 (aq), heat under reflux **OR** (b) $KMnO_4$, H_2SO_4 (aq), heat under reflux
Equation	- 1° alcohol e.g. ethanol  $CH_3CH_2OH + 2[O] \longrightarrow CH_3COOH + H_2O$ ethanoic acid - 2° alcohol e.g. propan-2-ol  $CH_3CH(OH)CH_3 + [O] \longrightarrow CH_3COCH_3 + H_2O$ propanone - 3° alcohol e.g. 2-methylpropan-2-ol  $(CH_3)_3COH \xrightarrow{[O]}$ no reaction
Observation	<u>For 1° & 2° alcohols</u> Orange dichromate(VI) turns green, **OR** purple $KMnO_4$ decolourises. <u>For 3° alcohols</u> Orange dichromate(VI) remains, **OR** purple $KMnO_4$ remains.
Remarks	<u>Distinguishing test</u> This reaction can be used to distinguish between 1° , 2° and 3° alcohols. Test: Add $K_2Cr_2O_7$, H_2SO_4 (aq), heat Observation: *Case 1*: Orange $K_2Cr_2O_7$ turns green ➔ 1° or 2° alcohol is present *Case 2:* Orange $K_2Cr_2O_7$ remains ➔ 1° and 2° alcohol is absent; 3° alcohol is present - Similarly, acidified $KMnO_4$ can be used to distinguish 1° and 2° alcohols from 3° alcohols.

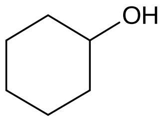
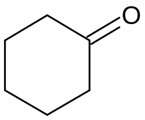
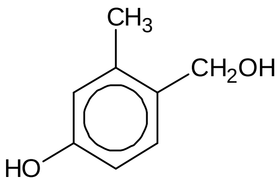
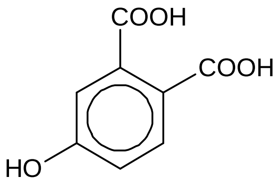
Type of Reaction	Oxidation
Reagents & Conditions	$K_2Cr_2O_7$, H_2SO_4 (aq), heat with ***immediate distillation***
Equation	$CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O$  $CH_3-CH_2(H)(H)-OH + [O] \longrightarrow CH_3-CH{=}O + H_2O$ *Ethanal*
Observation	orange dichromate(VI) turns green
Remarks	• If the reaction involves heating with potassium dichromate(VI), $K_2Cr_2O_7$, H_2SO_4 (aq), under reflux (ie no distillation), the 1° alcohol is oxidised to carboxylic acid <u>directly</u>. The aldehyde will not be obtained. • Acidified $KMnO_4$ <u>cannot</u> be used because it is a much stronger oxidising agent. The primary alcohol will be oxidised to a carboxylic acid directly. The aldehyde will not be obtained even with immediate distillation.

What is the difference between "heat under reflux" and "heat with distillation"?

heat under reflux	heat with distillation
	
Many organic reactions are slow and require prolonged heating to increase the rate of reaction. However, many organic compounds have low boiling points and will vapourise upon exposure to high heat, preventing the reaction from proceeding. To address this, heating under reflux is used. This refers to heating a solution with an attached condenser to prevent reagents from evaporating away. Any vapour will condense on the cool surface of the attached condenser and flow back into the flask.	In the case of controlled oxidation to form aldehydes from primary alcohols, the aldehyde formed is immediately removed by <u>distillation</u> as it is formed, preventing it from further oxidation to give carboxylic acids. This method makes use of the higher volatility of the aldehyde (lack of hydrogen bonding). The reaction mixture is warmed to a temperature above the boiling point of the aldehyde, but below that of the alcohol. The aldehyde distils as soon as it is formed, avoiding any further contact with the oxidation agent.

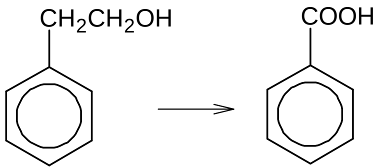
Worked example 1

Give the structural formulae of the organic products for each of the following oxidation reactions.

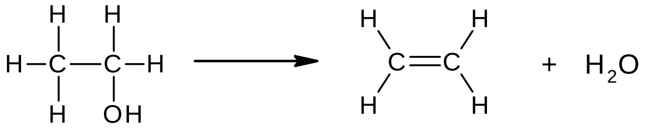
Reactant	Reagents and Conditions	Organic product
$(CH_3)_2CHCH_2OH$	$K_2Cr_2O_7$, H_2SO_4 (aq), heat with immediate distillation	$(CH_3)_2CHCHO$
	$K_2Cr_2O_7$, H_2SO_4 (aq), heat under reflux	$(CH_3)_2CHCOOH$
 cyclohexanol	$KMnO_4$, H_2SO_4 (aq), heat under reflux	 cyclohexanone
	$KMnO_4$, H_2SO_4 (aq), heat under reflux	

Putting it together

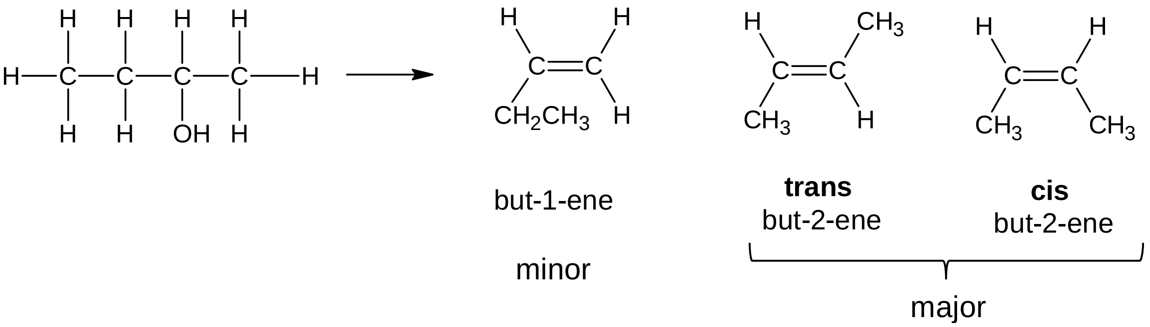
We can deduce the type of alcohols from the change in molecular formula (useful for deductive qns)

Oxidation reaction	**Change in molecular formula**	**Example**
Primary alcohol → carboxylic acid	Gain of 1 O atom, loss of 2 H atoms	$RCH_2OH \rightarrow RCOOH$
Aldehyde → carboxylic acid	Gain of 1 O atom	$RCHO \rightarrow RCOOH$
Primary alcohol → aldehyde	No change in number of O atoms, loss of 2 H atoms	$RCH_2OH \rightarrow RCHO$
Secondary alcohol → ketone	No change in number of O atoms, loss of 2 H atoms	$R_2CHOH \rightarrow R_2CO$
Oxidation of carbon containing side chain of benzene	Loss of C atoms	

4.2.4 **Dehydration** (Alcohol → Alkenes + Water)

Type of Reaction	Elimination
Reagents & Conditions	(a) Excess conc. H_2SO_4 at 170°C, **OR** (b) Heat with Al_2O_3 to 350°C.
Equation	$CH_3CH_2OH \longrightarrow CH_2 = CH_2 + H_2O$  ethanol ethene
Remarks	Primary alcohols give a **single** product. Secondary and tertiary alcohols may give a **mixture** of products.

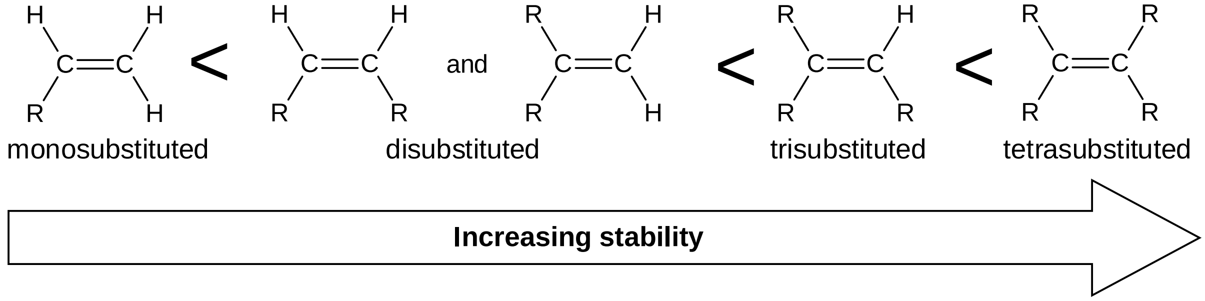
Example:



<u>Saytzeff's rule</u>

In an elimination reaction, the products with the **most highly substituted double bond** (more alkyl groups) will predominate (major product).

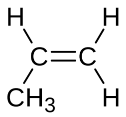
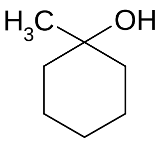
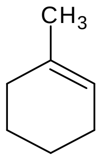
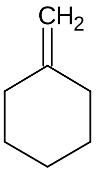
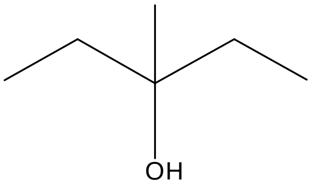
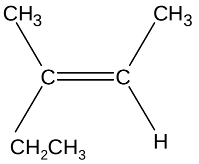
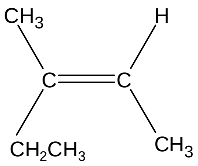
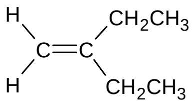
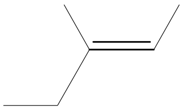
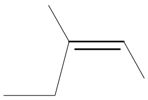
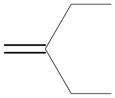
(Note that this is unlike the Markovnikov's Rule where only the most stable product forms.)



If any of the major and minor products possesses *cis-trans* isomerism, both the *cis* and *trans* isomers will be formed. (Refer to Halogen derivatives Lecture Notes)

Worked example 2

Give the structural formulae of all the possible organic products of following reactions.

Reactant	**Reagents and Conditions**	**Organic product**
$CH_3CH_2CH_2OH$	Al_2O_3, 350°C	
	Excess conc. H_2SO_4 , 170 °C	 major  minor
	Excess conc. H_2SO_4 , 170 °C	   minor cis trans major OR answers in skeletal form:    cis trans minor major

4.2.5 Halogenation

$$ROH \rightarrow RX$$

Alcohols can be converted to halogenoalkanes via the following reactions:

- Reactions involving hydrogen halides, HX
- Reacting alcohols with phosphorus halides, PCl_5 , PBr_3, PI_3
- Reacting alcohols with thionyl chloride, $SOCl_2$

(i) Chlorination (to form RC*l*):

Type of Reaction	Nucleophilic substitution
Reagents & Conditions	(a) $SOCl_2$ (thionyl chloride) at room temperature **OR** (b) PCl_3 or PCl_5 at room temperature **OR** (c) HC*l*(g)
Equation	(a) $CH_3CH_2OH + SOCl_2 \rightarrow CH_3CH_2Cl + SO_2 + HCl$ (b) $3\ CH_3CH_2OH + PCl_3 \rightarrow 3\ CH_3CH_2Cl + H_3PO_3$ $CH_3CH_2OH + PCl_5 \rightarrow CH_3CH_2Cl + POCl_3 + HCl$ (c) $CH_3CH(OH)CH_3 + HCl \rightarrow CH_3CH(Cl)CH_3 + H_2O$
Observation	For reaction with $SOCl_2$ and PCl_5: Steamy white fumes of HC*l* observed.
Remarks	➢ Distinguishing test PCl_5 or $SOCl_2$ can be used as a test for the presence of –OH group in alcohols and carboxylic acids. Test: Add PCl_5 at room temp **OR** $SOCl_2$ at room temp Observation: Steamy white fumes observed. HC*l* is formed Therefore, –OH group is present. ➢ $SOCl_2$ is a preferred reagent for chlorination as the products, SO_2 and HC*l* are gases. Hence, it gives a very **clean reaction**. The halogenoalkane formed can be easily isolated from the other gaseous products.

(ii) Bromination (to form RBr):

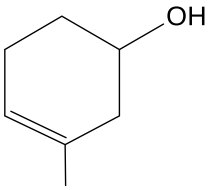
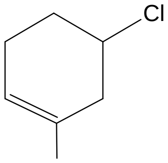
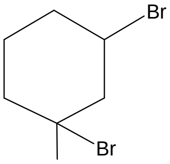
Type of Reaction	Nucleophilic substitution
Reagents & Conditions	(a) PBr_3 at room temperature **OR** (b) HBr(g)
Equation	(a) $3\ CH_3CH_2OH + PBr_3 \rightarrow 3\ CH_3CH_2Br + H_3PO_3$ (b) $CH_3CH(OH)CH_3 + HBr \rightarrow CH_3CH(Br)CH_3 + H_2O$

(iii) Iodination (to form RI):

Type of Reaction	Nucleophilic substitution
Reagents & Conditions	(a) PI_3 **OR** (b) HI(g)
Equation	(a) $3\ CH_3CH_2OH + PI_3 \rightarrow 3\ CH_3CH_2I + H_3PO_3$ (b) $CH_3CH(OH)CH_3 + HI \rightarrow CH_3CHICH_3 + H_2O$

Worked example 3

Give the structural formulae of all the possible organic products of following reactions.

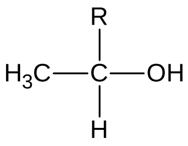
Reactant	**Reagents and Conditions**	**Organic product**	**Type of reaction(s)**
$CH_3CH_2CH_2OH$	HCl(g)	$CH_3CH_2CH_2Cl$	Nucleophilic substitution
	$SOCl_2$,		Nucleophilic substitution
	HBr(g)		Nucleophilic substitution *and* Electrophilic addition

4.2.6 Tri-iodomethane (Iodoform) test

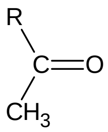
- The reaction of iodine and NaOH(aq) with methyl alcohols or methyl carbonyls results in the appearance of a very pale yellow precipitate of triiodomethane, CHI_3 (previously known as iodoform).

- This reaction is positive for **alcohols** with a **<u>methyl group</u>** and a **<u>hydrogen atom</u>** attached to the carbon with the **<u>–OH group</u>**.

- For **carbonyl compounds**, the reaction is positive for **<u>methyl carbonyls</u>**. (refer to *Carbonyl Compounds* Lecture)



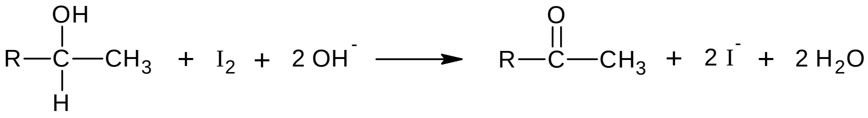
$$H_3C-\overset{R}{\underset{H}{C}}-OH$$



(R = H atom, alkyl or aryl group)

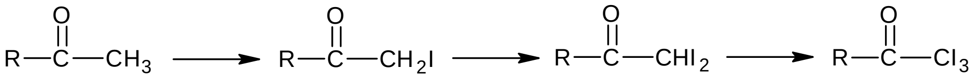
<u>Steps for the formation of tri-iodomethane (mechanism is NOT required for syllabus)</u>

1. Oxidation of the alcohol to a methyl ketone.



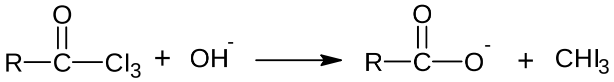
$$R-\overset{OH}{\underset{H}{C}}-CH_3 + I_2 + 2\,OH^- \longrightarrow R-\overset{O}{\overset{\|}{C}}-CH_3 + 2\,I^- + 2\,H_2O$$

2. Substitution of the hydrogens to form tri-iodoketone.

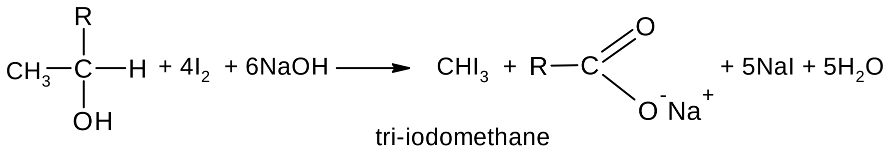


$$R-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow R-\overset{O}{\overset{\|}{C}}-CH_2I \longrightarrow R-\overset{O}{\overset{\|}{C}}-CHI_2 \longrightarrow R-\overset{O}{\overset{\|}{C}}-CI_3$$

3. Attack by the OH^- causing the C–C bond to break.

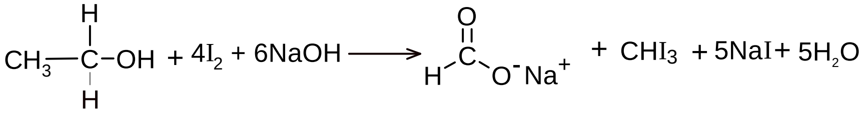
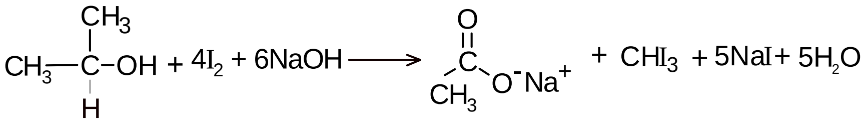


$$R-\overset{O}{\overset{\|}{C}}-CI_3 + OH^- \longrightarrow R-\overset{O}{\overset{\|}{C}}-O^- + CHI_3$$

Type of Reaction	Oxidation
Reagents & Conditions	NaOH(aq), I_2(aq), warm
Equation	$CH_3CH(OH)R + 4I_2 + 6NaOH \rightarrow CHI_3 + RCO_2^-Na^+ + 5NaI + 5H_2O$ 
Observation	Yellow ppt of CHI_3 formed (antiseptic smell)
Remarks	<u>Distinguishing Test</u> Alkaline aqueous iodine is used to test for the presence of (i) methyl alcohols (ii) methyl carbonyls Test: Add NaOH(aq), I_2(aq), warm Observation: Yellow ppt of CHI_3 is formed Therefore, methyl alcohol or methyl carbonyl is present

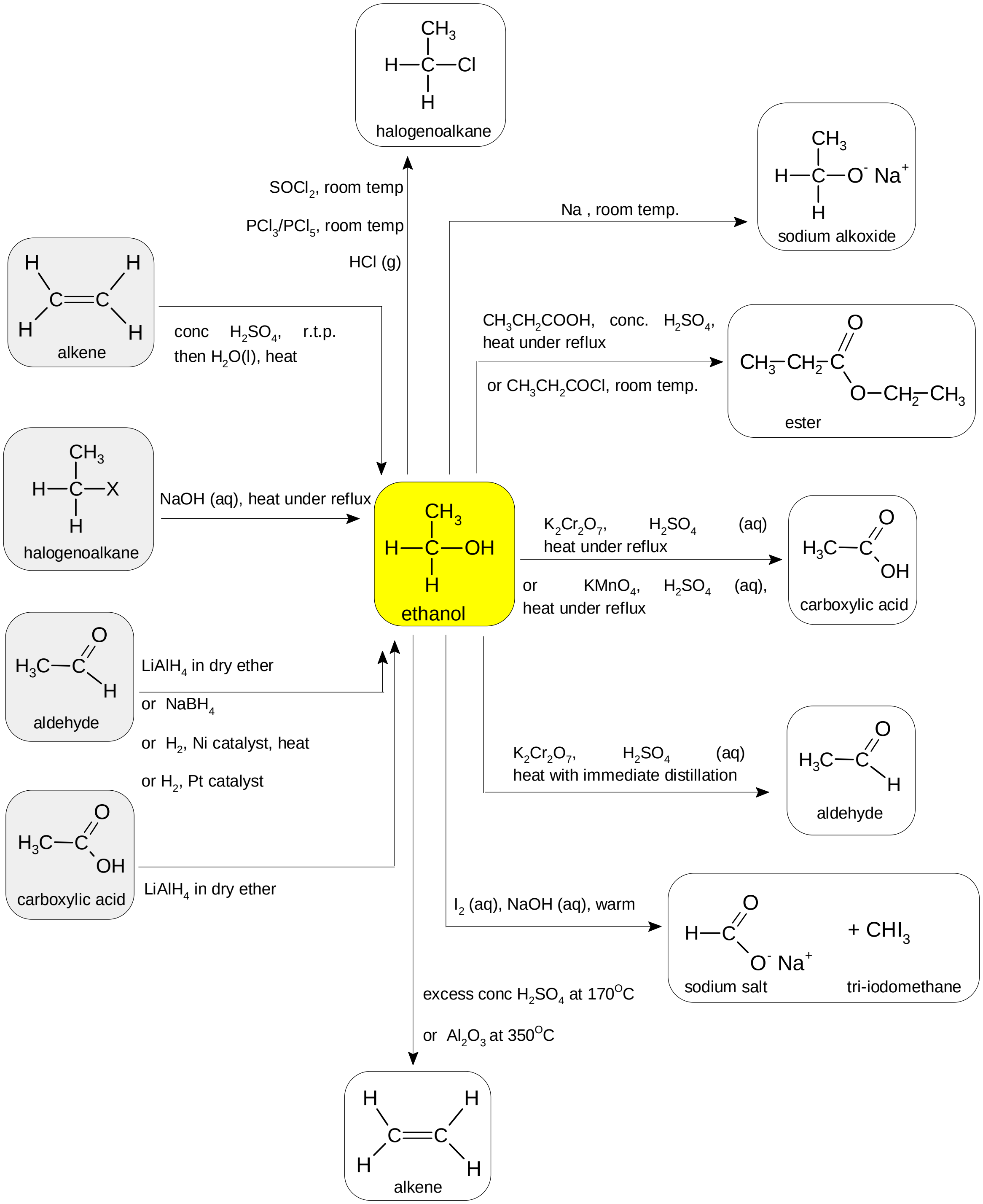
<u>Worked example 4</u>

Which of the following alcohols will give a positive triiodomethane test? If there is any reaction, give the balanced equation for the reaction.

(a) Methanol	No reaction
(b) Ethanol	Yellow ppt of CHI_3 formed. 
(c) propan-1-ol	No reaction
(d) propan-2-ol	Yellow ppt of CHI_3 formed. 

✍ *Self check: Tutorial Q1 – Q4*

Summary of reactions for a primary alcohol



Organic Summary by Reagent (Alkanes → Phenols)

1. This summary gives you an overview of different reagents react with the different functional groups you have learnt so far.
2. For each organic functional group, the conditions required for the reaction is stated. "Nil" indicates that the reagent does not react with the functional group.
3. Expand on this summary by thinking of an example for each functional group and writing out the products formed, or any other reagent not listed here.
4. Finally, recall what type of reaction occurs for each reaction.

Reagent	**Functional Group**								
	Alkanes	**Alkenes**	**Arenes**	**Arenes with carbon containing side chain e.g. methylbenzene**	**Halogenoalkanes**	**Halogenoarenes**	**Primary alcohols**	**Secondary alcohols**	**Phenols**
HCl (g)	NIL	✓ Electrophilic addition	NIL	NIL	NIL	NIL	✓nucleophilic substitution	✓nucleophilic substitution	NIL
PBr_3 , room temp	NIL	NIL	NIL	NIL	NIL	NIL	✓nucleophilic substitution	✓ nucleophilic substitution	NIL
$SOCl_2$, room temp	NIL	NIL	NIL	NIL	NIL	NIL	✓nucleophilic substitution	✓nucleophilic substitution	NIL
$K_2Cr_2O_7$ H_2SO_4 (aq), heat	NIL	NIL	NIL	NIL	NIL	NIL	✓ oxidation	✓oxidation	NIL
$KMnO_4$ H_2SO_4 (aq), heat	NIL	✓Oxidation * Mild oxidation takes place with cold dil $KMnO_4$,H_2SO_4 (aq)	NIL	✓Oxidation	NIL	NIL	✓Oxidation	✓Oxidation	NIL
NaOH (aq), room temp	NIL	NIL	NIL	NIL	*NaOH (aq), ***heat*** nucleophilic substitution	NIL	NIL	NIL	✓acid base reaction
Na (s), room temp	NIL	NIL	NIL	NIL	NIL	NIL	✓reduction	✓ reduction	✓ reduction
CH_3COCl room temp	NIL	NIL	NIL	NIL	NIL	NIL	✓condensation /nucleophilic acyl substitution	✓ condensation /nucleophilic acyl substitution	✓ condensation /nucleophilic acyl substitution
Br_2 (aq), room temp	***Br_2 (g), UV or heat** Free radical substitution	✓ Electrophilic addition	***Br_2, anhydrous $FeBr_3$ rm temp** Electrophilic substitution	***Br_2, anhydrous $FeBr_3$ rm temp** Electrophilic substitution	NIL	***Br_2, anhydrous $FeBr_3$ rm temp** Electrophilic substitution	NIL	NIL	✓Electrophilic substitution

* Indicates a variation of reagent and conditions for possible reactions

Appendix

(I) Alcohol reaction with *very* strong bases

Other than reacting with alkali metals like Na, alcohols react with **strong bases** such as sodium hydride (**NaH**), sodium amide (**$NaNH_2$**) and Grignard reagents (**RMgX**).

Alkoxide (**RO^-**) ions are formed in all these reactions.

- With sodium hydride ($Na^+ H^-$),

$CH_3OH + NaH \rightarrow CH_3O^- Na^+ + H_2$

- With sodium amide ($NaNH_2$),

$CH_3CH_2OH + NaNH_2 \rightarrow CH_3CH_2O^- Na^+ + NH_3$

- With Grignard reagent,

$CH_3CH_2OH + CH_3MgBr \rightarrow CH_3CH_2O^- \, ^+MgBr + CH_4$

- *formation of Grignard reagent, CH_3MgBr*: $CH_3Br + Mg \rightarrow CH_3MgBr$

In all these cases, the alcohol loses the hydrogen to form the RO^- ion.

The RO^- ion is a stronger nucleophile than ROH, the original alcohol.

Purpose of this reaction

The alkoxide ions that are formed are nucleophiles that are frequently used as reagents in organic reactions.

[Recall: Nucleophiles are electron-rich species that carries a negative or partial negative charge and attacks positive centres in other molecules or ions.]

Example:
Once ethoxide ion is formed from ethanol using any of the 3 strong bases above, the ethoxide ion can reaction with 1-bromopropane as follows:

$$CH_3CH_2\overset{\delta+}{C}H_2Br + CH_3CH_2O{:}^- \longrightarrow CH_3CH_2CH_2OCH_2CH_3 + Br^- \quad \text{--- } \mathbf{(1)}$$

An ether (functional group not in syllabus)

Compare reaction **(1)** with the equation below (from *Halogen Derivatives*):

$$CH_3CH_2CH_2Br + OH^- \longrightarrow CH_3CH_2CH_2OH + Br^-$$

You learnt that hydroxide ions are good nucleophiles. When halogenoalkane reacts with sodium hydroxide solution, the hydroxide ion replaces the halogen atom.

The ethoxide ion can behave in the same way as the hydroxide ions. The ethoxide ion is able to replace the halogen atom as well (as shown by equation **(1)**).

(II) Ethanol as a chemical, drug and poison

The production of ethanol by fermentation of grains and sugars is one of the oldest known organic reactions, going back at least 2500 years. Fermentation is carried out by adding yeast to an aqueous sugar solution, where enzymes break down carbohydrates (sugars and starches) into ethanol and carbon dioxide:

In Singapore, binge drinking (defined as having 4 or more alcoholic drinks in one session for women, and 5 or more for men) is more common among 18 to 29 year olds – 18.7% of men and 12.2% of women. In 2010, the Singapore Mental Health Study found that about 3.5% of our citizens suffered from alcohol abuse at some point in their lives and 0.5% from alcohol addiction (or alcoholism).

A person's brain develops until the age of about 24. During this time, alcohol abuse can result in learning difficulties and social problems. Alcohol is also a known cause of cancers of the mouth, throat (pharynx), voice box (larynx), esophagus, liver, colon and rectum, and breast. Alcohol may increase the risk of cancer of the pancreas too.

The blood alcohol concentration in drivers can be tested by the Breathalyser test. It makes use of the colour change that occurs when the expired air reduces the bright orange oxidising agent potassium dichromate ($K_2Cr_2O_7$) to green chromium(III) ion, Cr^{3+}.

(III) Alternative Form of Fuel – Bioethanol

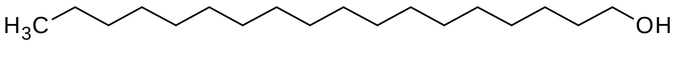
Bioethanol is an alcohol made by fermentation, mostly from carbohydrates in the form of sugar and starch produced by crops such as corn and sugarcane.

However, there are concerns about the production of bioethanol, such as the fact that it requires more energy for production than it can supply and that it directly competes for land for growing crops.

(IV) Solubility of alcohol and its application

Alcohols are good solvents and are used in perfumes and flavourings to dissolve fats and oils. Heavier alcohols with long chains of hydrocarbons act as emulsifiers and surfactants, bringing oil and water together.

- Ethanol is used as a fast-drying (due to its low b.p.) solvent in cosmetics and hairsprays.
- Stearyl alcohol (1-octadecanol) is a non-ionic surfactant used as a hair coating in shampoos and conditioners. As water and oil do not dissolve in each other, a surfactant has to be added to the mixture to keep it from separating into layers. Stearyl alcohol can be used as a surfactant as it has both hydrophobic and hydrophilic ends.

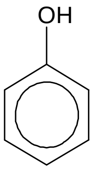


Stearyl alcohol (1-octadecanol)

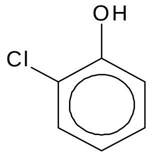
PHENOLS

1 Nomenclature

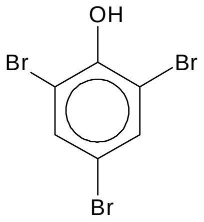
- Phenols have an –OH group attached directly to the benzene ring.



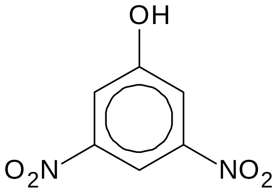
phenol



2-chlorophenol



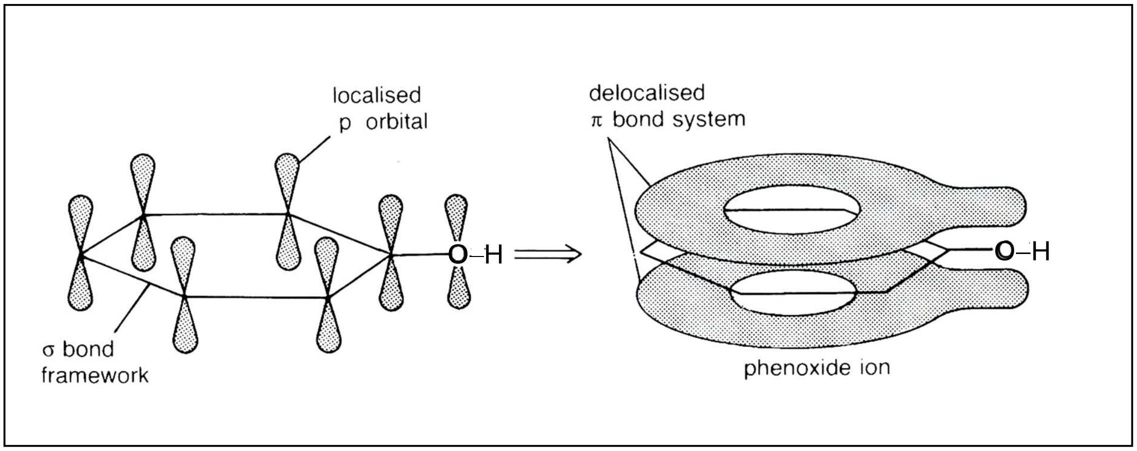
2,4,6-tribromophenol



3,5-dinitrophenol

2 Structure of Phenol

- Recall: Benzene ring has a delocalised cloud of π electrons due to the overlapping 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 atom overlaps with the π electron cloud of the benzene ring**, forming a delocalised cloud.



As a result,

- The **C – O bond is strengthened**, while the **O– H bond is weakened**.
- Phenol is a relatively stronger acid than alcohol. Hence phenols can react with NaOH while alcohols cannot. (Refer to acidity of Phenols)

3 Physical Properties

3.1 Appearance

- Phenol is a colourless, hygroscopic, crystalline solid (m.p. 42 °C, b.p. 181 °C) with an antiseptic smell.

3.2 Boiling point

- Phenols have much higher boiling points compared to alkanes of similar M_r.

compound	M_r	b.p. / °C
phenol C_6H_5OH	92.0	181
$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	100.0	98

Reason:
Phenol is able to form stronger intermolecular **hydrogen bonds**, which require more energy to overcome than the weaker intermolecular **instantaneous dipole-induced dipole interactions** found between alkanes of similar M_r.

3.3 Solubility

- Although the –OH group can form hydrogen bonds with water, the non-polar benzene ring is hydrophobic. Hence, phenols are only partially soluble in water.

3.4.1 Acidity

- Phenols are slightly acidic.

$$C_6H_5OH + H_2O \rightleftharpoons \underset{\textit{phenoxide ion}}{C_6H_5O^-} + H_3O^+$$

  - It has no effect on litmus paper.
  - It does not react with carbonates. (Only carboxylic acids and strong mineral acids like HCl, HNO_3 react with carbonates)

What affects acid strength?

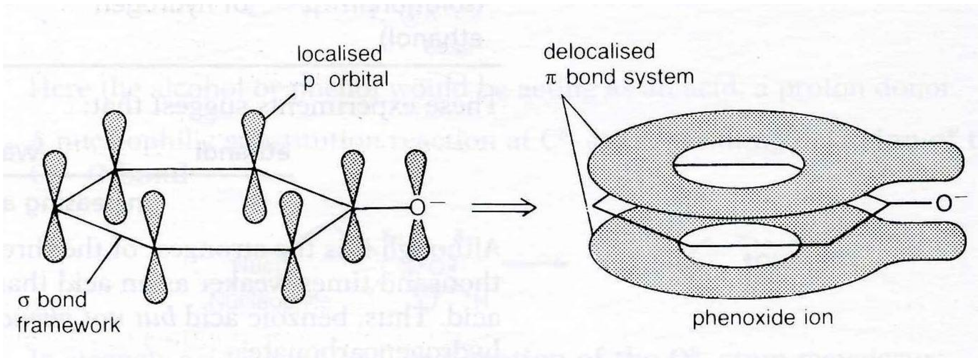
- A stronger acid is one that dissociates more to produce conjugate base and proton. Position of equilibrium lies further to the right.

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

- The strongest acid forms the most stable conjugate base.
- Therefore, the relative **strength** of an acid depends on the **stability of its conjugate base** formed.
  - When a **more stable conjugate base** formed,
  - the POE of dissociation lies **more to the right**,
  - hence the respective acid is **stronger**.

Comparing the acidities of alcohol, water and phenol

	Ethanol	**Water**	**Phenol**
Equation for dissociation	(1) $CH_3CH_2OH + H_2O \rightleftharpoons$ $CH_3CH_2O^- + H_3O^+$	(2) $2H_2O \rightleftharpoons OH^- + H_3O^+$	(3) $C_6H_5OH + H_2O \rightleftharpoons$ $C_6H_5O^- + H_3O^+$
K_a / mol dm^{-3} (at 25 ^{o}C)	1.3×10^{-16}	1.8×10^{-16}	1.3×10^{-10}
Acid strength	**Increasing acidity** →		
Conjugate base and relative stability	$CH_3CH_2O^-$ **(least stable)**	OH^-	$C_6H_5O^-$ **(most stable)**
Reason	**Ethanol, water and phenol are Bronsted-Lowry acids as they are proton donors.** **The ethoxide ion ($CH_3CH_2O^-$) is the least stable conjugate base.** The negative charge on O atom is intensified by electron donating alkyl group, hence destabilising the conjugate base. Therefore, ethanol is the least acidic, and POE (1) lies more to the left and ethanol donates a proton less readily than water. **The phenoxide ion is the most stable** as the p orbital of O overlaps with the π orbital of the benzene ring resulting in the delocalisation of lone pair of electrons on the O atom into the benzene ring. The negative charge on O atom is dispersed over the benzene ring and one oxygen atom, hence stabilising the conjugate base. Therefore, phenol is the most acidic and POE (3) lies more to the right and phenol donates a proton more readily than water.		

	Ethanol	**Water**	**Phenol**
			
Reaction with Na	ROH + Na → $RO^-Na^+ + ½ H_2$	H_2O + Na → NaOH+ ½ H_2	C_6H_5OH + Na → $C_6H_5O^-Na^+ + ½ H_2$
Reaction with NaOH	No reaction	NaOH dissociates in water, no reaction	C_6H_5OH + NaOH → $C_6H_5O^-Na^+ + H_2O$
Reaction with Na_2CO_3	No reaction	No reaction	No reaction

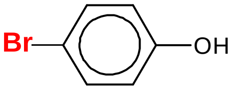
[You should be able to compare the reactions of carboxylic acids with the above reagents after the completion of the *Carboxylic Acid* & Derivatives lecture.]

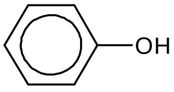
Effect of Substituents on Acidity

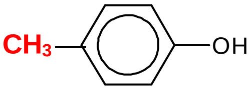
Phenols are **more acidic** when the ring is substituted with **electron withdrawing groups**.

The electron withdrawing groups **stabilises** the phenoxide ion by **further dispersing the negative charge on the oxygen**.

Conversely, phenols substituted with **electron donating groups** are **less acidic** than phenol.







4-bromophenol pKa = 9.35 phenol pKa = 10.00 4-methylphenol pKa = 10.26

4 Chemical Properties

4.1 Combustion

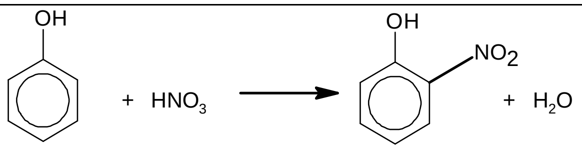
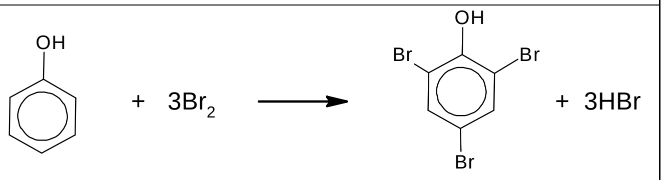
Similar to benzene, phenol is highly inflammable and burns in air with a smoky flame due to its high carbon content.

$$C_6H_5OH + 7O_2 \rightarrow 6CO_2 + 3H_2O$$

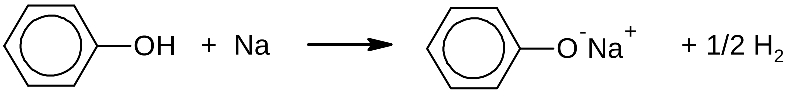
4.2 **Other reactions of phenol** can be divided **two groups: those that occur at**

- the O–H bond and
- those that occur in the benzene ring

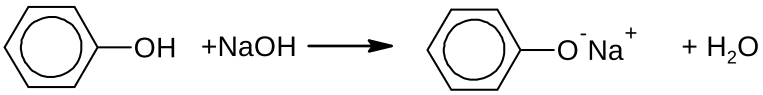
Overview of reactions of phenol

	Type of reaction	**Equations**
Reaction at O-H bond	Reduction of phenol	$C_6H_5OH + Na \rightarrow C_6H_5O^{-}Na^{+} + \frac{1}{2} H_2$
	Acid base	$C_6H_5OH + NaOH \rightarrow C_6H_5O^{-}Na^{+} + H_2O$
	Condensation / Nucleophilic acyl substitution	$C_6H_5OH + \mathbf{RCO}X \rightarrow C_6H_5O\mathbf{COR} + HX$ Acyl chloride ester
Reaction of the Benzene Ring in Phenol	Electrophilic substitution	
	Electrophilic substitution	

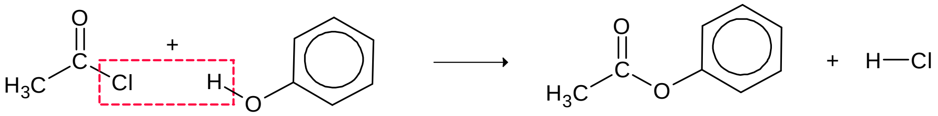
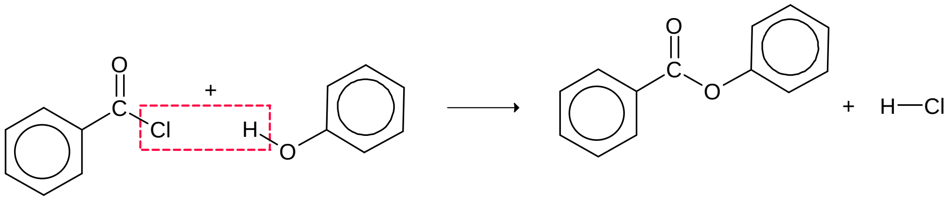
4.2.1 Reaction with Sodium

Type of Reaction	Reduction of phenol
Reagents & Conditions	Sodium metal at room temperature
Purpose	This reaction can be used to generate a phenoxide ion that is a strong nucleophile for subsequent reactions.
Equations	$C_6H_5OH + Na \rightarrow C_6H_5O^-Na^+ + \frac{1}{2}H_2$ sodium phenoxide 
Observations	**Distinguishing test** **This reaction is used to test for the presence of –OH groups in alcohols, phenols and carboxylic acids** **Test:** • Add a small piece of Na metal **Observation:** • Strong effervescence, gas evolved gives a 'pop' sound with lighted splint. • H_2 gas is formed. ∴ –OH group is present

4.2.2 Reaction with Bases

Type of Reaction	Acid-base
Reagents & Conditions	Aqueous NaOH at room temperature
Purpose	This reaction can be used to generate the phenoxide ion that is a strong nucleophile for subsequent reactions. (Refer to Phenol reaction with aromatic acyl chlorides)
Equations	$C_6H_5OH + NaOH \rightarrow C_6H_5O^-Na^+ + H_2O$ sodium phenoxide 
Observations	Phenol dissolves to form a colourless solution. The sodium phenoxide is able to form ion-dipole interactions with water, hence it is miscible with water.
Note	**Distinguishing Test** **This reaction is useful to distinguish phenol from non-polar organic liquids that do not react with NaOH (aq)** **Test:** • Add NaOH(aq) to phenol **Observation:** • Resulting mixture is a homogenous colourless solution Other organic liquids (e.g. alcohols) that do not react with NaOH will result in 2 immiscible layers being observed.

4.2.3 Formation of esters

Type of reaction	Condensation (Nucleophilic acyl substitution)
Reagents & Conditions	Anhydrous acyl chloride, room temperature
Equations	(i) $CH_3COCl + C_6H_5OH \rightarrow CH_3CO_2C_6H_5 + HCl$  (ii) $C_6H_5COCl + C_6H_5OH \rightarrow C_6H_5CO_2C_6H_5 + HCl$ 
Observations	Sweet-smelling ester produced as an immiscible layer from water, steamy white fumes of HCl produced.

Self-check : How are esters synthesised?

Reactants			Ester formed?
Alcohol	+	Carboxylic acid	yes
Alcohol	+	Acyl Chloride	yes
Phenol	+	Carboxylic acid	**no**
Phenol	+	Acyl chloride	yes

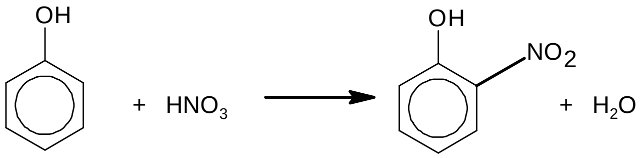
5 Reactions of the Benzene Ring in Phenol

- The –OH group in phenol is a strong **electron-donating** group, hence it **activates** the ring strongly towards electrophilic substitution.

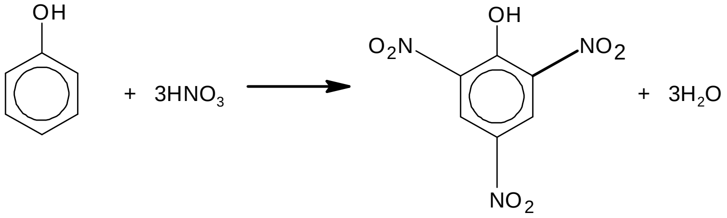
  The –OH group increases the electron density in the benzene ring, hence, increasing its reactivity towards electrophiles. Therefore, phenol undergoes nitration and bromination readily at room temperature, without the presence of a catalyst (as compared to benzene).
- The –OH group is **2, 4-directing**. The electron density on the carbons of 2- and 4- positions increases, thus makes them more vulnerable to attack by an electrophile at these positions. (Recall from Arenes notes)

5.1 Nitration

5.1.1 Formation of mono-substituted products (2-nitrophenol or 4-nitrophenol):

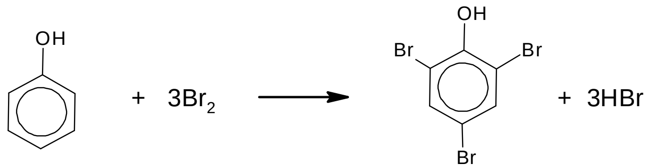
Type of Reaction	Electrophilic Substitution
Reagents & Conditions	Dilute HNO$_3$ at room temperature
Equation	 *4-nitrophenol can **also** be formed.

5.1.2 Formation of multi-substituted product (2,4,6-trinitrophenol):

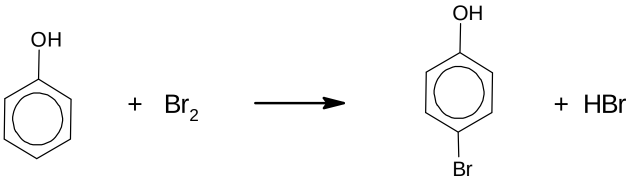
Type of Reaction	Electrophilic Substitution
Reagents & Conditions	Concentrated HNO$_3$ at room temperature
Equation	
Remarks	• Phenol undergoes nitration much more easily than benzene. Hence concentrated H$_2$SO$_4$ is not required to generate the strong NO$_2^+$ electrophile. The weak electrophile HNO$_3$ is sufficient to attack the benzene ring in phenol. • When concentrated HNO$_3$ is used, **multiple substitutions** can take place.

5.2 Bromination

5.2.1 *Formation of multi-substituted product (2,4,6-tribromophenol):*

Type of Reaction	Electrophilic Substitution
Reagents & Conditions	$Br_2(aq)$ at room temperature
Equation	 2,4,6-tribromophenol
Observation	Orange colour of bromine decolourised and white precipitate of 2,4,6-tribromophenol formed. Steamy white fumes of $HBr(g)$ may also be observed.
Remarks	**Compare this reaction with halogenation of benzene.** Halogen carrier is not required in this case. **Distinguishing test** **Test for phenol or phenylamine group** **Test:** • Add a few drops of aqueous Br_2 at room temperature **Observation:** • Orange aqueous Br_2 decolourised and production of white precipitate. ∴ phenol or phenylamine is present (Refer to *Nitrogen compounds* Lecture Notes that will be taught later)

5.2.2 Formation of mono-substituted products (2-bromophenol or 4-bromophenol):

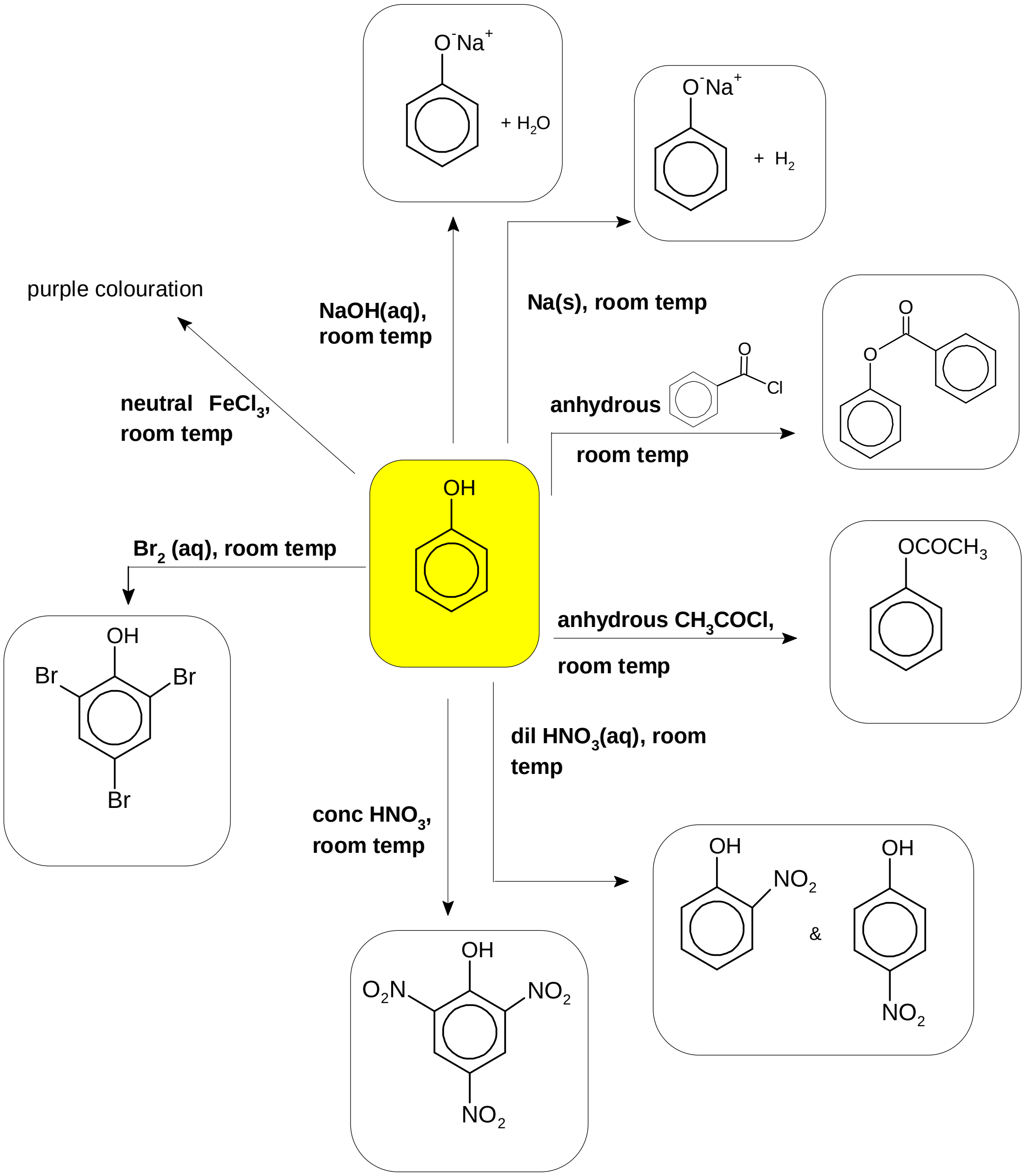
Type of Reaction	Electrophilic Substitution
Reagents & Conditions	Br_2 in CCl_4 at room temperature
Equation	 4-bromophenol 2-bromophenol can also be formed.
Observation	Orange-red colour of bromine decolourised. Steamy white fumes of HBr(g) may also be observed.
Remarks	Recall that alkenes also react with Br_2 in CCl_4, decolourising the orange-red bromine. However, no white fumes (HBr) will be formed.

6 Reaction with neutral Iron(III) Chloride

Reagents & Conditions	Neutral $FeCl_3$(aq) at room temperature
Observation	Purple colouration
Remarks	<u>Distinguishing test</u> To test for phenol group Test: Add neutral $FeCl_3$(aq) at room temperature Observation: Purple colouration observed. Therefore, phenol is present

✍ *Self check: Tutorial Q5 – Q7*

Summary of reactions for Phenol

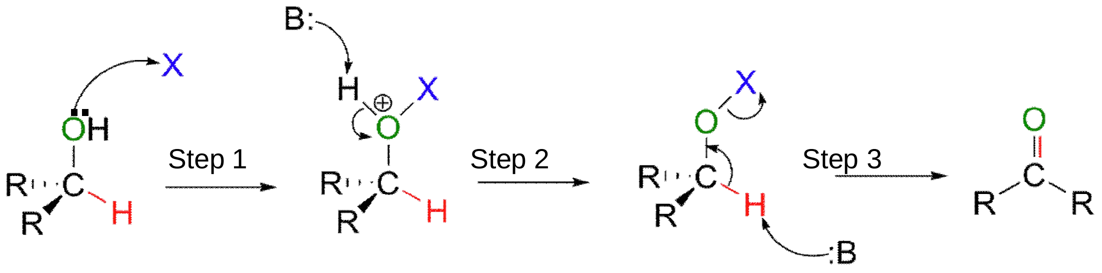


Appendix

- **Why tertiary alcohols and phenols cannot be oxidised**

The general mechanism of oxidation is illustrated below.

(i) The hydrogen of the alcohol group is replaced by a leaving group (X in the figure below) in steps 1 and 2.

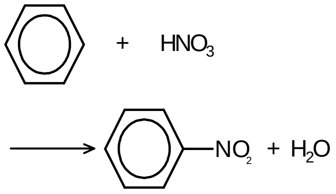
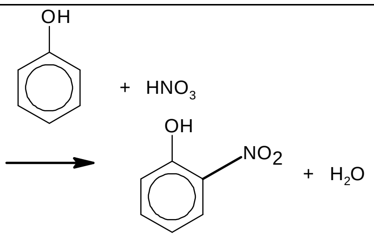


(ii) A base abstracts the proton bound to the alcohol carbon (step 3), which results in elimination of the X leaving group and formation of a new carbon-oxygen double bond.

Tertiary alcohols, phenols, and carboxylic acids cannot be oxidised as they do not have a hydrogen atom on the alcohol carbon atom.

Source: **Organic Chemistry With a Biological Emphasis** by Tim Soderberg (University of Minnesota, Morris)

- **Comparison of electrophilic substitution of benzene and phenol**

	Benzene	**Phenol**
Reagents and conditions	**Concentrated nitric acid**, concentrated sulfuric acid, **heat under reflux at 55°C**	**Dilute HNO_3** at **room temperature**
Equation		
Electrophile involved	NO_2^+	HNO_3
Remarks	The phenolic group strongly activates the benzene ring towards electrophilic substitution, and phenol can react with dilute HNO_3 (a weaker electrophile than NO_2^+) while benzene only reacts in the presence of the stronger NO_2^+ electrophile. For phenol, the –OH group **increases the electron density in the benzene ring, as the lone pair of electrons on the oxygen atom can be delocalised over the benzene ring,** making the ring to be more electron rich, hence, increasing its reactivity towards electrophiles. The weak electrophile HNO_3 is sufficient to attack the benzene ring in phenol, and there is no need to generate a stronger electrophile, NO_2^+.	