16

Extension Topic – Organic Chemistry Hydroxy Compounds

GUIDING QUESTIONS

- How are alcohols synthesised?
- Which classses of reagents do alcohols react with and why? What types of reactions do alcohols undergo and why?
- Which classses of reagents do phenols react with and why? What types of reactions do phenols undergo and why?
- How does the reactivity of phenol compare to benzene towards electrophiles?
- How do we compare the relative acidity of hydroxy compounds?

LEARNING OUTCOMES

Students should be able to:

11.5(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
11.5(b) suggest characteristic distinguishing reactions for the different classes of alcohols (primary, secondary and tertiary alcohols), e.g. mild oxidation
11.5(c) deduce the presence of a $CH_3CH(OH)–$ group in an alcohol from its reaction with alkaline aqueous iodine to form tri-iodomethane
11.5(d) recall the chemistry of phenol, as exemplified by the following reactions:
  (i) with bases
  (ii) with sodium
  (iii) nitration of, and bromination of, the aromatic ring
11.5(e) explain the relative acidities of water, phenol and ethanol in aqueous medium (interpret as Brønsted–Lowry Acids)

REFERENCES

1. Cann, P.; Hughes, P. *Cambridge International AS and A Level Chemistry;* Hodder Education: London, 2015; pp 281–293, 432–439.
2. McMurry, J. *Organic Chemistry,* 6th ed.; Brooks/Cole: Belmont, CA, 2004; pp 587–638.
3. Bailey, P. S.; Bailey, C. A. *Organic Chemistry – A Brief Survey of Concepts and Applications,* 6th ed.; Prentice Hall: Upper Saddle River, NJ; 2000.

LOOKING BACK

In Topic 4 Reactions and Stoichiometry, we discussed various definitions of acids and bases. In Topic 15 Acid-Base Equilibria, we further learnt that the strength of weak acids and bases can be indicated by the equilibrium constants K_a and K_b. In our continuation of organic chemistry, we will see the application of the above acid-base concepts in the context of relatively weak organic acids (e.g. alcohols, phenols and carboxylic acids) and organic bases (e.g. amines). Fundamental concepts in Introduction and Isomerism (e.g. types of reactions, polar/non-polar mechanisms, electronic/resonance/steric effect and isomerism) continue to play an important role in explaining the nature and reactions of these acidic and basic functional groups in organic chemistry. The use of halogen derivatives as a starting material to prepare these compounds will also be revisited.

1 INTRODUCTION

LO 11.1(a) part: interpret, and use the nomenclature, general formulae and displayed formulae of the following classes of compound: (iii) hydroxyl compounds (alcohols and phenols)

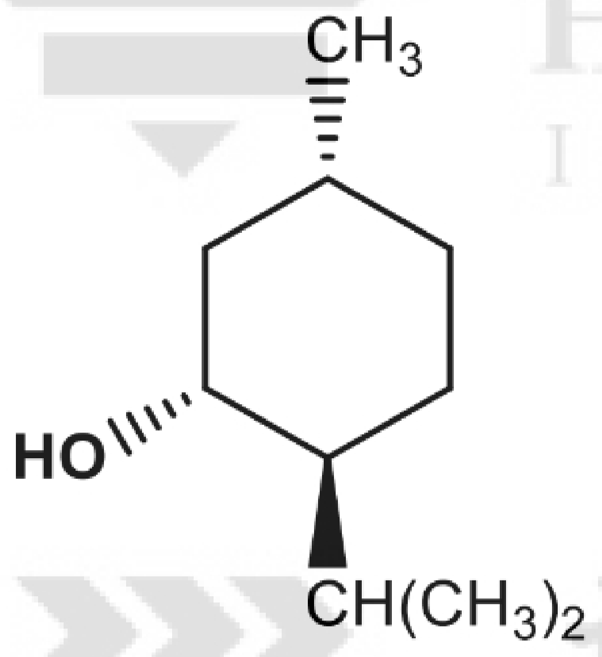
LO 11.1(b) part: interpret, and use the following terminology associated with organic reactions: (iii) degree of substitution: primary, secondary, tertiary, quaternary

Alcohols are compounds of the general formula R–**OH**, where R is any alkyl or substituted alkyl group. All alcohols contain the hydroxy (–**OH**) group, which determines the properties characteristic of this family of compounds.

$CH_3CH_2\mathbf{OH}$

ethanol

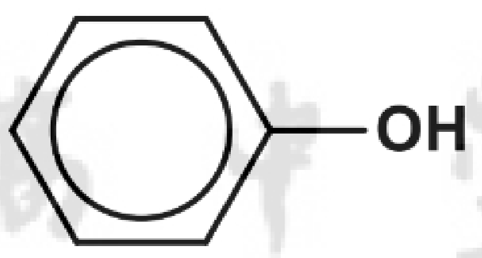
Present in alcoholic beverages and in some modern thermometers.



menthol

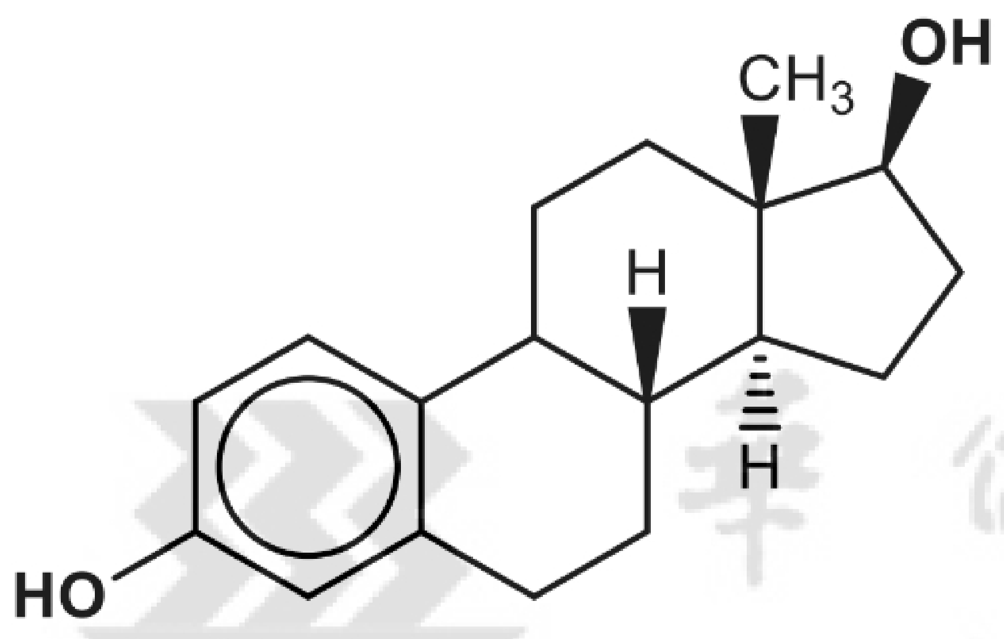
Occurs naturally in peppermint oil. It is well-known for the cooling sensation that it provokes when inhaled, eaten or applied to the skin.

Phenols are compounds in which the hydroxy (–**OH**) group is directly attached to an aromatic ring. Phenols differ markedly from alcohols in both physical and chemical properties.



phenol

An important chemical produced industrially as a precursor to many different compounds, including polycarbonates, herbicides, and pharmaceutical drugs.

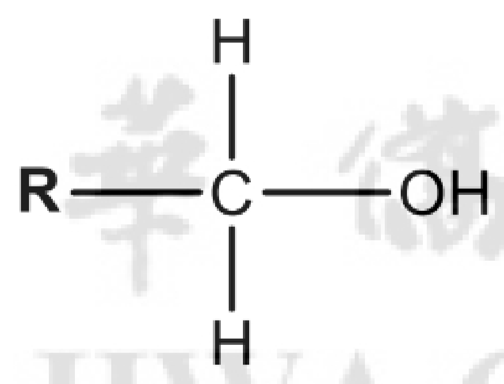


estradiol

The primary female sex hormone is an important hormone not only in reproductive and sexual functioning, and also affects other organs including the bones.

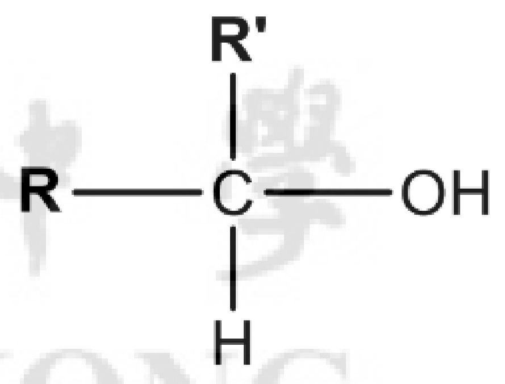
1.1 Classification of alcohols

Alcohols can be subdivided into **three** different classes (similar to halogenoalkanes). An alcohol is classified as **primary (1°)**, **secondary (2°)**, or **tertiary (3°)** according to the number of carbon atoms bonded to the carbon that bears the –OH group:



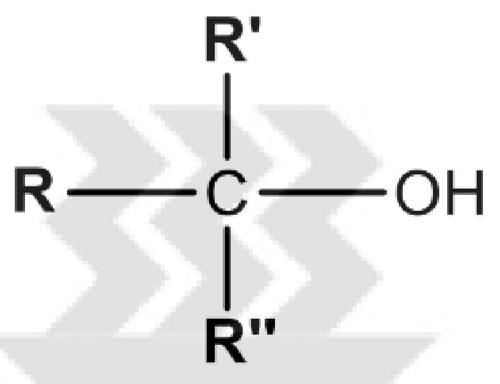
$\mathrm{R{-}\overset{H}{\underset{H}{C}}{-}OH}$

primary alcohol



$\mathrm{R{-}\overset{R'}{\underset{H}{C}}{-}OH}$

secondary alcohol



$\mathrm{R{-}\overset{R'}{\underset{R''}{C}}{-}OH}$

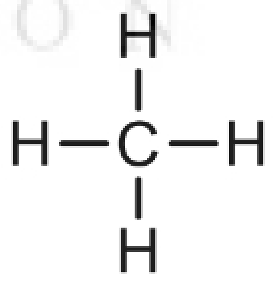
tertiary alcohol

R = alkyl or aryl group

Each class of alcohol undergoes chemical reactions differently. When asked to identify the alcohol functional group in a compound, you should state whether it is a primary, secondary or tertiary alcohol explicitly and not just a generic "alcohol".

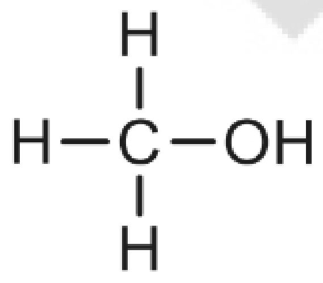
1.2 Nomenclature

Alcohols are named by replacing the terminal ***-e*** of the corresponding alkane name with ***-ol***.



$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}H}$

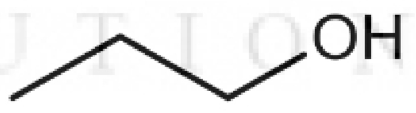
methan**e**



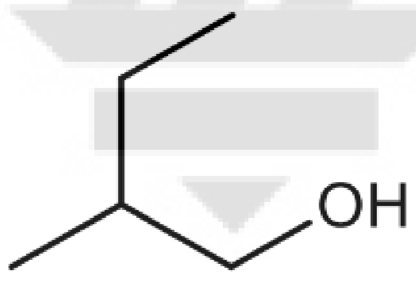
$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}OH}$

methan**ol**

The longest carbon chain containing the hydroxy group is considered the parent structure.

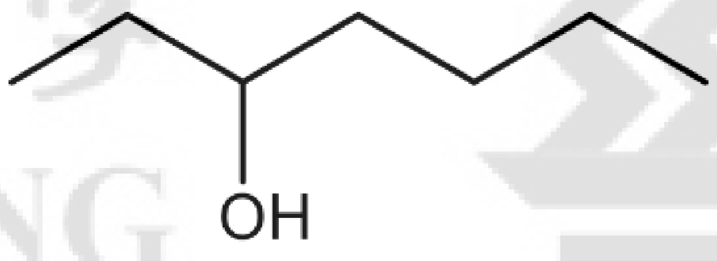


propan-1-ol



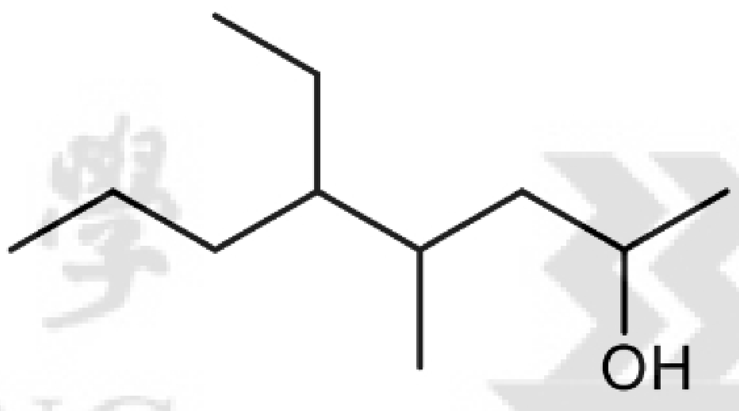
2-methylbutan-1-ol

Number the alkane chain beginning at the end nearer the hydroxy group, and use the appropriate number to indicate the position of the –OH group.



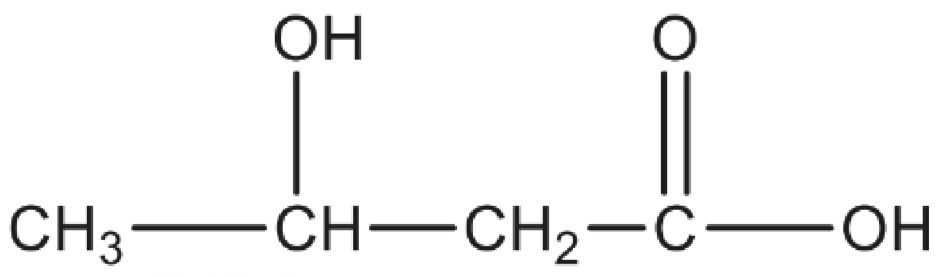
heptan-3-ol

Number any substituents according to their positions on the chain, and list the substituents in alphabetical order.



5-ethyl-4-methyloctan-2-ol

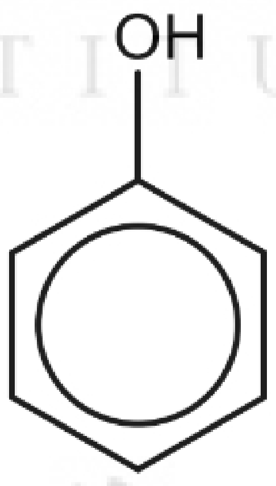
As a substituent, the –OH group is named "hydroxy", i.e. when it appears on a structure with a higher priority functional group, i.e. ketone, aldehyde, nitrile, amide, acid halide, ester and carboxylic acid.



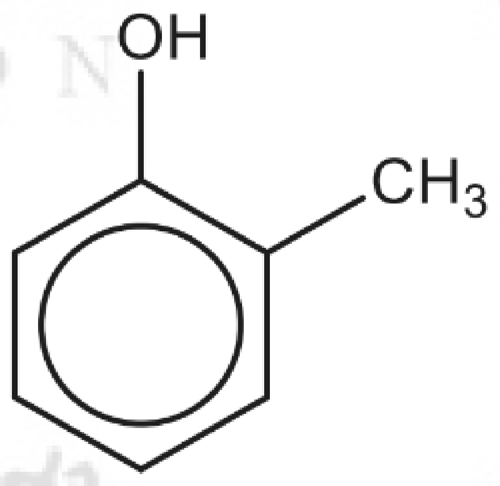
$CH_3-\overset{OH}{\overset{|}{C}H}-CH_2-\overset{O}{\overset{\|}{C}}-OH$

3-hydroxybutanoic acid

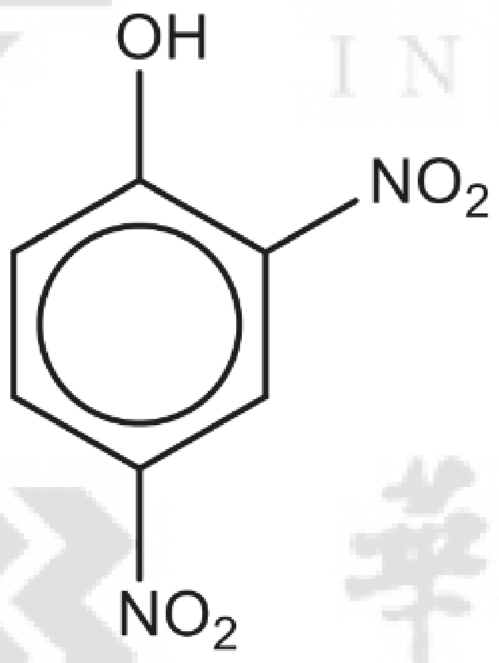
Compounds that have an –OH group directly attached to a benzene ring are called phenols.



phenol



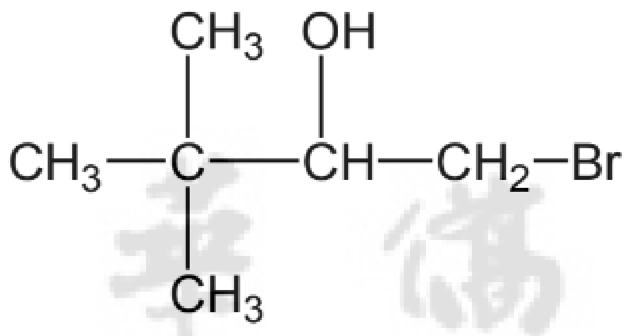
2-methylphenol



2,4-dinitrophenol

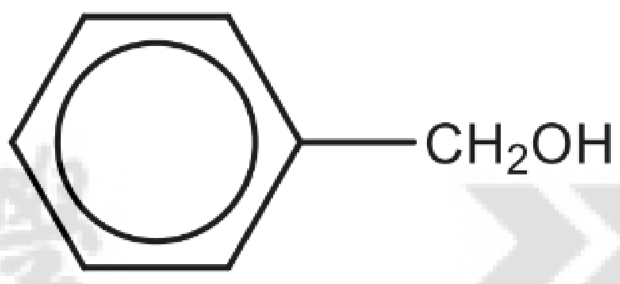
Lecture Exercise 1.1
Name and classify the following alcohols or phenols.

(i)

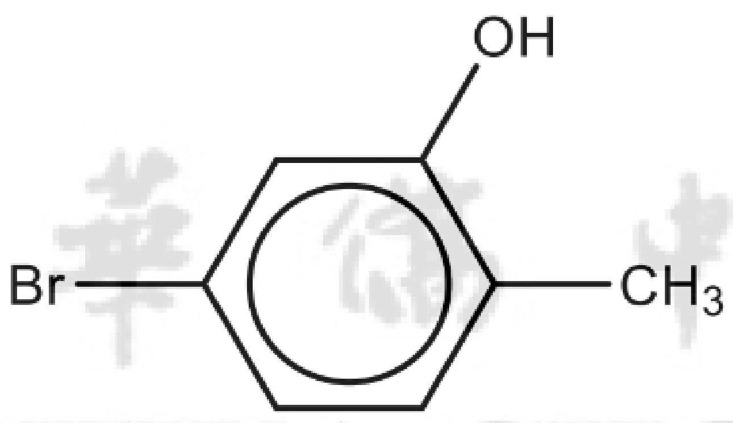


$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{OH}{C}H-CH_2-Br$

(ii)



(iii)

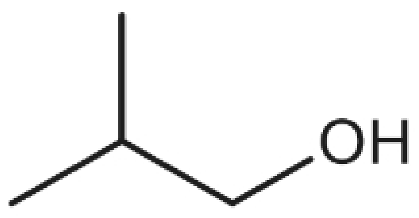


1.3 Isomerism

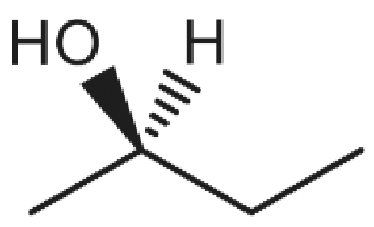
Isomerism in alcohols

Alcohols can exhibit constitutional isomerism, as well as enantiomerism. Of the five isomers with the formula C_4H_9OH, two (**A** and **B**) are primary alcohols, two (**C** and **D**) are secondary alcohols, and one (**E**) is a tertiary alcohol.

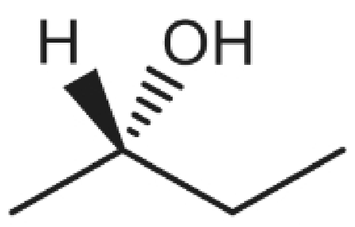
A



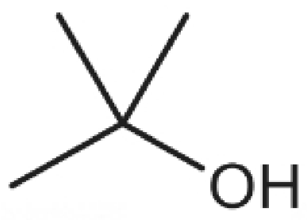
B



C



D



E

Isomerism of alcohols and ethers

Ethers are constitutional isomers of alcohols. Ethers do not contain the –OH group and so have none of the reactions of alcohols, and do not form intermolecular hydrogen bonds. Hence, ethers are fairly inert compounds with boiling points lower than those of the isomeric compounds. For example:

butan-1-ol, b.p. 118 °C

diethyl ether, b.p. 35 °C

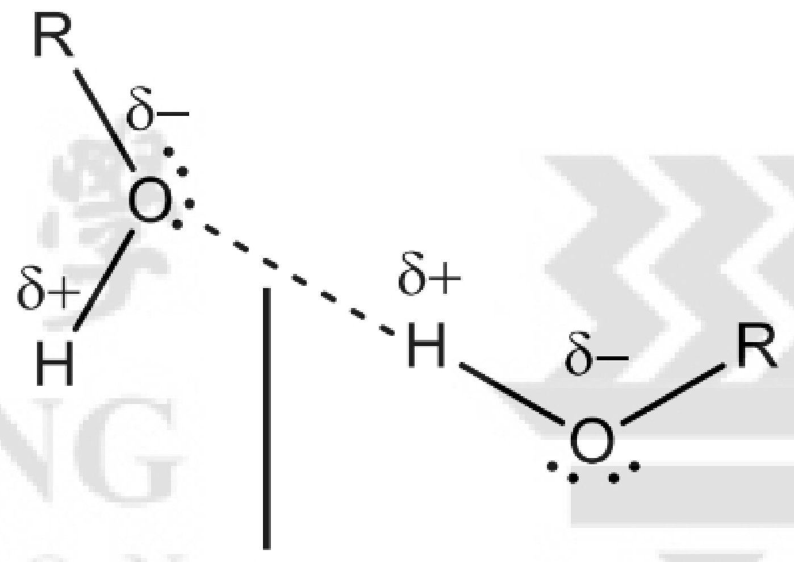
2 PHYSICAL PROPERTIES OF ALCOHOLS AND PHENOLS

2.1 Boiling Points

Alcohols and phenols have significantly higher boiling points than those of corresponding (isoelectronic) hydrocarbons.

no. of electrons in molecule	alkane		alcohol	
	formula	b.p. / °C	formula	b.p. / °C
18	C_2H_6	−88	CH_3OH	65
26	C_3H_8	−42	C_2H_5OH	78
34	C_4H_{10}	0	C_3H_7OH	97
42	C_5H_{12}	36	C_4H_9OH	118
50	C_6H_{14}	69	$C_5H_{11}OH$	138
50	$C_6H_5CH_3$ (methylbenzene)	111	C_6H_5OH (phenol)	182

- The boiling point of an alcohol is **higher** than that of the corresponding isoelectronic alkane (same number of electrons).
    - While the strength of the dispersion forces in the alcohol and in the alkane is about the same due to the similar sizes of the electron clouds, more energy is required to overcome the intermolecular **hydrogen bonding** in alcohols which is stronger than the dispersion forces in alkanes.



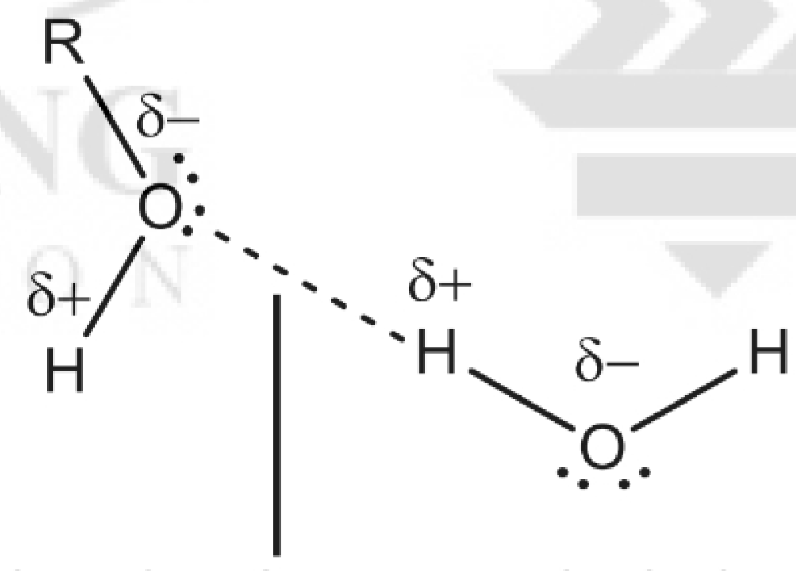
hydrogen bonding between alcohol molecules

- The boiling point of alcohols **increases** as the alkyl chain length increases.
    - While the strength of intermolecular hydrogen bonding remains largely similar for all the alcohols, the size of the electron cloud increases as the length of the alkyl chains increases. More energy is thus required to overcome the stronger **dispersion forces** between the alcohol molecules.

- Phenol and its derivatives are colourless solids. The melting point of phenol is 42 °C. The presence of hydrogen bonds makes the melting point of phenols higher than those of hydrocarbons with similar numbers of electrons.

2.2 Solubility in water

Alcohols are more soluble in water compared to their corresponding alkanes due to their ability to form hydrogen bonds with water molecules.



hydrogen bonding between alcohol and water

The solubility of alcohols in water decreases with increasing carbon number due to the increasing length of the non-polar alkyl chain.

$$\underbrace{CH_3CH_2CH_2CH_2CH_2CH_2}_{\text{non-polar}}\underbrace{-O-H}_{\text{polar}}$$

As the length of the alkyl chain increases, the strength of the dispersion forces between alcohol molecules increases. Energy released from hydrogen bonding formed between the alcohol molecule and water is less able to overcome the increasingly stronger dispersion forces, as well as the existing hydrogen bonding in water. In addition, the hydrogen bonding with water is disrupted by the larger non-polar alkyl chain.

Phenols are only moderately soluble in water due to their large non-polar aryl group; but dissolve completely when warmed.

Self-Practice 2.1

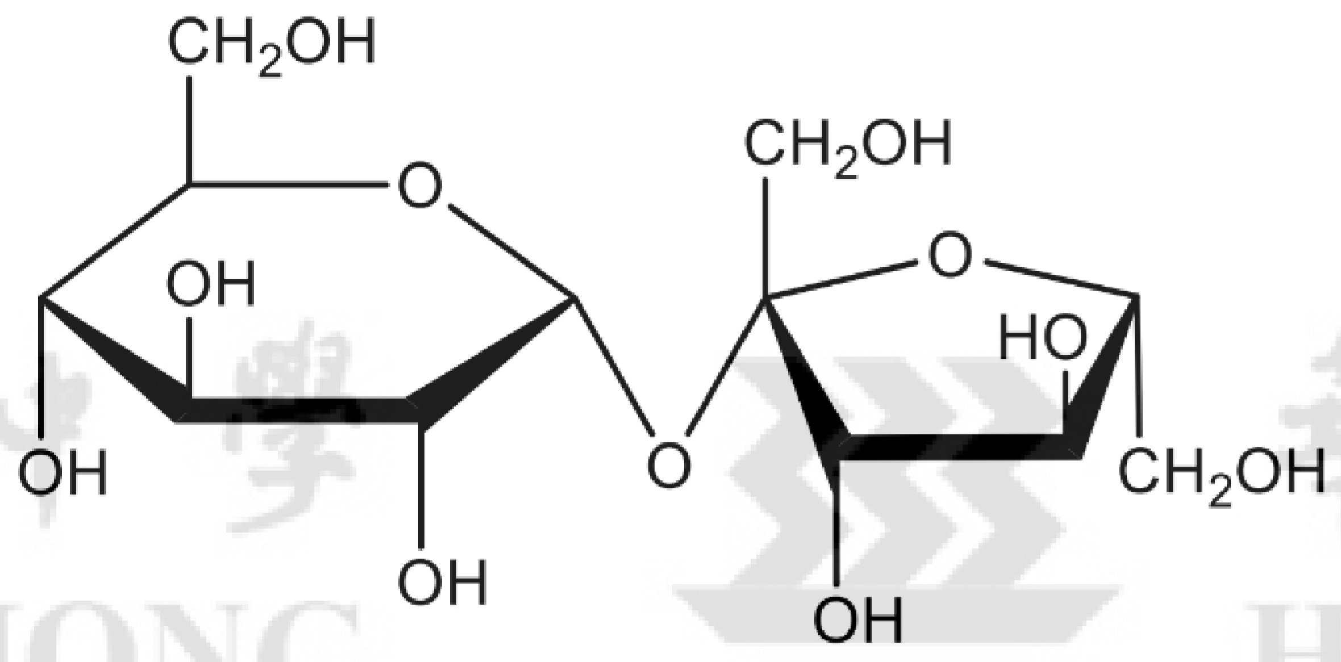
1. Arrange ethanol, ethane and ethane-1,2-diol in order of increasing boiling point. Explain your answer.

2. Hexan-1-ol has a boiling point of 158 °C whereas 3,3-dimethylbutan-2-ol has a boiling point of 120 °C. Explain the difference in boiling points.

3. The table below shows the solubility of various alcohols in water. Explain the trend.

name	formula	solubility / mol dm^{-3}
methanol	CH_3OH	miscible
ethanol	C_2H_5OH	miscible
propanol	C_3H_7OH	miscible
butanol	C_4H_9OH	1.1
pentanol	$C_5H_{11}OH$	0.30
hexanol	$C_6H_{13}OH$	0.058
heptanol	$C_7H_{15}OH$	0.008

4. The structure of sucrose is shown below. Predict the physical state and solubility of the compound under standard conditions.



3 PREPARATION OF ALCOHOLS

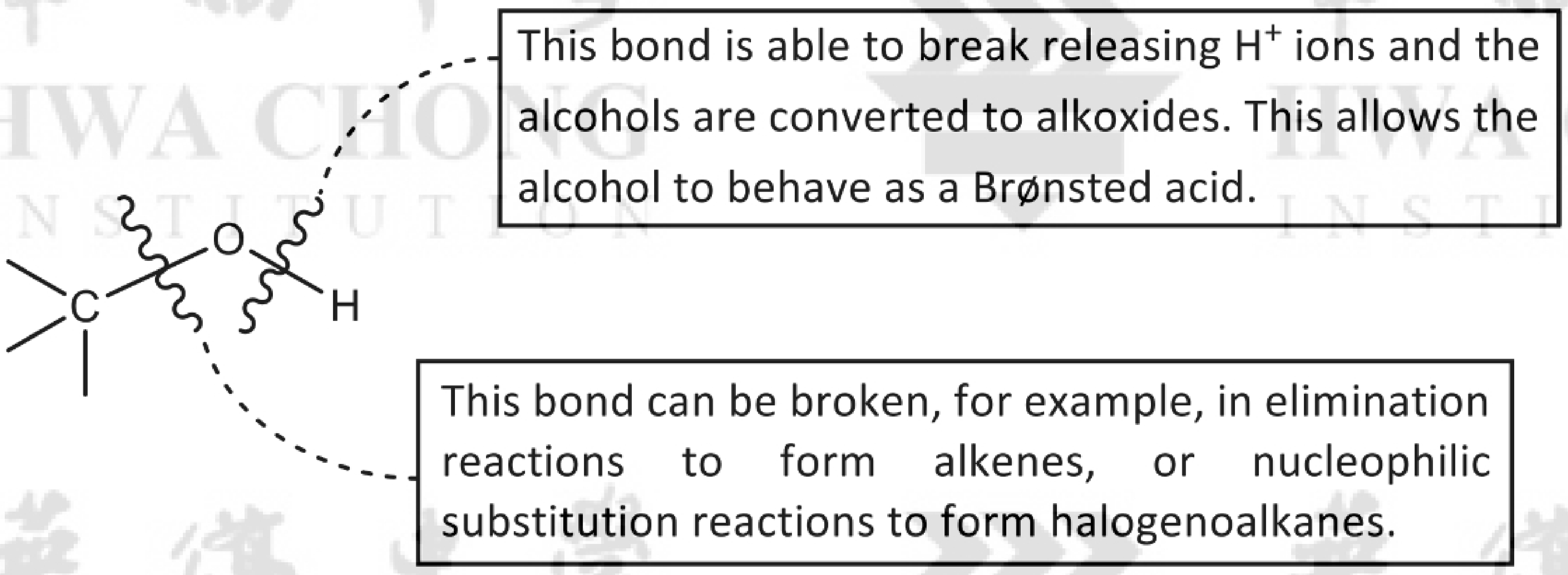
Alcohols can be prepared from:

- Electrophilic addition of water or steam to alkenes (Topic 11 Alkenes)
- Nucleophilic substitution of halogenoalkanes (Topic 13 Halogen Derivatives)
- Reduction of aldehydes and ketones (to be covered in Topic 17 Carbonyl Compounds)
  - Reduction of aldehydes yields primary alcohols
  - Reduction of ketones yields secondary alcohols
- Reduction of carboxylic acids (to be covered in Topic 18 Carboxylic Acids and Derivatives)
  - Reduction of carboxylic acids yields only primary alcohols

4 CHEMICAL PROPERTIES AND REACTIONS OF ALCOHOLS AND PHENOLS

LO 11.5(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

The reactivity of the –OH group allows alcohols to be versatile starting materials for the preparation of a variety of organic compounds. The alcohol functional group can undergo various reactions involving the cleavage of either the C–O or O–H bonds of the –OH group.



This bond is able to break releasing H^+ ions and the alcohols are converted to alkoxides. This allows the alcohol to behave as a Brønsted acid.

This bond can be broken, for example, in elimination reactions to form alkenes, or nucleophilic substitution reactions to form halogenoalkanes.

4.1 Combustion

All alcohols burn well in air to form carbon dioxide and water, but only the combustion of ethanol has significance in everyday life:

$$CH_3CH_2OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) \qquad \Delta H_c = -1367 \text{ kJ mol}^{-1}$$

4.2 Acid-Base reactions of Alcohols and Phenols

LO 11.5(e): explain the relative acidities of water, phenol and ethanol in aqueous medium (interpret as Brønsted–Lowry Acids)

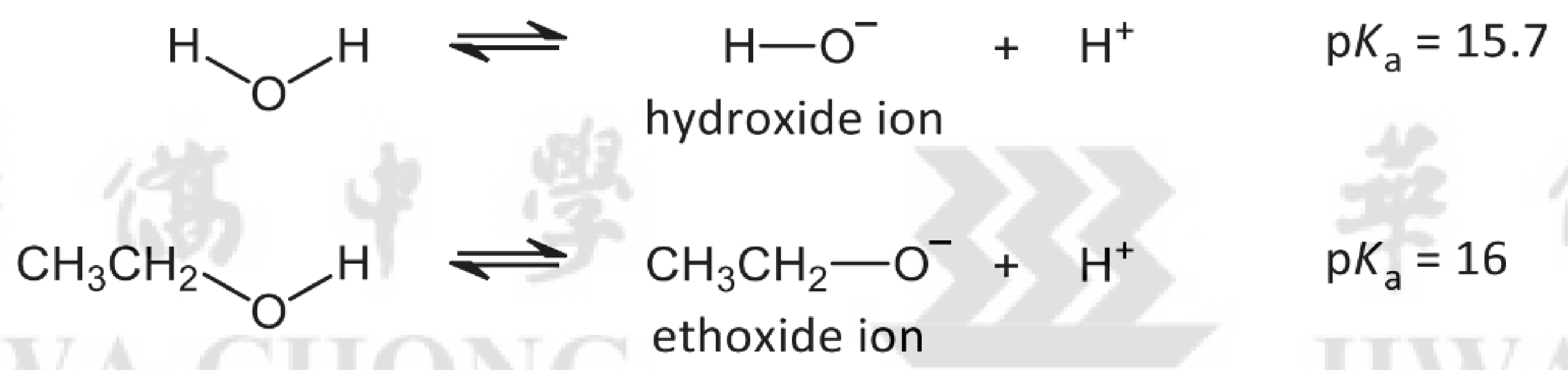
Due to the presence of the –OH group, alcohols and phenols can act as either Brønsted acids or Brønsted bases. The electron-deficient hydrogen can be removed in the presence of a sufficiently strong base, while the electron-rich oxygen can be protonated in the presence of a sufficiently strong acid.

While this section mainly focuses on alcohols and phenols acting as Brønsted acids, we do see alcohols acting as Brønsted bases later in Section 4.3.

In general, the strength of an acid depends on the **stability** of the conjugate base formed after dissociation. When a more stable conjugate base is formed, it is less likely to accept a proton to re-form the acid. Hence, the extent of dissociation is greater, resulting in a stronger acid and a larger K_a (Topic 15 Acid-Base Equilibria).

4.2.1 Acidity of Alcohols

In alcohols, the O–H bond can break to give H^+ and $R\text{–}O^-$ (alkoxide ion). The extent of dissociation is lower than that of water. Therefore alcohols do not turn blue litmus red.



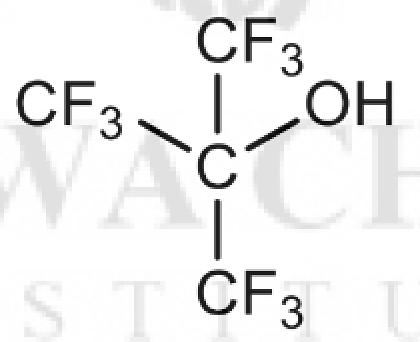
Why are alcohols weaker acids than water?

Alkyl groups are inductively electron-donating and will **intensify** the negative charge on the alkoxide ion. The alkoxide ion has a greater tendency to accept a proton to re-form the alcohol molecule. Thus the alkoxide ion is said to be **destabilised**, and deprotonation of the alcohol does not take place as easily. (Note: the length of the alkyl chain does not have a significant impact on the acidity.)

Effect of substituents on acidity of alcohols

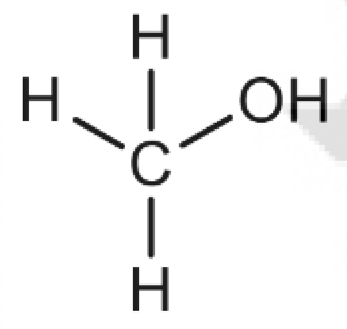
The presence of electron-withdrawing groups (e.g. $-NO_2$, –F, –Cl, –Br, –I, $-COCH_3$, $-CO_2H$, –CN, $-CO_2R$, $-NH_2$, –OH, $-OCH_3$) help to stabilise the alkoxide ion formed by dispersing the negative charge on the alkoxide ion, thus promoting the ionisation of the alcohol.

However, the presence of electron-donating groups (e.g. $-CH_3$) decreases the acidic strength of alcohols by intensifying the negative charge on the alkoxide ion, destabilising the alkoxide ion.



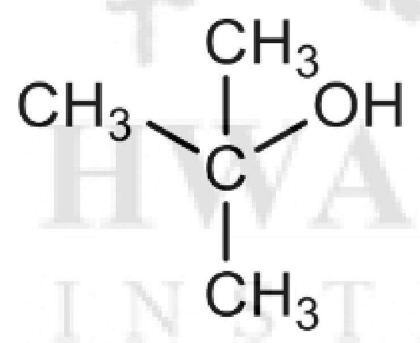
nonafluoro-tert-butylalcohol

pK_a = 5.4



methanol

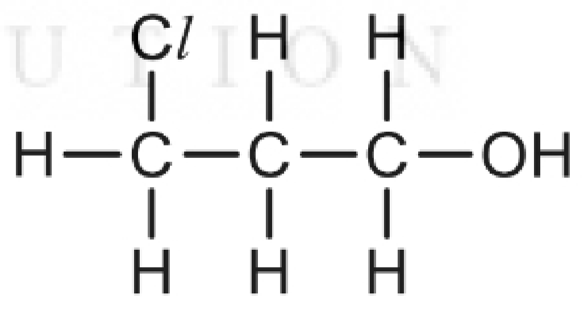
pK_a = 15.5



2-methylpropan-2-ol

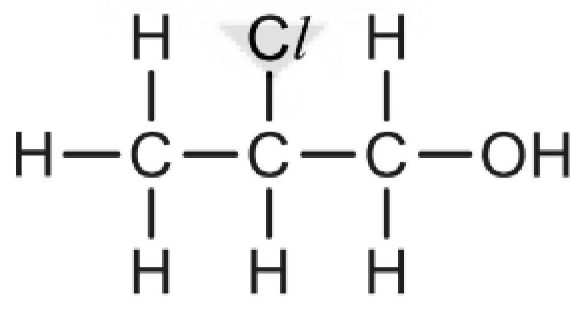
pK_a = 18

The distance of the electron-withdrawing group from the alkoxide group also affects the degree of dispersion of the negative charge on the alkoxide group, as the inductive effect decreases with increasing distance. Thus, the nearer the electron-withdrawing group is to the alkoxide group, the greater the degree of dispersion of the negative charge and the greater the acid strength of the alcohol.



3-chloropropan-1-ol

pK_a = 15.9



2-chloropropan-1-ol

pK_a = 14.5

Lecture Exercise 4.1

Arrange the alcohols in order of increasing acid strength, giving your reasoning.

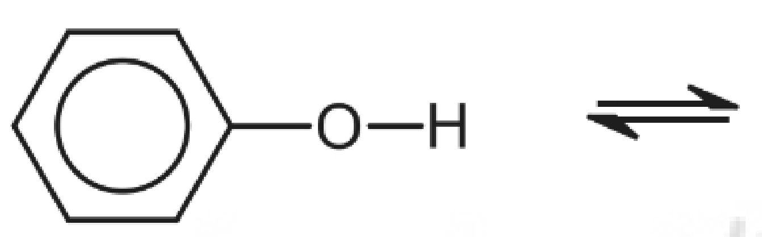
$CH_3CH_2CH_2OH$ $CH_3CHClCH_2OH$ $(CH_3)_2CHOH$ $CH_3CH_2CH(Cl)OH$

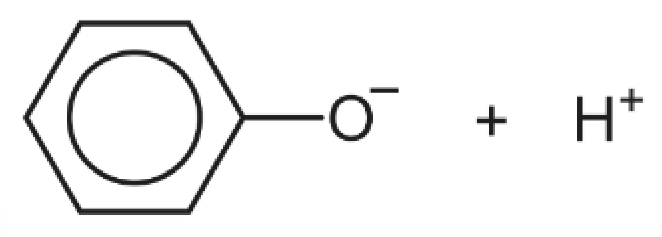
4.2.2 Acidity of Phenols

Phenols are more acidic than alcohols (and water). The pH of a 0.1 mol dm^{-3} phenol solution in water is 5.4, so a solution of phenol will turn blue litmus red.

$$CH_3CH_2{-}O{-}H \rightleftharpoons CH_3CH_2{-}O^- + H^+ \qquad pK_a = 16$$

ethoxide ion

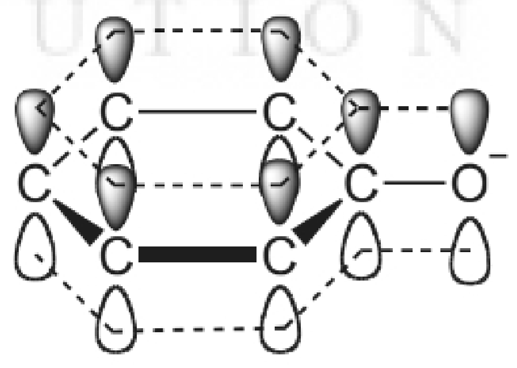


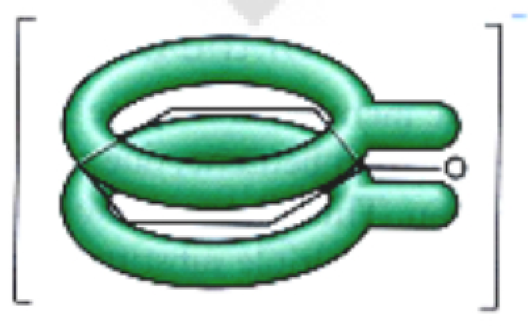


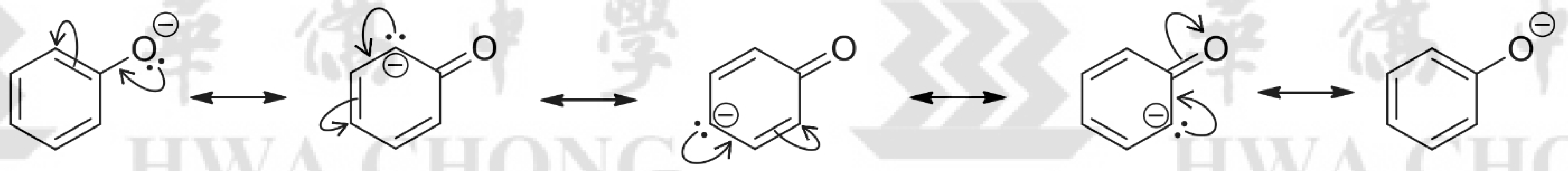
phenoxide ion

$pK_a = 10$

The negative charge on the phenoxide ion can be delocalised over the benzene ring as shown in the following diagrams.



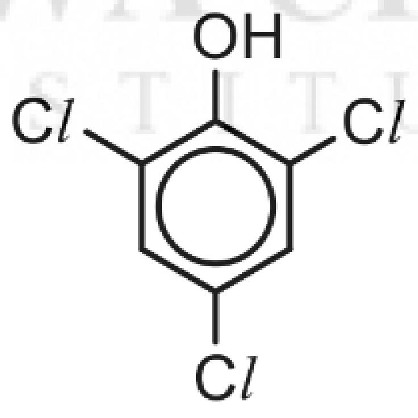




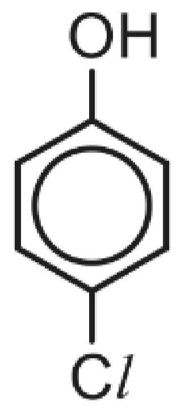
In the phenoxide ion, a p orbital of the oxygen atom is able to overlap with the π-electron cloud of the benzene ring. The negative charge is able to delocalise into the benzene ring to some extent, thus the phenoxide anion is **stabilised by resonance**. The phenoxide anion is less likely to accept a proton to re-form phenol. This makes phenols stronger acids than both aliphatic alcohols and water.

Effect of ring substituents on acidity of phenols

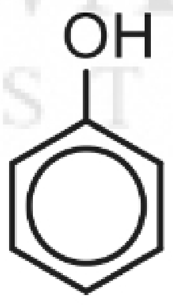
Similar to alcohols, the presence of electron-withdrawing groups (e.g. $-NO_2$, $-F$, $-Cl$, $-Br$, $-I$, $-COCH_3$, $-CO_2H$, $-CN$, $-CO_2R$), in the ring enables the ring in turn to withdraw more electron density from the oxygen, thus stabilising the phenoxide ion further and promoting the ionisation of the phenol.



2,4,6-trichlorophenol
pK_a = 7.6

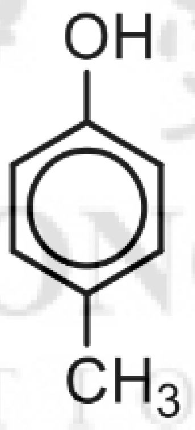


4-chlorophenol
pK_a = 9.4

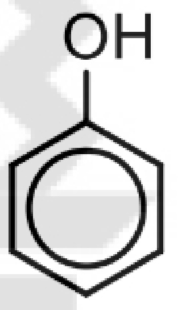


phenol
pK_a = 10

The presence of electron-donating groups (e.g. $-CH_3$, $-NH_2$, $-OH$, $-OCH_3$) decreases the acid strength of phenols by reducing the delocalisation of the negative charge on the oxygen atom into the ring (or by intensifying the negative charge on the phenoxide ion), thus destabilising the conjugate base.



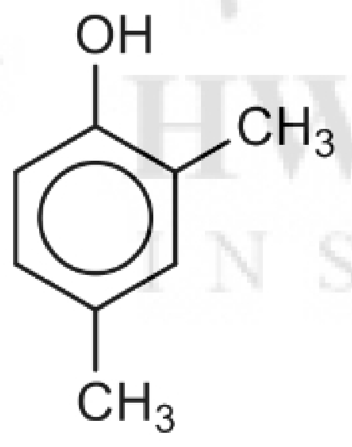
4-methylphenol
pK_a = 10.3

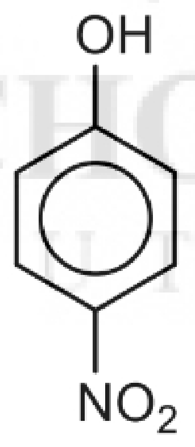


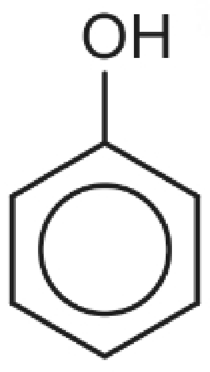
phenol
pK_a = 10

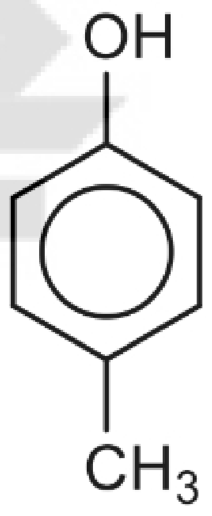
Self-Practice 4.1

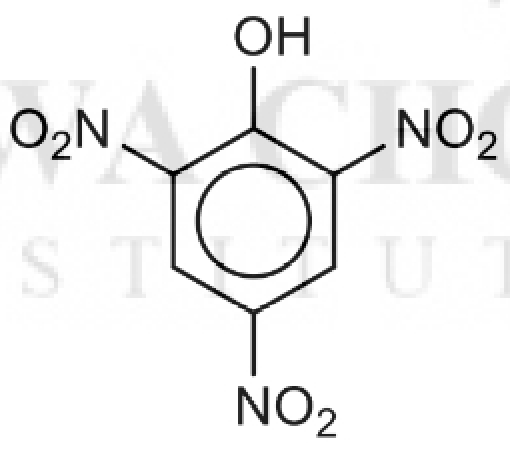
Arrange the following phenols in order of acid strength (1 for the most acidic, 5 for the least acidic).











4.2.3 Acid-metal Reaction with sodium (redox)

Alcohols and phenols react with Group 1 metals such as sodium and potassium to form alkoxides or phenoxides respectively and hydrogen gas. This reaction involves the breaking of the O–H bond.

$$CH_3CH_2OH + Na \longrightarrow \underset{\text{sodium ethoxide}}{CH_3CH_2O^-Na^+} + \tfrac{1}{2} H_2$$

Reagents & Conditions: Na(s), room temperature
Observation: slow effervescence of hydrogen gas

Reagents & Conditions: Na(s), room temperature
Observation: rapid effervescence of hydrogen gas

Alcohols and phenols both act as acids, liberating H^+, which is then reduced by sodium to H_2. Both reactions are similar to that of sodium with water. However, alcohols react more slowly as they are weaker acids than water. Phenols, being stronger acids than water, react more vigourously.

4.2.4 Acid-base reaction with sodium hydroxide

Phenols are acidic enough to react with bases like sodium hydroxide (and potassium hydroxide) to yield phenoxide salts and water. Phenol will form a cloudy mixture when mixed with water due to its poor solubility. Upon addition of aqueous NaOH, the phenol will dissolve to form a homogeneous colourless solution.

Reagents & Conditions: NaOH(aq), room temperature
Observation: cloudy mixture dissolves to form colourless homogeneous solution–

Note that phenols are not acidic enough to react with carbonates to liberate CO_2 gas.

Alcohols, being weaker acids than water, are not acidic enough to react with aqueous sodium hydroxide to form the corresponding alkoxides.

$$CH_3CH_2OH \ + \ NaOH \not\longrightarrow \text{no acid-base reaction}$$

4.3 Nucleophilic substitution (mechanism not required)

Alcohols can be converted to halogenoalkanes by nucleophilic substitution. In this reaction, the C–O bond is broken.

We have seen in Topic 13 Halogen Derivatives that the OH^- ion can attack a halogenoalkane, e.g. RCl, to form an alcohol. In this reaction, the halide ion, Cl^-, is called the **leaving group**.

Recall also from Topic 15 Acid-Base Equilibria, that Cl^- and OH^- ions are conjugate bases of acids HCl and H_2O respectively.

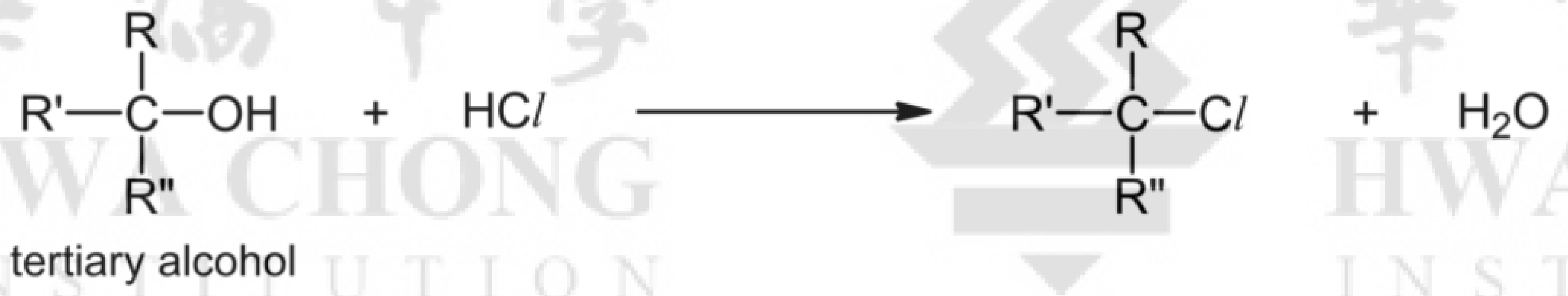
Since HCl is a stronger acid than H_2O, its conjugate base Cl^- is a weaker base than OH^-. Weaker bases are generally better leaving groups. Hence Cl^-, being a better leaving group than OH^-, is readily substituted by OH^- ions in halogenoalkanes to form alcohols in nucleophilic substitutions. This also applies to Br^- and I^-.

On the other hand, as OH^- is a poor leaving group, the conversion of alcohols to halogenoalkanes involves reagents such as acid or $SOCl_2$. These reagents first convert the –OH group into a better leaving group before the halide ion attacks, forming the halogenoalkane.

4.3.1 Nucleophilic substitution with hydrogen halides

Reaction with hydrochloric acid

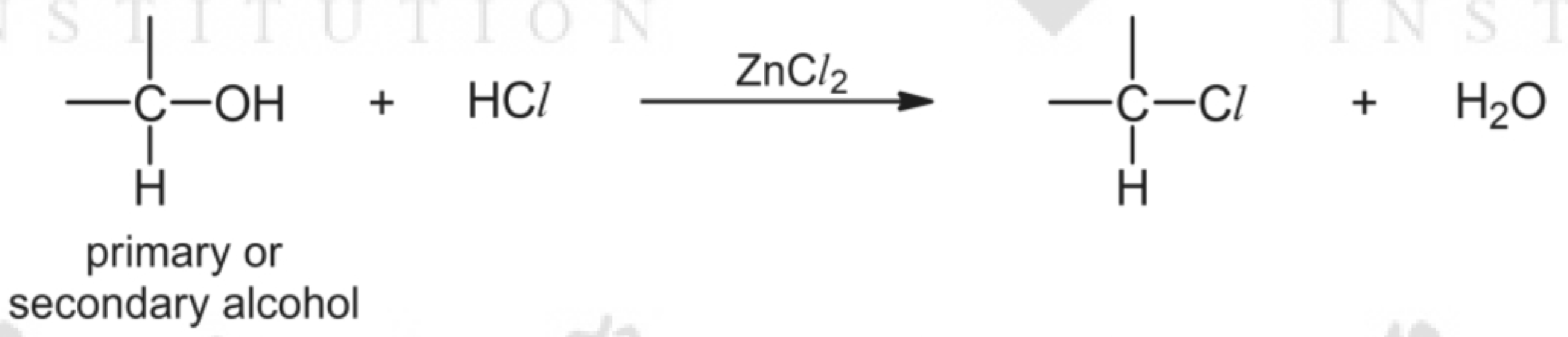
Tertiary alcohols react readily with concentrated hydrochloric acid upon shaking at room temperature to form the corresponding chloroalkane.



$$R'\!-\!\overset{\displaystyle R}{\underset{\displaystyle R''}{C}}\!-\!OH \ + \ HCl \longrightarrow R'\!-\!\overset{\displaystyle R}{\underset{\displaystyle R''}{C}}\!-\!Cl \ + \ H_2O$$

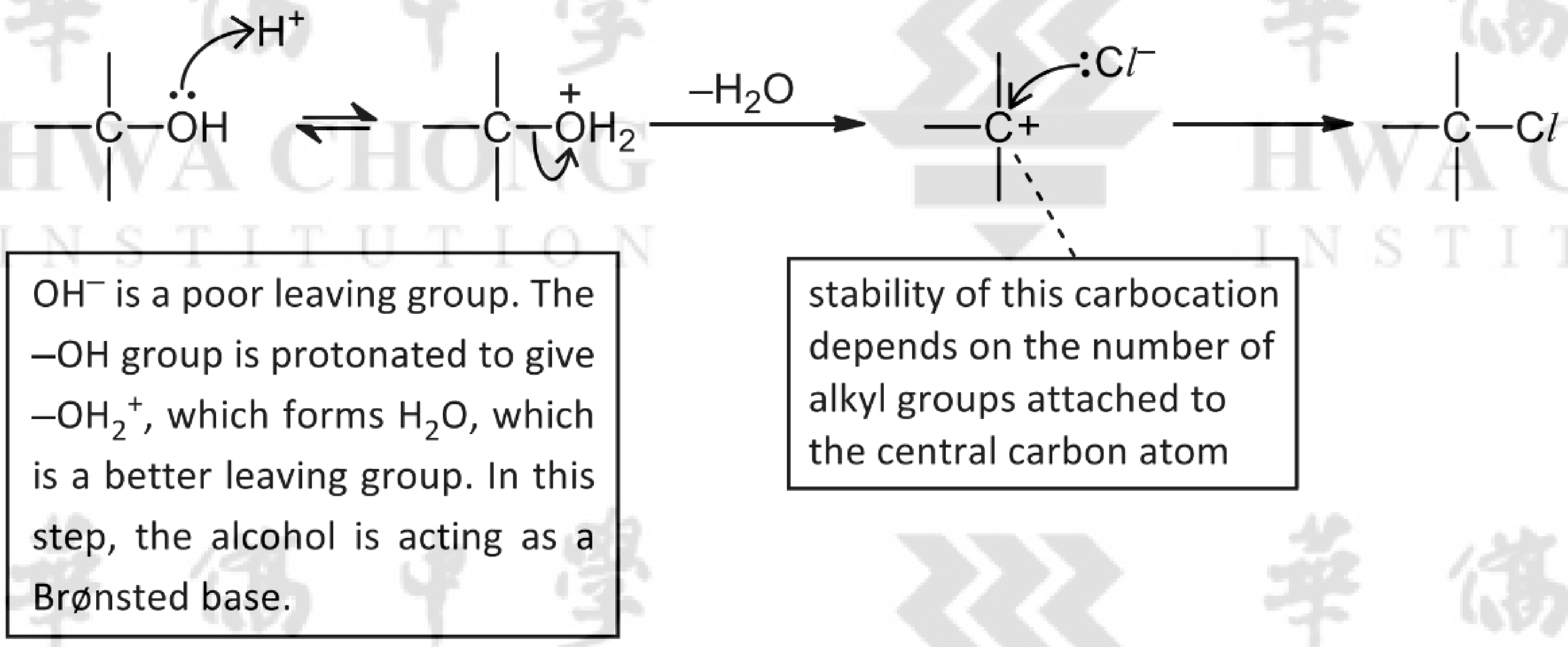
Reagents & Conditions: concentrated HCl, room temperature
Observation: solution turns cloudy

Primary and secondary alcohols also can react with concentrated hydrochloric acid, but at a slower rate. Anhydrous zinc chloride must be added as a catalyst, and the reaction mixture must be heated.



Reagents & Conditions: concentrated HC*l*, ZnC*l*₂, heat
Observation: solution turns cloudy

The reaction takes place via an S_N1 mechanism, forming a carbocation intermediate. The rate of reaction depends on the stability of the carbocation formed (See Topic 13 Halogen Derivatives). Carbocations formed from tertiary alcohols have three electron-donating alkyl groups and hence are the most stable. As such, the insoluble chloroalkanes are formed fastest with tertiary alcohols, and the reaction with primary alcohols is very slow at room temperature.



OH^- is a poor leaving group. The –OH group is protonated to give $-OH_2^+$, which forms H_2O, which is a better leaving group. In this step, the alcohol is acting as a Brønsted base.

stability of this carbocation depends on the number of alkyl groups attached to the central carbon atom

Figure 1: General mechanism of nucleophilic substitution of alcohols using HCl

These reactions form the basis of the **Lucas Test** to distinguish between primary, secondary and tertiary alcohols. The cloudiness of the solution is due to the relative insolubility of the chloroalkane.

type of alcohol	observation on adding conc HC*l* + ZnC*l*₂
R_3COH (tertiary)	immediate cloudiness appears in solution
R_2CHOH (secondary)	cloudiness appears within 5 min (at room temperature)
RCH_2OH (primary)	no cloudiness appears unless warmed

Reaction with hydrogen bromide

An alcohol can be converted to a bromoalkane by reacting it with either concentrated hydrobromic acid (HBr) or a mixture of sodium bromide with concentrated acid to generate HBr *in situ*.

$$R{-}OH + HBr \longrightarrow R{-}Br + H_2O$$

Reagents & Conditions: concentrated HBr, heat
-or- NaBr, conc. H_2SO_4 (to generate HBr *in situ*), heat

4.3.2 Nucleophilic substitution with phosphorus halides

Reaction with phosphorus trihalides:

Alcohols react with the various phosphorus trihalides to form the corresponding halogenoalkanes and phosphoric(III) acid.

$$3R{-}OH + PCl_3 \longrightarrow 3R{-}Cl + H_3PO_3$$

$$6R{-}OH + 2P + 3Br_2 \longrightarrow 6R{-}Br + 2H_3PO_3$$

$$6R{-}OH + 2P + 3I_2 \longrightarrow 6R{-}I + 2H_3PO_3$$

Reagents & Conditions: PCl_3, room temperature
-or- P, Br_2, heat
-or- P, I_2, heat

Comment: PBr_3 and PI_3 are prepared *in situ* by heating red phosphorus with bromine and iodine respectively.
$2P + 3X_2 \rightarrow 2PX_3$ X = Br, I

Reaction with phosphorus(V) chloride:

Phosphorus(V) chloride converts an alcohol into the corresponding chloroalkane with the evolution of hydrogen chloride. As it is highly reactive with water, the reagents must be free of water or moisture. PCl_5 is a good distinguishing test for an alcohol functional group if a carboxylic acid is absent (as PCl_5 will also react with carboxylic acids to produce HCl gas; see Topic 18 Carboxylic Acids and derivatives).

$$R{-}OH + PCl_5 \longrightarrow R{-}Cl + POCl_3 + HCl$$

Reagents & Conditions: PCl_5, room temperature

Observation: dense white fumes of HCl produced

Comment: Good distinguishing test for alcohol group (if carboxylic acid is absent)

4.3.3 Nucleophilic substitution with thionyl chloride

Another good reagent to convert alcohols to chloroalkanes is thionyl chloride, $SOCl_2$. Thionyl chloride and PCl_5 will react with both alcohols and carboxylic acids, liberating HCl in the process. The use of thionyl chloride confers an additional advantage over the use of PCl_5 in that both byproducts are acidic gases and are hence more easily separated from the chloroalkane product. Also, since both by-products are gases, the reaction is entropically driven (entropy change more positive, reaction more thermodynamically feasible).

$$R{-}OH + SOCl_2 \xrightarrow{\text{warm}} R{-}Cl + SO_2 + HCl$$

Reagents & Conditions: $SOCl_2$, warm

Observation: SO_2 gas and white fumes of HCl produced

Comments: Good distinguishing test for alcohol group (if carboxylic acid is absent)

Gaseous by-products easy to separate from the liquid product

Thionyl bromide, $SOBr_2$, may also be used to produce bromoalkanes with HBr and SO_2 as by-products.

4.3.4 Non-reactivity of phenols towards nucleophilic substitution

Phenols are very much less susceptible towards nucleophilic sustitution, in which the –OH group is replaced by a halide, than alcohols. Extremely harsh conditions are required for conversion of phenols to halogenoarenes (which will not be discussed in this syllabus).

Reasons for the inertness of phenols towards nucleophilic substitution

There are several reasons for the reduced susceptibility of phenols to form halogenoarenes. These reasons are similar to those given for the reduced susceptibility of halogenoarenes to nucleophilic substitution reactions (see Topic 13 Halogen Derivatives).

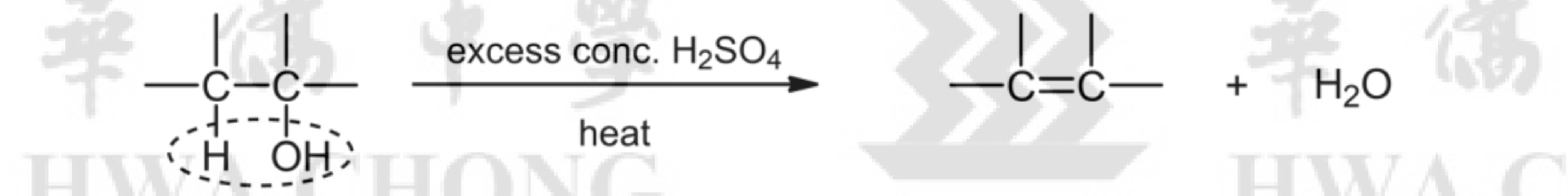
1. The lone pair of electrons on the O atom in phenol delocalises into the benzene ring, resulting in partial double bond character in the C–O bond. The C–O bond strength in phenols is higher than in an alcohol, making it more difficult to break.

2. Sterically, the approach of a nucleophile to the rear side of the C–O bond in phenols is hindered by the benzene ring. The π-electron cloud of the benzene ring will also repel the lone pair of electrons on the approaching nucleophile.

These two factors make the attack by the nucleophile difficult.

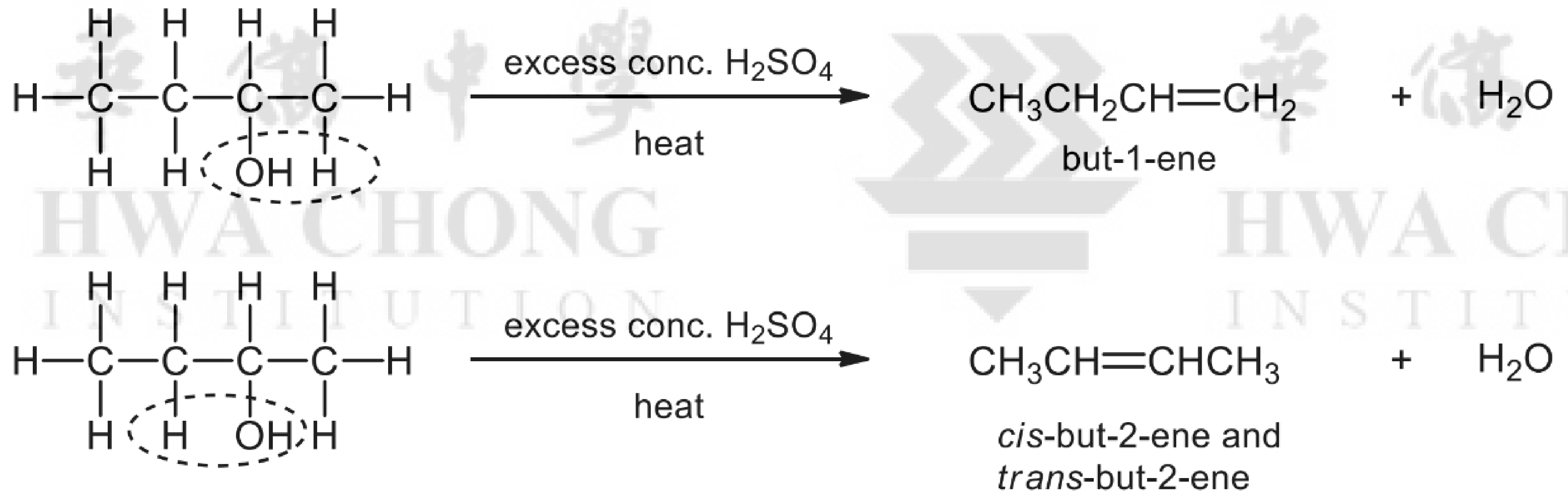
4.4 Dehydration (Elimination)

Dehydration of alcohols is carried out by heating the alcohol in the presence of a suitable catalyst. The loss of the hydroxy group together with a H atom bonded to an adjacent carbon will result in the formation of an alkene and a water molecule.



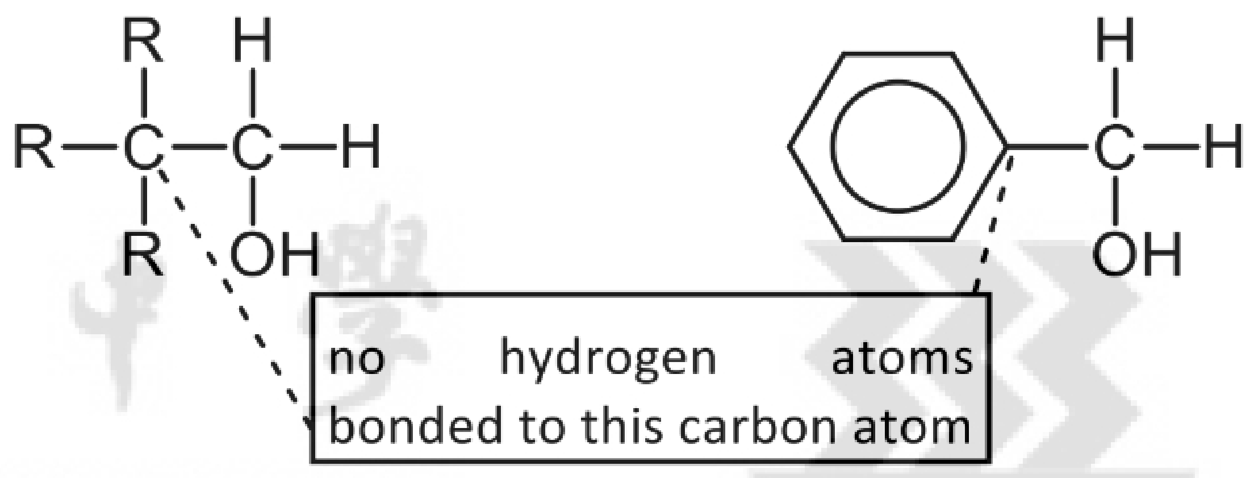
Reagents & Conditions:	excess concentrated H_2SO_4, heat -or- concentrated H_3PO_4, heat -or- Al_2O_3, heat
Comments:	Only alcohols with at least one H atom on the carbon atom adjacent to the carbon atom bearing the hydroxy group can undergo dehydration (shown in diagram above). Concentrated phosphoric(V) acid is sometimes preferred over sulfuric acid as sulfuric acid may act as an oxidising agent, producing unwanted side products. Phosphoric(V) acid is not an oxidising agent so side product formation is

Dehydration may form a mixture of alkenes, depending on the position of the hydroxy group. Consider the reaction of butan-2-ol with excess concentrated sulfuric acid:

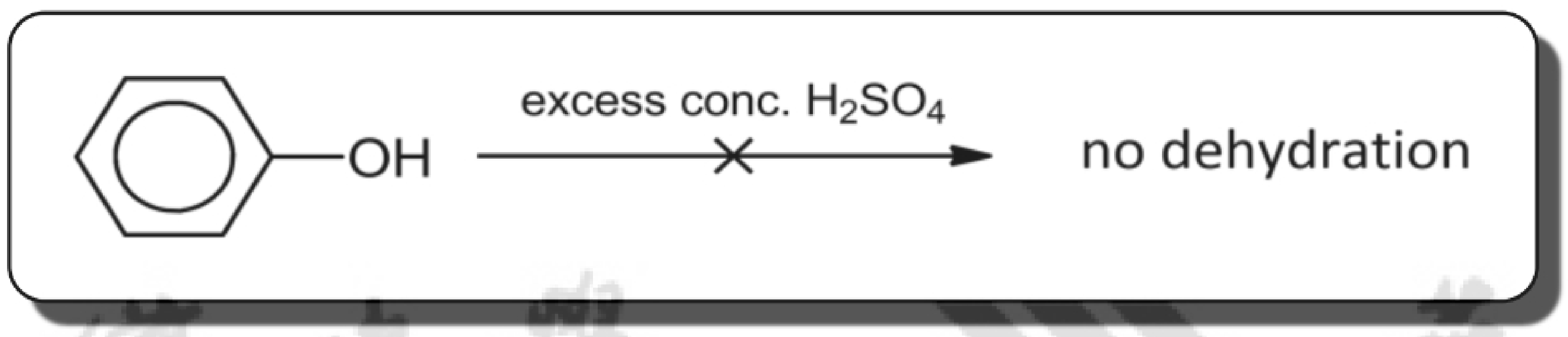


Note: There are some similarities and differences between the dehydration reaction of alcohols and elimination of halogenoalkanes. In both cases, an alkene is formed, but the differences are in the reagents used, as well as formation of H_2O and HX in the cases of alcohols and halogenoalkanes respectively. (See Topic 13 Halogen Derivatives)

If there are no hydrogen atoms bonded to the carbon atom that is adjacent to the carbon atom bearing the hydroxy group, dehydration cannot take place:

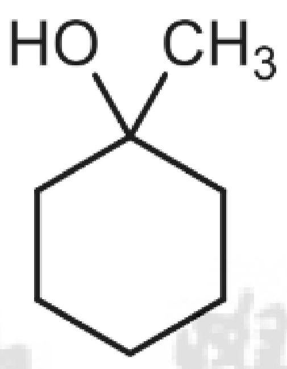


Phenols cannot undergo dehydration. This is because the C–O bond is very strong as explained in the previous section on nucleophilic substitution.



Lecture Exercise 4.2

Give structures of all products formed when 1-methylcyclohexanol reacts with each of the following reagents.



1-methylcyclohexanol

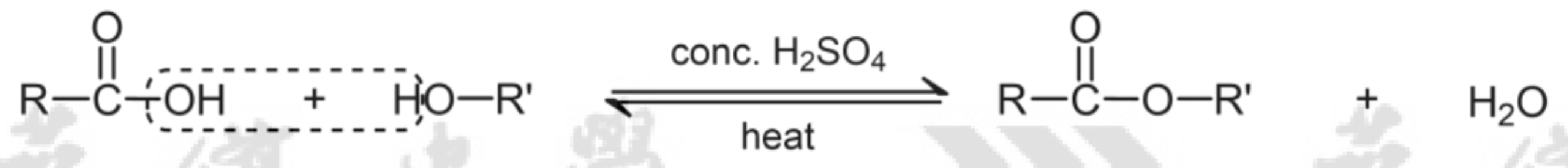
- **a)** phosphorus pentachloride
- **b)** NaBr, conc H_2SO_4, heat
- **c)** hot concentrated sulfuric acid (excess)

4.5 Condensation

Alcohols and phenols possess a –OH group with two lone pairs of electrons on the oxygen atom. This allows them to act as nucleophiles (Lewis base) in their reaction with carboxylic acids and acyl chlorides to form esters in a condensation process.

4.5.1 Condensation with carboxylic acids

Alcohols will react with carboxylic acids in a slow and reversible reaction, with a few drops of concentrated sulfuric acid as catalyst, to form the ester with the condensation of a water molecule. Note that concentrated sulfuric acid acts as a catalyst for both dehydration (to alkenes) and condensation. In this case, only a few drops of concentrated sulfuric acid are used, making the sulfuric acid less likely to act as a dehydrating agent.

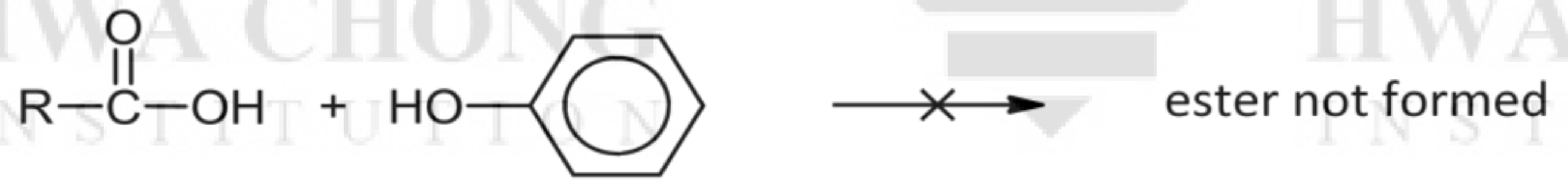


$$\mathrm{R-\overset{\overset{O}{\|}}{C}-OH + HO-R' \xrightleftharpoons[heat]{conc.\ H_2SO_4} R-\overset{\overset{O}{\|}}{C}-O-R' + H_2O}$$

Reagents & Conditions: alcohol, carboxylic acid, few drops of concentrated H_2SO_4, heat

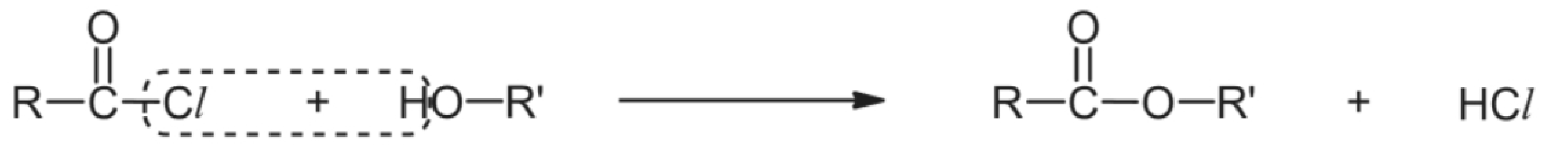
Comment: reaction slow and reversible

Unlike alcohols, phenols cannot react with carboxylic acids in a similar condensation reaction. This is due to the delocalisation of the lone pair of electrons on the oxygen atom into the benzene ring. The lone pair of electrons is thus less available to attack the carboxyl carbon of the carboxylic acid to form the ester.



4.5.2 Condensation with acyl chlorides

Acyl chlorides react much more readily with alcohols in condensation reactions than their corresponding carboxylic acids. No heating and no catalysts are required, and the reaction goes to completion instead of establishing an equilbrium.

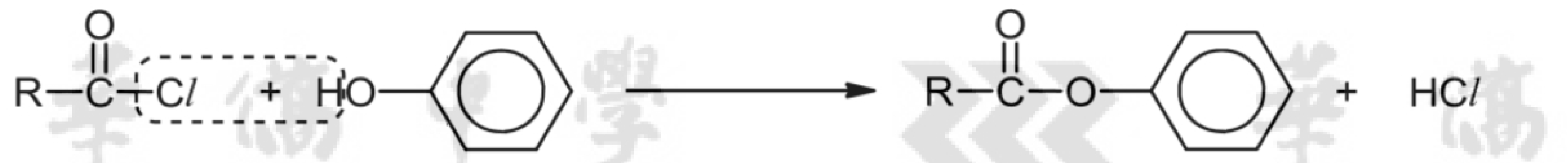


$$\mathrm{R-\overset{\overset{O}{\|}}{C}-C\mathit{l} + HO-R' \longrightarrow R-\overset{\overset{O}{\|}}{C}-O-R' + HC\mathit{l}}$$

Reagents & Conditions: acyl chloride, alcohol, room temperature

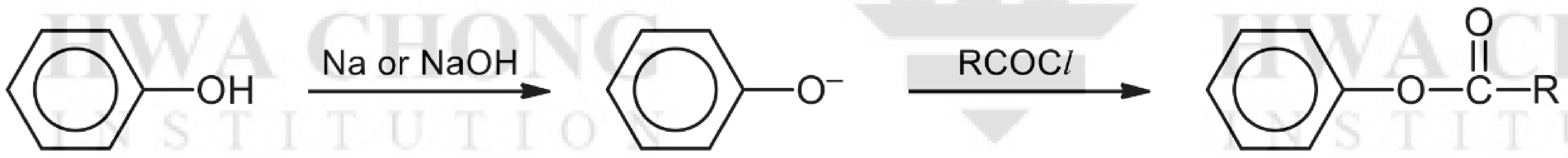
Observation: white fumes of HC*l* produced

The only method to form a phenyl ester is from the condensation reaction between a phenol and an acyl chloride. As the lone pair of electrons on the oxygen atom in phenol is delocalised into the π-electron cloud of the benzene ring, phenols are less nucleophilic than alcohols. As a result, only the acyl chloride and not the carboxylic acid is used for this condensation reaction.



Reagents & Conditions: acyl chloride, phenol, room temperature
Observation: white fumes of HC*l* produced

For a better yield, the reaction is carried out under basic conditions (by using Na or NaOH) to first generate the phenoxide ion. The negative charge of the phenoxide ion increases the electron density around the oxygen atom, making it a stronger nucleophile than phenol. Hence the phenoxide ion attacks the acyl chloride more readily.



4.6 Oxidation

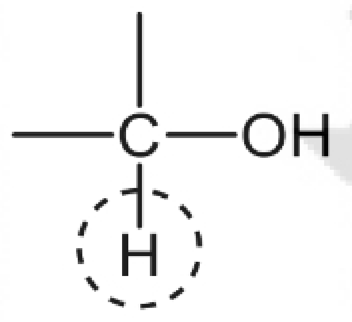
Two common sets of reagents and conditions are used for the oxidation of alcohols:

- $K_2Cr_2O_7$ / dilute H_2SO_4, heat
- $KMnO_4$ / dilute H_2SO_4, heat

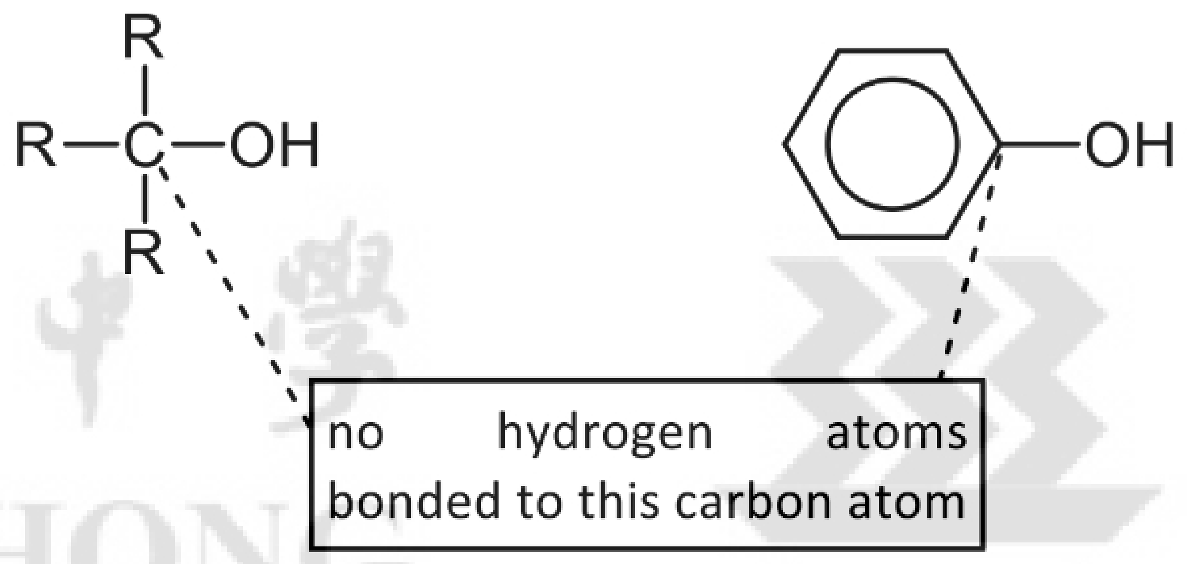
The product of oxidation is determined largely by the type of alcohol.

Note:

For the oxidation of an alcohol to occur (using the above reagents), the alcohol must have at least one hydrogen atom bonded to the carbon atom bearing the –OH group:



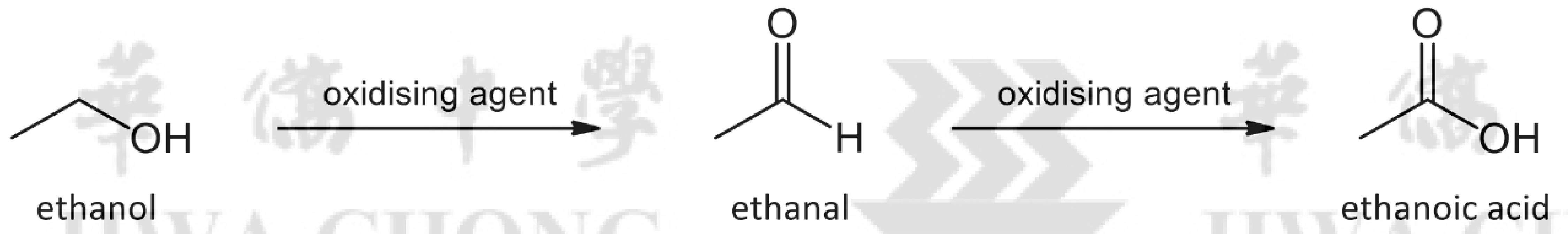
For this reason, tertiary alcohols and phenols cannot be oxidised using the above reagents:



no hydrogen atoms bonded to this carbon atom

4.6.1 Oxidation of Primary Alcohols

Primary alcohols are readily oxidised to aldehydes on heating. With excess oxidising agent, the reaction proceeds further, yielding carboxylic acids. The oxidation pathway for ethanol is shown below.



Oxidation to aldehydes

- Controlled oxidation of primary alcohols yields aldehydes.

- Once the aldehyde is formed in the reaction vessel, it will come into contact with more oxidant and this will lead to further oxidation, forming a carboxylic acid. This can be avoided by distilling the aldehyde away from the reaction mixture as soon as it forms. This is possible as the aldehyde lacks intermolecular hydrogen bonding and thus has a lower boiling point than the corresponding alcohol.
- The distillation setup is shown in diagram below.

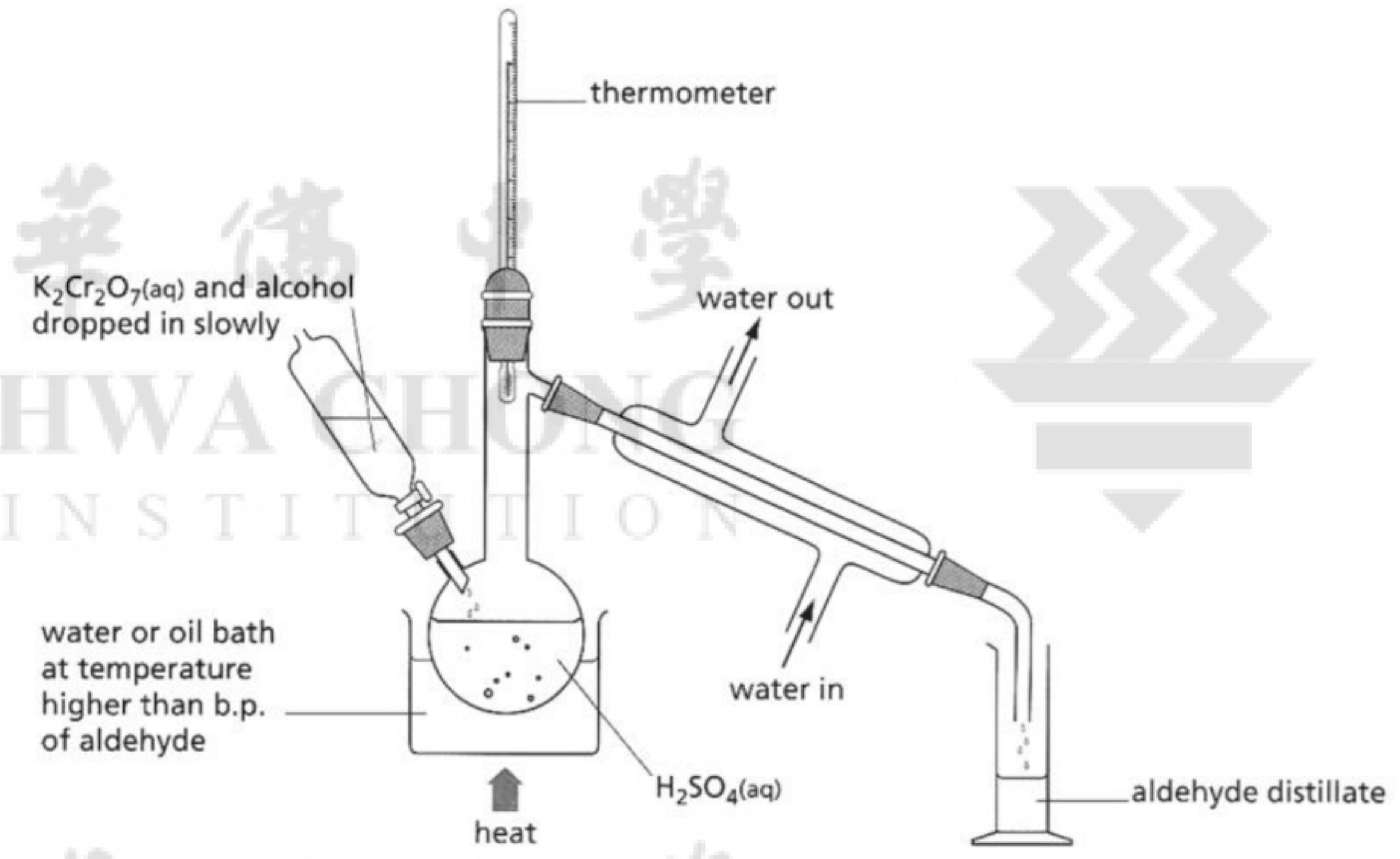
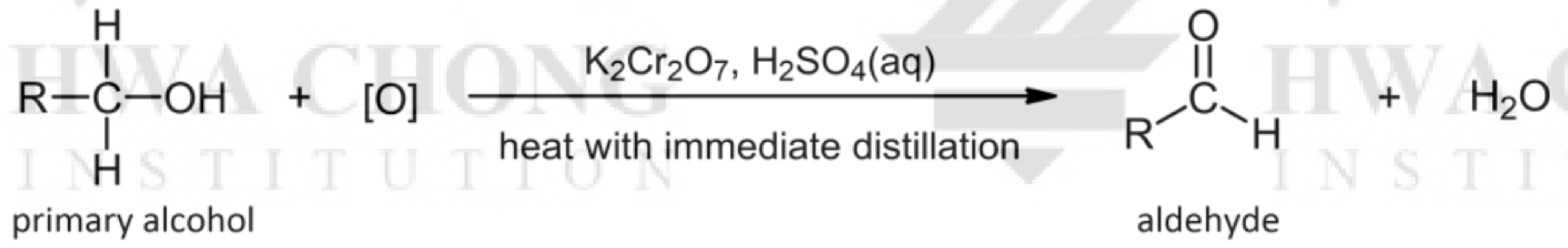


Figure 2. Experimental setup for the distillation of aldehydes by oxidising primary alcohols. (Diagram taken from Chemistry for Advanced Level by P. Cann and P. Hughes; Hodder Murray)



$$RCH_2OH + [O] \xrightarrow[\text{heat with immediate distillation}]{K_2Cr_2O_7,\ H_2SO_4(aq)} RCHO + H_2O$$

Reagents & Conditions: $K_2Cr_2O_7$, $H_2SO_4(aq)$, heat with immediate distillation

Observations: orange solution ($Cr_2O_7^{2-}$) turns green (Cr^{3+})

Comments: Only $K_2Cr_2O_7$ is selective enough to oxidise primary alcohols to the aldehydes. $KMnO_4$, being a stronger oxidising agent, will oxidise them directly to carboxylic acids.

Oxidation to carboxylic acids

To obtain carboxylic acids from primary alcohols, the reacting solution needs to be heated under reflux. This prevents the aldehyde formed from evaporating and allows further oxidation to the carboxylic acid.

The reflux setup is shown in the diagram below.

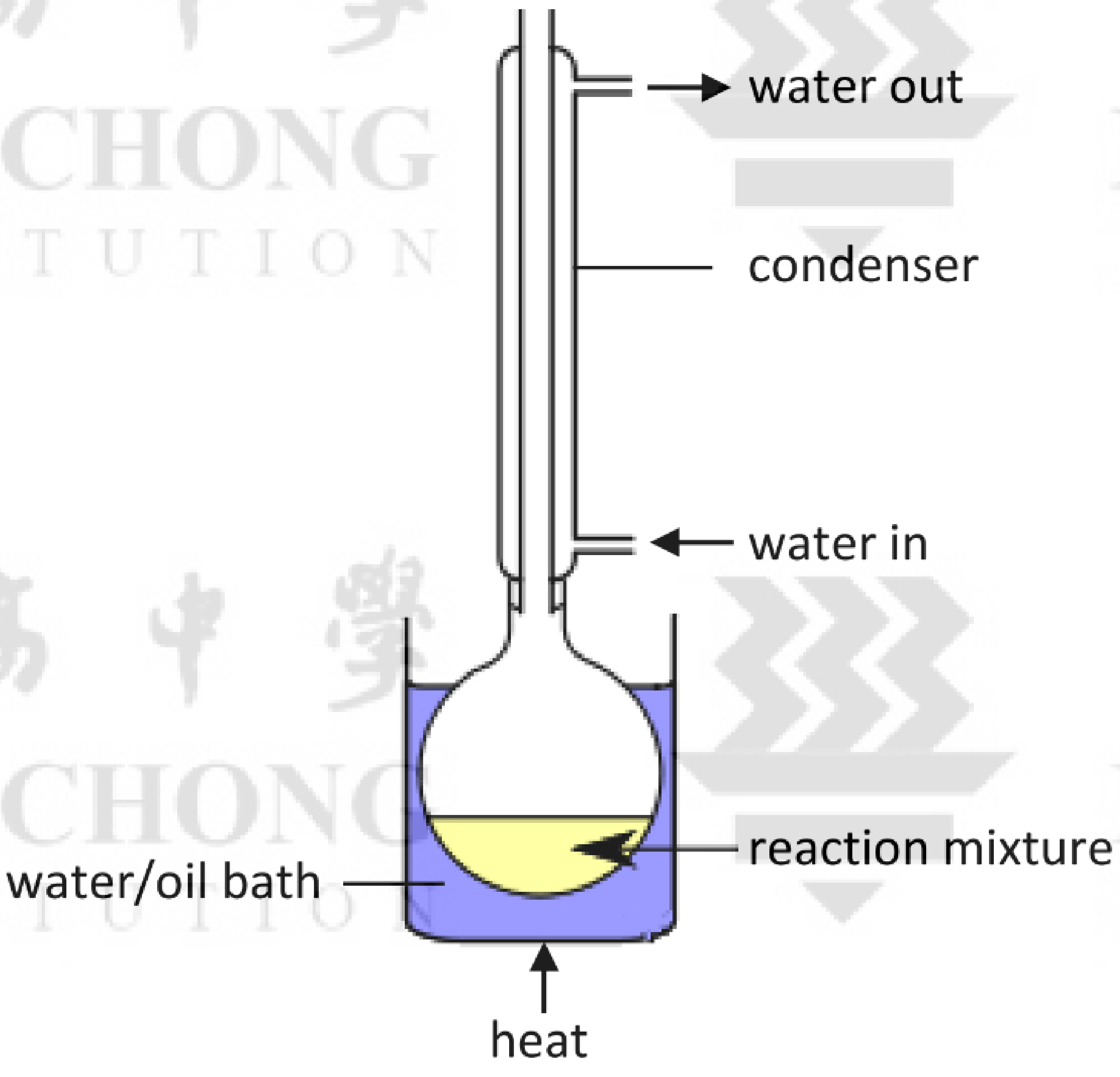
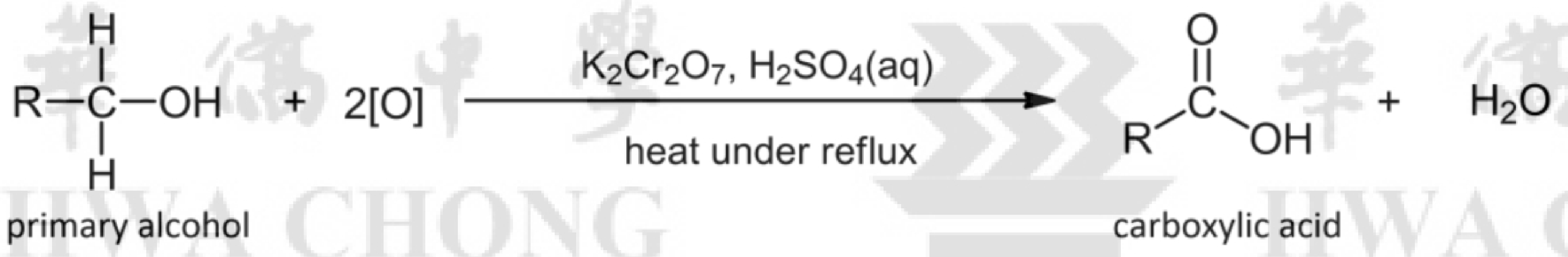


Figure 3. Example of a typical reflux setup

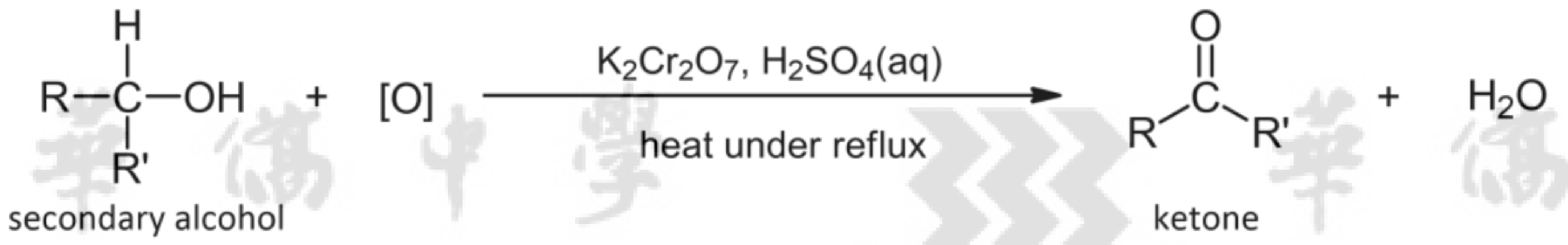


Reagents & Conditions: $K_2Cr_2O_7$, H_2SO_4(aq), heat under reflux
-or- $KMnO_4$, H_2SO_4(aq), heat under reflux

Observations: orange solution ($Cr_2O_7^{2-}$) turns green (Cr^{3+})
-or- purple solution (MnO_4^{-}) turns colourless (Mn^{2+})

4.6.2 Oxidation of Secondary Alcohols

Secondary alcohols are oxidised to ketones which are resistant to further oxidation.



Reagents & Conditions: $K_2Cr_2O_7$, H_2SO_4(aq), heat under reflux
-or- $KMnO_4$, H_2SO_4(aq), heat under reflux
Observations: orange solution ($Cr_2O_7^{2-}$) turns green (Cr^{3+})
-or- purple solution (MnO_4^-) turns colourless (Mn^{2+})

Oxidation as a distinguishing test to identify primary, secondary and tertiary alcohols
LO 11.5(b): suggest characteristic distinguishing reactions for the different classes of alcohols (primary, secondary and tertiary alcohols), e.g. mild oxidation

Oxidation may be used as a method to distinguish between the various classes of alcohols (primary, secondary or tertiary), based on the products of oxidation (if any). The alcohol is first **heated under reflux** with **excess** potassium dichromate(VI) and dilute sulfuric acid. Tertiary alcohols will not be oxidised by $K_2Cr_2O_7$, so the colour of the reaction mixture remains orange.

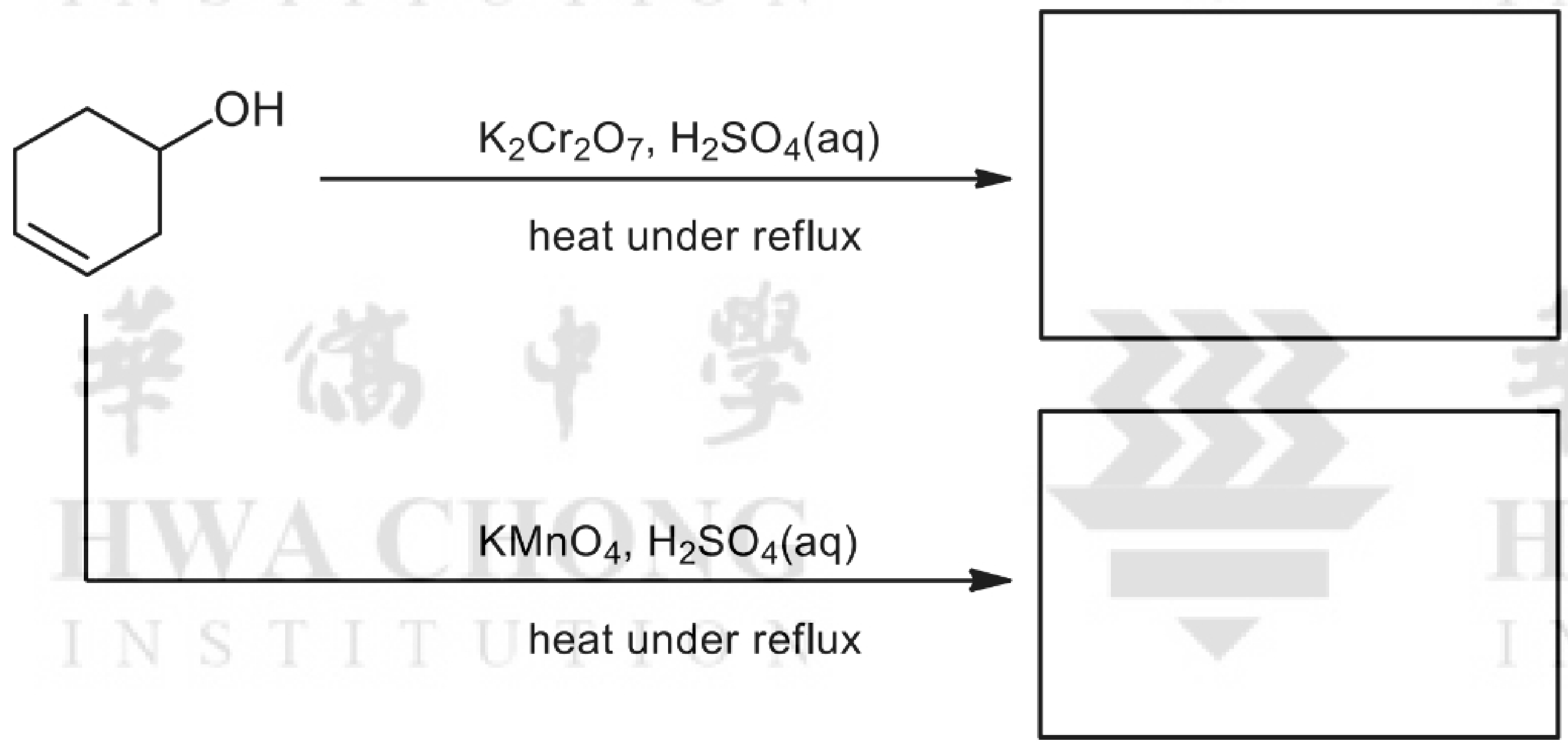
Primary and secondary alcohols will be oxidised by $K_2Cr_2O_7$ to carboxylic acids and ketones respectively, causing the orange solution to turn green. To distinguish between these two classes of alcohols, the organic product must be **isolated** (e.g. by distillation), and distinguishing tests for the carboxylic acid or the ketone should be carried out on the product to identify the class of alcohol. (These distinguishing tests will be covered in Topic 17 Carbonyl Compounds and Topic 18 Carboxylic Acids and Derivatives.)

Note that in simple chemical tests, reflux and distillation setups are not used.

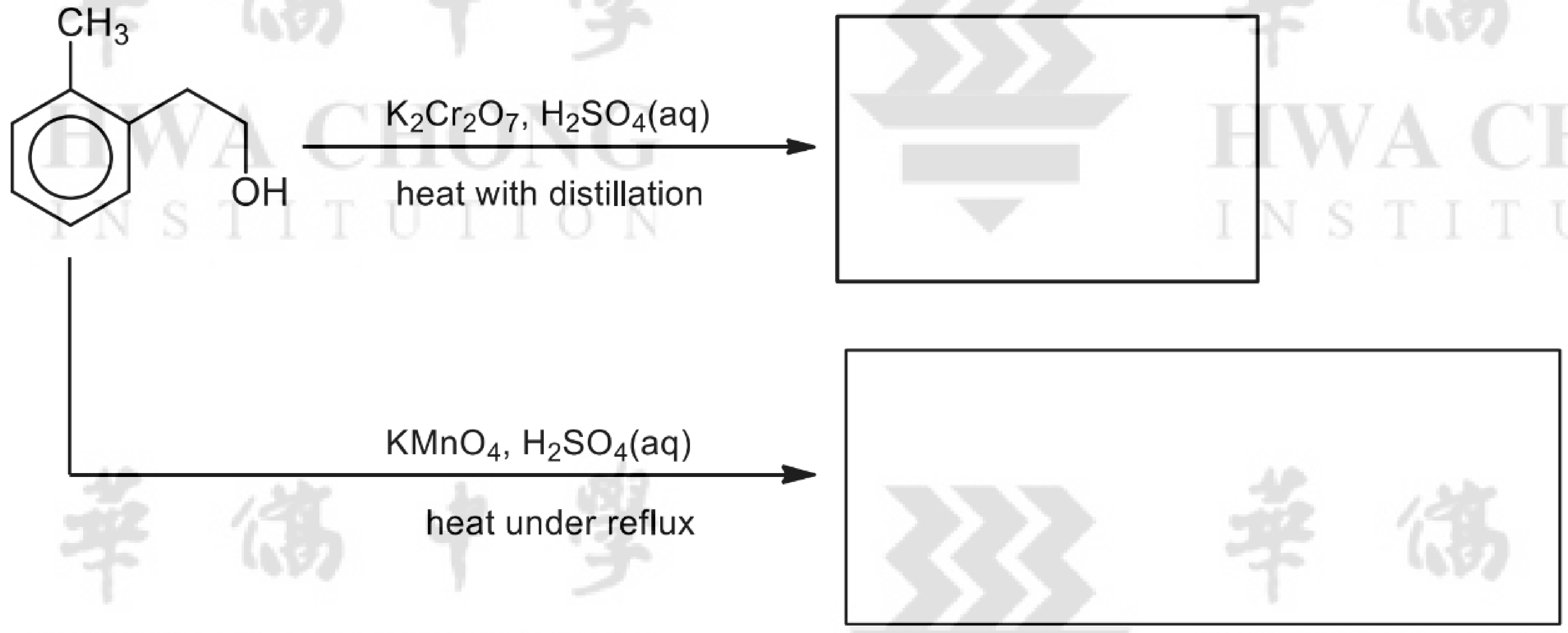
Lecture Exercise 4.3

Draw the structures of the compounds formed by oxidation of each of the following compounds.

(a)



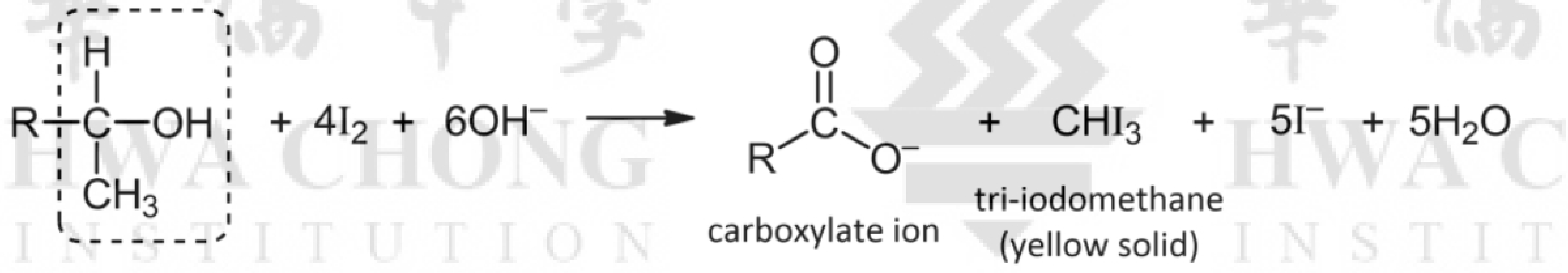
(b)



4.2 The Tri-iodomethane (iodoform) Test

LO 11.5(c): deduce the presence of a $CH_3CH(OH)$– group in an alcohol from its reaction with alkaline aqueous iodine to form tri-iodomethane

Alcohols with a $CH_3CH(OH)$– group will react with warm alkaline aqueous iodine. In this reaction, the carbon bearing the hydroxy group is oxidised to a carboxyl carbon.

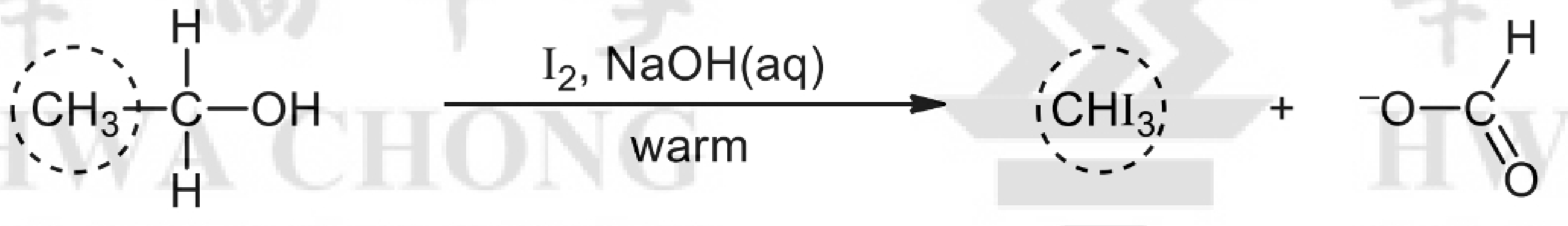


Reagents & Conditions:	I_2(aq), NaOH(aq), warm
Observations:	yellow ppt (CHI_3) formed (Note that CHI_3 is an organic compound.)
Comment:	Another name for tri-iodomethane is iodoform.

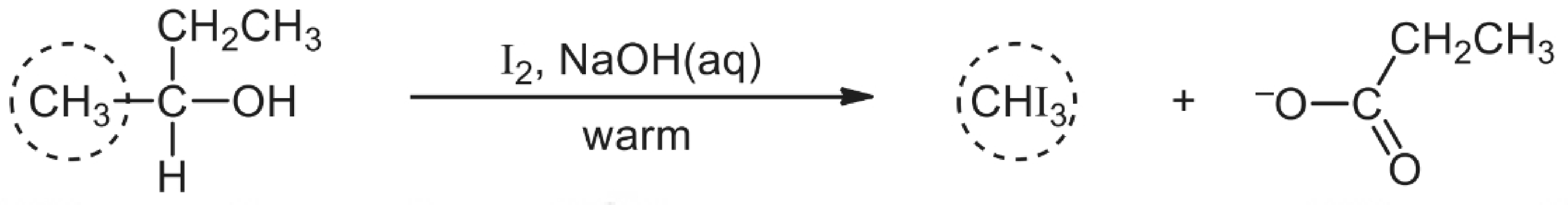
All of these alcohols are secondary alcohols, with the exception of ethanol (primary alcohol), where the R group is replaced by a hydrogen atom.

Note that this reaction involves the **breaking of a C–C bond** with the removal of the methyl ($-CH_3$) group. It is therefore a useful method to **shorten a carbon chain by a single carbon** (known as a **step-down reaction**).

Examples:



ethanol

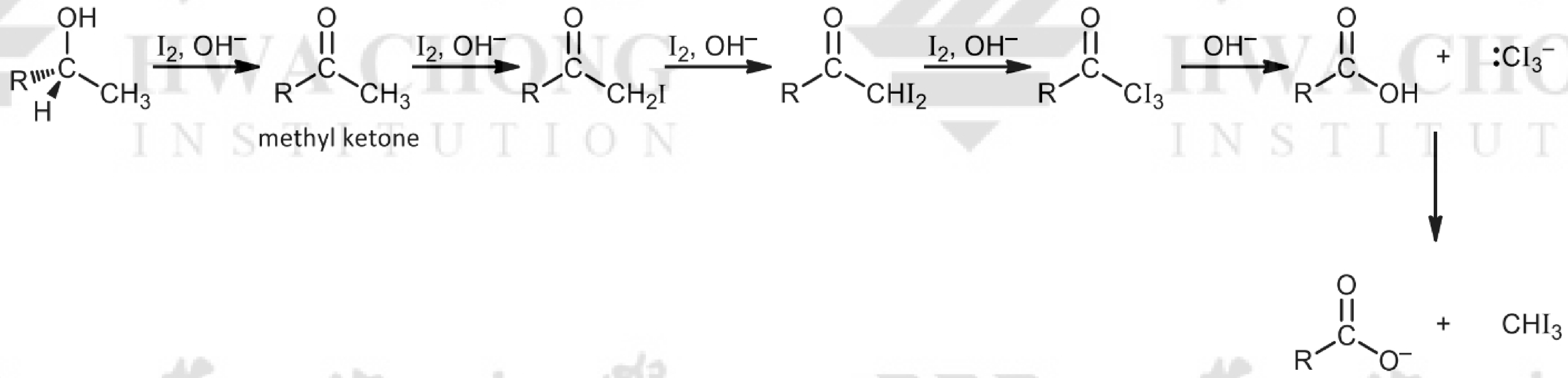


butan-2-ol

Background Information:

Why do both the $CH_3CH(OH)$– and the CH_3CO– groups give a positive iodoform test?
(Mechanism not required)

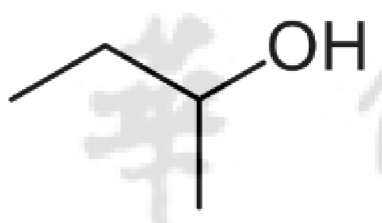
In this reaction, the $CH_3CH(OH)$– group is first oxidised *in-situ* to the corresponding CH_3CO– group (a methyl ketone) by the iodate(I) ion. This is then followed by a series of substitutions, leading to cleavage of the –CI_3 group to give CHI_3.



Hence, methyl ketones also give a positive iodoform test, forming CHI_3 (to be covered in Topic 17 Carbonyl Compounds).

Lecture Exercise 4.4

1 Which of the following alcohols would give a positive tri-iodomethane reaction?



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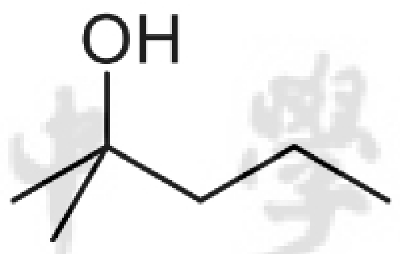

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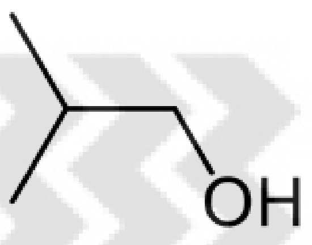

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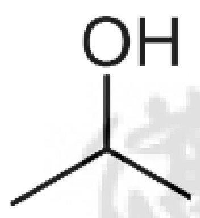


4

2 Chemical tests were carried out on four organic compounds are labelled **A**, **B**, **C** and **D**.

The compounds are ethanol, propan-1-ol, 2-methylpropan-2-ol and cyclohexene but not necessarily in that order.

The observations of each test are detailed in the table below.

chemical test	observations			
	A	**B**	**C**	**D**
add Na(s)	effervescence	no effervescence	effervescence	effervescence
add $K_2Cr_2O_7$ and dilute H_2SO_4, heat	orange solution remains orange	orange solution remains orange	orange solution turns green	orange solution turns green
add aqueous I_2, aqueous NaOH, heat	no yellow ppt formed	no yellow ppt formed	yellow ppt formed	no yellow ppt formed

Deduce the identity of the four compounds.

4.8 Other reactions of Phenols

In addition to the reactions discussed in earlier sections, phenol also undergoes some other reactions of interest.

4.8.1 Electrophilic substitution of the benzene ring

LO 11.5(d): recall the chemistry of phenol, as exemplified by the following reactions: (i) with bases, (ii) with sodium, (iii) nitration of, and bromination of, the aromatic ring

Due to the delocalisation of the lone pair of electrons of oxygen into the benzene ring, the electron density in the ring is greatly increased, making phenol much more susceptible to electrophilic attack than benzene (contrast this to the reagents and conditions required for electrophilic substitution of benzene in Topic 12 Arenes). Hence, the presence of the –OH group highly activates the benzene ring towards electrophilic substitution. Two general observations are noted:

1. Electrophilic substitution of the benzene ring in phenols takes place under milder conditions compared to benzene: **no catalyst** and **no heating** required.

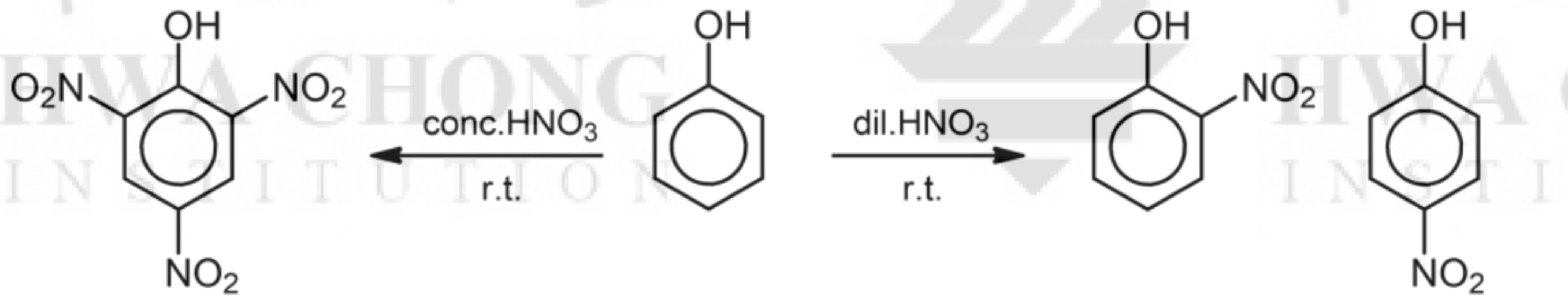
2. The –OH group is strongly activating and 2,4- directing, which may result in **multi-substituted products** at the 2-, 4-, and 6- positions easily.

Note: as the $-NH_2$ group in phenylamine is even more strongly activating than the –OH group in phenol, similar observations will be made regarding electrophilic substitution of the benzene ring in phenylamine (to be covered in Topic 19 Nitrogen Compounds).

Electrophilic substitution with nitric acid (nitration)

When phenol is treated with dilute aqueous nitric acid at room temperature, mono-substitution occurs to form a mixture of 2- and 4- nitrophenol.

If concentrated nitric acid at room temperature is used, 2,4,6-trinitrophenol is produced.

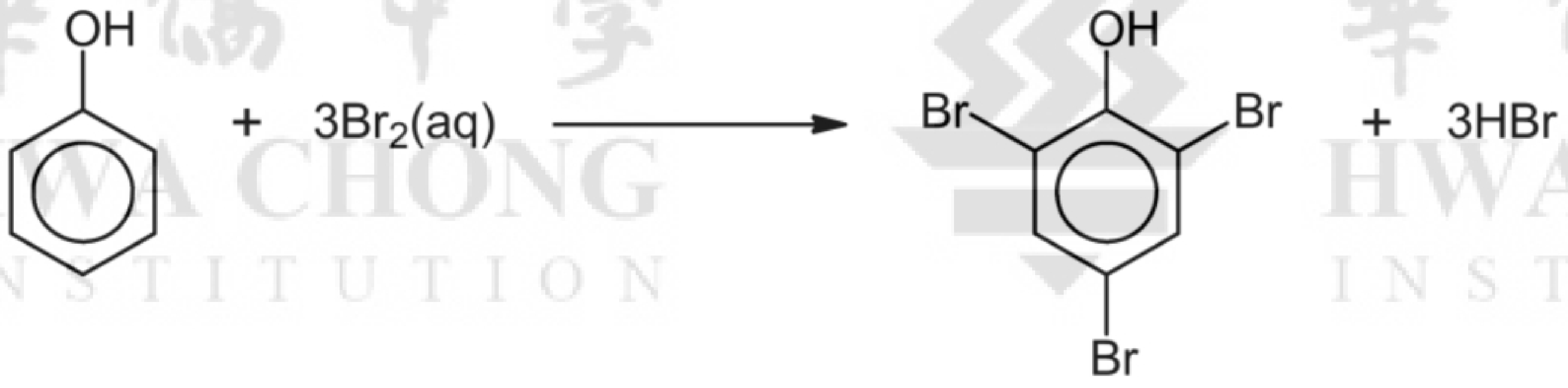


2,4,6-trinitrophenol 2-nitrophenol 4-nitrophenol

Reagents & Conditions: dilute HNO_3, room temperature
-or- concentrated HNO_3, room temperature
Observation: pale yellow liquid formed

Electrophilic substitution with bromine (bromination)

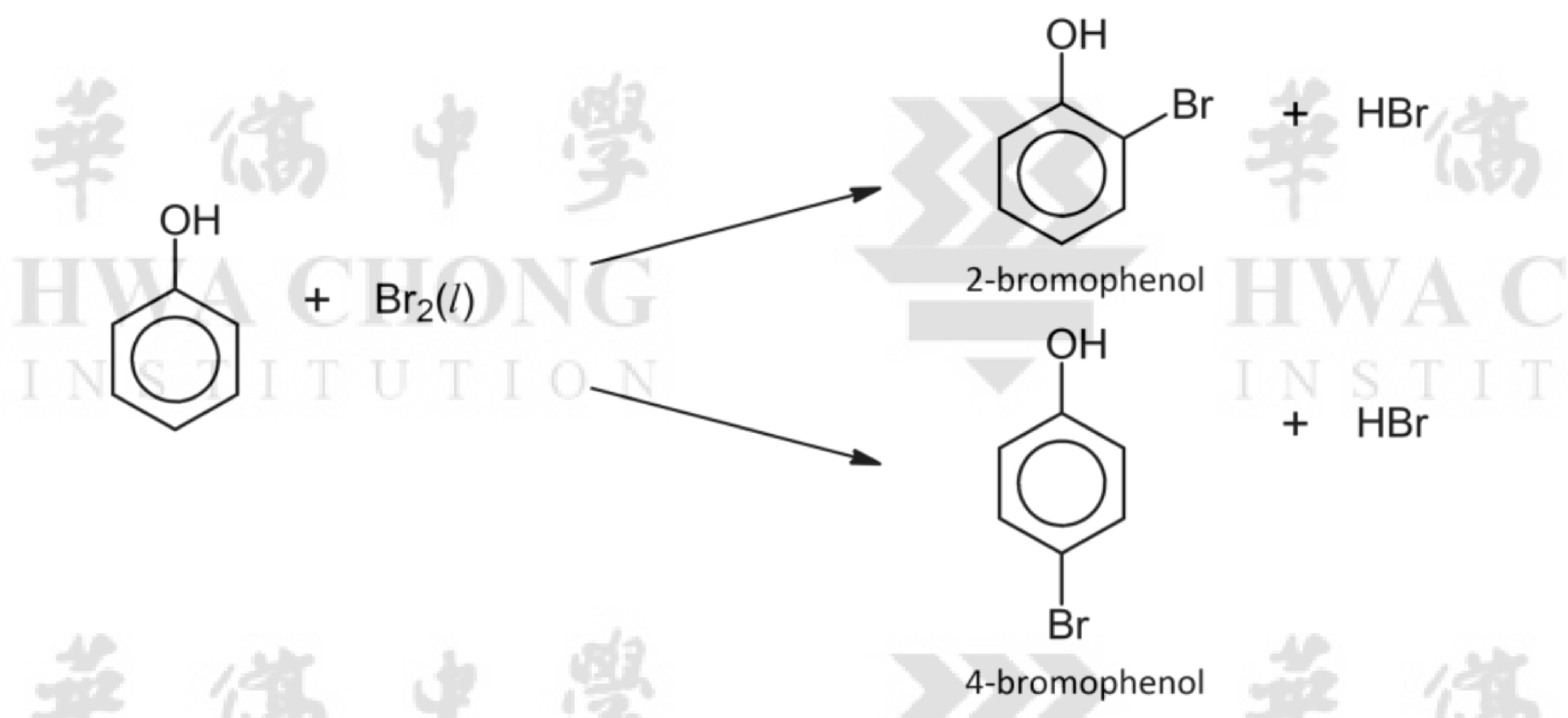
Phenol will react with **aqueous bromine** at room temperature to form a white precipitate of 2,4,6-tribromophenol. No Lewis acid catalyst is required.



2,4,6-tribromophenol
(white ppt)

Reagents & Conditions: aqueous bromine (bromine water), room temperature
Observation: yellow-orange solution decolourised, white ppt formed

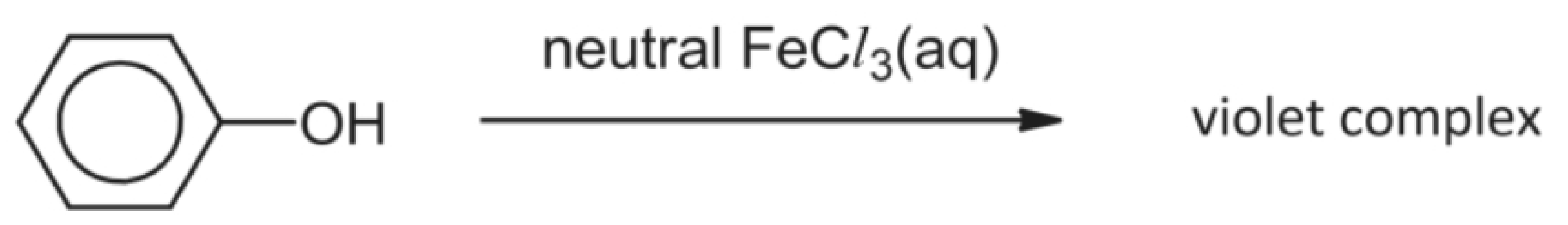
In order to achieve mono-bromination of phenol, **low** temperatures must be used as the –OH group is strongly activating. Also, the reaction must be carried out using either liquid bromine or bromine dissolved in a non-polar organic solvent (such as CCl_4) with a 1:1 ratio of phenol to bromine.



Reagents & Conditions: $Br_2(l)$ –or- Br_2 dissolved in CCl_4
Observation: reddish-brown liquid decolourised, white fumes of HBr evolved

4.8.2 Complex formation with iron(III) chloride

When a neutral solution of iron(III) chloride is added to a dilute solution of a phenol, a coloured complex is formed. (The reason for the complex having colour will be discussed in Topic 22 Chemistry of the Transition Elements.) The colour of the complex depends on the other substituents (if any) on the benzene ring. With phenol, a violet colour is observed.

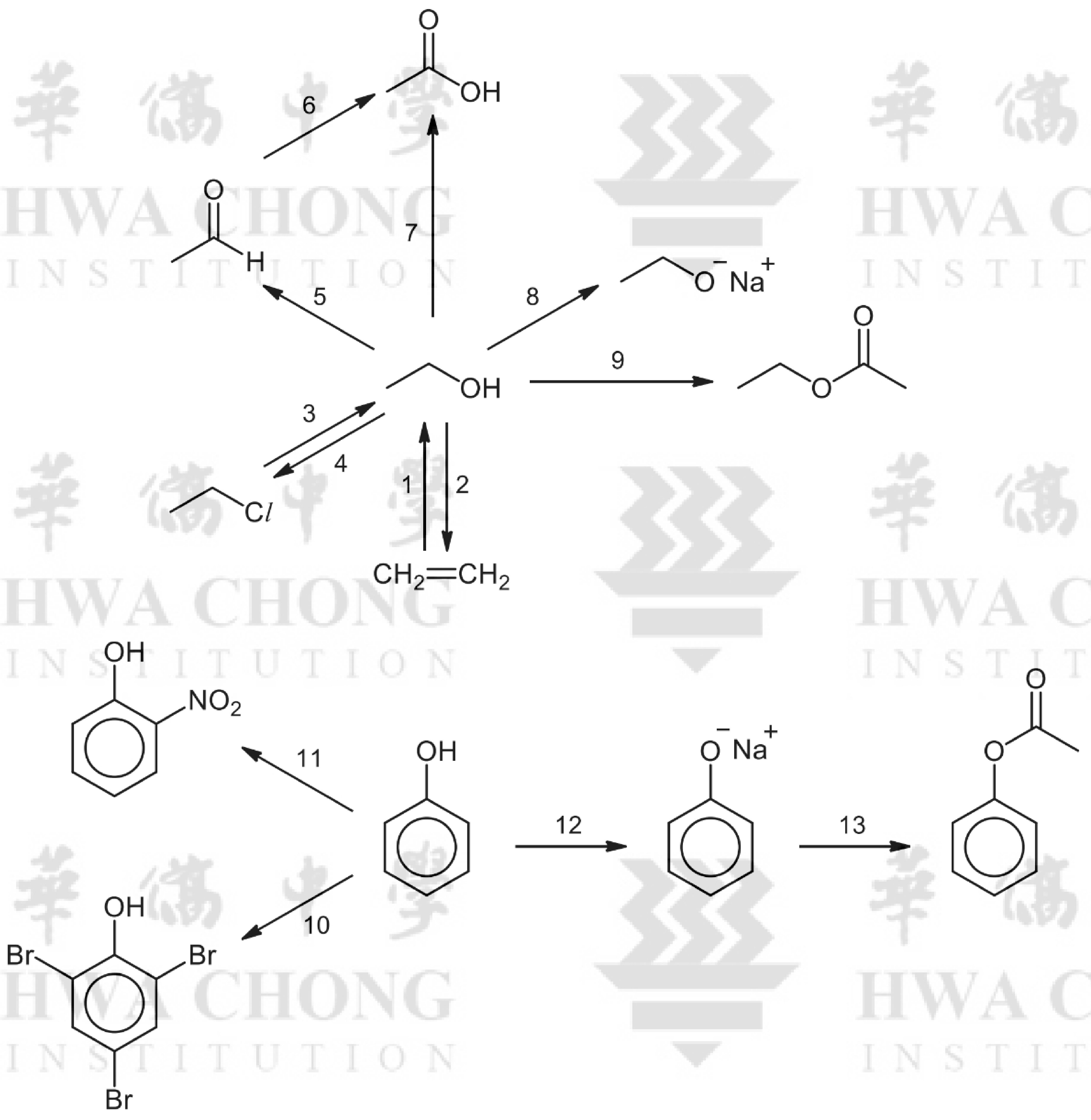


Reagents & Conditions: neutral $FeCl_3(aq)$, room temperature
Observation: violet colouration

This reaction is used as a **distinguishing test** for the presence of a phenolic group in an organic compound.

Summary of Reactions of alcohols and phenols

State the reagents and conditions needed for the conversions on the arrows below.



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