

**Pioneer Junior College
Higher 2 Chemistry (9647)
Organic Chemistry**

References:

1. A Level Chemistry (4th Edition) by E.N. Ramsden
2. Chemistry for Advanced Level by Peter Canns and Peter Hughes

Content**Part I - Alcohols**

1. Introduction
2. Nomenclature and Classification
3. Physical Properties
 - (i) Boiling point
 - (ii) Solubility
4. Laboratory Preparation
 - (i) Hydration of Alkenes through Electrophilic Addition Reaction
 - (ii) Alkaline Hydrolysis of Halogenoalkanes through Nucleophilic Substitution Reactions
 - (iii) Reduction of Carboxylic Acids, Aldehydes or Ketones
 - (iv) Acid Hydrolysis of Esters
 - (v) Alkaline Hydrolysis of Esters
5. Chemical Properties
 - (i) Combustion
 - (ii) Reactions involving the fission of RO–H bond
 - (iii) Reactions involving the fission of R–OH bond
 - (iv) Oxidation
 - (v) Tri-iodomethane (Iodoform) Formation/ Test

Part II - Phenols

1. Nomenclature
2. Physical Properties
 - (i) Appearance
 - (ii) Boiling point
 - (iii) Solubility
3. Structure of Phenol
4. Acidity of Phenol, Alcohol and Water
 - (i) Acidity of Phenol
 - (ii) Acidity of Alcohol
 - (iii) Comparing Relative Acidities of Water, Alcohol and Phenol
 - (iv) Effect of substituents on the acid strength of phenol
5. Chemical Properties
 - (i) Reactions of the –OH group
 - (ii) Reactions involving the benzene ring
 - (iii) Distinguishing Test for Phenols using FeCl_3 (aq)
6. Comparison of reactions of Ethanol and Phenol

Learning Outcomes

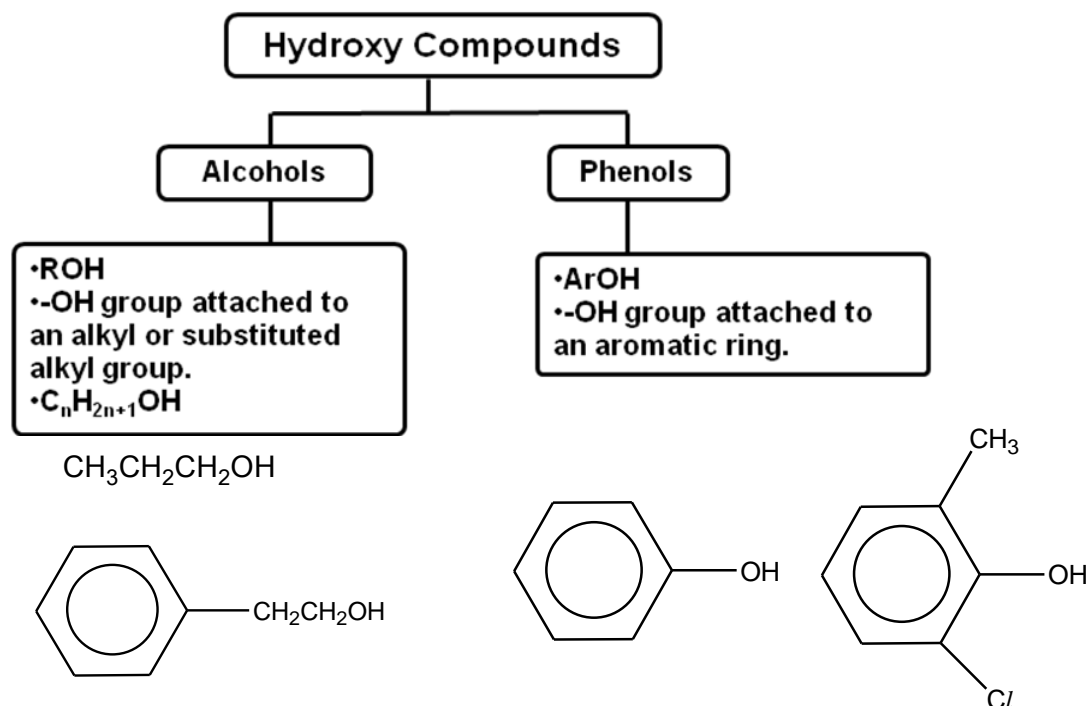
Candidates should be able to:

- (a) 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.
- (b) Explain the relative acidities of water, phenol and ethanol.
- (c) Recall the chemistry of alcohols, exemplified by the following reactions of ethanol:
 - (i) Combustion
 - (ii) Substitution to give halogenoalkanes
 - (iii) Reaction with metals (e.g. sodium)
 - (iv) Oxidation to carbonyl compounds and carboxylic acids
 - (iv) Dehydration to alkenes.
- (d) Classify hydroxyl compounds into primary, secondary and tertiary alcohols.
- (e) Suggest characteristic distinguishing reactions, e.g. mild oxidation.
- (f) Deduce the presence of a $\text{CH}_3\text{CH}(\text{OH})$ - group in an alcohol from its reaction with alkaline aqueous iodine to form tri-iodomethane.

1. INTRODUCTION – What are hydroxy compounds?

Hydroxy compounds are compounds containing the hydroxyl ($-\text{OH}$) functional group. It does NOT include the compounds that contain the OH^- ion produced by alkalis or bases.



2. NOMENCLATURE & CLASSIFICATION

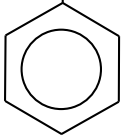
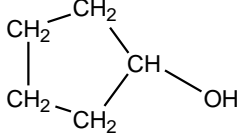
- (1) General formula of $\text{C}_n\text{H}_{2n+1}\text{OH}$.
E.g. Ethanol $\text{C}_2\text{H}_5\text{OH}$, where $n = 2$.
- (2) Ending '-ane' of corresponding alkane is replaced by suffix '-ol'.
- (3) Nomenclature:
 - Step 1: Select as parent the longest C chain that contains the hydroxyl group and replace the '-ane' ending with '-ol'.
 - Step 2: Number the Cs beginning at the end nearer the hydroxyl group.
 - Step 3: Position of OH group in carbon chain is specified by inserting the appropriate number between the stem of the name and 'ol'.
 - Step 4: Number other substituents present in the chain accordingly.

(4) Classification:

Alcohols are classified based on the **number of alkyl groups** attached to the carbon atom to which the hydroxyl group is attached.

Type	Primary (1°)	Secondary (2°)	Tertiary (3°)
No. of R groups bonded to the C with the hydroxyl group	0 or 1	2	3
Structure of alcohols (R = alkyl or aryl group)	$\begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}-\text{OH} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{R}' \\ \\ \text{R}-\text{C}-\text{OH} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{R}' \\ \\ \text{R}-\text{C}-\text{OH} \\ \\ \text{R}'' \end{array}$
No. of H atoms on C to which the -OH is attached	2 or 3	1	0

Lecture E.g. 1: Complete the following table.

Formula		IUPAC Name	Classification
CH ₃ CH ₂ OH	$\begin{array}{c} \text{H} \\ \\ \text{CH}_3-\text{C}-\text{OH} \\ \\ \text{H} \end{array}$	Ethanol	
(CH ₃) ₂ CH(OH)	$\begin{array}{c} \text{H} \\ \\ \text{CH}_3-\text{C}-\text{OH} \\ \\ \text{CH}_3 \end{array}$	Propan-2-ol	
(CH ₃) ₃ COH	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{OH} \\ \\ \text{CH}_3 \end{array}$		Tertiary
C ₆ H ₅ CH ₂ CH ₂ OH	$\begin{array}{c} \text{H}_2\text{C}-\text{CH}_2-\text{OH} \\ \\ \text{C}_6\text{H}_5 \end{array}$ 	2-phenylethanol	
C ₅ H ₉ OH		Cyclopentanol	

3. PHYSICAL PROPERTIES

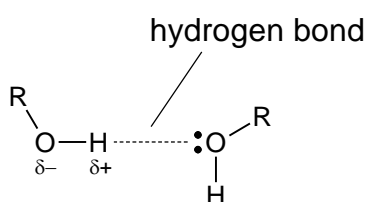
3.1 Boiling point

Boiling points of alcohols are much higher than alkanes with similar M_r .

Example:

Compound	Condensed Formula	M_r	Boiling point / °C
Butane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$	58	0
Propan-1-ol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	60	97

Comparing $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, propan-1-ol has a much higher boiling point because of its **hydrogen bonding**, compared to instantaneous dipole-induced dipole (id-id) interactions between butane molecules. (Both have relatively similar molecular mass.)



Note:

- (1) Draw out lone pair on O.
- (2) Indicate the δ^+ and δ^- .
- (3) Draw the dotted line and label the hydrogen bond.

Note: Hydrogen bonding is *not* the only intermolecular force present between alcohols molecules.

Van der Waals' interactions are also *present* and the strength of the force increase with the length of the carbon chain.

Factors Affecting Boiling Points (*Recall Chemical Bonding)

- (i) **Length of alkyl chain:** Boiling point increases with increasing length of alkyl chain.

Alcohol	Methanol	Ethanol	Propan-1-ol
Structural formula	CH_3OH	$\text{CH}_3\text{CH}_2\text{OH}$	$\text{CH}_3(\text{CH}_2)_2\text{OH}$
Boiling point / °C	65	78	97

- The relative molecular mass increases with an increase of the alkyl chain length.
- As the relative molecular mass increases, the **number of electrons that can be polarised increases** and hence the **strength of the van der Waals' interactions between the molecules increases**.
- More energy is required** to overcome these interactions and hence boiling point increases.

- (ii) **Branching:** Branching of the carbon skeleton lowers boiling point.

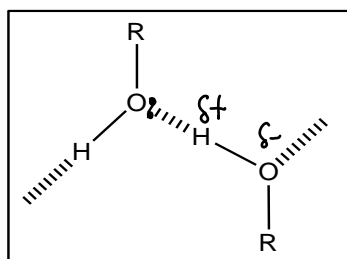
Alcohol	Butan-1-ol	2-methylpropan-1-ol
Structural formula	$ \begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{CH}_3 - \text{C} - \text{C} - \text{C} - \text{H} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{OH} \end{array} $	$ \begin{array}{c} \text{CH}_3 \quad \text{H} \\ \quad \\ \text{CH}_3 - \text{C} - \text{C} - \text{H} \\ \quad \\ \text{H} \quad \text{OH} \end{array} $
Boiling point / °C	118	108

- As **degree of branching** of the carbon skeleton increases, **surface area of electron cloud** exposed decreases.
- 2-methylpropan-1-ol has a **more compact** (and spherical) **electron cloud** than butan-1-ol, which has a more cylindrical (or rod-shaped) electron cloud, leading to **less extensive van der Waals' interactions** between 2-methylpropan-1-ol molecules.
- Less energy is hence required to overcome the **less extensive** interactions. Boiling point of 2-methylpropan-1-ol is hence lower than butan-1-ol (i.e. as branching of carbon skeleton increases, boiling point decreases).
- In addition, the $-OH$ group in 1° alcohols are **less hindered** for hydrogen bonding, but **most hindered** (overcrowded) in 3° alcohols. Less energy is required to overcome the weaker interactions in 3° alcohols. Thus, the boiling point of 2-methylpropan-1-ol is lower than butan-1-ol (i.e. as branching of carbon skeleton increases, boiling point decreases).

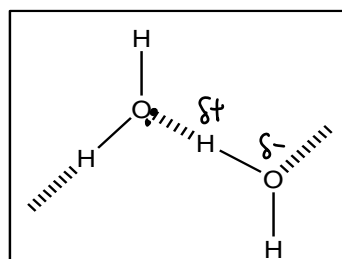
3.2 Solubility

In water

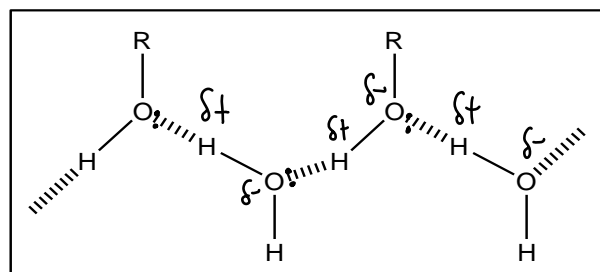
Alcohols are **more** soluble in water, compared to corresponding alkanes as alcohols are able to form **hydrogen bonds** with water.



Solute-solute interactions



Solvent-solvent interactions



Solute-solvent interactions

- However, as the hydrocarbon chain becomes longer, the respective alcohol shows a marked **decrease** in solubility.
- This is because, in the larger alcohol molecules, the energy released during the formation of the solute-solvent (alcohol – water) interaction cannot compensate for the energy required to break the solute-solute (alcohol - alcohol) and the solvent-solvent (water - water) interactions. In general, alcohols with 5 carbons or more are effectively insoluble in water.

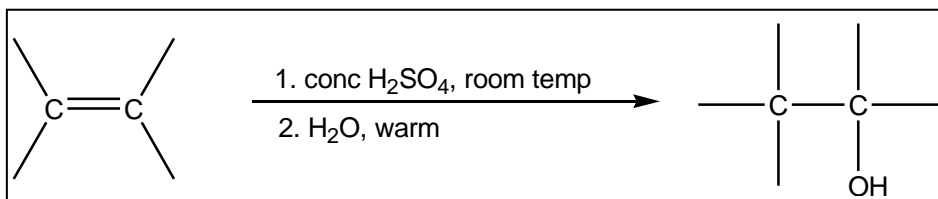
In organic solvents

All alcohols are miscible with most organic solvents. Some are useful organic solvents themselves. An example is propan-2-ol, an alcohol commonly used as a solvent in glue.

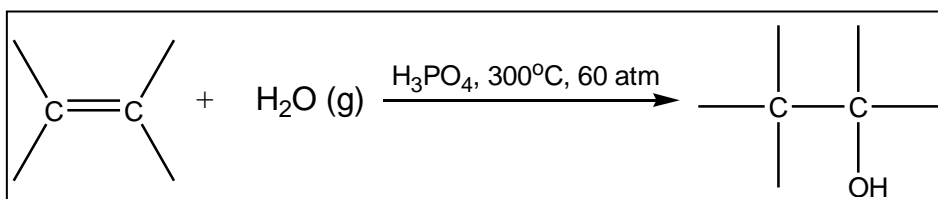
4. LABORATORY PREPARATION

4.1 Electrophilic Addition of H₂O to Alkenes

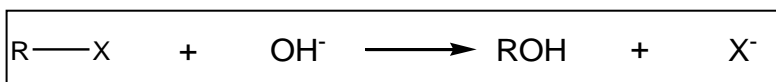
Laboratory method:



Industrial method:



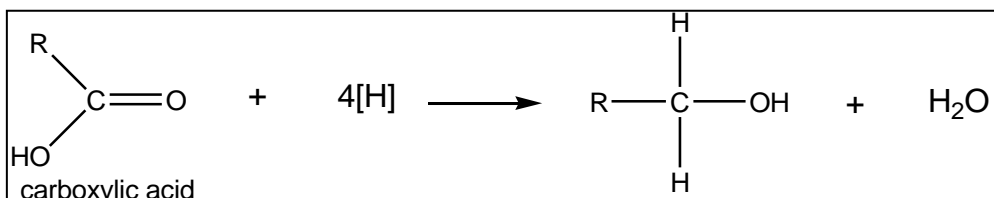
4.2 Nucleophilic Substitution of Halogenoalkanes



Reagents & conditions: Aqueous NaOH or KOH, heat

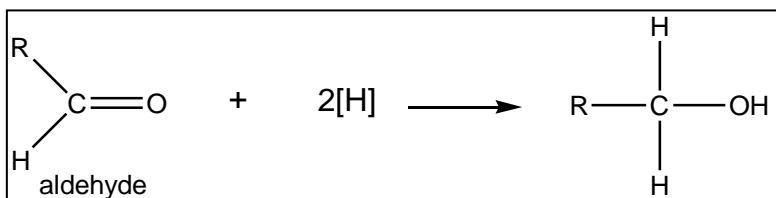
4.3 Reduction of Carboxylic Acids, Aldehydes or Ketones

Carboxylic acids and **aldehydes** are reduced to the corresponding **primary alcohols**:



Reagents & conditions: LiAlH₄ (Lithium Aluminium Hydride) in dry ether

⚡ H₂(g), Ni catalyst, 200°C CANNOT reduce carboxylic acids!

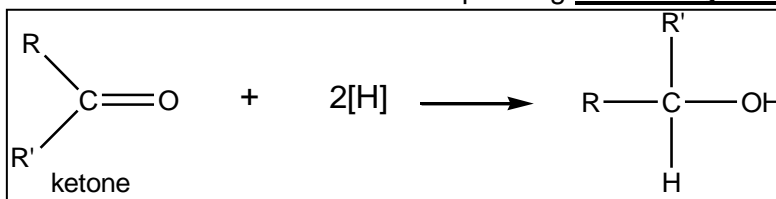


Reagents & conditions: LiAlH₄ (Lithium Aluminium Hydride) in dry ether

OR

H₂(g), Ni catalyst at 200°C

Ketones are reduced to the corresponding **secondary alcohols**:

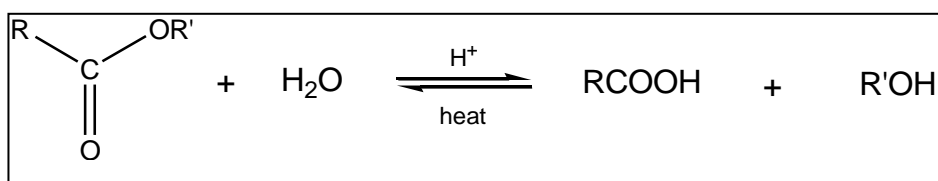


Reagents & conditions: LiAlH₄ (Lithium Aluminium Hydride) in dry ether

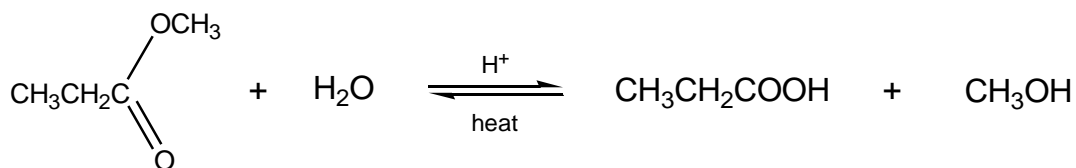
OR

H₂(g), Ni catalyst at 200°C

4.4 Acid Hydrolysis of Esters

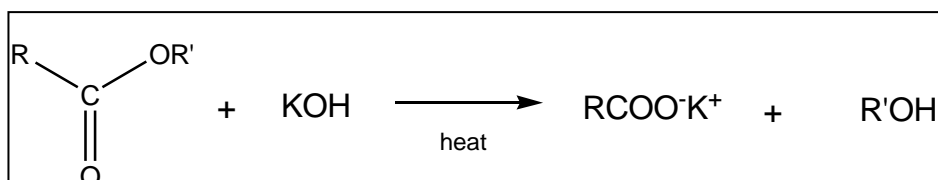


Example:

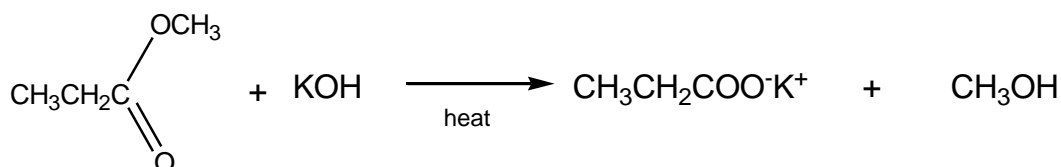


Reagents & conditions: Heat with dilute acid, e.g. H₂SO₄(aq), HCl(aq).

4.5 Alkaline Hydrolysis of Esters



Example:



Reagents & conditions: Heat with dilute base, e.g. KOH(aq).



Alkaline hydrolysis generally gives **higher yields** than the reversible acid-catalysed reaction. Why?

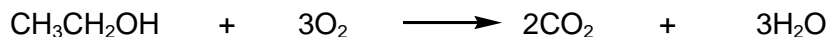
:OH⁻ ion (used in alkaline hydrolysis) is a **stronger nucleophile** than H₂O: (used in acid hydrolysis).

:OH⁻ ions can attack the electron deficient carbonyl carbon more readily during hydrolysis reaction, accounting for its irreversibility and higher yields.

5. CHEMICAL PROPERTIES

5.1 Combustion

Alcohols burn in excess air (oxygen) with a non-luminous (pale blue) flame, to form CO_2 and H_2O .

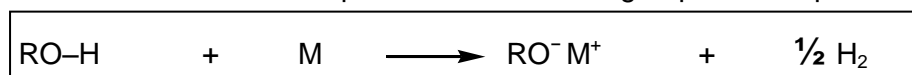


5.2 Reactions involving the fission of the RO–H bond

5.2.1 Reaction with reactive metal

Alcohols react with reactive metals, e.g. Na, to form alkoxides and $\text{H}_2(\text{g})$ is evolved.

This can be a test for the presence of the –OH group in a compound.



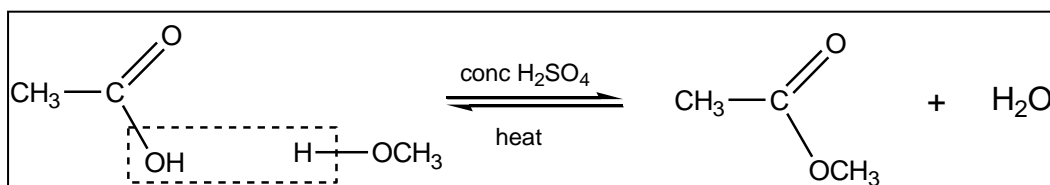
Condition: Room temperature

Observation: Colourless gas evolved extinguishes a burning splint with a “pop” sound.

- This is a **redox** reaction:
Na is oxidised: Oxidation state of Na increases from 0 in Na to +1 in Na^+ .
H is reduced: Oxidation state of H decreases from +1 in ROH to 0 in H_2 .

5.2.2 Esterification

Alcohols react with carboxylic acids to form ester:



Type of reaction: **Condensation**

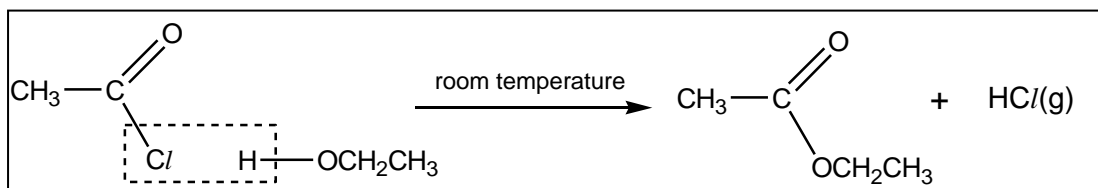
Reagent and condition: Concentrated H_2SO_4 (as a catalyst) and heat

Observation: Sweet smell of esters (Note: Do not use this as a diagnostic observation.)

- This reaction is slow and reversible.
- **Question:** What do you think is the purpose of **concentrated** H_2SO_4 ? Two purposes:
 1. It supplies **H^+ ions** to catalyse the reaction.
 2. As a **dehydrating** agent, it **absorbs** the H_2O produced in the reaction, and this shifts the position of equilibrium to the **right**, and **increases** the yield of the ester formed.

5.2.3 Acylation

Alcohols react with acid chlorides to form ester and HCl:



Type of reaction: **Condensation**

Reagent and condition: Room temperature



Comparison between esterification and acylation:

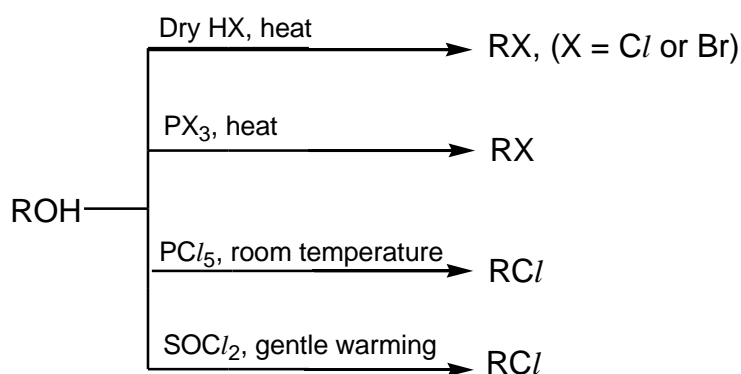
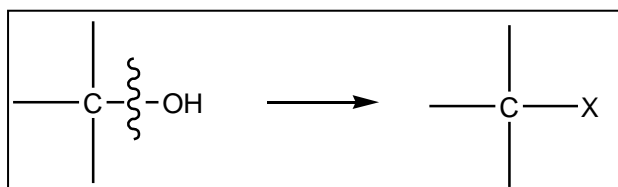
- Acylating agents are **more** reactive than carboxylic acids.*
 - Acylation is **complete**, rapid, gives **high** yield and does not require heating.*
- * Reasons for higher reactivity of acyl halides will be learnt in Carboxylic Acids & Derivatives.

5.3 Reactions involving the fission of the R-OH bond

5.3.1 Halogenation

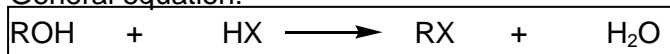
Alcohols can undergo halogenation. Halogenation involves the substitution of the hydroxyl functional group with a halogen with the cleavage of the C-O bond.

Type of reaction: **Nucleophilic substitution**

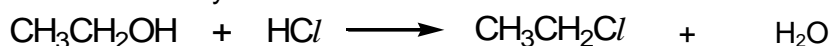


- With hydrogen halides

General equation:

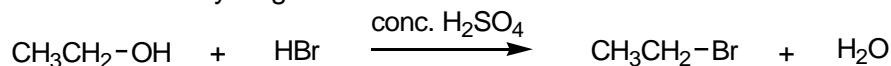


- Reaction with hydrochloric acid



Reagent and conditions: Conc HCl, ZnCl₂ (catalyst) & heat.

- Reaction with hydrogen bromide



Reagent and conditions: Conc H_2SO_4^* , KBr^* , and heat

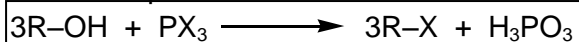
*HBr is generated *in situ* when KBr is reacted with conc. H_2SO_4 :



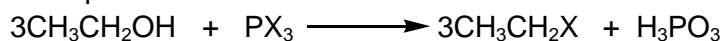
- With phosphorus halides

- Reaction with PX_3

General equation:



Example:

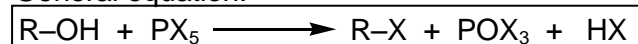


(X = Cl, Br or I)

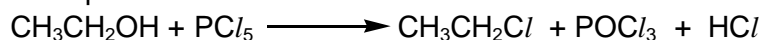
Reagent and conditions: heat

- Reaction with PX_5

General equation:



Example:

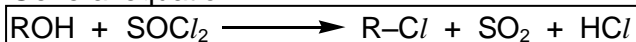


Reagents and conditions: Room temperature

Observation: Steamy white fumes (of HCl) produced.

- With thionyl chloride

General equation:



Reagent and conditions: Warm gently.

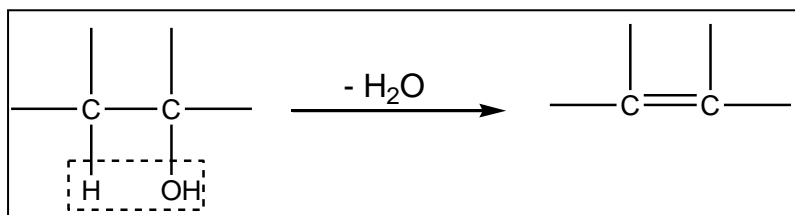
Observation: White fumes (of HCl) produced.



This reagent (SOCl_2) is preferred in preparing RCl as all its side products (i.e. SO_2 and HCl) are gases, which can be removed easily.

5.3.2 Dehydration

Alcohols undergo dehydration to yield the follow alkene:

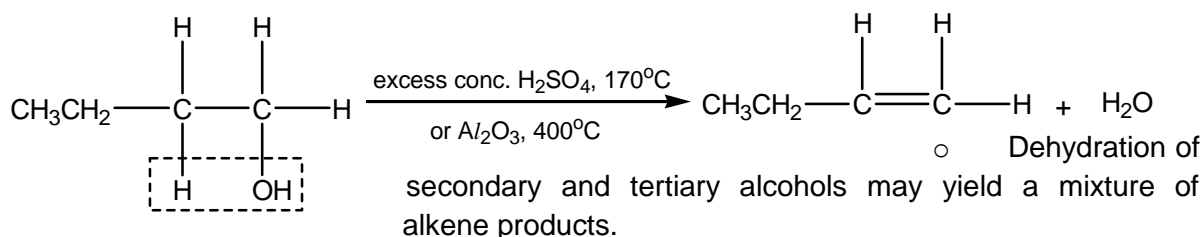


Type of reaction: **Elimination**

Reagents and conditions: Excess conc H_2SO_4 , 170°C (Laboratory conditions)

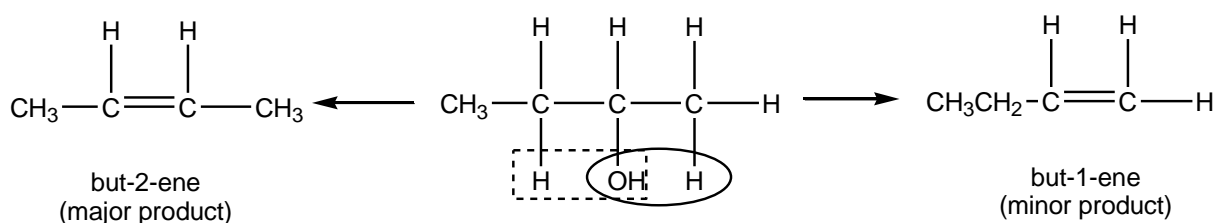
OR Al_2O_3 catalyst, 400°C (Industrial conditions)

- Dehydration is only possible on alcohols with at least 1 hydrogen atom on adjacent C atom(s).



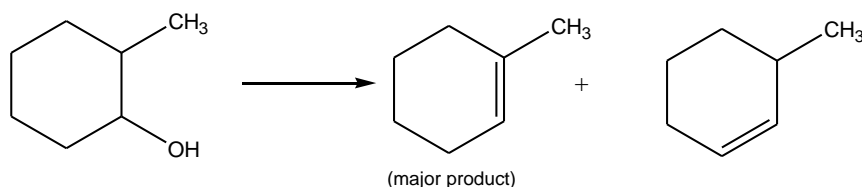
Zaitsev's Rule:

When dehydration (a type of elimination) occurs, the **more substituted** alkene (i.e. the one containing a higher number of alkyl groups on the $\text{C}=\text{C}$ bond) is formed as the major product.

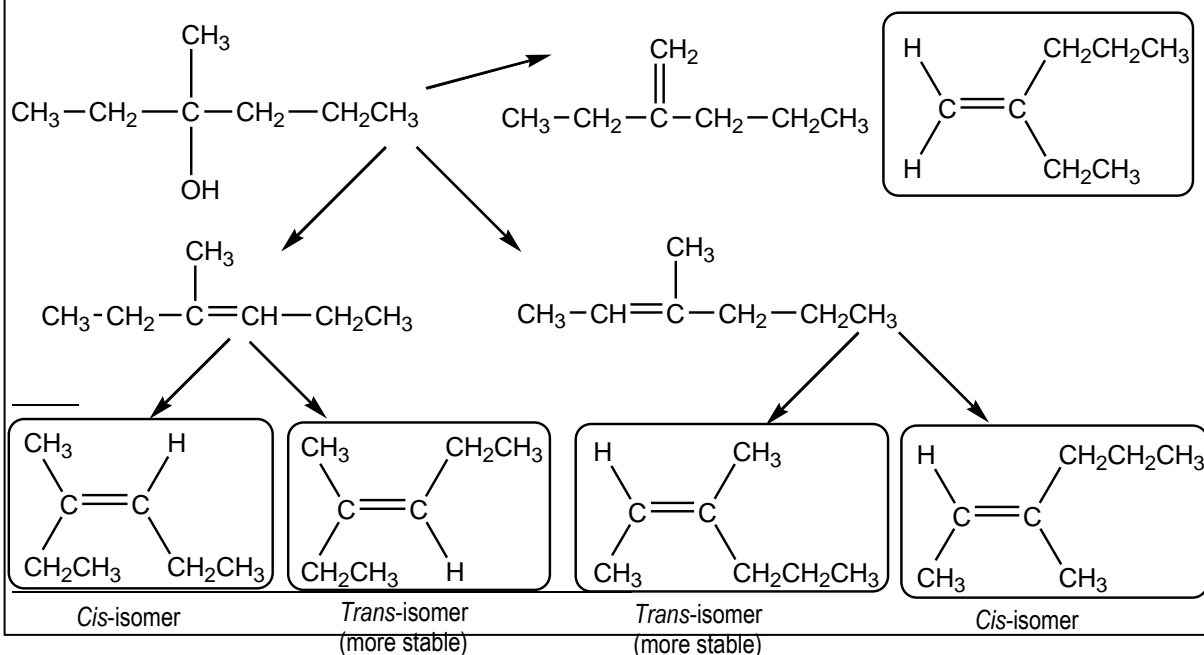


Lecture E.g. 2: Give the structural formulae of all the possible alkenes formed when the following alcohols are dehydrated using concentrated sulfuric acid, at 170°C .

(a) 2-methylcyclohexanol



(b) 3-methylhexan-3-ol



5.4 Oxidation

The oxidation of an alcohol involved the loss of one or more hydrogens from the carbon bearing the –OH group.

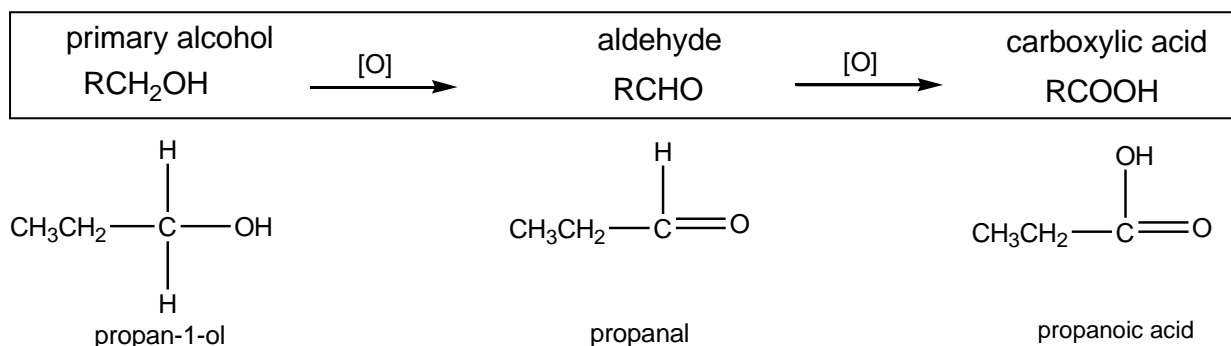
Suitable oxidising agents: $\text{KMnO}_4(\text{aq})$, $\text{H}_2\text{SO}_4(\text{aq})$,
OR
 $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$, $\text{H}_2\text{SO}_4(\text{aq})$.

Condition: heat

Alcohol Type	Alcohol	Aldehyde/ Ketone	Carboxylic Acid
Primary (1°)	$\begin{array}{c} \text{H} \\ \\ \text{CH}_3\text{CH}_2-\text{C}-\text{OH} \\ \\ \text{H} \end{array}$	$\xrightarrow{\text{Mild oxidation}} \begin{array}{c} \text{H} \\ \\ \text{CH}_3\text{CH}_2-\text{C}=\text{O} \end{array}$	$\xrightarrow{\text{Strong oxidation}} \begin{array}{c} \text{OH} \\ \\ \text{CH}_3\text{CH}_2-\text{C}=\text{O} \end{array}$
	$\begin{array}{c} \text{H} \\ \\ \text{CH}_3\text{CH}_2-\text{C}-\text{OH} \\ \\ \text{H} \end{array}$	$\xrightarrow{\text{Strong oxidation}} \begin{array}{c} \text{OH} \\ \\ \text{CH}_3\text{CH}_2-\text{C}=\text{O} \end{array}$	
Secondary (2°)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CH}_2-\text{C}-\text{OH} \\ \\ \text{H} \end{array}$	$\xrightarrow{\text{Mild/ strong oxidation}} \begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CH}_2-\text{C}=\text{O} \end{array}$ <p style="text-align: center;">Ketone</p>	\nrightarrow
Tertiary (3°)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CH}_2-\text{C}-\text{OH} \\ \\ \text{CH}_3 \end{array}$	\nrightarrow	

5.4.1 Primary Alcohols

Primary alcohols are oxidised to aldehydes, which is further oxidised to carboxylic acids.

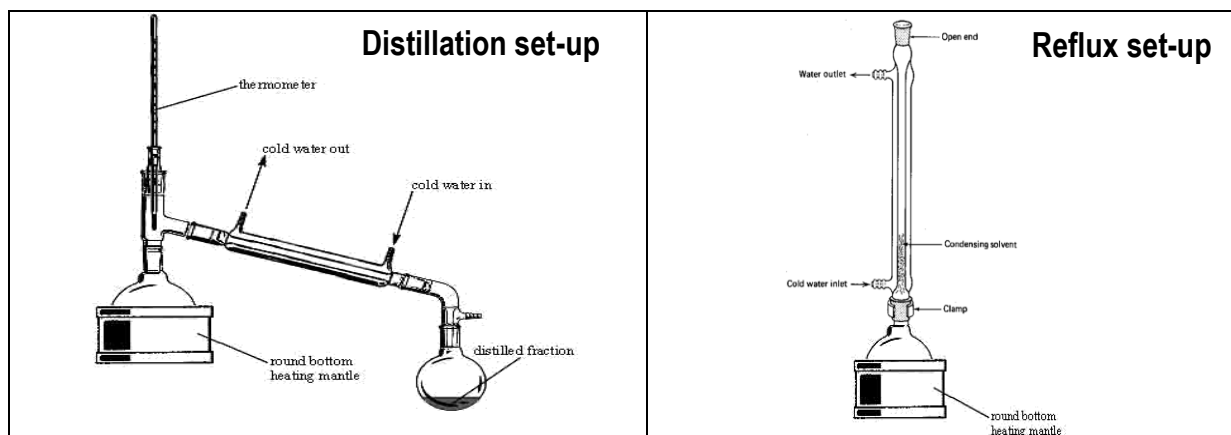


To oxidise to aldehyde only

Reagent and condition: $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$, $\text{H}_2\text{SO}_4(\text{aq})$, and then **distill**.

Observation: Orange solution ($\text{Cr}_2\text{O}_7^{2-}$) turns green (Cr^{3+}).

Be able to draw both set-ups! (Increasingly tested in the A-Levels)



Point of discussion: To obtain the aldehyde, why must the aldehyde be distilled from the reaction mixture? What will happen if it is not distilled out?

- **Distillation** of the aldehyde from the reaction mixture **prevents the aldehyde from being acted on further by the oxidising agent** to form carboxylic acid instead.
- Distillation is a suitable method of separation of aldehyde (product) from the starting alcohol (reactant) as the **aldehyde has a lower boiling point than the alcohol**.
- **Less** energy is required to overcome the **weaker permanent dipole-dipole** (pd-d) interactions that exist between aldehyde molecules than **stronger hydrogen bonds** between alcohol molecules, accounting for a lower boiling point of the aldehyde.
- **Aldehyde** (product) can hence be collected as the **distillate** first.

To completely oxidise to carboxylic acid

Reagent and condition: $\text{KMnO}_4(\text{aq})$, $\text{H}_2\text{SO}_4(\text{aq})$, and then **heat (under reflux)**.

OR

$\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$, $\text{H}_2\text{SO}_4(\text{aq})$, and then **heat (under reflux)**.

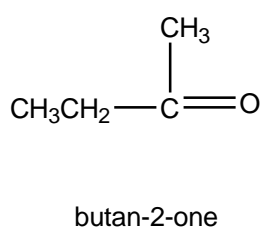
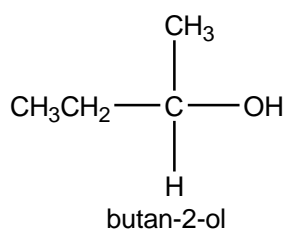
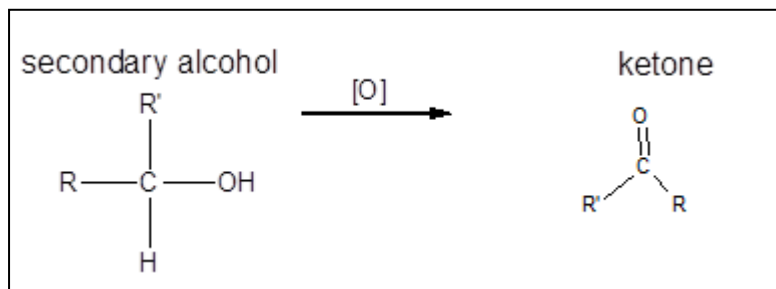
Observation: Purple solution (MnO_4^-) decolourises to give a colourless solution (Mn^{2+}).

OR

Orange solution ($\text{Cr}_2\text{O}_7^{2-}$) turns green (Cr^{3+}).

5.4.2 Secondary Alcohols

Secondary alcohols are oxidised to ketones.



Reagent and condition: **KMnO₄(aq)**, H₂SO₄(aq), and then **heat (under reflux)**.

OR

K₂Cr₂O₇(aq), H₂SO₄(aq), and then **heat (under reflux)**.


Observation: Purple solution (MnO₄⁻) decolourises to give a colourless solution (Mn²⁺).

OR

Orange solution (Cr₂O₇²⁻) turns green (Cr³⁺).

5.4.3 Tertiary Alcohols

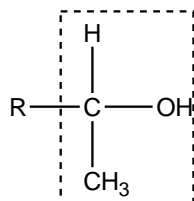
Tertiary alcohols **cannot** be oxidised.

 **Tip!** Oxidation of alcohols can be employed to distinguish between the different classes of alcohols → Distinguishing test for 1° / 2° and 3° alcohols.

5.5 Tri-iodomethane (Iodoform) Formation/ Test

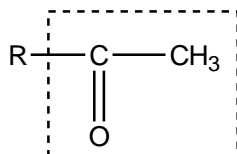
This reaction is only positive (i.e. yellow precipitate formed) for

- (i) an alcohol containing the following structure:



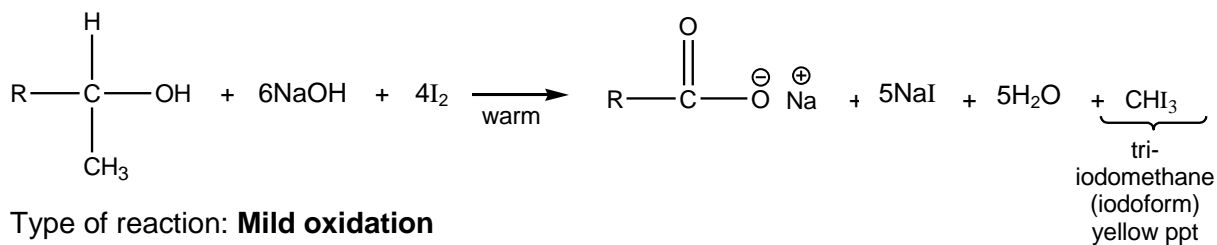
where R = H, alkyl or aryl group

- (ii) carbonyl compound (aldehydes/ ketones) with the structure:



where R = H, alkyl or aryl group

General equation:



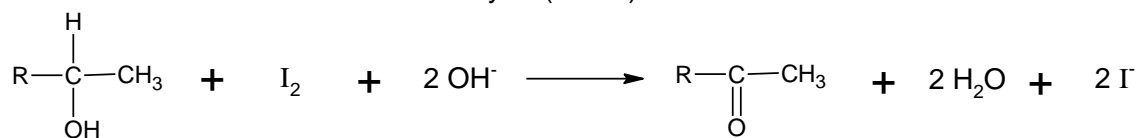
Reagent and condition: $\text{I}_2(\text{aq})$, $\text{NaOH}(\text{aq})$, warm

Observation: Yellow precipitate of CHI_3 is formed.

Note: This is a method to decrease the number of carbons by one.

Mechanism of Iodoform test (For self-reading)

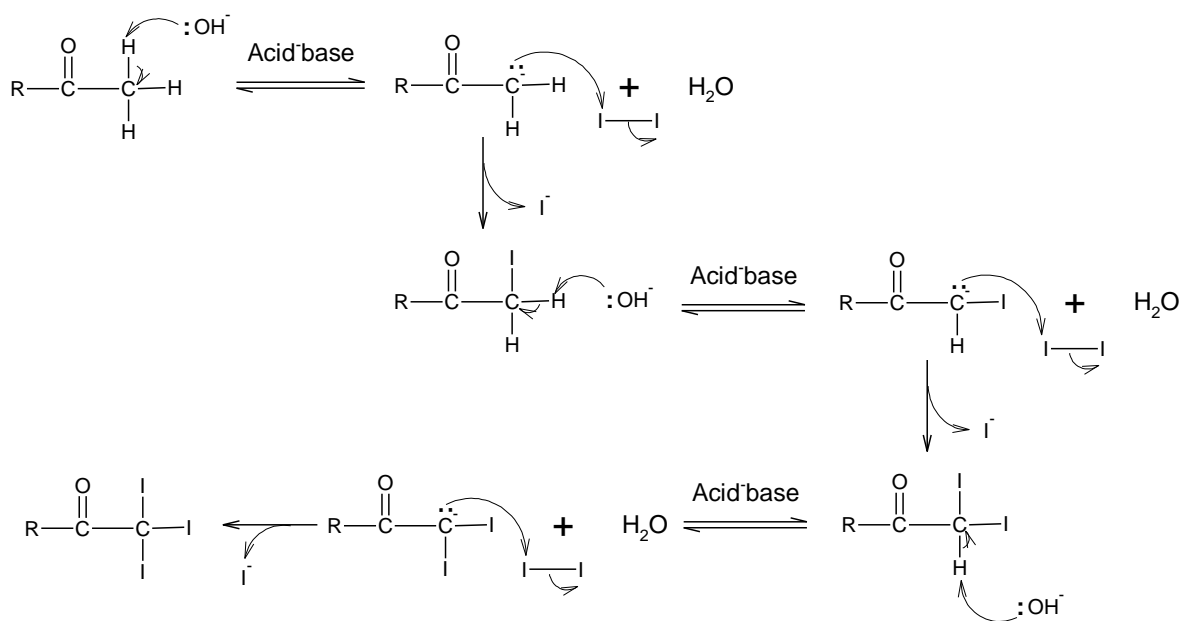
Step 1: **Oxidation** of 2° alcohol to ketone (R=alkyl group)/
Oxidation of 1° alcohol to aldehyde (R = H)



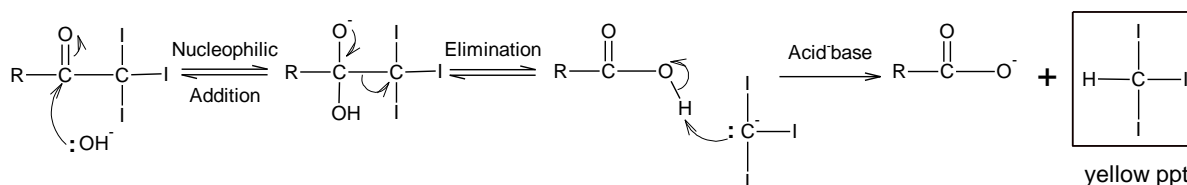
methyl alcohol

methyl ketone

Step 2: OH^- serves as base to remove acidic proton, forming carbanion.
(Acid-base reaction)



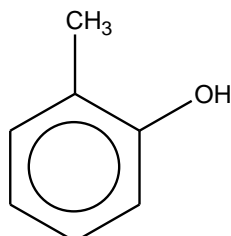
Step 3: **Nucleophilic addition-elimination**, then **acid-base reaction** to form CHI_3 .



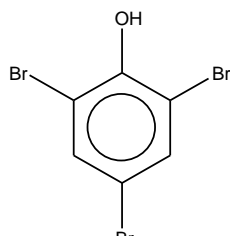
PART II – PHENOL COMPOUNDS

1. NOMENCLATURE

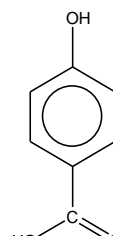
Phenols are compounds containing a hydroxyl (-OH) group attached **directly** to the aromatic ring. It has a general formula of ArOH.



2-methylphenol



2,4,6-tribromophenol



4-hydroxybenzoic acid

2. PHYSICAL PROPERTIES

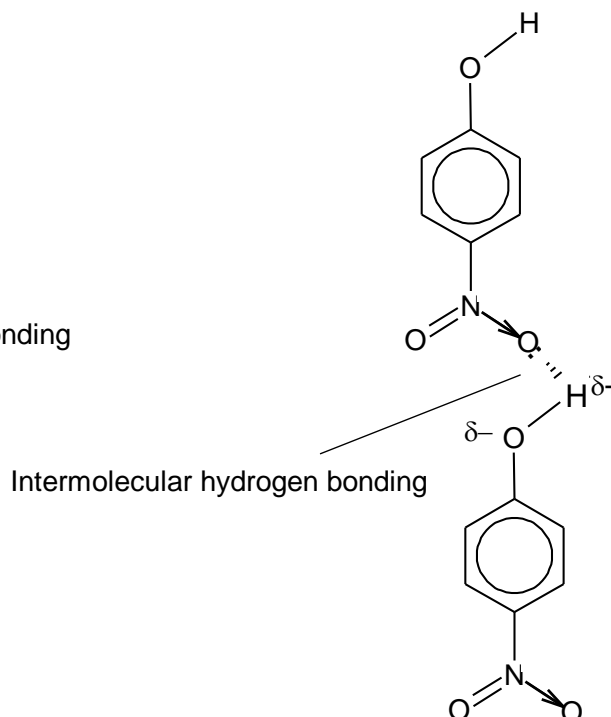
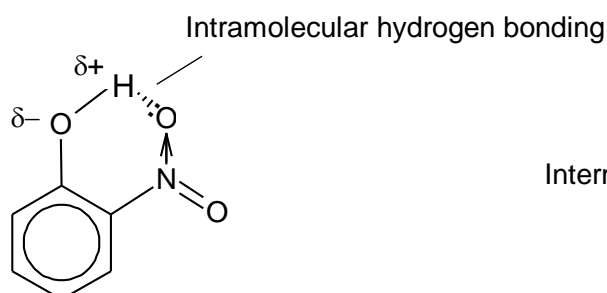
2.1 Appearance

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

2.2 Boiling point

Phenols have a relatively high boiling point of 181 °C, compared to other organic compounds of similar molecular masses due to **hydrogen bonding**.

Boiling point depends on extent of intermolecular hydrogen bonding e.g. 2-nitrophenol (217°C) versus 4-nitrophenol (245°C). In 2-nitrophenol, intramolecular hydrogen bonding occurs, thus, the ability to form hydrogen bonding with neighbouring molecules decreases, resulting in a lower boiling point.

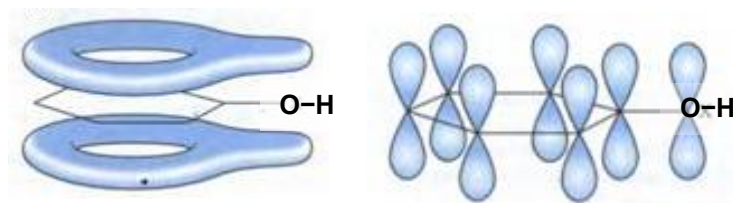


2.3 Solubility

Phenols are only partially soluble in water at room temperature. Although it can form hydrogen bonding with water molecules, its large, bulky hydrophobic benzene ring interferes with hydrogen bonding. Upon heating to above 68.5 °C, it becomes completely soluble.

3. STRUCTURE OF PHENOL

The aromatic ring has a delocalised electron cloud of electrons. The 2p orbital of the oxygen overlaps side-way with the 2p orbitals of C atoms of the benzene ring to form a delocalised π -electron cloud system. Therefore, the C–O bond is being strengthened (has partial double bond character), while the O–H bond is weakened.



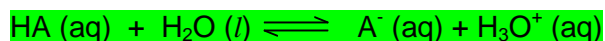
Side-way overlap of the 2p orbital of O atom with 2p orbitals of the C atoms of benzene confers strength to the C–O bond.

4.

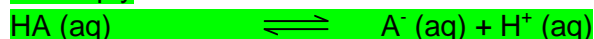
PHENOL, ALCOHOL AND WATER

4 Acidity

- An *acid* is a proton, H^+ donor.
- A weak acid is one that undergoes partial dissociation in aqueous solution.
- Consider the dissociation of a weak monobasic acid HA in aqueous solution:

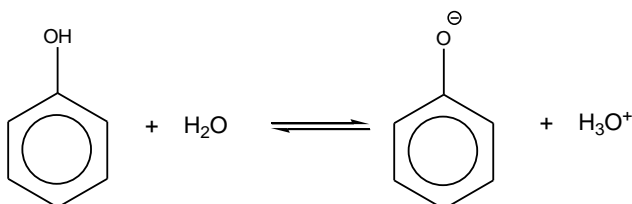


Or simply



4.1 Acidity of Phenol

Phenol can donate a proton to water, forming the phenoxide ion.

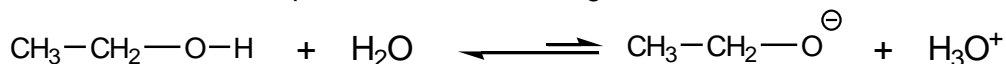


The phenoxide ion is **stabilised** by charge dispersion:

- The p-orbital of oxygen overlaps side-way with the π -electron cloud of the phenyl ring.
- This results in delocalisation of negative charge on oxygen into the ring (i.e. the negative charge density on the oxygen atom is dispersed across the ring).
- The intensity of negative charge on oxygen atom is **lowered**, **stabilising** the phenoxide ion. (*the more stable the ion, the more likely it forms, and the greater the extent of acid dissociation*)
- The equilibrium position in the equation lies comparatively **more** to the right, indicating phenol is a relatively **stronger** acid (compared to water).

4.2 Acidity of Alcohol

Alcohol can donate a proton to water, forming the alkoxide ion.



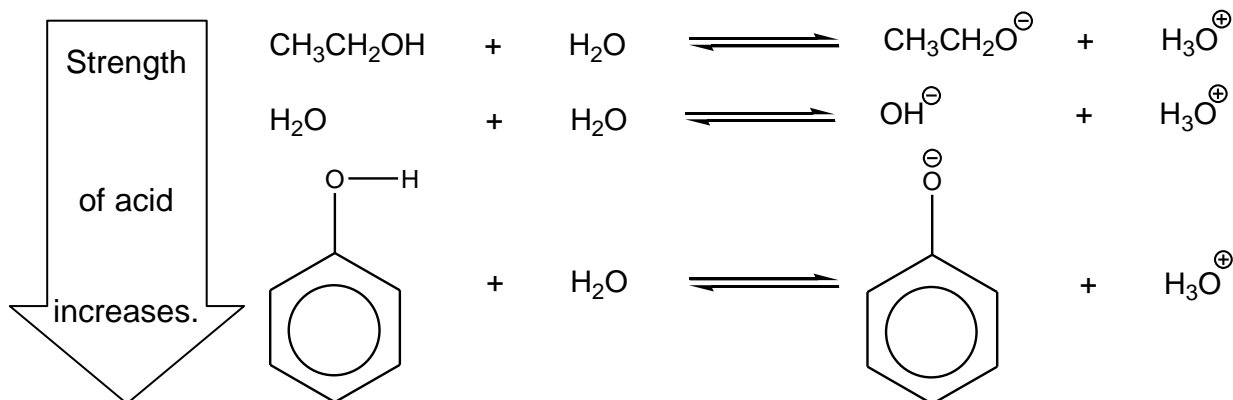
The alkoxide ion is **destabilised** as:

- The negatively charged oxygen is attached to an electron-donating alkyl group, which increases the electron density on the negatively charged oxygen of the ethoxide ion.
- This **destabilises** the ion (and make it more ready to accept protons),
- thus, the equilibrium position lies comparatively **less** to the right (more to the left), indicating that ethanol is a weaker **er** acid (compared to water).

Note: While alcohols can exhibit acidic properties, they do **NOT** protonate in water to form acidic solutions. Alcohols are considered neutral.

4.3 Comparing the relative acidities of water, ethanol and phenol

Strong acid releases H^+ more readily, while weak acid releases H^+ less readily.



Due to the electron-donating nature of the $-\text{R}$ group, this increases the negative charge density on the oxygen, making it less stable. Therefore, ethanol is a weaker acid than water.

In phenoxide ion, the negative charge on oxygen atom is delocalised to the benzene ring. This reduces the negative charge on the oxygen, the phenoxide anion is thus stabilised (and accepts protons less readily). Thus, phenol is a stronger acid compared to water or ethanol.

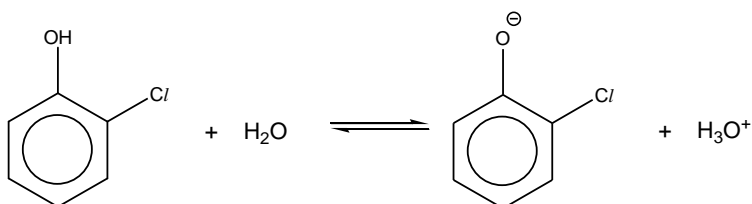
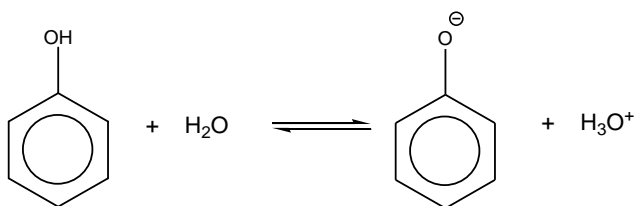
Acidity: **Phenol > Water > Alcohol** (e.g. ethanol)

4.4 Effect of substituents on the acid strength of phenol

The **more dispersed the negative charge density** on O of the phenoxide ion
 → the **more stable the ion** → the **more strongly acidic the phenol**.

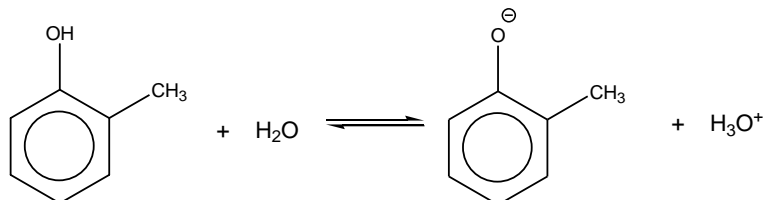
Presence of electron-withdrawing groups (e.g. $-\text{Cl}$, $-\text{NO}_2$) in the ring increases the acid strength of phenol.

- The electron-withdrawing group further **disperses** the negative charge density on the oxygen, thus further stabilising the phenoxide ion.
- Equilibrium position shifts comparatively more to the right, thus chlorophenol and nitrophenol are **stronger** acids than phenol.

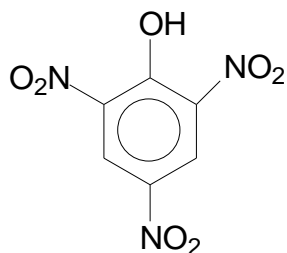
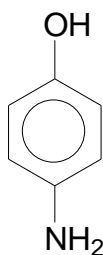
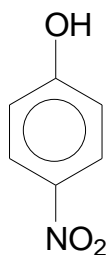
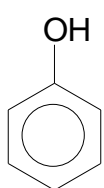


Presence of electron-donating groups (e.g. $-\text{CH}_3$) in the ring decreases the acid strength of phenol.

- The electron-donating group **intensifies** the negative charge electron density on the oxygen, thus, destabilising the phenoxide ion.
- Equilibrium position shifts comparatively less to the right, thus methyl phenol is a **weaker** acid than phenol.



Lecture E.g. 3: Arrange the following phenols in the order of increasing acidity.

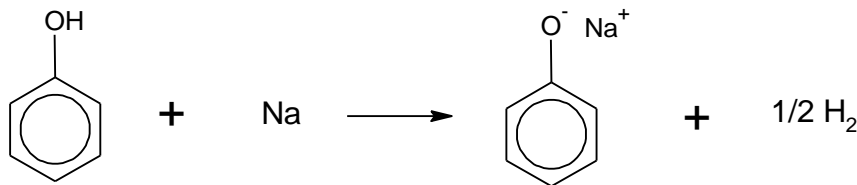


5. CHEMICAL PROPERTIES

5.1 Reactions of the –OH group

5.1.1 Reaction with reactive metal

Phenol can react with reactive metals such as Na to liberate hydrogen gas.



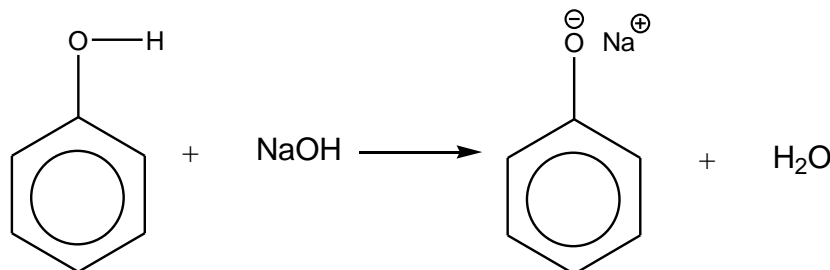
Type of reaction: **Redox**

Condition: Room temperature

Observation: Colourless gas evolved extinguishes a burning splint with a “pop” sound.

5.1.2 Reaction with sodium hydroxide

Due to the acidity of phenol, it also reacts with bases, such as sodium hydroxide, to give a salt and water. This is often used as a test to differentiate alcohols from phenols.



Type of reaction: **Acid-base**

Condition: Room temperature

5.1.3 Reaction with sodium carbonate

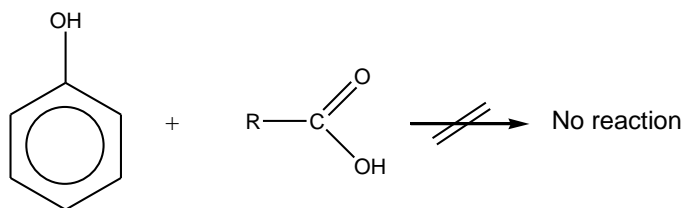
No reaction.

Tip! These 3 reagents are commonly used to distinguish between the three classes of organic compounds (i.e. alcohols, phenols and carboxylic acids).

	Sodium metal (Na)	Sodium hydroxide (NaOH)	Sodium carbonate (Na ₂ CO ₃)
Alcohol	√	X	X
Phenol	√	√	X
Carboxylic Acid (To be learnt later)	√	√	√

5.1.4 Esterification

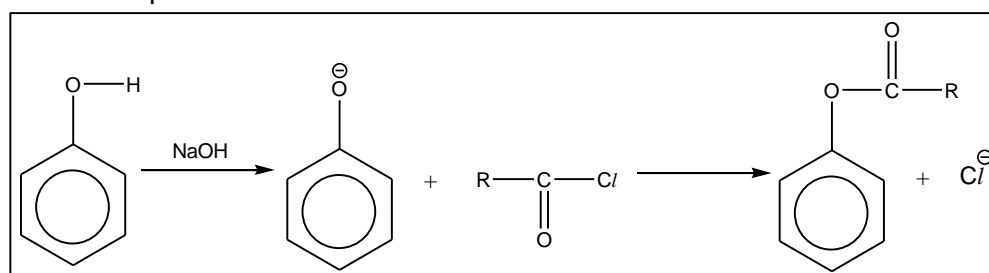
Phenol does not react with carboxylic acids.



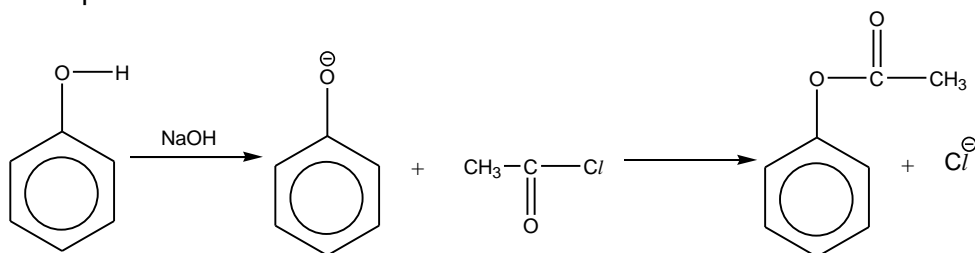
Phenol reacts with acid chlorides to form phenyl esters.

Esterification is particularly effective in NaOH (aq), as the alkali first reacts with phenol to form the **phenoxide** ion, which is a **stronger nucleophile than phenol** itself:

General Equation:



Example:



Reagent and condition:

1. Add NaOH(aq) (Type of reaction: **Acid-base**)
2. Add acid chloride at room temperature (Type of reaction: **Condensation**)

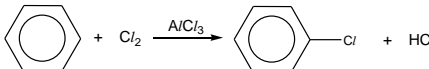
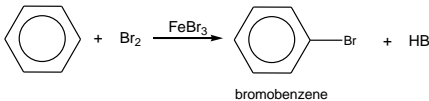
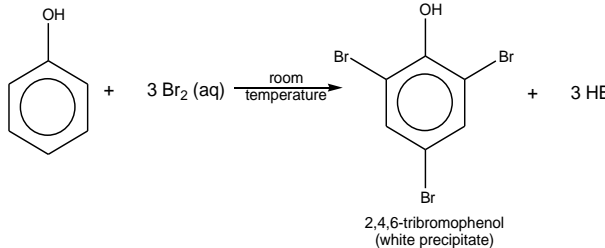
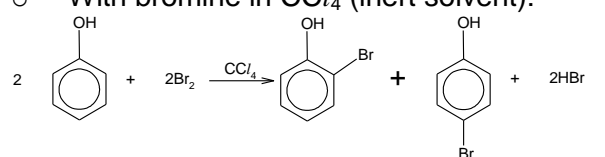
5.2 Reactions involving the benzene ring

The hydroxyl group is **2, 4-directing** and **electron-donating**. The delocalisation of lone pair of electrons on oxygen into the benzene ring **increases** the electron density in the ring, **activating** it. Hence, phenol undergoes **electrophilic substitution** much more readily than benzene. Reactions are carried out under **milder** conditions, and polysubstitution occurs.

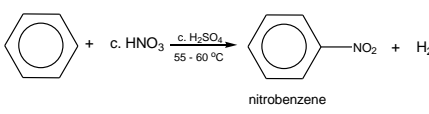
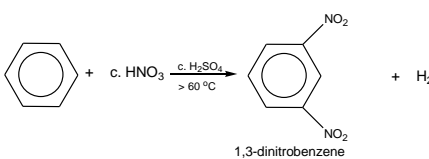
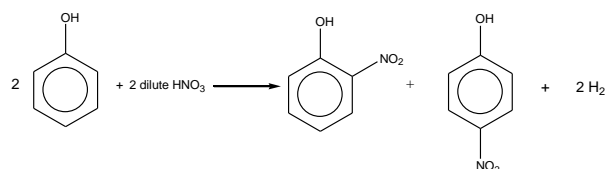
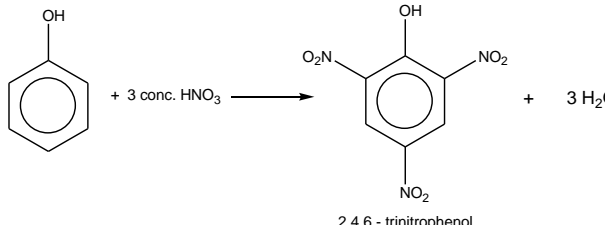
Two main types of reactions occur at the benzene ring:

5.2.1 Halogenation

	Benzene	Phenol
Reagents and conditions:	Iron filings/ iron(III) halide/ anhydrous aluminium halide Heat	Br ₂ (aq) (Halogen carrier is NOT required.) Room temperature

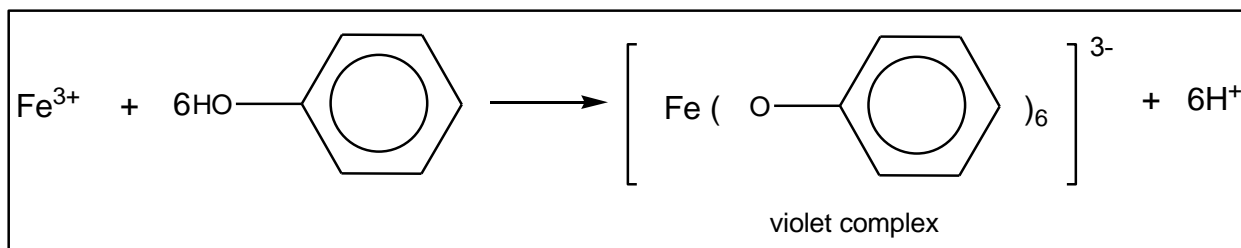
<p>Type of reaction:</p>	<p>Electrophilic substitution</p> <ul style="list-style-type: none"> With anhydrous $AlCl_3$:  <ul style="list-style-type: none"> With $FeBr_3$:  <p style="text-align: center;">bromobenzene</p>	<p>Electrophilic substitution</p> <ul style="list-style-type: none"> With aqueous bromine:  <p style="text-align: center;">2,4,6-tribromophenol (white precipitate)</p> <p>Observations: Orange $Br_2(aq)$ is decolourised, and a white precipitate of 2,4,6-tribromophenol is formed.</p> <ul style="list-style-type: none"> With bromine in CCl_4 (inert solvent):  <p>Observation: Reddish-brown $Br_2(l)$ is decolourised</p>
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5.2.2 Nitration

	Benzene	Phenol
Reagents and conditions:	<p>Conc HNO_3, conc H_2SO_4</p> <p>Warm at $55 - 60^\circ C$</p>	<p>Conc/ dilute HNO_3,</p> <p>Room temperature</p>
Type of reaction:	<p>Electrophilic substitution</p>  <p style="text-align: center;">nitrobenzene</p> <p>If temperature increases $>60^\circ C$,</p>  <p style="text-align: center;">1,3-dinitrobenzene</p>	<p>Electrophilic substitution</p> <ul style="list-style-type: none"> With dilute HNO_3, at room temperature:  <ul style="list-style-type: none"> With concentrated HNO_3, at room temperature:  <p style="text-align: center;">2,4,6 - trinitrophenol</p>

5.3 Distinguishing test for Phenols using $\text{FeCl}_3(\text{aq})$

Phenol reacts with aqueous iron(III) chloride to form a **violet** complex.



Type of reaction: **Complex ion formation**

Reagent and conditions: Aqueous FeCl_3 , neutral conditions, room temperature.

Observations: A violet complex is formed in the presence of phenol.

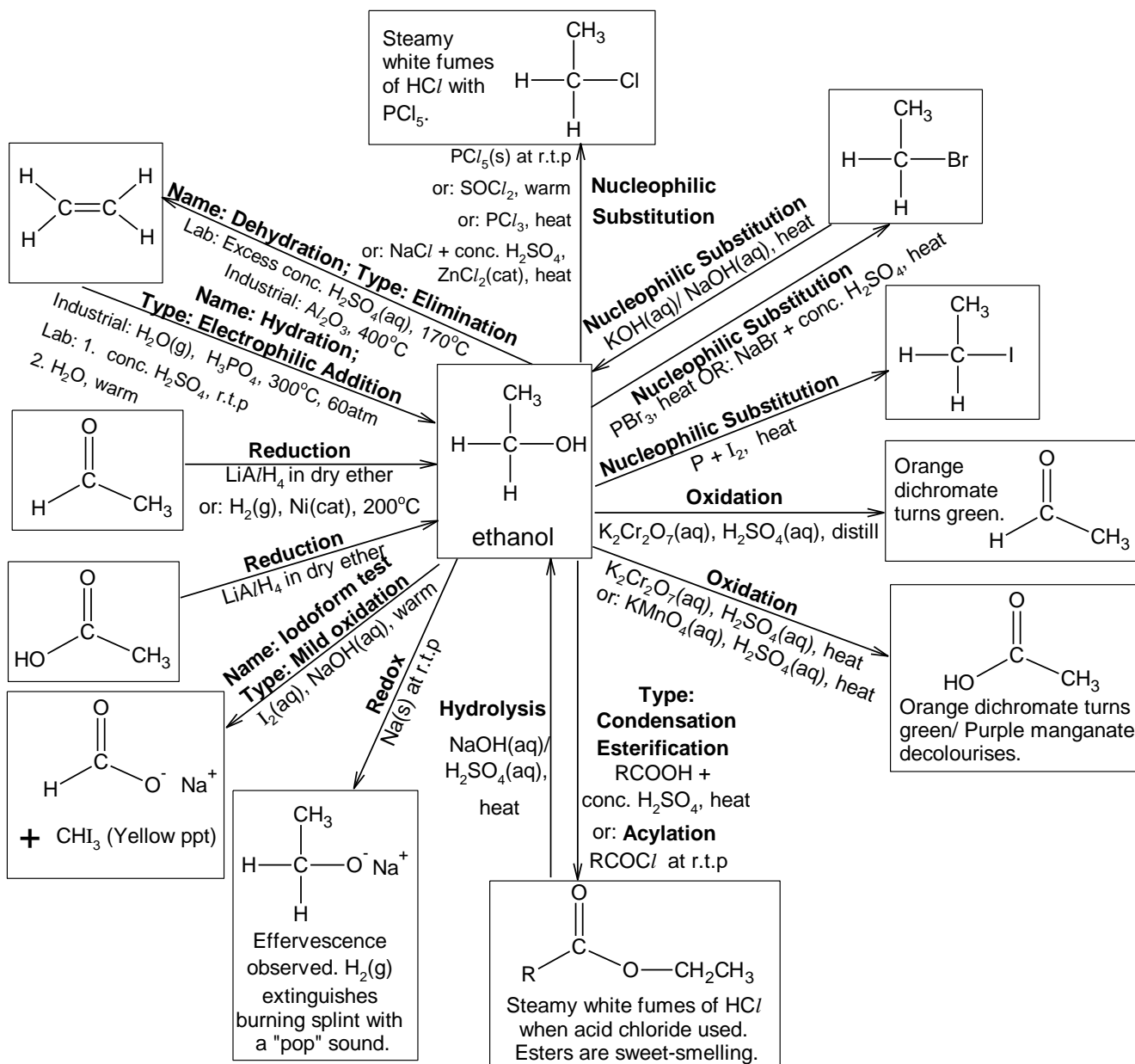
Note! These reactions are used to test for the presence of phenol. The colour of the complex may vary if other substituents are bonded to the benzene ring.

6. COMPARISON OF REACTIONS OF ETHANOL AND PHENOL WITH SOME COMMON REAGENTS

Reagent		Ethanol $\text{CH}_3\text{CH}_2\text{OH}$	Phenol $\text{C}_6\text{H}_5\text{OH}$
Physical Properties			
1.	With water	Miscible in all proportions for lower alcohols	Sparingly soluble
Chemical Reactivity			
1.	Na(s)	Redox reaction. $\text{CH}_3\text{CH}_2\text{O}^-\text{Na}^+$ and H_2 formed.	Redox reaction. $\text{C}_6\text{H}_5\text{O}^-\text{Na}^+$ and H_2 formed.
2.	NaOH(aq)	No reaction.	Acid-base reaction. $\text{C}_6\text{H}_5\text{O}^-\text{Na}^+$ formed.
3.	HX	Nucleophilic substitution (halogenation) Halogenoethane formed	No reaction.
4.	$\text{PCl}_5(\text{s})$	Nucleophilic substitution (halogenation) Vigorous reaction, HCl evolved.	No reaction.
5.	RCOCl Acid chloride	Condensation (acylation) Ester formed readily.	Condensation (acylation) Ester formed. Rate increased in presence of NaOH (aq) .
6.	RCOOH Carboxylic acid	Condensation (esterification) Ester formed.	No reaction.
7.	Dilute HNO_3	No reaction.	Electrophilic substitution $-\text{NO}_2$ group directed to 2- and 4- positions
8.	$\text{Br}_2(\text{aq})$	No reaction.	Electrophilic substitution White ppt. of 2,4,6-tribromophenol formed.
9.	$\text{I}_2, \text{OH}^-(\text{aq})$	Mild oxidation (iodoform test) Yellow ppt. of CHI_3 formed (reaction positive only for alcohols with $-\text{CH}(\text{CH}_3)\text{OH}$).	No reaction.
10.	$\text{MnO}_4^-/\text{H}^+$	Oxidation Ethanoic acid formed.	No reaction.
11.	Neutral $\text{FeCl}_3(\text{aq})$	No colour observed.	Complex ion formation Violet complex formed.

7. SUMMARY

7.1 Summary of Part I – Alcohols



7.2 Summary of Part II – Phenols

