2023 JC2 H2 CHEMISTRY (9729)
EXTENSION TOPIC – ORGANIC CHEMISTRY Topic 5: HYDROXY COMPOUNDS

Name: ____ Civics Group: _________

(a) recall the chemistry of alcohols, exemplified by ethanol:
  - (i) combustion
  - (ii) nucleophilic substitution to give halogenoalkanes
  - (iii) reaction with sodium
  - (iv) oxidation to carbonyl compounds and carboxylic acids
  - (v) dehydration to alkenes

(b) suggest characteristics distinguishing reactions for the different classes of alcohols (primary, secondary and tertiary alcohols), e.g. mild oxidation

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

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

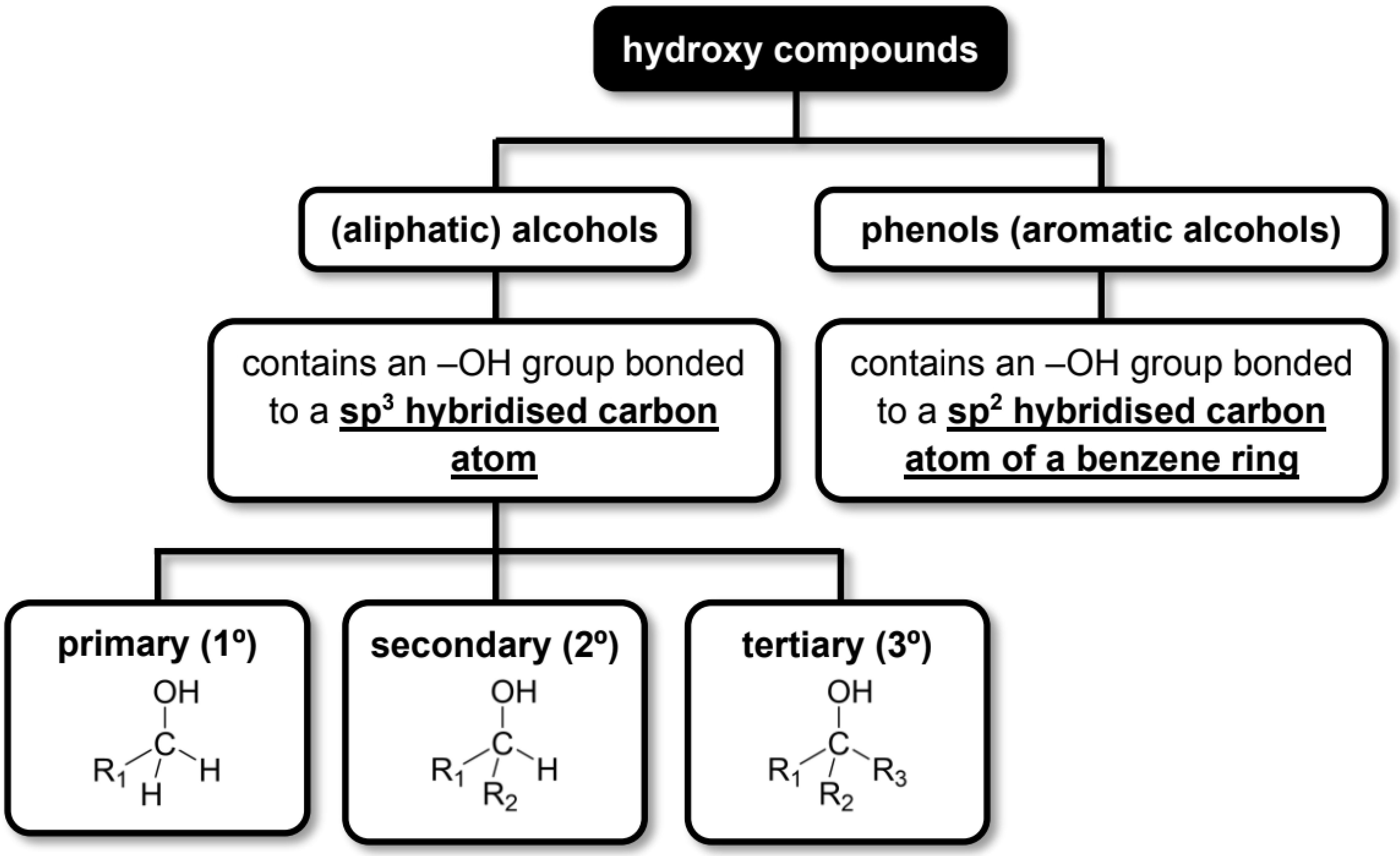
(e) explain the relative acidities of water, phenol and ethanol in aqueous medium (interpret as Brønsted-Lowry acids)

References

1 **Chemistry (for CIE AS & A Level)** by Peter Cann & Peter Hughes

2 **Cambridge International AS and A Level Chemistry Revision Guide** by Judith Potter and Peter Cann

LECTURE CONTENT



1 Introduction to Aliphatic Alcohols

- Aliphatic alcohols are classified as *primary*, *secondary* or *tertiary* depending on the number of alkyl (or aryl) groups attached to the α-carbon, *i.e.* the carbon linked to the –OH group.

1.1 Nomenclature

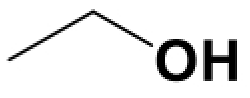
- The hydroxyl group is treated as a *principal functional group* of the hydrocarbon and named in the *suffix*.

- The *position* of the –OH groups are indicated (if necessary) by *numbering* the carbon atoms of the hydrocarbon.

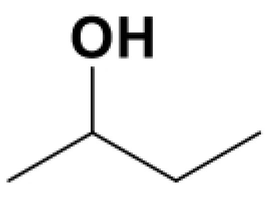
- *Multipliers* such as di-, tri-, tetra-, *etc.* are used to indicate the *number of* –OH groups present.

- *E.g.*

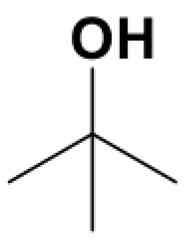
methanol



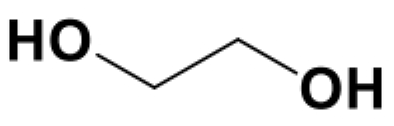
ethanol
(primary alcohol)



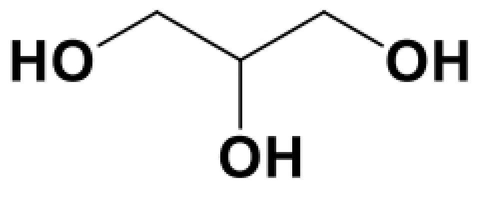
butan-2-ol
(secondary alcohol)



2-methylpropan-2-ol
(tertiary alcohol)



ethane-1,2-diol
(ethylene glycol)



propane-1,2,3-triol
(glycerol)

Self-Check 1A

1 Write the structural formulae and the names of all the isomers of **butanol**.
Classify them into primary, secondary and tertiary alcohols.

1.2 Physical Properties of Aliphatic Alcohols

1.2.1 Boiling Points of Alcohols

compound	**M_r**	**no. of electrons**	**boiling point / °C**	**intermolecular forces of attraction**
C_2H_5OH	46.0	26	78.4	**hydrogen bonding** permanent dipole-permanent dipole instantaneous dipole-induced dipole
CH_3Cl	50.5	26	–24.2	permanent dipole-permanent dipole instantaneous dipole-induced dipole
C_3H_8	44.0	26	–42.0	instantaneous dipole-induced dipole

- Boiling points of alcohols are **higher** than boiling points of alkanes of comparable M_r.

  Reason: Larger amount of energy is needed to overcome the **stronger hydrogen bonds** between the alcohol molecules than the weaker instantaneous dipole-induced dipole interactions between the alkane molecules.

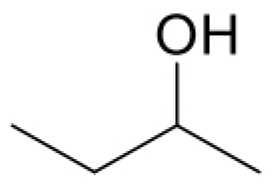
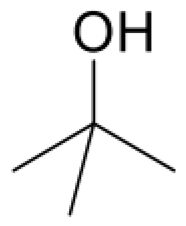
- Factors Affecting Boiling Points

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

alcohol	methanol	ethanol	propan-1-ol
structural formula	CH_3OH	CH_3CH_2OH	$CH_3(CH_2)_2OH$
boiling point / °C	64.7	78.4	97.0

Reason: Instantaneous dipole-induced dipole interactions **strengthen** with **increase in size (*i.e.* number of electrons)** and hence **polarisability of electron cloud**.

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

alcohol	butan-1-ol	butan-2-ol	2-methylpropan-2-ol
structural formula			
boiling point / ºC	118	108	82

Reason: With branching, molecules become more **<u>spherical</u>**. Compared with straight chain isomers, there is **<u>less</u> surface area of contact** and hence **<u>less</u> <u>extensive</u> instantaneous dipole-induced dipole interactions** between molecules.

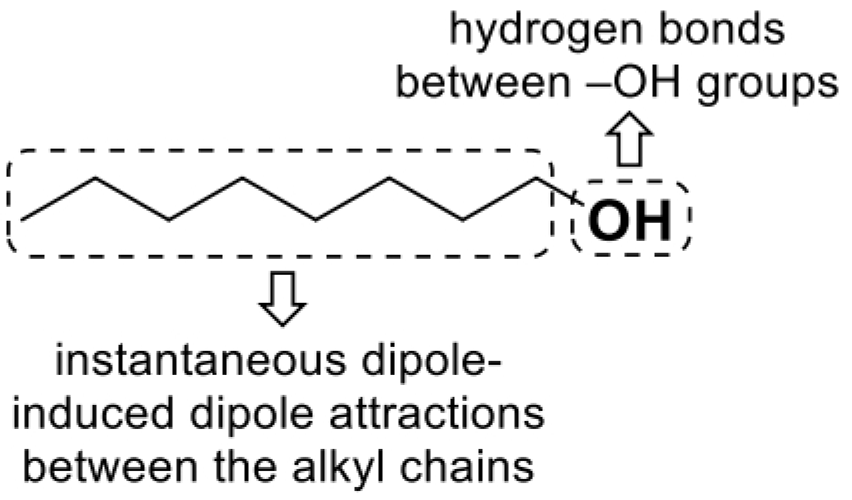
1.2.2 Solubility

- Alcohols are relatively more soluble in water than alkanes due to the **presence of the –OH group** which enables them to form **hydrogen bonds** with water molecules.

- Solubility decreases as the number of carbon atoms increases.

  Reason: The bulky non-polar alkyl/aryl groups in the higher alcohols **hinder** the formation of effective hydrogen bonds between alcohol and water molecules.

name	**structural formula**	**solubility ($g/100\ g\ H_2O$)**
methanol	CH_3OH	miscible
ethanol	CH_3CH_2OH	miscible
propan-1-ol	$CH_3CH_2CH_2OH$	miscible
butan-1-ol	$CH_3(CH_2)_2CH_2OH$	7.9
penta-1-ol	$CH_3(CH_2)_3CH_2OH$	2.3
hexan-1-ol	$CH_3(CH_2)_4CH_2OH$	0.6



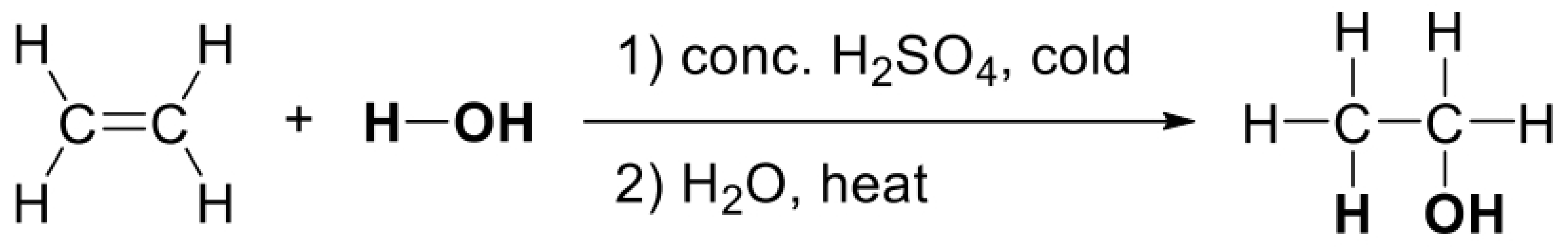
- All alcohols are miscible with most organic solvents. Some are useful organic solvents themselves.

- As a result of having a polar –OH group and a non-polar hydrocarbon chain, alcohols can act as **good solvents** to dissolve **both** water-soluble species (*e.g.* KOH, NaOH) and organic ones (*e.g.* alkyl halides).

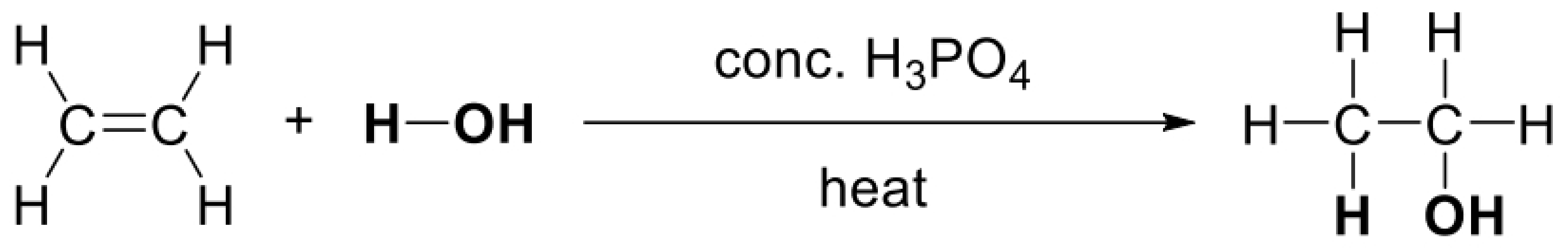
1.3 Preparation of Alcohols

1.3.1 From Alkenes

Type of reaction: Electrophilic Addition



Reagents and conditions: 1) concentrated H_2SO_4, cold
(laboratory method) 2) H_2O, heat

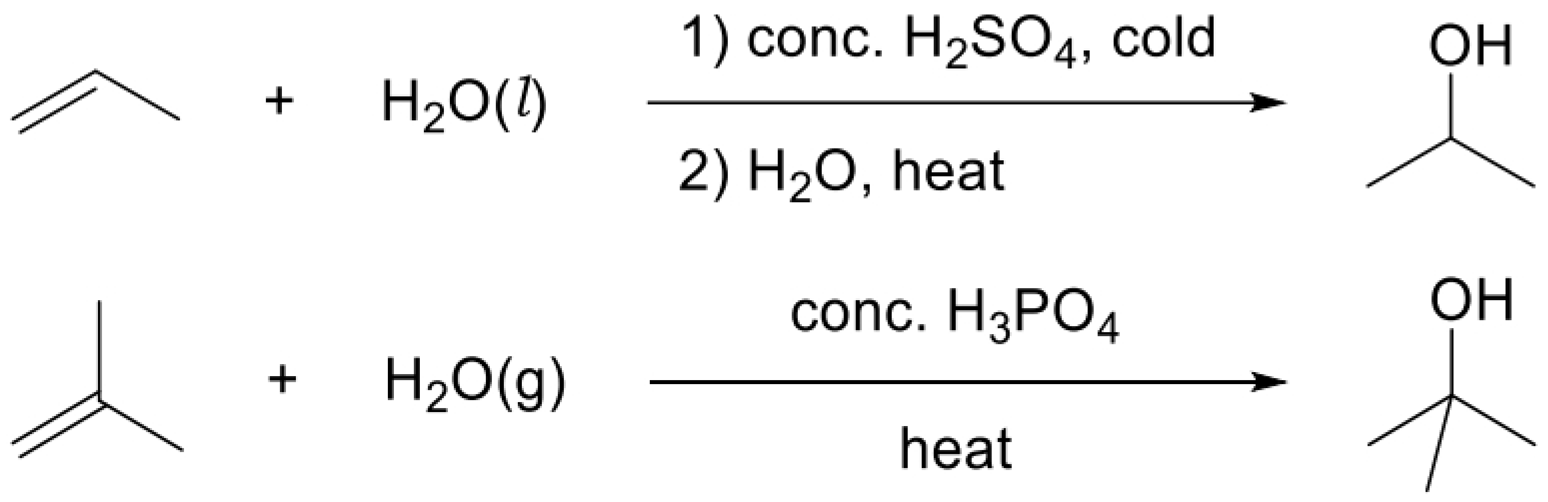


Reagents and conditions: steam, conc. H_3PO_4 catalyst,
(industrial method) heat

Note:

Markovnikov's rule applies for asymmetrical alkenes.

E.g.



1.3.2 From Halogenoalkanes / Alkyl Halides

Type of reaction: Nucleophilic Substitution

$$R{-}X + OH^- \xrightarrow{\text{heat}} R{-}OH + X^-$$

(X = C*l*, Br, I)

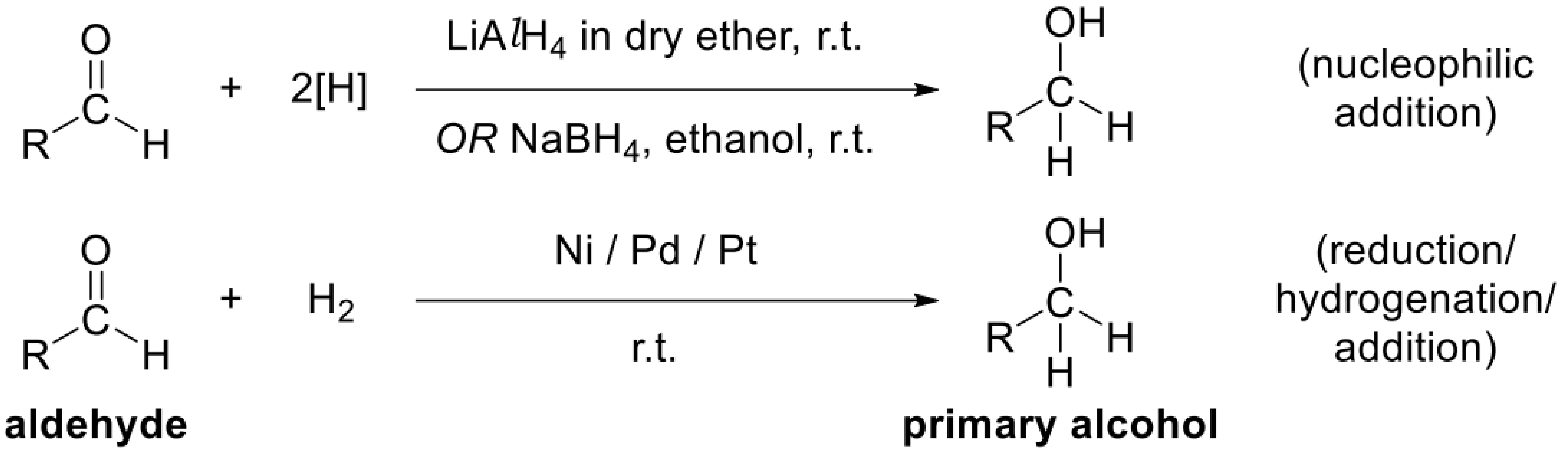
Reagents and conditions: aqueous NaOH or KOH, heat

E.g.

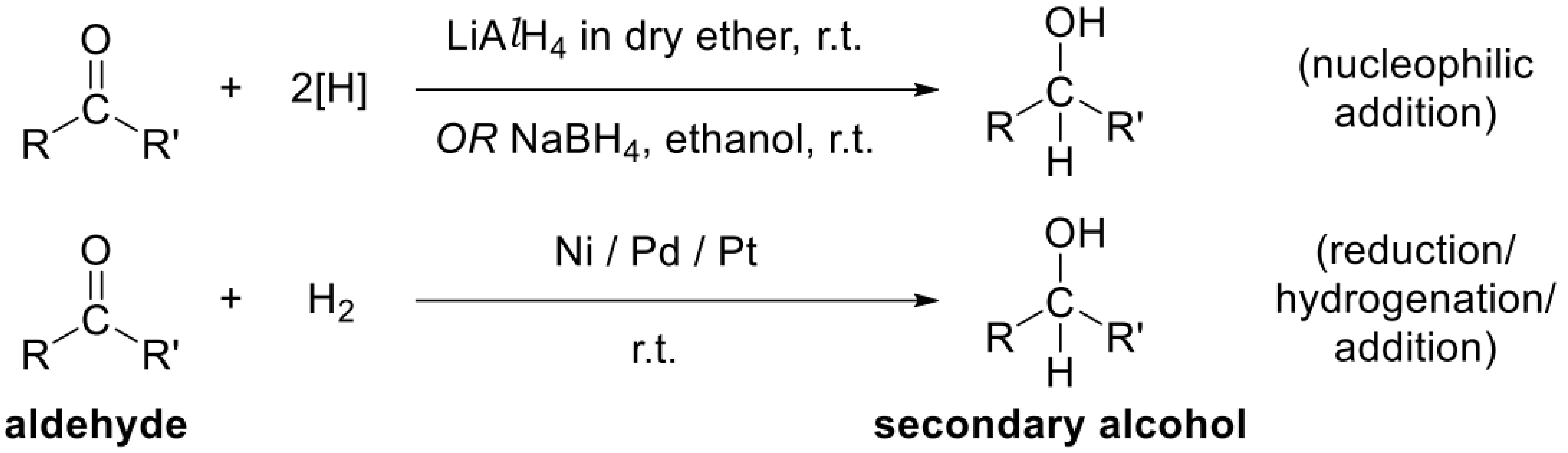
1.3.3 From Aldehydes and Ketones

Type of reaction: Reduction

Aldehydes (reduced to primary alcohols)



Ketones (reduced to secondary alcohols)



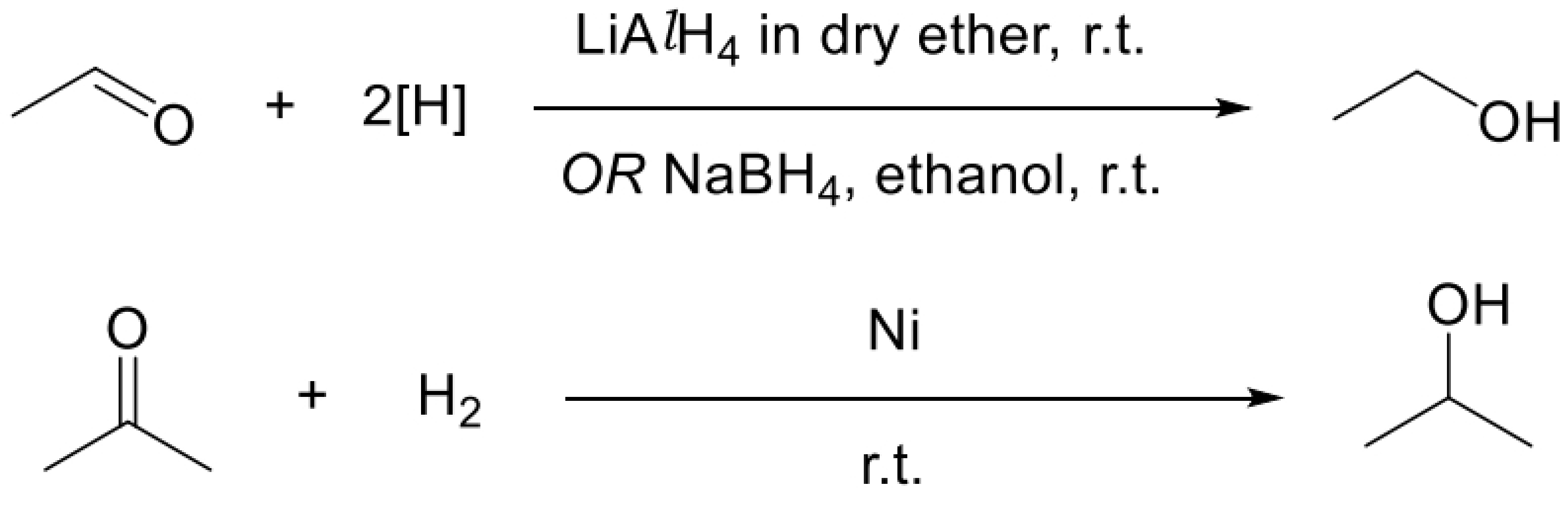
Reagents and conditions: $LiAlH_4$ in dry ether, r.t.
OR $NaBH_4$ in ethanol, r.t.
OR H_2, Ni / Pd / Pt catalyst, r.t.

Note:

$LiAlH_4$ and $NaBH_4$ are metal **hydride** reducing agents. The active reducing species can be viewed as the nucleophilic hydride anion, **$H:^-$**.

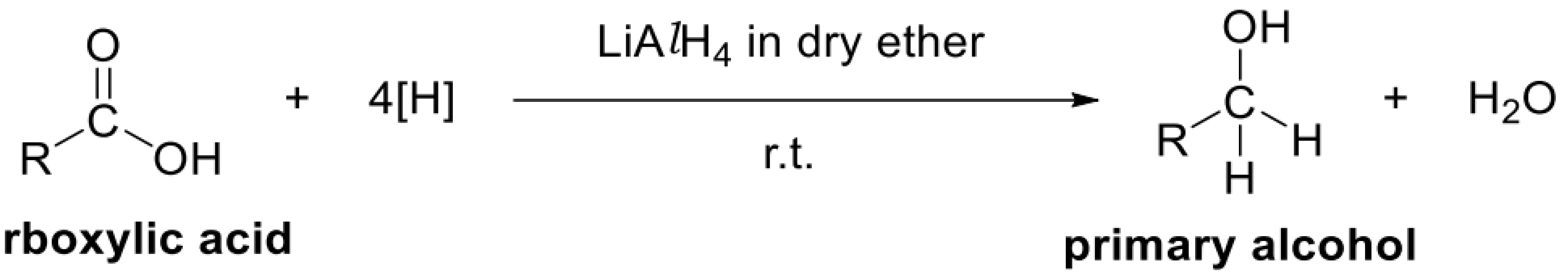
- **$NaBH_4$ can only** reduce aldehydes and ketones. It **cannot** reduce alkenes, nitriles and carboxylic acids.
- **$LiAlH_4$ can** reduce aldehydes, ketones, nitriles and carboxylic acids. It **cannot** reduce alkenes (*why?*)

E.g.



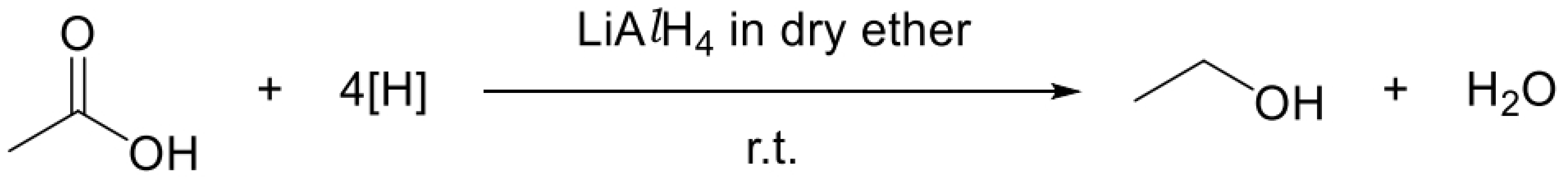
1.3.4 From Carboxylic Acids

Type of reaction: Reduction



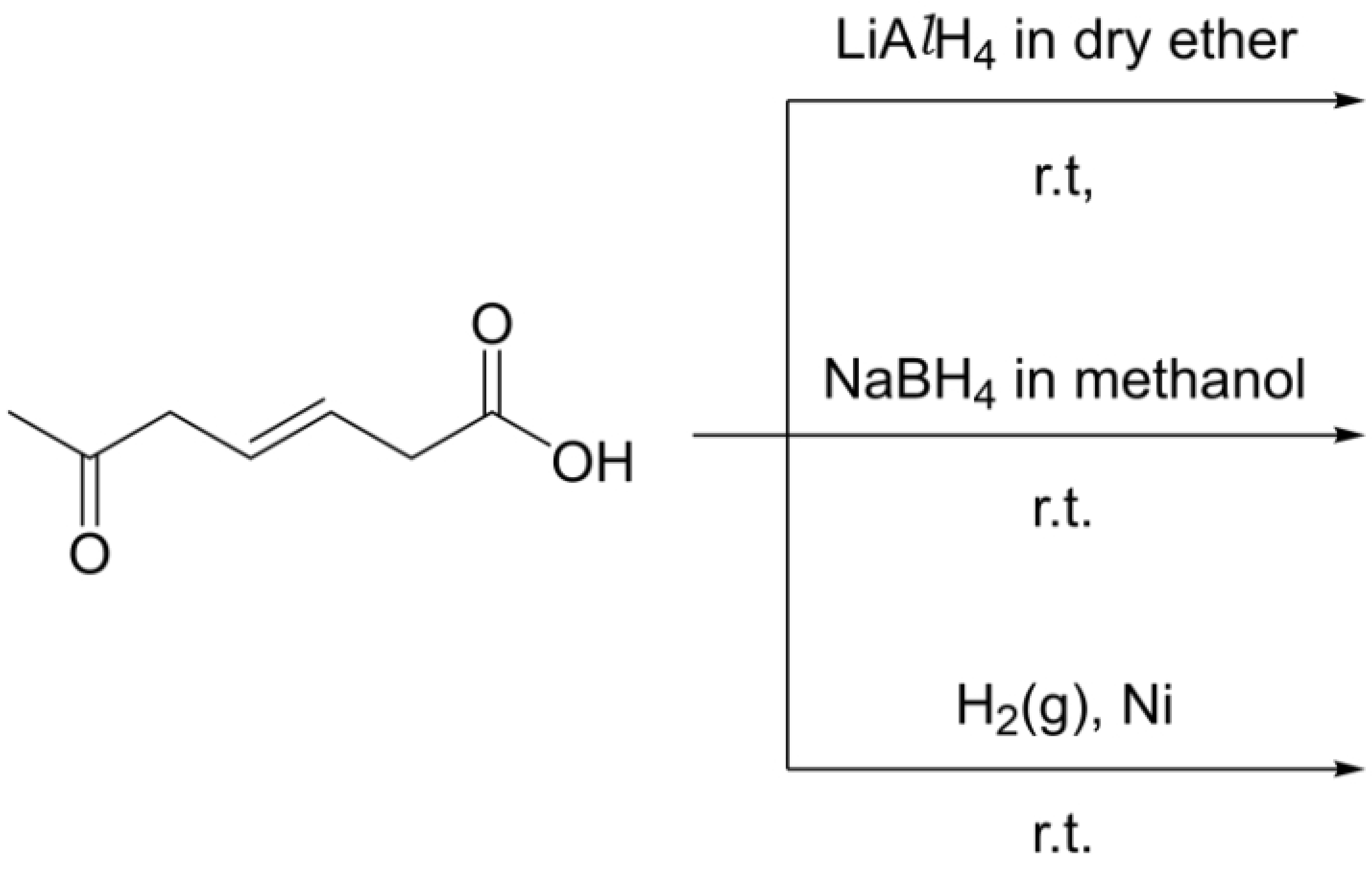
Reagents and conditions: LiA*l*H_4 in dry ether, r.t.

E.g.



Example 1A

1 Draw the products of the following reactions:



Checkpoint for §1

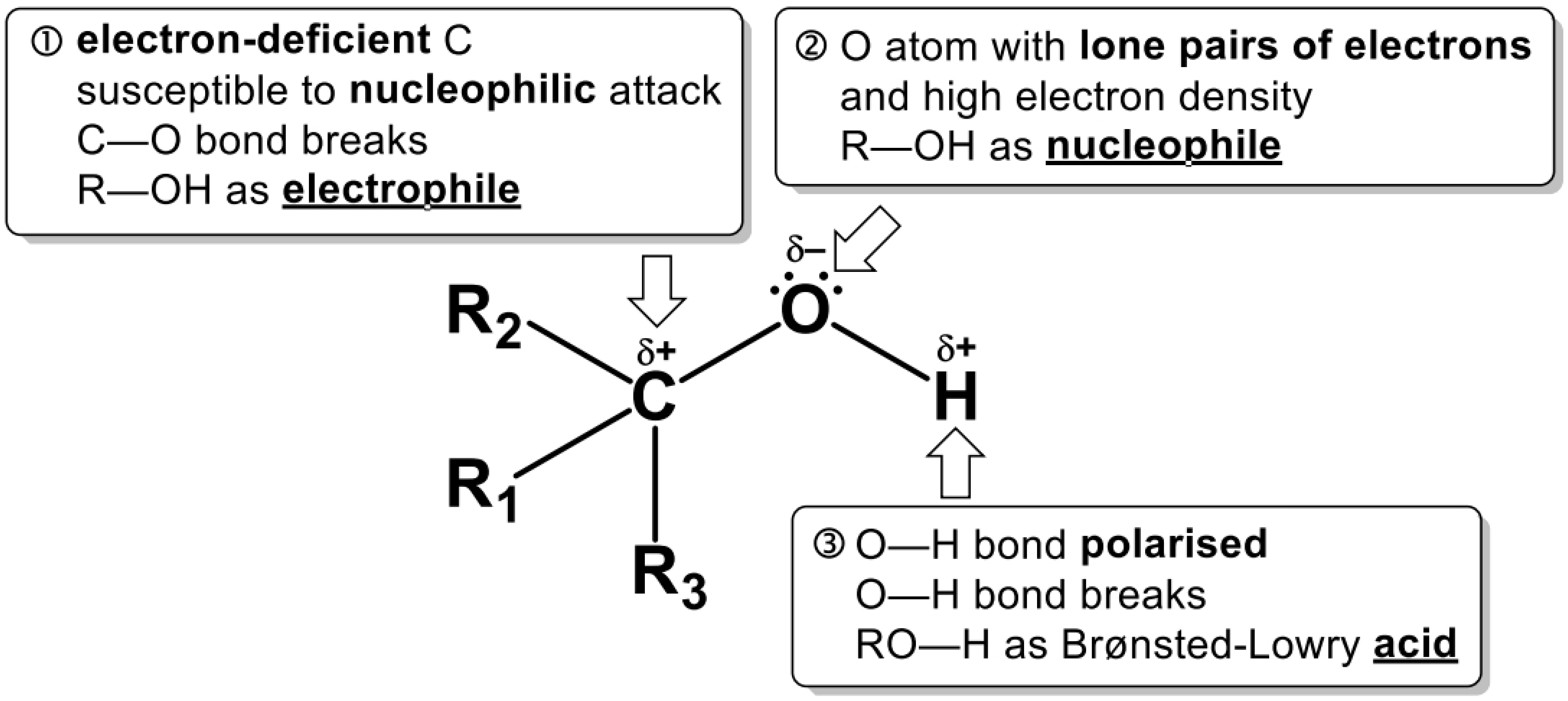
At the end of this section, you must be able to:

- write IUPAC names of simple alcohols given the structural formula and *vice versa*.
- relate the physical properties (boiling point and solubility) of alcohols to their structure and bonding.
- describe the reagents and conditions for the preparation of alcohols from:
  - Alkenes
  - Halogenoalkanes / Alky halides
  - Aldehydes and Ketones
  - Carboxylic acids

2 Chemical Reactions of Aliphatic Alcohols

LO **(a)** recall the chemistry of alcohols, exemplified by ethanol: (i) combustion, (ii) nucleophilic substitution to give halogenoalkanes, (iv) oxidation to carbonyl compounds and carboxylic acids, (v) dehydration to alkenes
(b) suggest characteristic distinguishing reactions for the different classes of alcohols (primary, secondary and tertiary alcohols), e.g. mild oxidation

- There are three sites of reactivity in aliphatic alcohols:



① **electron-deficient** C
susceptible to **nucleophilic** attack
C—O bond breaks
R—OH as **electrophile**

② O atom with **lone pairs of electrons** and high electron density
R—OH as **nucleophile**

③ O—H bond **polarised**
O—H bond breaks
RO—H as Brønsted-Lowry **acid**

① Due to the electronegative O atom attached to the C atom, the C atom becomes **electron-deficient** and is susceptible to nucleophilic attack, resulting in a heterolytic fission of the C–O bond. ROH **acts as an electrophile**. (**§2.3**)

② The O atom of the –OH group has lone pairs of electrons and a high electron density. This makes it electron-rich and therefore **acts as a nucleophile**. Upon nucleophilic attack, the O–H bond will break, forming a new bond with the electrophile. **(§2.5**)

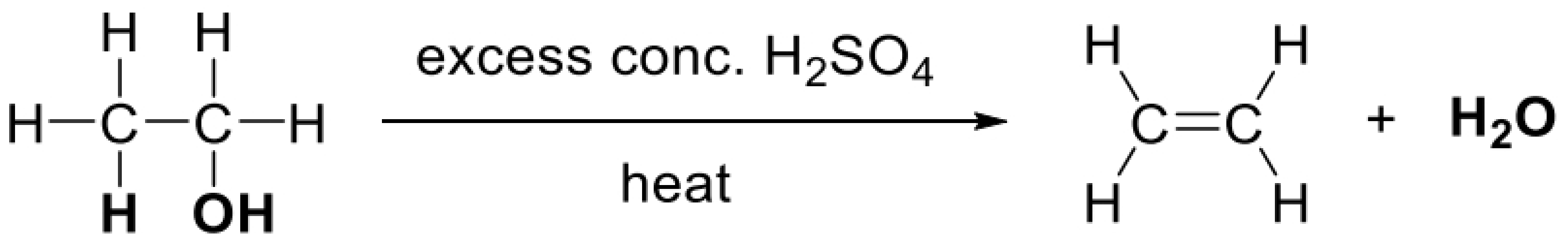
③ The O–H bond is polarised such that **deprotonation may occur** and therefore **acts as a Brønsted-Lowry acid**. (**§0**)

2.1 Combustion

- Alcohols burn in air (or excess oxygen) with a clear, hot flame to produce CO_2 and H_2O. With a good supply of air, the flame is pale blue. They are called 'clean' fuels.

E.g. $CH_3CH_2OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

2.2 Dehydration of Alcohol (Elimination Reaction)

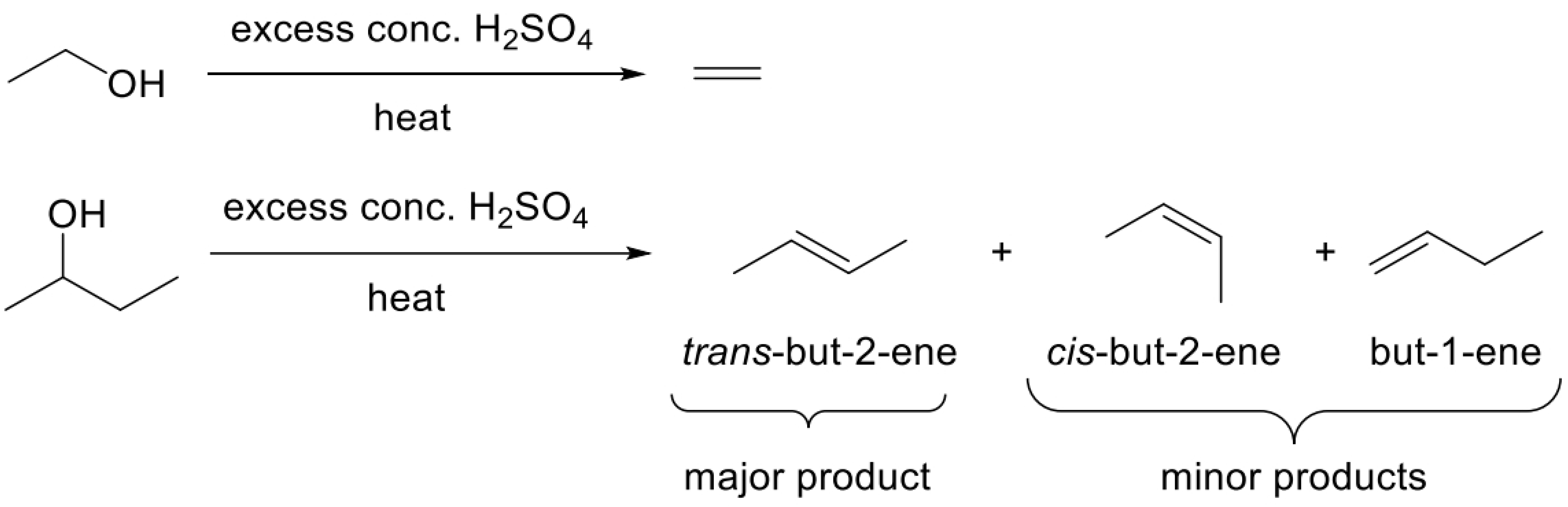


Reagents and conditions: excess conc. H_2SO_4, heat
OR Al_2O_3 catalyst, heat
OR conc. H_3PO_4 catalyst, heat

Note:

Dehydration of secondary and tertiary alcohols that contain more than three C atoms will give **a mixture of alkenes**. The major product can be determined using **Saytzeff's Rule**.

E.g.



Think:

Why is *trans*-but-2-ene the major product instead of the minor products?

2.3 Nucleophilic Substitution

Reagents and conditions:

$$R\text{—}\mathbf{OH} \xrightarrow[\text{}]{\text{conc. HC}l\text{, ZnC}l_2\text{ catalyst, heat } \textit{OR} \text{ HBr(g), r.t. } \textit{OR} \text{ HI(g), r.t.}} R\text{—}\mathbf{X} + H_2O(l)$$
$(\mathbf{X} = Cl, Br, I)$

$$R\text{—}\mathbf{OH} \xrightarrow{\text{anhydrous PC}l_3\text{, heat } \textit{OR} \text{ anhydrous PBr}_3\text{, heat } \textit{OR} \text{ anhydrous PI}_3\text{, heat}} R\text{—}\mathbf{X} + H_3PO_3(l)$$
$(\mathbf{X} = Cl, Br, I)$

$$R\text{—}\mathbf{OH} \xrightarrow{\text{anhydrous PC}l_5\text{, r.t.}} R\text{—}\mathbf{C}\boldsymbol{l} + POCl_3(l) + HCl(g)$$

$$R\text{—}\mathbf{OH} \xrightarrow{\text{anhydrous SOC}l_2\text{, heat}} R\text{—}\mathbf{C}\boldsymbol{l} + SO_2(g) + HCl(g)$$

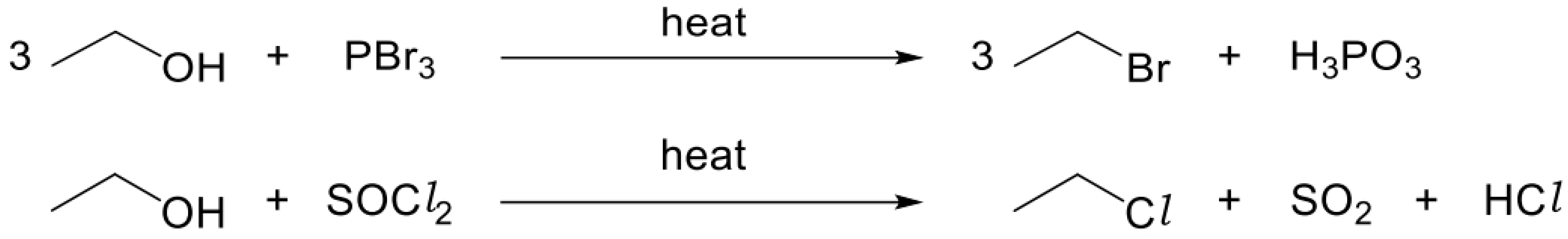
Observations: For reaction with PCl_5 and $SOCl_2$, white fumes of HCl are produced, which turn damp blue litmus paper red.

Note:

Unlike halogenoalkanes, aliphatic alcohols are generally poor electrophiles, despite the α-carbon being more electron-deficient.

- Bond strength: C–O (360 kJ mol^{-1}) comparable to C–Cl (340 kJ mol^{-1})
- OH^- is a very poor *leaving group* compared to the halides, X^-, since it is a much stronger base (*why?*).
- To make the O a better leaving group,
  - *Protonation* (with a strong Brønsted-Lowry acid) converts –OH into $-OH_2^+$, where neutral H_2O is a much better leaving group.
  - *Appending* to sulfur (*e.g.* $SOCl_2$) or phosphorus (*e.g.* PBr_3, PCl_5).

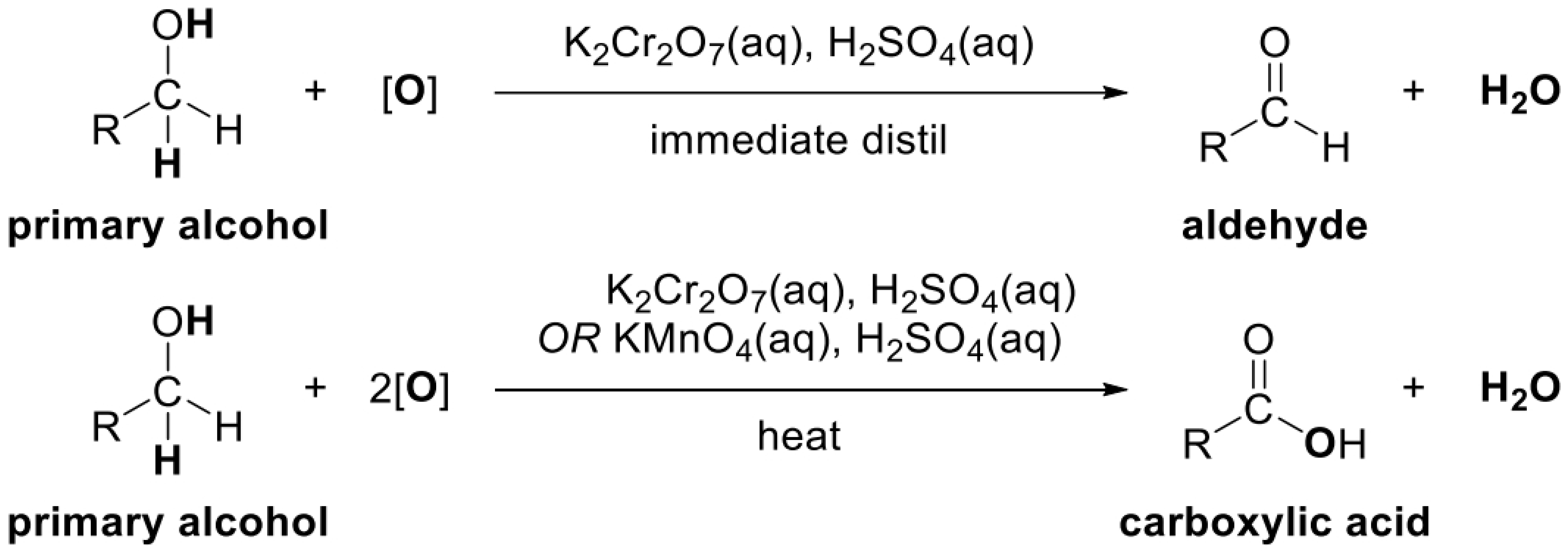
E.g.



2.4 Oxidation of Aliphatic Alcohols

2.4.1 Oxidation of Primary Alcohols

For the oxidation of **primary alcohols**, the identity of the final products (**aldehyde** or **carboxylic acid**) depends on the choice of oxidising agent and the mode of heating.



For Formation of Aldehydes

Reagents and conditions: $K_2Cr_2O_7(aq)$, $H_2SO_4(aq)$, immediate distil

Observations: Orange $K_2Cr_2O_7$ turns green.

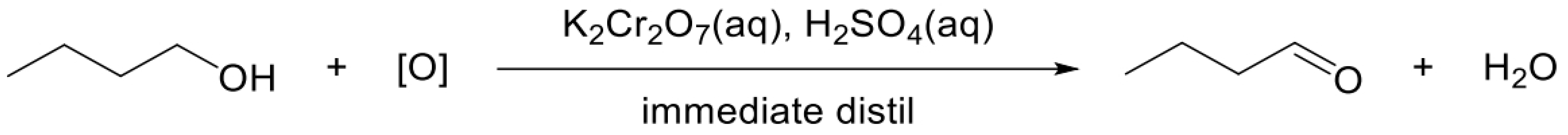
For Formation of Carboxylic Acids

Reagents and conditions: $K_2Cr_2O_7(aq)$, $H_2SO_4(aq)$, heat

OR $KMnO_4(aq)$, $H_2SO_4(aq)$, heat

Observations: Orange $K_2Cr_2O_7$ turns green *OR* Purple $KMnO_4$ turns colourless.

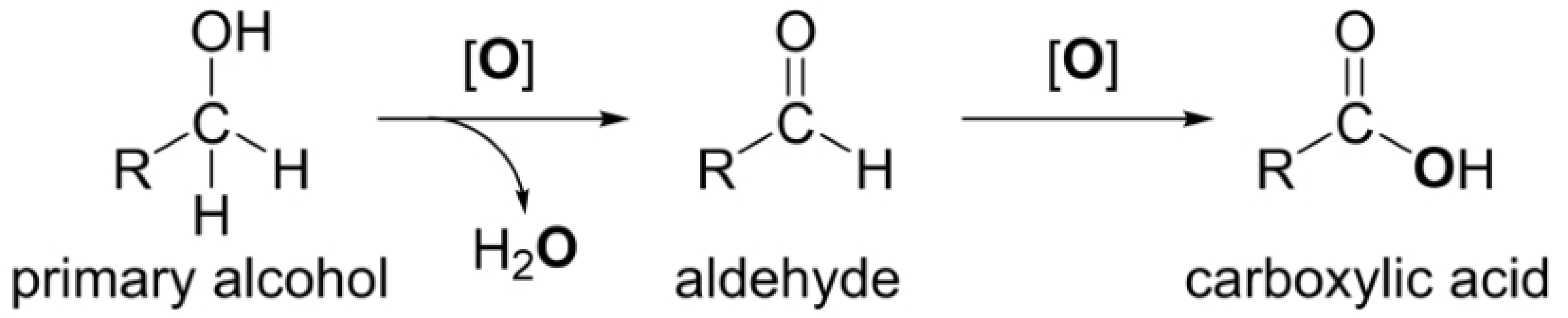
E.g.



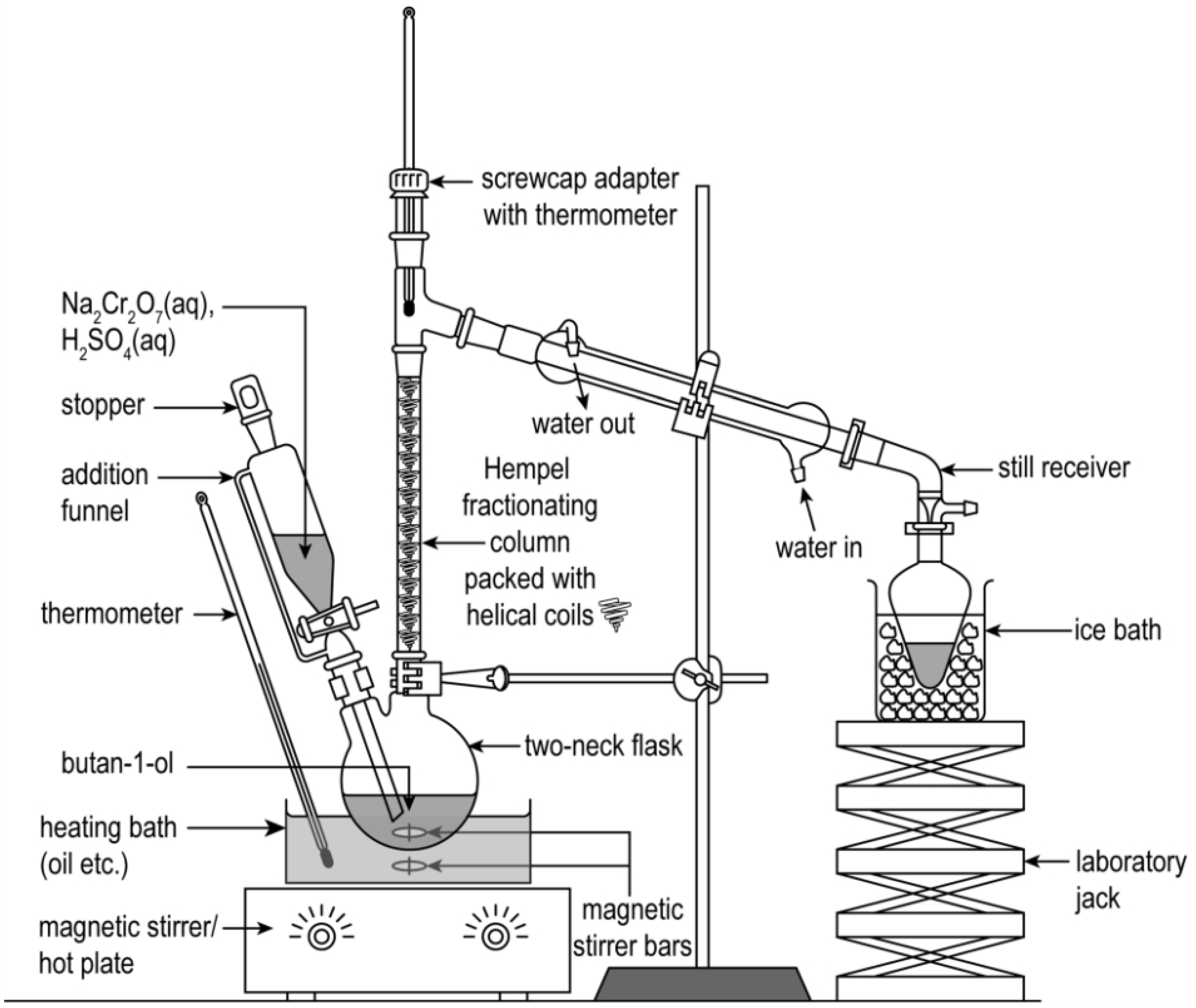
Note:

To isolate the aldehyde formed by the oxidation of a primary alcohol, we must use acidified $K_2Cr_2O_7$ as the oxidising agent and perform **<u>immediate distillation</u>**.

This is to prevent further oxidation of the aldehyde to form the corresponding carboxylic acid:

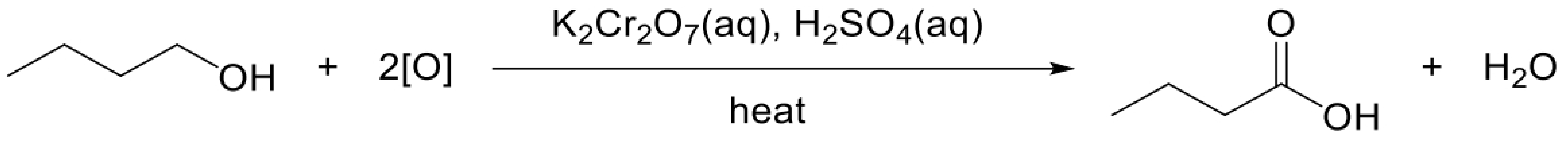


Experimental setup:



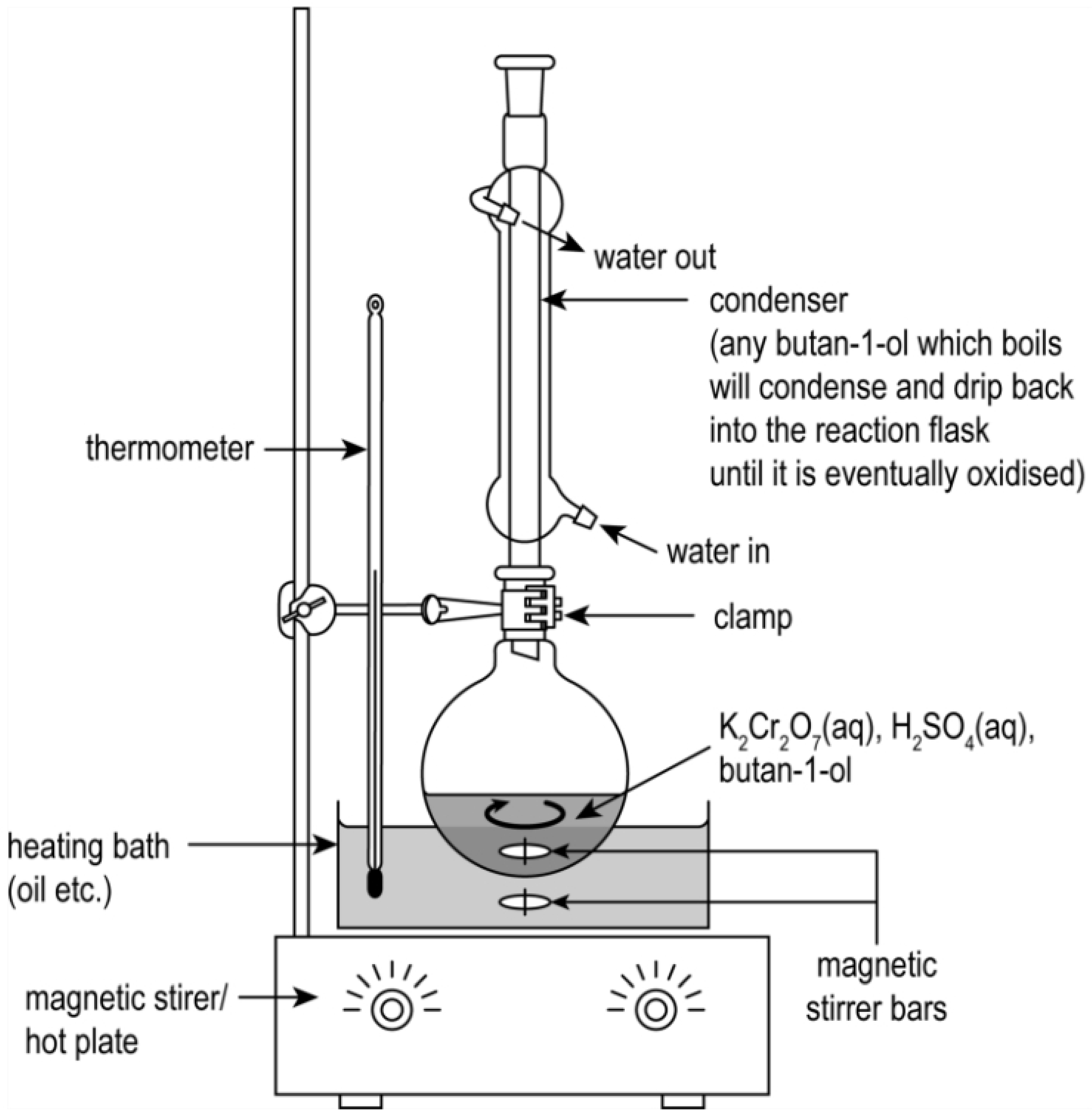
- $Na_2Cr_2O_7$ is added slowly to the alcohol (instead of *vice versa*). Why?
- Alcohols and aldehydes generally form *lower boiling* **azeotropes** with water.
  - Butan-1-ol (b.p. : 117.7 ºC) forms an azeotrope boiling at 92.3 ºC.
  - Butanal (b.p. : 74.8 ºC) forms an azeotrope boiling at 68.0 ºC.
  - Why is a fractionating column needed?
- All that passes over below 90 ºC is collected.
  - Water is separated from the distillate (*how?*)
  - Residue is dried with a drying agent (*e.g.* anhydrous Na_2SO_4)
  - Dried distillate is distilled using the same column to give fairly pure butanal.
- Why is it that we can isolate the aldehyde by immediate distillation?

E.g.



Note:

Experimental setup (prolonged heating under reflux conditions):

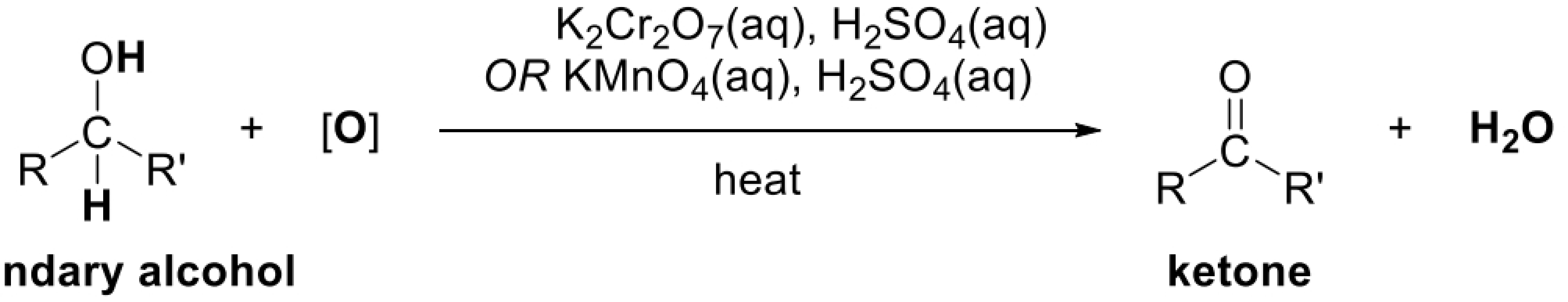


Did You Know?

The redox reaction between ethanol and acidified $K_2Cr_2O_7$ is employed in 'breathalyzers', which contains orange crystals of $K_2Cr_2O_7$, that are reduced to green Cr^{3+} ions by ethanol. The colour change provides an indication of the level of ethanol vapour in a motorist's breath.

2.4.2 Oxidation of Secondary Alcohols

- For the oxidation of **secondary alcohols**, the products formed are **ketones**.

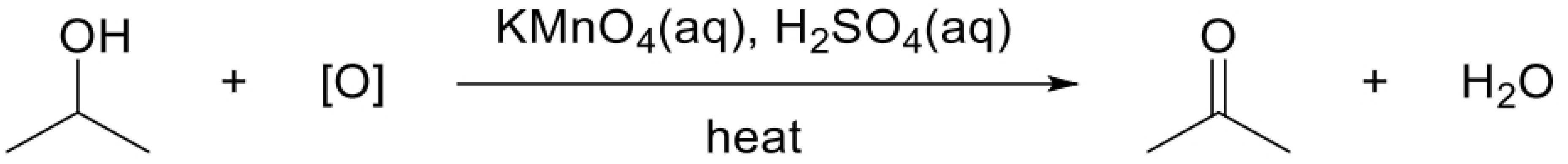


Reagents and conditions: $K_2Cr_2O_7(aq)$, $H_2SO_4(aq)$, heat

OR $KMnO_4(aq)$, $H_2SO_4(aq)$, heat

Observations: Orange $K_2Cr_2O_7$ turns green *OR* Purple $KMnO_4$ turns colourless.

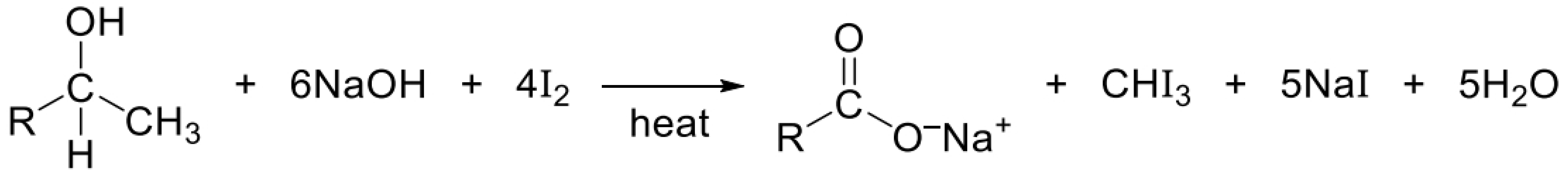
E.g.



2.4.3 Oxidation of Tertiary Alcohols

- Tertiary alcohols are **resistant to oxidation** by $KMnO_4$ and $K_2Cr_2O_7$ due to absence of α-hydrogens.

2.4.4 Tri-iodomethane / Iodoform Reaction

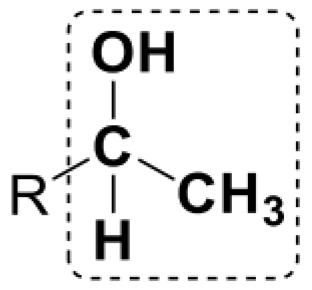


$$RCH(OH)CH_3 + 6NaOH + 4I_2 \xrightarrow{\text{heat}} RCOO^-Na^+ + CHI_3 + 5NaI + 5H_2O$$

Reagents and conditions: Iodine, aqueous NaOH (alkaline aqueous I_2), heat
Observations: Brown I_2 **decolourises** and a **pale-yellow ppt. of CHI_3** is formed.

- Oxidative cleavage reaction, or **step-down reaction** (leading to a shorter carbon chain).

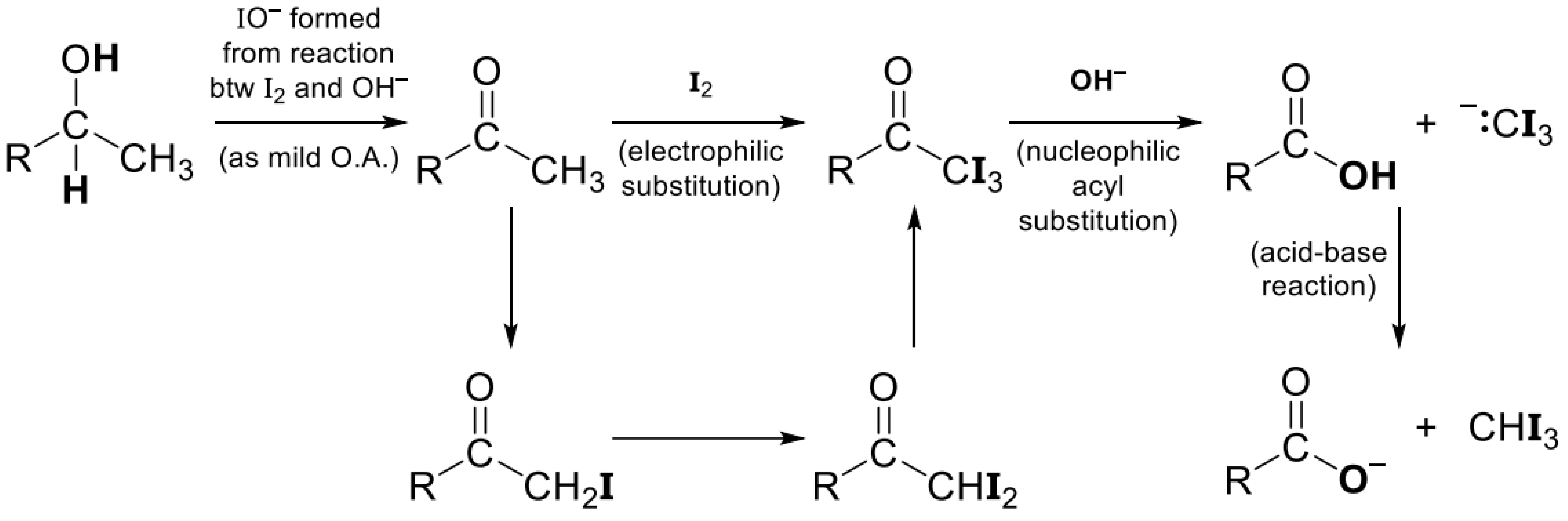
- Only alcohols with the following structure will react to give the iodoform reaction:



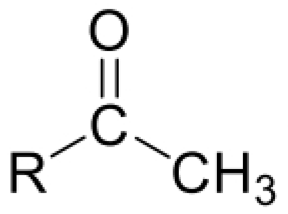
where R = H, alkyl, or aryl group

  - All are **secondary alcohols** (secondary methyl carbinols), with the exception of **ethanol** (R = H), which is a primary alcohol.

- Sequence of transformation involved in iodoform reaction (*not required at A-level*):



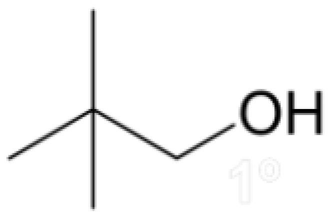
  - I_2 reacts with OH^- to give iodate(I), IO^-: $I_2 + 2OH^- \rightarrow I^- + IO^- + H_2O$
  - Since the 2° methyl carbinol is first oxidised by IO^- to the corresponding methyl ketone,



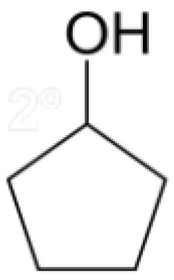
$RCOCH_3$, the latter also gives the iodoform reaction.

Example 2A

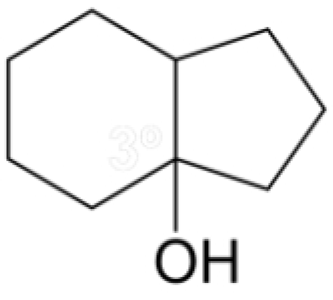
1 Classify the following alcohols and deduce the oxidation product (if any).

(a) 

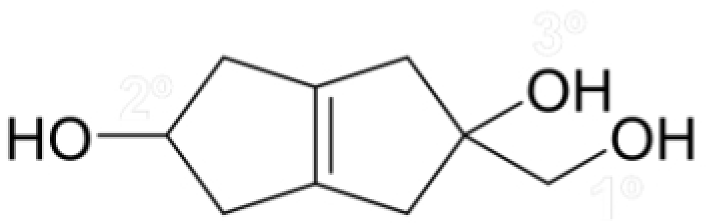
$\xrightarrow[\text{heat}]{KMnO_4(aq),\ H_2SO_4(aq)}$

(b) 

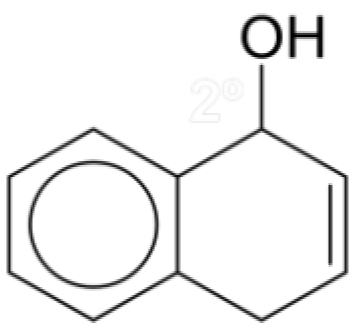
$\xrightarrow[\text{heat}]{K_2Cr_2O_7(aq),\ H_2SO_4(aq)}$

(c) 

$\xrightarrow[\text{heat}]{KMnO_4(aq),\ H_2SO_4(aq)}$

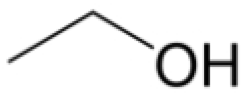
(d) 

$\xrightarrow[\text{heat}]{KMnO_4(aq),\ H_2SO_4(aq)}$

(e) 

$\xrightarrow[\text{heat}]{K_2Cr_2O_7(aq),\ H_2SO_4(aq)}$

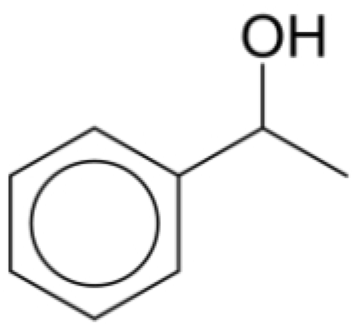
2 Draw the organic products (if any) of the following reactions.

(a) 

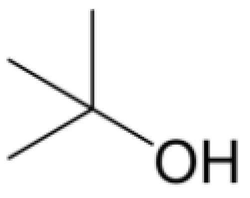
$\xrightarrow[\text{heat}]{\text{alkaline } I_2(aq)}$

(b) 

$\xrightarrow[\text{heat}]{I_2(aq),\ NaOH(aq)}$

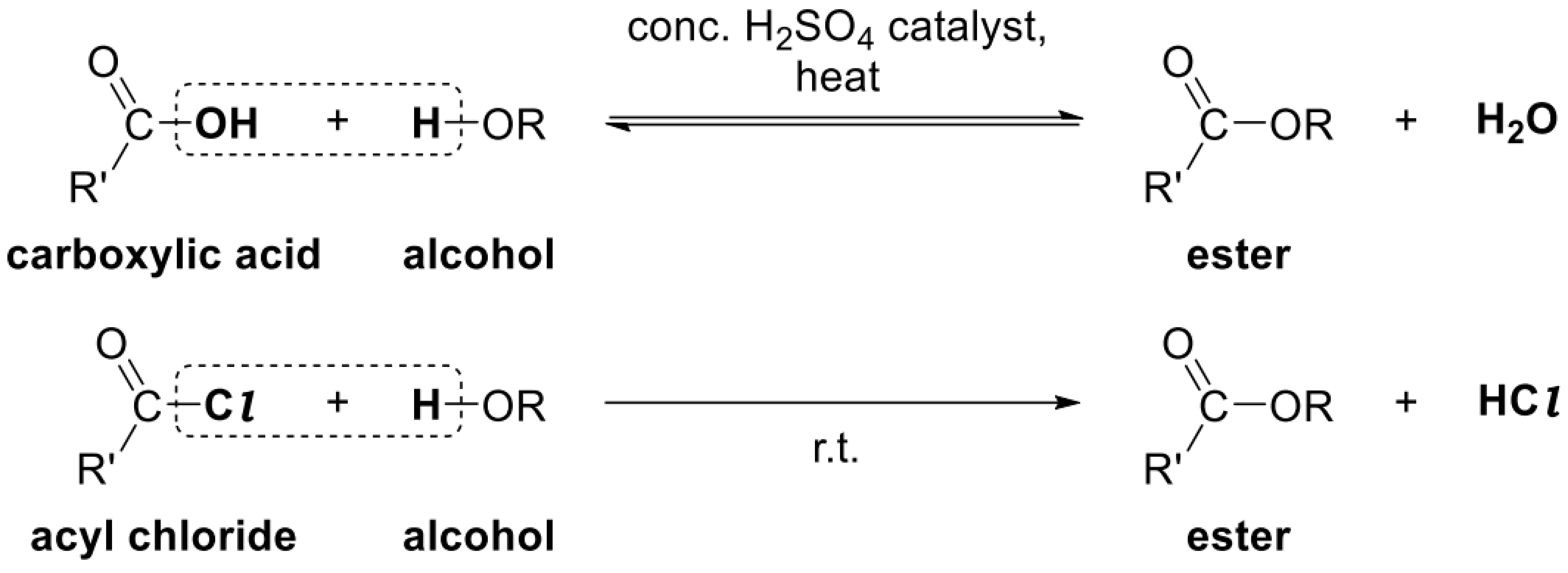
(c) 

$\xrightarrow[\text{heat}]{I_2(aq),\ NaOH(aq)}$

(d) 

$\xrightarrow[\text{heat}]{I_2(aq),\ NaOH(aq)}$

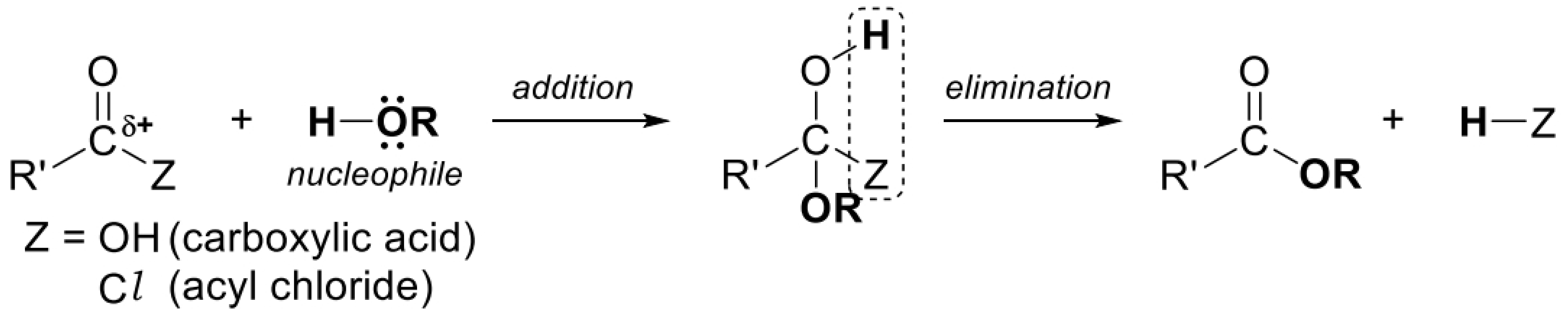
2.5 Ester Formation (Nucleophilic Acyl Substitution)



Reagents and conditions: RCO_2H, conc. H_2SO_4 catalyst, heat under reflux *(reversible)*
OR $RCOCl$, r.t.

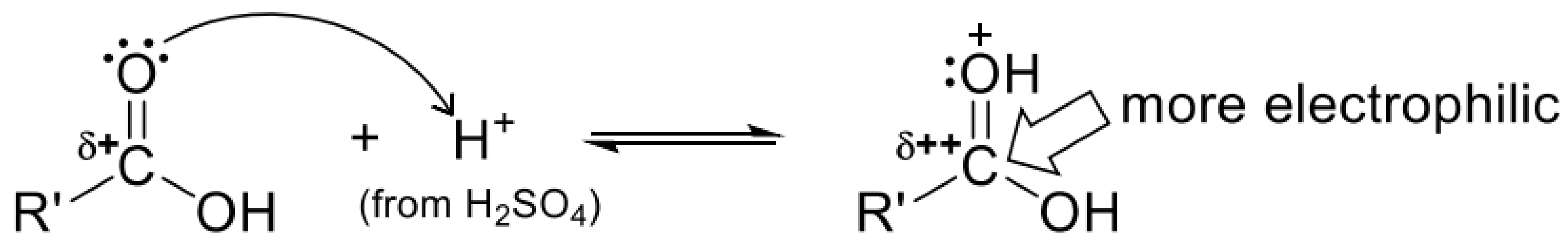
- The reaction between an alcohol and a carboxylic acid or acyl chloride, leading to the formation of an **ester**, is an example of a **condensation** reaction.
  - [IUPAC] Condensation reaction: a (usually stepwise) reaction in which two or more reactants (or remote reactive sites within the same molecular entity) yield a single main product with accompanying formation of water or of some other small molecule, *e.g.* ammonia, ethanol, acetic acid, hydrogen sulfide.

- Like many other condensation reactions, the mechanism for ester formation has been shown to comprise *consecutive* addition and elimination reactions (see **Appendix 1**):



  - Alcohol acts as a **nucleophile** (due to the lone pairs on O atom) and attacks the electron-deficient acyl carbon, $\overset{\delta+}{C}=\overset{\delta-}{O}$, of the carboxylic acid / acyl chloride, leading to **addition** of ROH across the C=O.
  - Subsequently, **elimination** of HZ regenerates the acyl C=O in the ester product.
  - Overall also known as a **nucleophilic (acyl) substitution** mechanism. (*Not required for A-level*. However, note the difference from the nucleophilic substitution, S_N1 and S_N2, mechanisms under halogenoalkanes.)

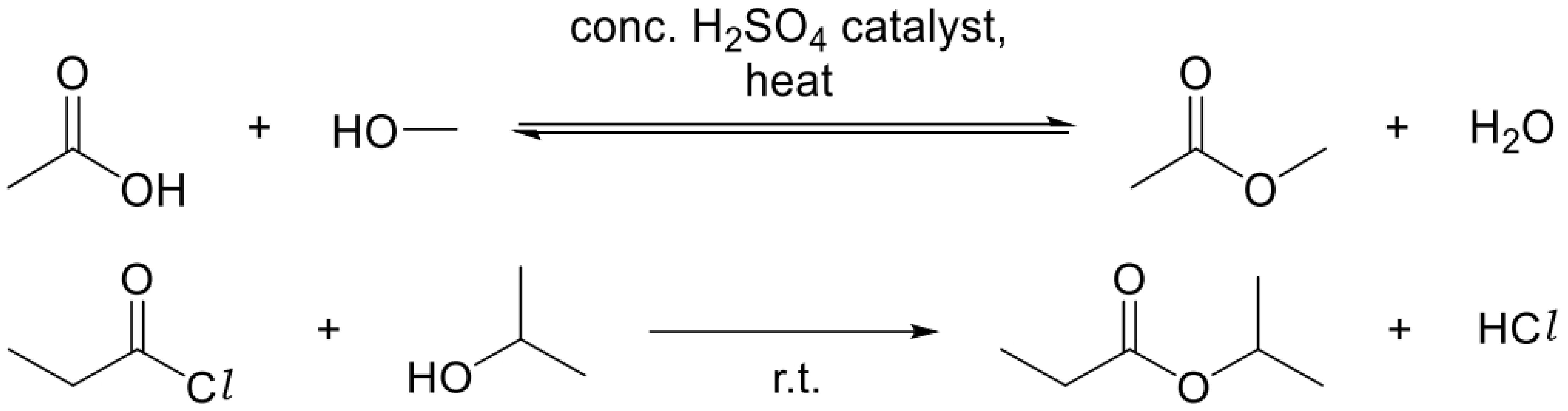
- In the reaction with carboxylic acid, the conc. H_2SO_4 acts as a **catalyst** by protonating the acyl oxygen, thereby increasing the electrophilicity of the acyl carbon (see **Appendix 1**):



- The reaction with carboxylic acid is reversible, while that with acyl chloride is irreversible.
  - H_2O is comparable to ROH in terms of nucleophilicity, while HCl is essentially non-nucleophilic.
  - HCl being a gas, readily escapes from the system, rendering the reverse reaction impossible.

- In the laboratory, reaction with acyl chloride is the **preferred method** because:
  - reaction goes to completion,
  - milder conditions are required (no catalyst, no heating), and
  - the by-product HCl is a gas and can be easily removed.

E.g.



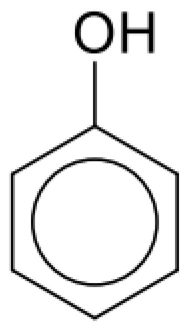
Checkpoint for §2

At the end of this section, you must be able to:

- relate differences in the reactivity of alcohols to the structure and bonding:
  - as electrophiles in nucleophilic substitution
  - as nucleophiles in nucleophilic substitution
  - as Brønsted-Lowry acid in acid-base reaction
- describe the reagents and conditions for the following reactions of alcohols:
  - dehydration (elimination) to form alkenes
  - nucleophilic substitution to form halogenoalkanes
  - oxidation of primary alcohols to aldehydes and carboxylic acids
  - oxidation of secondary aclohols to ketones
  - tri-iodomethane/iodoform reaction/oxidative cleavage of secondary methyl carbinols
  - nucleophilic (acyl) substitution to form esters
- relate the inertness of tertiary alcohols towards oxidation to the lack of α-hydrogen

3 Introduction to Phenols

- The parent compound, hydroxybenzene, was discovered in 1834 by Friedlieb Ferdinand Runge, who extracted it (in impure form) from coal tar. Runge called the compound “Karbolsäure” (coal-oil-acid, carbolic acid). Coal tar remained the primary source until the development of the petrochemical industry.



hydroxybenzene

- In 1841, the French chemist Auguste Laurent obtained hydroxybenzene in pure form.

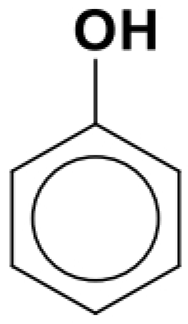
- In 1836, Auguste Laurent coined the name “phène” for benzene; this is the root of the word “phenol” and “phenyl”. In 1843, French chemist Charles Gerhardt coined the name “phenol”.

- Phenol is an important industrial commodity as a precursor to many materials and useful compounds. It is primarily used to synthesise plastics and related materials. Phenol and its chemical derivatives are essential for production of polycarbonates, epoxies, Bakelite, nylon, detergents, herbicides such as phenoxy herbicides, and numerous pharmaceutical drugs.

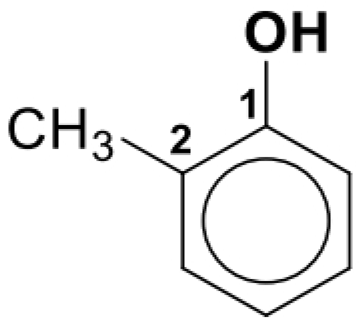
3.1 Nomenclature

3.1.1 Phenol as the parent

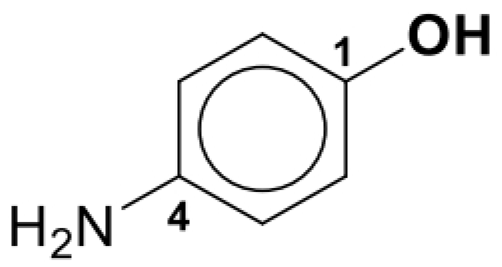
- In many simple compounds, *phenol* is the parent name and other substituents are simply indicated by a prefix added to the word *-phenol*.
  - When more than two substituents are present and the substituents are different, they are listed in alphabetical order.
  - The ring is numbered so as to give ***the lowest possible numbers to the substituents*** while the hydroxy group is assumed to be at position 1



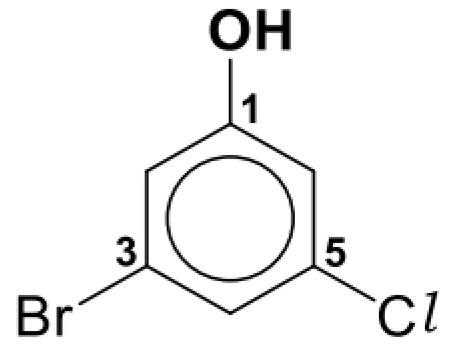
phenol



2-methylphenol



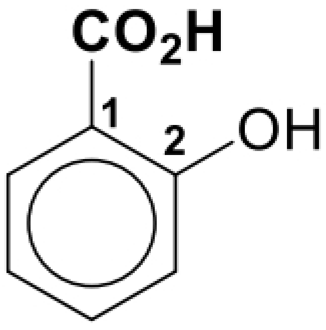
4-aminophenol



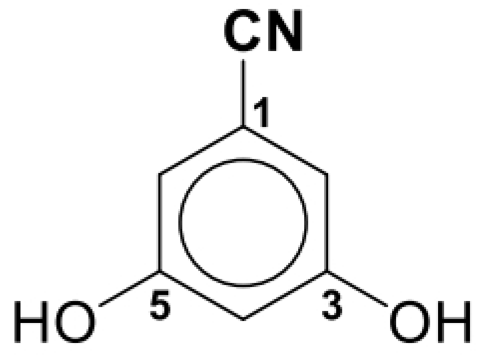
3-bromo-5-chlorophenol

3.1.2 Hydroxy group as the substituent

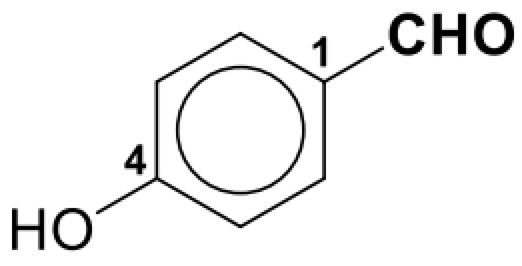
- In aromatic compounds containing the carboxyl group, acid derivatives, nitrile group, or carbonyl group, these form the parent and the –OH group is named as a substituent instead, indicated by the prefix *hydroxy*-, preceded by a number indicating it’s position relative to the major (parent) functional group.



2-hydroxybenzoic acid



3,5-dihydroxybenzonitrile



4-hydroxybenzaldehyde

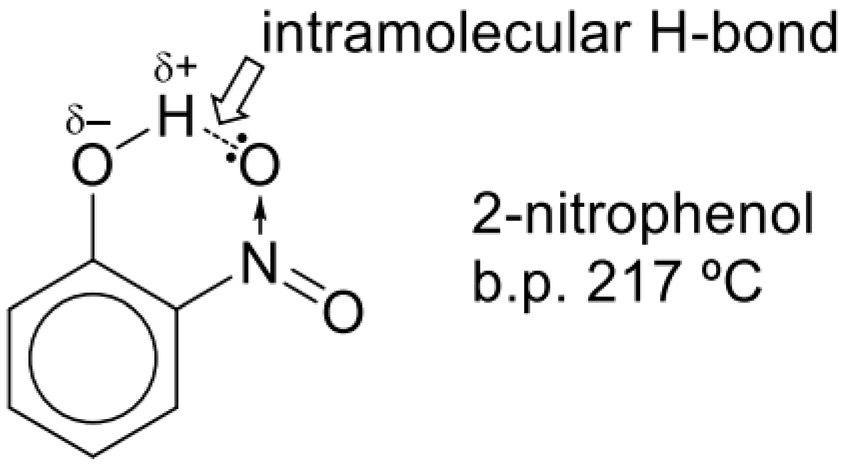
3.2 Physical Properties of Phenol

- Phenol is a colourless, crystalline, hygroscopic solid (m.p. 42 ºC; b.p. 181 ºC).

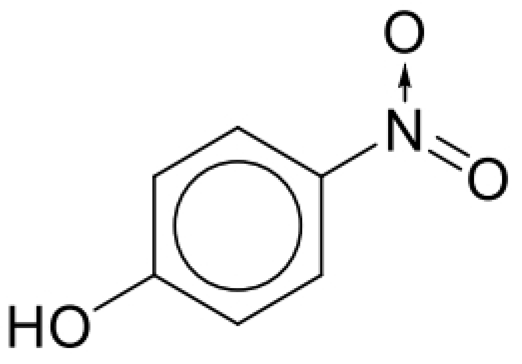
- It is **sparingly soluble in water** and the resultant solution is **weakly acidic** (pK_a = 9.98).

- Phenol and its **vapours** are corrosive to the eyes, the skin, and the respiratory tract.
  - Its corrosive effect on skin and mucous membranes is due to its ability to denature and coagulate proteins.
  - Repeated or prolonged skin contact with phenol may cause dermatitis, or even second and third-degree burns.

- The melting point and boiling point of phenol are higher than that of an alkane of similar M_r due to more energy required to overcome the stronger **hydrogen bonds** between phenol molecules than the weaker instantaneous dipole-induced dipole interactions between alkane molecules.
  - Boiling point depends on the *extent* of *intermolecular* hydrogen bonding.
    - *E.g.* In 2-nitrophenol, the proximity of the –OH and $-NO_2$ groups allows **intramolecular hydrogen bonding** to occur. Thus, intermolecular hydrogen bonding is **less extensive**, resulting in a lower boiling point than 4-nitrophenol.



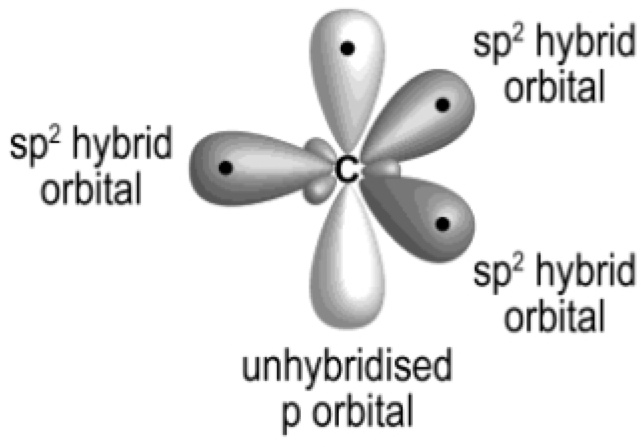
2-nitrophenol
b.p. 217 ºC



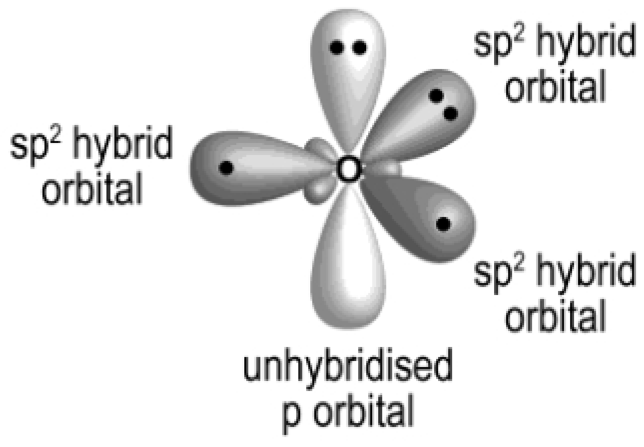
4-nitrophenol
b.p. 245 ºC

3.3 Structure of Phenol

- The oxygen atom of the OH group in phenol can be taken to be **sp^2-hybridised**, same as the six carbon atoms of the benzene ring.

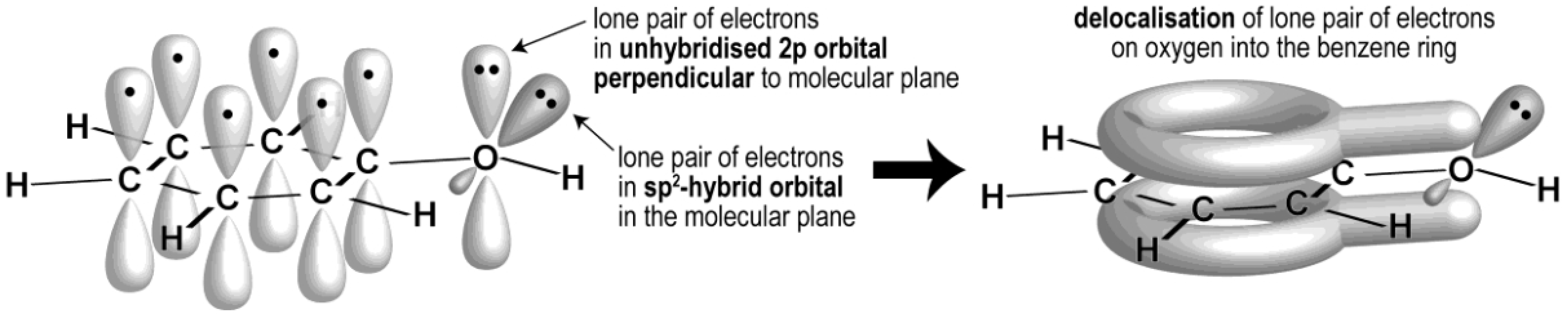


the carbon atom



the oxygen atom

- The **2p-orbital** on the oxygen atom of the –OH group, carrying a lone pair of electrons, can have a **side-on overlap** with the **π electron cloud** of the benzene ring. As a result, the lone pair of electrons on the oxygen atom is **delocalised into** the benzene ring.

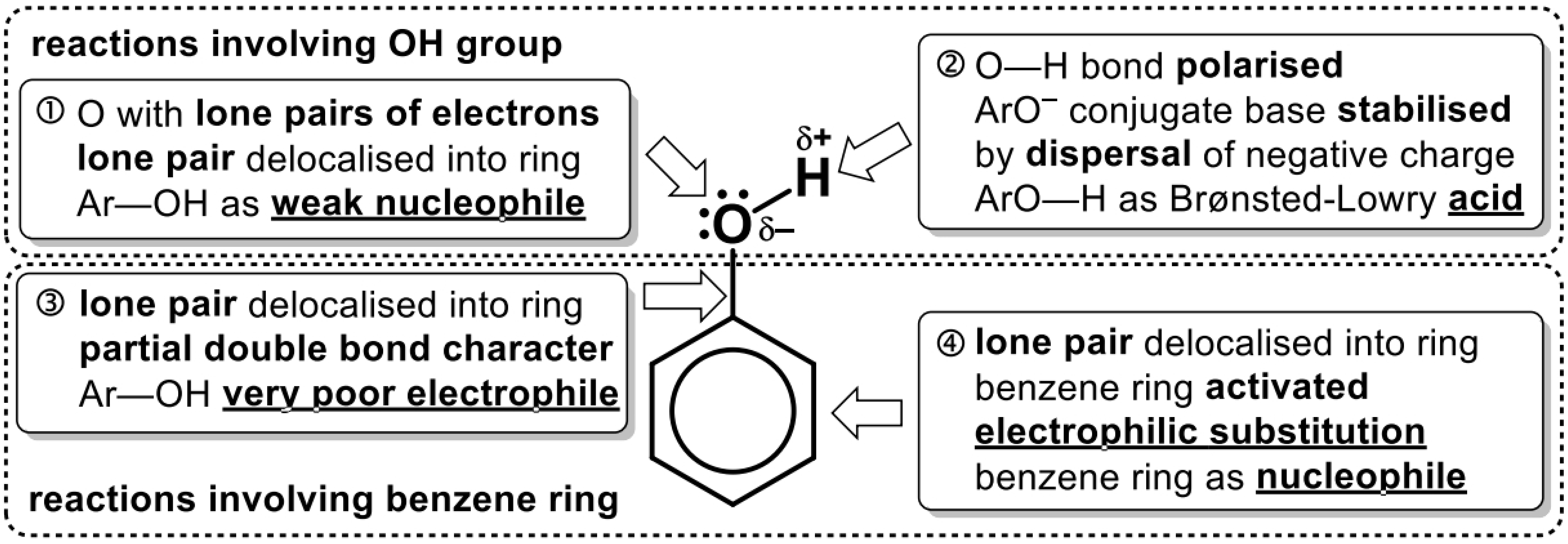


- The delocalisation of the lone pair of electrons on the oxygen atom into the benzene ring has profound influence on the reactivity of
  - the **–OH group** of phenol compared to that in aliphatic alcohols, and
  - the **benzene ring** of phenol compared to benzene itself.

4 Chemical Reactions of Phenols

LO **(d)** recall the chemistry of phenol, as exemplified by the following reactions: nitration of, and bromination of, the benzene ring

- There are four sites of reactivity in phenols, two involving the –OH group and two involving the benzene ring:



① Although the O atom of the –OH group has lone pairs of electrons, delocalisation of the lone pair into the benzene ring renders the lone pair **less available for donation**, hence a **weaker nucleophile** than ROH. **(§4.2.1**)

② Delocalisation of the lone pair of electrons on O into the benzene ring helps to **disperse the negative charge** on the phenoxide ion, **stabilising the conjugate base** and hence making ArOH a **stronger Brønsted-Lowry acid** than ROH. (**§5.2** and **§0**)

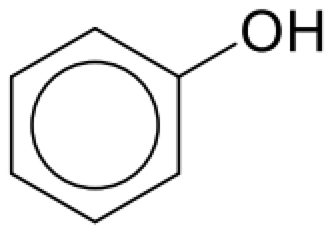
③ Delocalisation of the lone pair into the benzene ring imparts **partial double bond character** to the C–O, strengthening the C–O bond, rendering ArOH a **very poor electrophile**. **(§4.3.1**)

④ Due to delocalisation of the lone pair of electrons on O into the benzene ring, the benzene ring has higher electron density and is **activated** compared to benzene itself towards **electrophilic substitution**. (**§4.3.2**)

4.1 Combustion

- Phenol burns in a plentiful supply of oxygen to give carbon dioxide and water.

E.g.



$$+ \ 7O_2 \longrightarrow 6CO_2 + 3H_2O$$

- However, for compounds containing benzene rings, combustion is hardly ever complete, especially if they are burnt in air. The high proportion of carbon in phenol means that a very high proportion of oxygen to phenol is needed to get complete combustion.

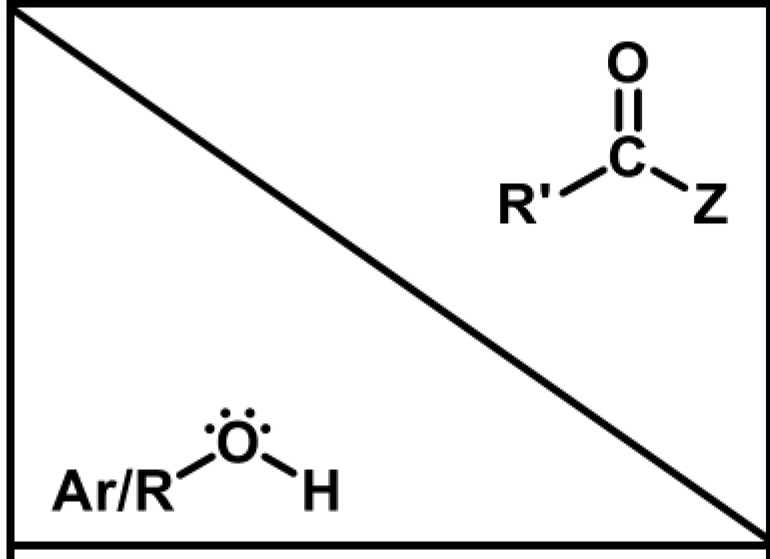
- Phenol tends to burn in air with an orange flame and an extremely smoky flame

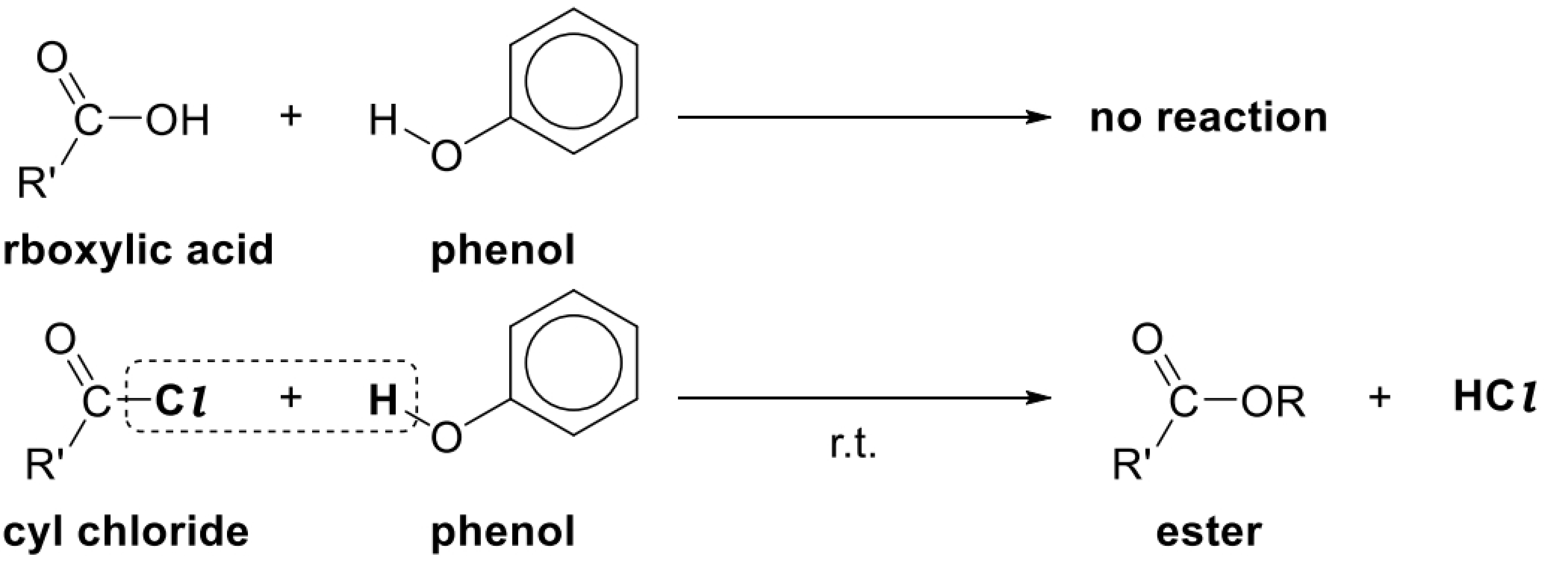
4.2 Reactions involving the OH group

4.2.1 Ester Formation (Nucleophilic Acyl Substitution)

- The 2p-orbital of the oxygen atom of the –OH group, carrying a lone pair of electrons, can have a **side-on overlap** with the π electron cloud of the benzene ring. As a result, the lone pair of electrons on the oxygen atom is **delocalised into** the benzene ring and hence the lone pair is **less available for donation** to an electrophile.
  - In other words, phenols are **less nucleophilic** or are **weaker nucleophiles** compared to aliphatic alcohols.

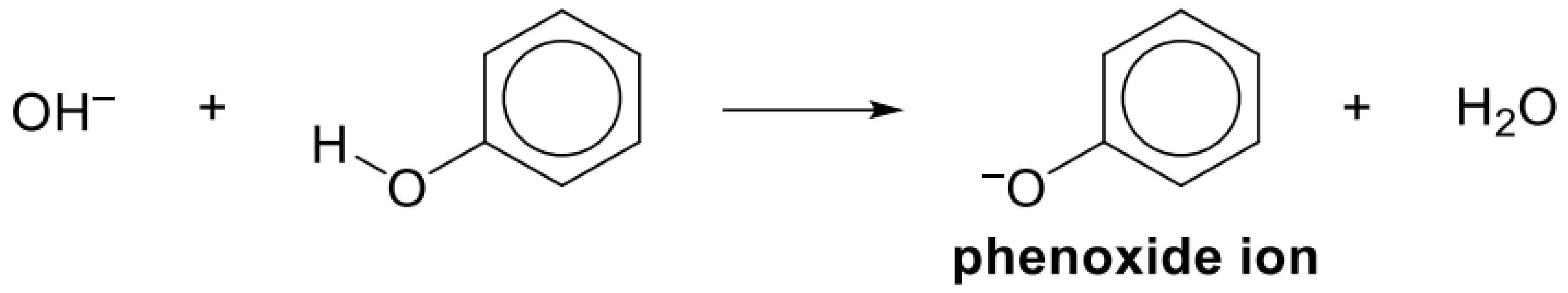
- Hence, ester formation reaction **only occurs** between a phenol and an **acyl chloride**. It is unable to react with a carboxylic acid unlike aliphatic alcohols (see **§2.5**).
  - Acyl chlorides are better acylating agents compared to carboxylic acids, as they are **more electrophilic** or are **stronger electrophiles**.

	**carboxylic acid (Z = OH)** • acyl C attached to two highly electronegative O • lone pair on O of OH delocalised into C=O • acyl C mildly e^--deficient • *weak electrophile*	**acyl chloride (Z = C*l*)** • acyl C attached to highly electronegative O and C*l* • lone pair on C*l* very weakly delocalised into C=O • acyl C highly e^--deficient • *strong electrophile*
phenol (ArOH) • lone pair delocalised into benzene ring • lone pair on O is less available for donation • *weak nucleophile*	**no reaction**	• sluggish reaction • convert to **more nucleophilic phenoxide ion** for faster reaction
aliphatic alcohol (ROH) • alkyl group is electron-donating (+I effect) • lone pair on O is more available for donation • *strong nucleophile*	• **reversible** reaction • very **slow equilibrium** • catalysed by conc. H_2SO_4 • heat to increase rate	• **irreversible** reaction • reacts **quickly** and **completely** • room temperature

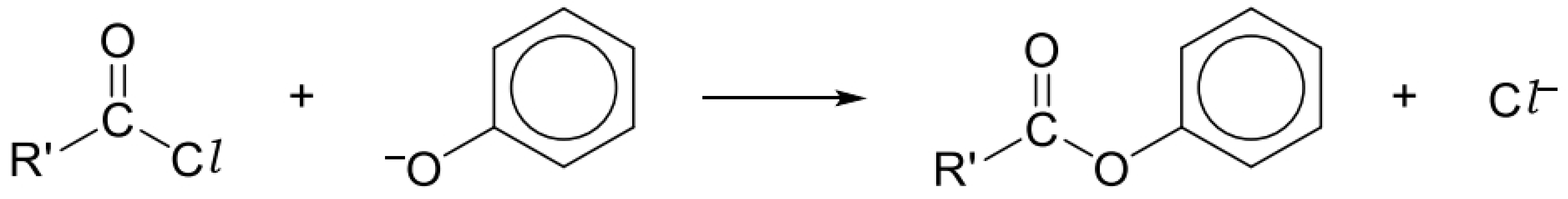


Reagents and conditions: 1) phenol in NaOH(aq), r.t.; 2) RCOC*l*, r.t.

- Phenol is **first reacted with NaOH(aq)** in an **acid-base reaction** and is converted to the **<u>negatively charged</u> phenoxide ion**, which is a **stronger nucleophile than phenol** itself.
  - Step 1: A base such as NaOH(aq) or pyridine (an organic base) helps to increase the rate of reaction by converting phenol to a **stronger nucleophile**.



  - Step 2: The phenoxide ion (a stronger nucleophile) will then react with the acyl chloride to form the ester.



4.3 Reactions involving the benzene ring

4.3.1 Nucleophilic Substitution as Electrophile

- Unlike aliphatic alcohols (see **§2.3**), phenol does **not** undergo nucleophilic substitution reaction with HX, PX_3, PCl_5 and $SOCl_2$. This is similar to why halogenoarenes generally do not undergo nucleophilic substitution reactions.

- **Explanation:**
  - The 2p-orbital of the oxygen atom of the –OH group, carrying a lone pair of electrons, can have a **side-on overlap** with the π electron cloud of the benzene ring. As a result, the lone pair of electrons on the oxygen atom is **delocalised into** the benzene ring.
  - This leads to the **partial double bond character** in the C–O bond, **strengthening the C–O bond**, and making the C–O bond more difficult to break.

- In addition, unlike the electrophilic α-carbon in aliphatic alcohols, the benzene ring of phenol is electron-rich and hence will **repel an incoming nucleophile**. The electron density of the benzene ring is further intensified by the delocalisation of the lone pair of electrons on O into the ring.

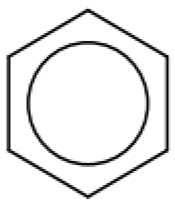
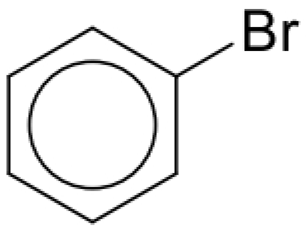
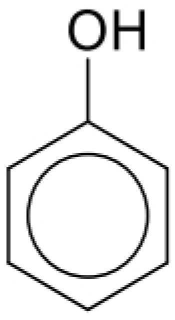
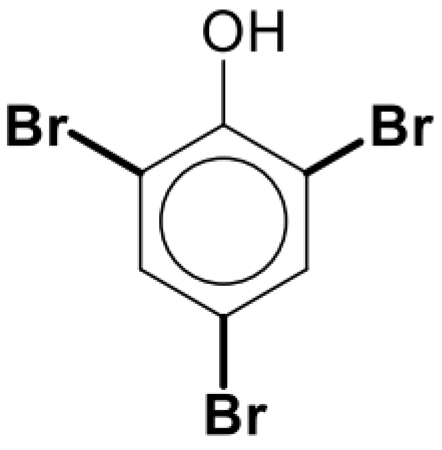
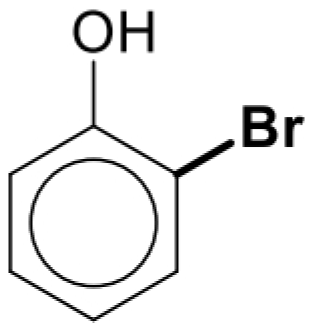
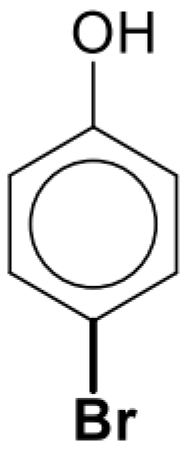
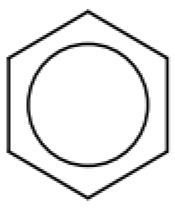
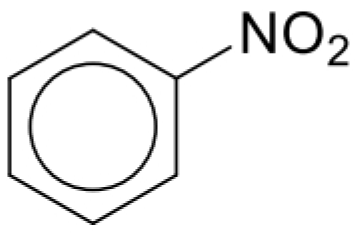
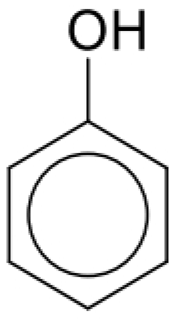
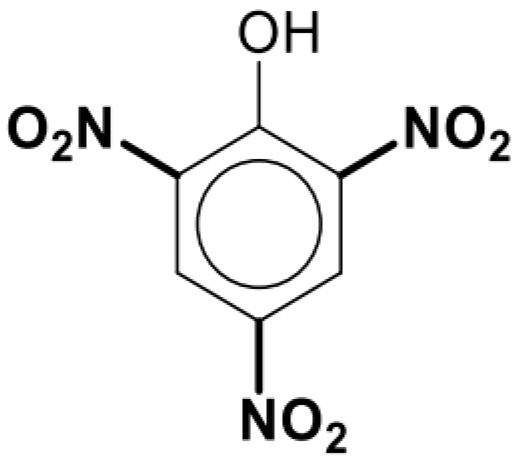
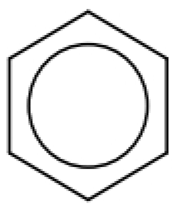
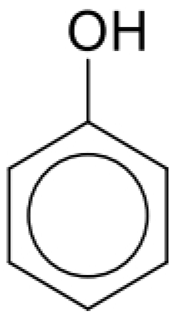
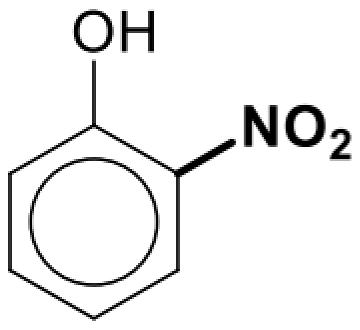
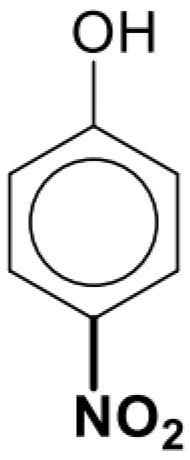
4.3.2 Electrophilic (Aromatic) Substitution as Nucleophile

- The benzene ring of phenol **undergoes electrophilic substitution**, but **under milder conditions** compared to benzene and methylbenzene.

- **Explanation:**
  - The 2p-orbital of the oxygen atom of the –OH group, carrying a lone pair of electrons, can have a **side-on overlap** with the π electron cloud of the benzene ring. As a result, the lone pair of electrons on the oxygen atom is **delocalised into** the benzene ring.
  - This makes the **benzene ring more electron-rich**, and hence, **more susceptible to electrophilic substitution**.

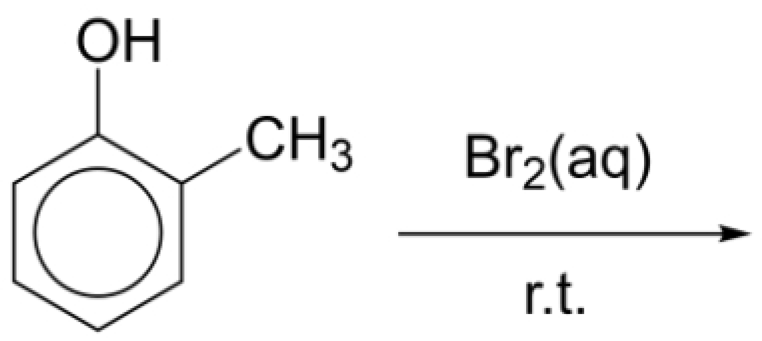
- The **<u>–OH group is STRONGLY ring-activating and 2,4-directing</u>**. Hence **tri-substitution** occurs at the **2, 4 and 6 positions** of phenol.

- Comparing benzene and phenol:

reactant		**reaction conditions**	**substitution products**
Br_2		$Br_2(l)$, anhydrous $FeBr_3$, heat	
		**Br_2(aq)**, r.t. (no catalyst and heating required)	 2,4,6-tribromophenol (white ppt)
		Br_2 in CCl_4, r.t.	 and 
conc. HNO_3		conc. HNO_3, conc. H_2SO_4, 55–60 °C	
		**conc. HNO_3**, r.t. (no catalyst and heating required)	 2,4,6-trinitrophenol
dil. HNO_3		**no reaction**	**no reaction**
		**dilute HNO_3**, r.t.	 and 

Example 4A

1 Draw the product for the following reaction:



Note:
The –OH group is a stronger ring-activating group than $–CH_3$. Hence the electron-donating effect of –OH dominates over $–CH_3$ and directs the electrophile to the 2-, 4- **AND** 6-positions relative to –OH.

Self-Check 4A

1 Write balanced equations for the reaction of phenol with

(a) aqueous Br_2

(b) concentrated HNO_3

(c) dilute HNO_3

2 State the observation for the reaction between phenol and aqueous Br_2.

Checkpoint for §3 & §4

At the end of section 3, you must be able to:

- write IUPAC names of simple substituted phenols given the structural formula and *vice versa*
- understand the structure of phenol in terms of the delocalisation of the lone pair of electrons on the oxygen into the benzene ring

At the end of section 4, you must be able to:

- relate differences in the reactivity of phenols to the structure and bonding, in particular, the delocalisation of the lone pair of electrons into the benzene ring:
  - as electrophiles in nucleophilic substitution
  - as nucleophiles in nucleophilic substitution
  - as nucleophiles in electrophilic (aromatic) substitution
  - as Brønsted-Lowry acid in acid-base reaction
- describe the reagents and conditions for the following reactions of phenols:
  - nucleophilic (acyl) substitution to form esters
  - electrophilic substitution of the benzene ring
- explain for the
  - high reactivity of phenols towards electrophilic (aromatic) substitution compared to benzene
  - low reactivity of phenols towards nucleophilic substitutions as both electrophiles and nucleophiles compared to alcohols

  in relation to the delocalisation of the lone pair of electrons on the oxygen into the benzene ring

5 Acid Behaviour of Alcohols and Phenols

LO **(a)** recall the chemistry of alcohols, exemplified by ethanol: (iii) reaction with sodium:
(b) recall the chemistry of phenol, as exemplified by the following reactions: (i) with bases, (ii) with sodium
(e) explain the relative acidities of water, phenol and ethanol in aqueous medium (interpret as Brønsted-Lowry acids)

5.1 Factors Affecting Acid Strength

- The **strength of acid**, **HA**, depends on the **relative stability** of the resulting **conjugate base**, **A⁻**, formed.

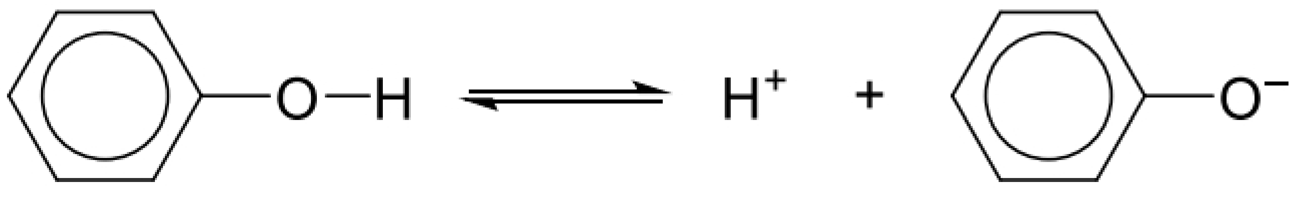
$$H{-}A(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

  - The **more stable** the resulting **conjugate base**, **A⁻**
    - the position of equilibrium will lie more to the **right**
    - **more H^+(aq) is formed** due to greater dissociation
    - the **stronger the acid**, **HA**

- Hence, to evaluate the acidity of an alcohol / phenol, we assess the **stability** of the corresponding **alkoxide / phenoxide** ion, with the **negative charge on the O atom**:

$$R{-}O{-}H \rightleftharpoons H^+ + R{-}O^-$$

alcohol **alkoxide**



phenol **phenoxide**

5.2 Relative Acidity of Water, Ethanol and Phenol

alcohol	equilibria	pK_a*	
ethanol	$CH_3CH_2OH \rightleftharpoons \mathbf{CH_3CH_2O^-} + H^+$	15.9	*(neutral)*
water	$H_2O \rightleftharpoons \mathbf{HO^-} + H^+$	15.7	*(reference)*
phenol	$C_6H_5OH \rightleftharpoons \mathbf{C_6H_5O^-} + H^+$	10.0	*(acidic)*

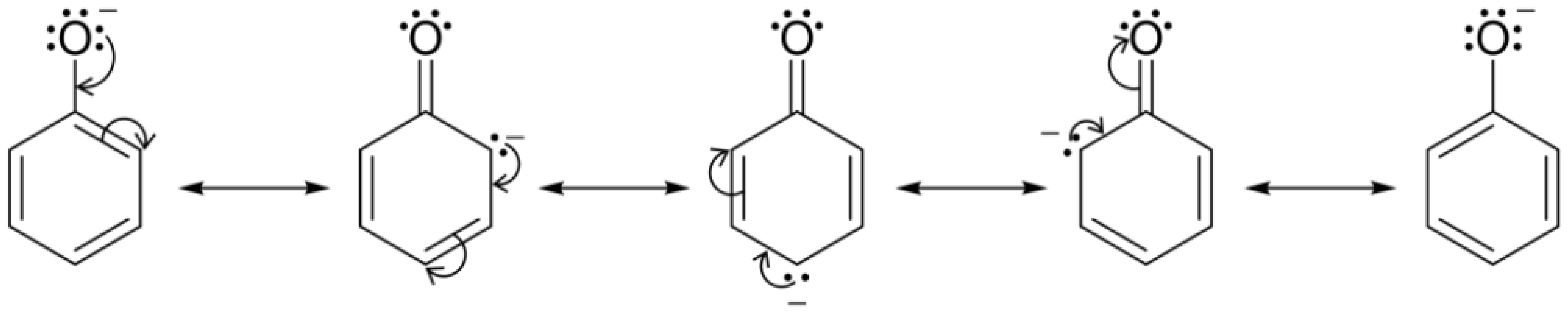
*The higher the value of pK_a, the less acidic is the compound.

- **Ethanol is a weaker acid than water**.
  - The electron-donating CH_3CH_2– group **intensifies** the negative charge, thereby **destabilising** the ethoxide ion, $CH_3CH_2O^-$, relative to the hydroxide ion.

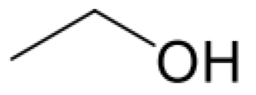
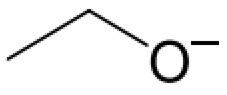
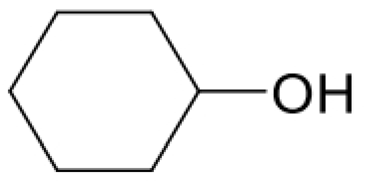
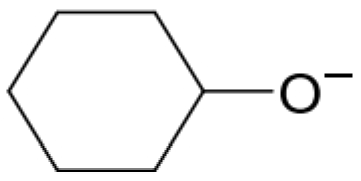
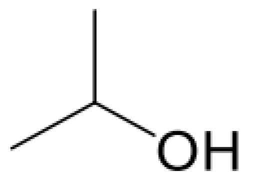
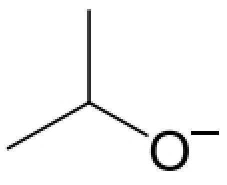
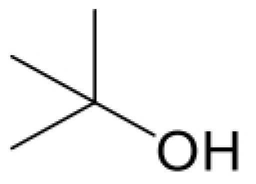
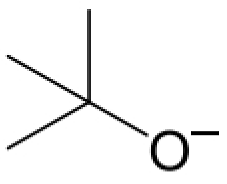
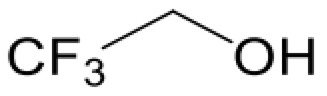
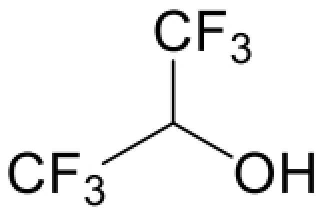
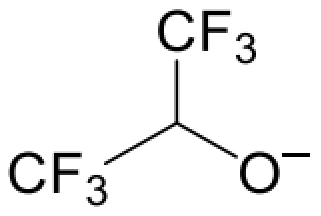
- **Phenol is a stronger acid than alcohol and water**.
  - The 2p-orbital of the oxygen atom of the O^- group, carrying a lone pair of electrons, can have a **side-on overlap** with the π electron cloud of the benzene ring. As a result, the lone pair of electrons on the oxygen atom is **delocalised** into the benzene ring, which **disperses** the negative charge, **stabilising the phenoxide ion**. The phenoxide ion is said to be **resonance-stabilised**.

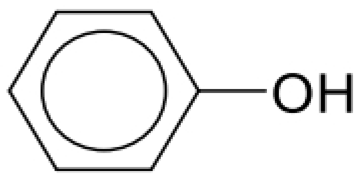
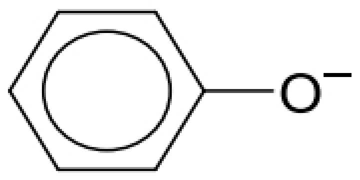
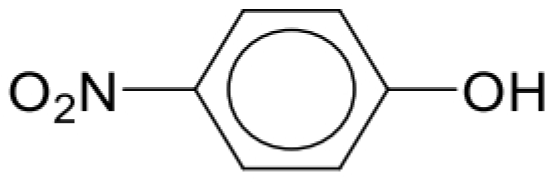
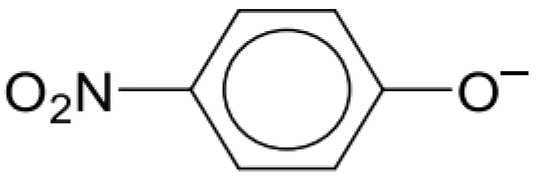
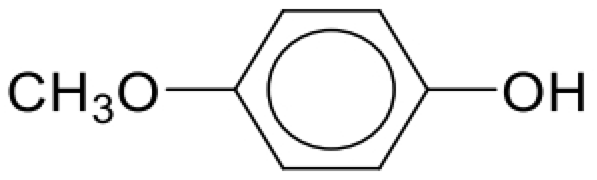
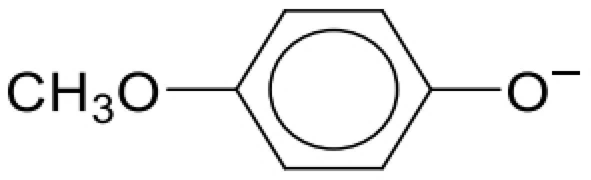
For your information:

How the phenoxide ion is resonance-stabilised can be seen from the following resonance structures. The negative charge is delocalised into the ring, dispersing the charge:



- **Stability** of the resulting anionic RO^- and ArO^- formed is further affected by:
  - **Electron-donating** groups, which **intensify** the negative charge, thereby **destabilising** the RO^- or ArO^- ion.
  - **Electron-withdrawing** groups, which **disperses** the negative charge, thereby **stabilising** the RO^- or ArO^- ion.

alcohol		**alkoxide**	**pK_a**
methanol	—OH	—O^-	15.5
ethanol (primary)			15.9
cyclohexanol (secondary)			16.0
propan-2-ol (secondary)			16.5
2-methylpropan-2-ol (tertiary)			17.0
2,2,2-trifluoroethanol			12.5
1,1,1,3,3,3-hexafluoro-propan-2-ol			9.3

phenol		**phenoxide**	**pK_a**
phenol			10.0
4-nitrophenol (NO_2 : EWG)			7.2
4-methoxyphenol (CH_3O : EDG)			10.2

5.3 Reaction with Sodium and Bases

- Alcohols and phenols can react with reactive metals such as Na and K to form **alkoxides and phenoxides** respectively, and hydrogen gas. It involves **cleavage** of the **O–H bond**.

$$\text{Ar/R–O–H} + \text{Na} \longrightarrow \text{Ar/R–O}^-\text{Na}^+ + \frac{1}{2}H_2$$

  - For every 1 mole of metal that has reacted with 1 mole of alcohol or phenol, **half a mole of hydrogen gas** will be produced.

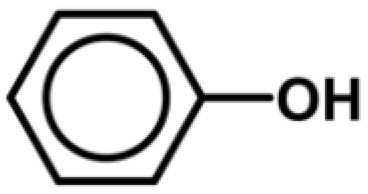
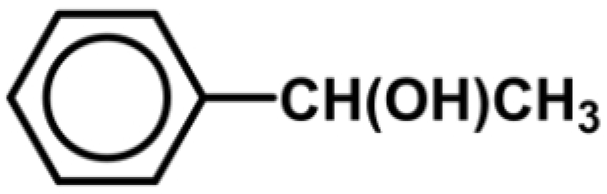
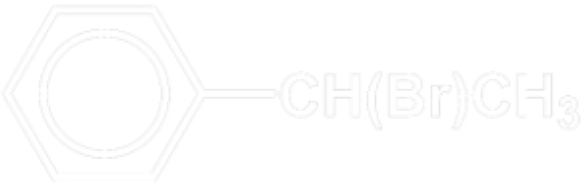
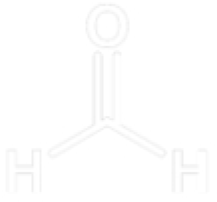
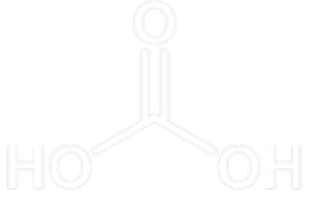
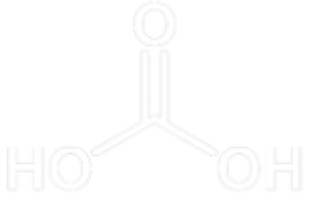
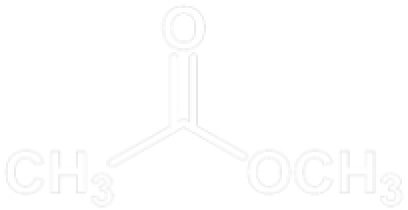
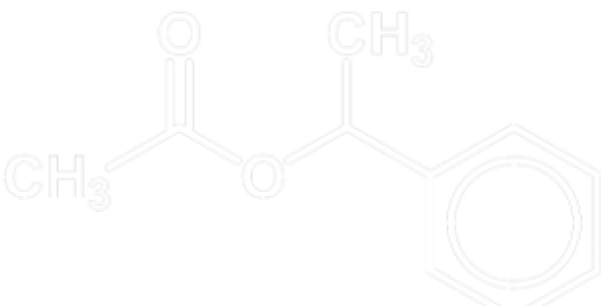
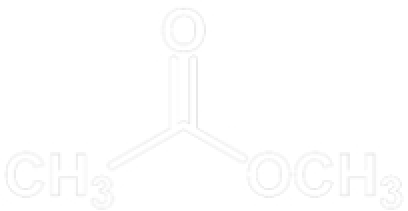
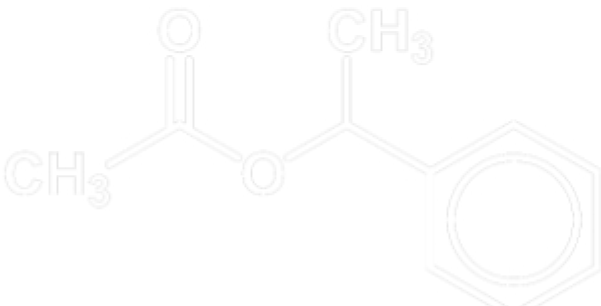
- The relative acidity can also be illustrated through the reactions of aliphatic alcohol, phenol and carboxylic acid with sodium metal and bases.

<table>
<tr><th>acid
reagent</th><th>CH_3CH_2OH
(pK_a = 15.9)</th><th>C_6H_5OH
(pK_a = 10.0)</th><th>CH_3COOH
(pK_a = 4.76)</th></tr>
<tr><td>Na(s)</td><td>$CH_3CH_2OH + Na \rightarrow$
$CH_3CH_2O^-Na^+ + ½H_2$</td><td>$C_6H_5OH + Na \rightarrow$
$C_6H_5O^-Na^+ + ½H_2$</td><td>$CH_3COOH + Na \rightarrow$
$CH_3COO^-Na^+ + ½H_2$</td></tr>
<tr><td colspan="4">Type of reaction: redox reaction (or Acid-Metal reaction)
Alcohols are much weaker acids than water, hence they react less vigorously with Na.</td></tr>
<tr><td>NaOH(aq)</td><td>No reaction</td><td>$C_6H_5OH + NaOH \rightarrow$
$C_6H_5O^-Na^+ + H_2O$</td><td>$CH_3COOH + NaOH \rightarrow$
$CH_3COO^-Na^+ + H_2O$</td></tr>
<tr><td colspan="4">Type of reaction: acid-base reaction
Alcohols are weaker acids than water, and thus cannot undergo acid-base reactions with strong bases.</td></tr>
<tr><td>Na_2CO_3(aq)</td><td>No reaction</td><td>$C_6H_5OH + Na_2CO_3 \rightarrow$
$C_6H_5O^-Na^+ + \mathbf{NaHCO_3}$</td><td>$CH_3COOH + Na_2CO_3 \rightarrow$
$CH_3COO^-Na^+ + \mathbf{CO_2} + H_2O$</td></tr>
<tr><td colspan="4">Type of reaction: acid-carbonate reaction
Reaction with CO_3^{2-} takes place in a step-wise manner, first giving HCO_3^-, then CO_2 :
$$CO_3^{2-} \underset{pK_a(HCO_3^-)=10.25}{\overset{H^+}{\rightleftharpoons}} HCO_3^- \underset{pK_a(H_2CO_3)=6.37}{\overset{H^+}{\rightleftharpoons}} H_2CO_3 \longrightarrow H_2O + CO_2$$
Both carboxylic acids and phenols are acidic enough to react with CO_3^{2-} to give HCO_3^-
However, <i>only carboxylic acids</i> are sufficiently acidic $(pK_a(RCO_2H) < pK_a(H_2CO_3))$ to react further with HCO_3^- to give CO_2 (and H_2O).
The effervescence of CO_2 which gives a white ppt with limewater, $Ca(OH)_2$, is a distinguishing test for the presence of the carboxyl ($–CO_2H$) group.
Phenols can react with Na_2CO_3 to produce $NaHCO_3$. However, this does not give an observable change and should not be used as a distinguishing test.</td></tr>
</table>

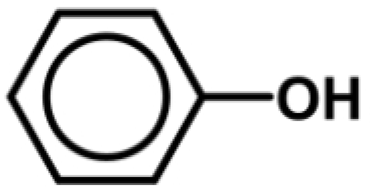
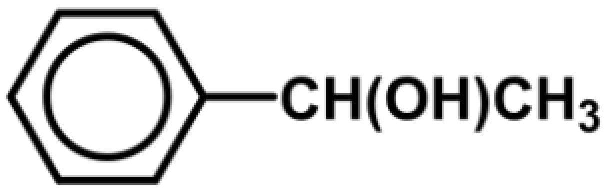
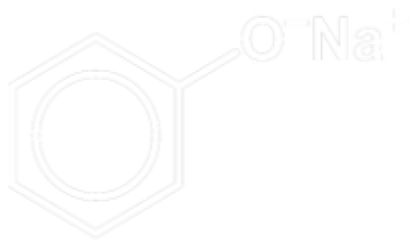
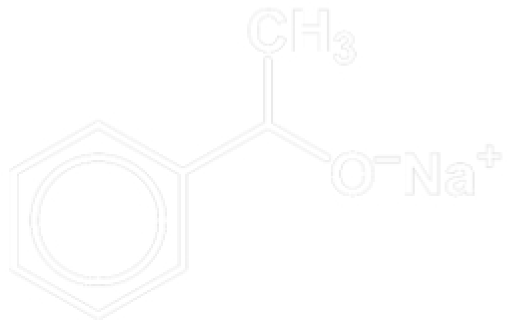
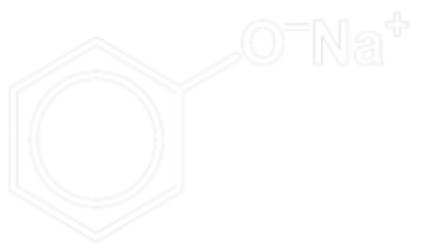
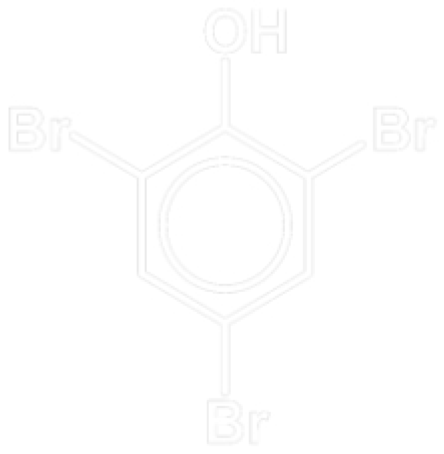
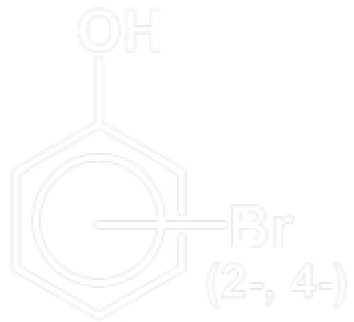
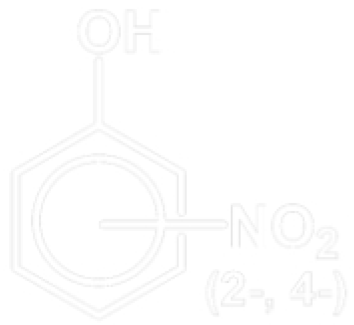
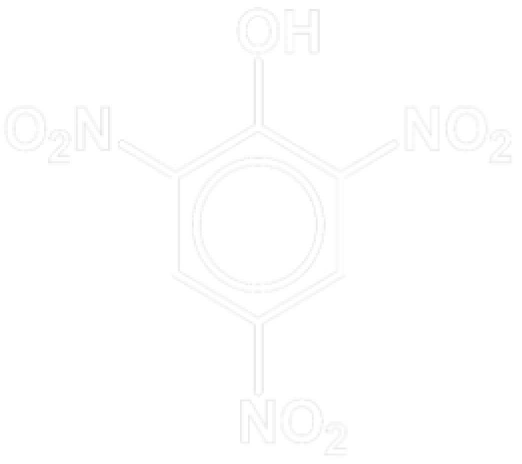
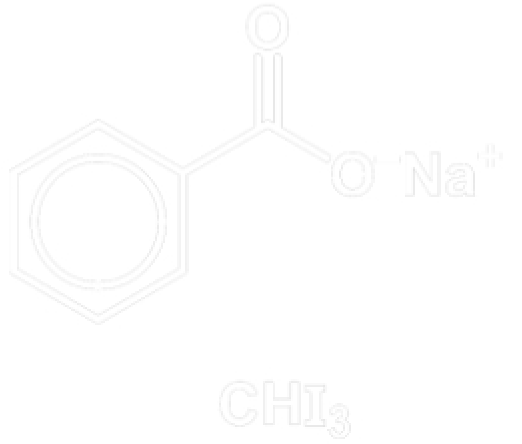
- In qualitative analysis:
  - to differentiate **hydroxyl** group from other functionalities, **Na metal** can be added, which results in the production of **H_2 gas** that produces a ‘pop’ sound with a lighted splint.
  - to differentiate **carboxyl** group from other functionalities, **Na_2CO_3** can be added, which results in the production of **CO_2 gas** that forms **white precipitate** with $Ca(OH)_2$.

Self-Check 5A

1 Draw the carbon-containing products for the reactions of methanol, phenol and 1-phenylethanol with the following reagents. Write “no reaction” is there is no reaction.

reagent and conditions	**type of reaction**	**methanol, CH_3OH**	**phenol,** 	**1-phenylethanol,** 
excess conc. H_2SO_4, heat	*elimination*			
PCl_5(s), r.t.	*nucleophilic substitution*			
HBr(g), r.t.				
$SOCl_2$, heat under reflux				
$K_2Cr_2O_7$ (aq), H_2SO_4 (aq), distil immediately	*oxidation*			
$K_2Cr_2O_7$ (aq), H_2SO_4 (aq), heat				
$KMnO_4$ (aq), H_2SO_4 (aq), heat				
CH_3COOH, conc. H_2SO_4, heat	*condensation (form ester)*			
CH_3COCl, r.t.				

Self-Check 5A (cont'd)

reagent and conditions	type of reaction	methanol, CH_3OH	phenol, 	1-phenylethanol, 
Na(s), r.t.	*redox*			
NaOH (aq), r.t.	*acid-base*			
Br_2(aq), r.t.	*electrophilic substitution*			
Br_2 in CCl_4, r.t.				
dilute HNO_3, r.t.				
concentrated HNO_3, r.t.				
I_2, aqueous NaOH, heat	*iodoform reaction / oxidation*			

Checkpoint for §5

At the end of this section, you must be able to:

- understand the inverse relationship between the acidity of an acid to the stability of its conjugate base
- explain the relative acidity of phenol > water > alcohol *via* the stability of respective conjugate bases in terms of electronic effects
- compare the acidity of different phenols and alcohols
- describe the reagents and conditions for the following reactions of alcohols:
  - acid-metal reaction with sodium
- describe the reagents and conditions for the following reactions of phenols:
  - neutralisation reaction with bases
  - acid-metal reaction with sodium

6 Identification Test for Alcohols and Phenols

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

6.1 Identification Tests for Aliphatic Alcohols

6.1.1 Nucleophilic Substitution with $PC\ell_5$(s) [§2.3]

Test: Add **anhydrous $PC\ell_5$(s)** to the sample in a test-tube.

Observations: [For **primary**, **secondary**, and **tertiary alcohols**]
White fumes of $HC\ell$(g) will be evolved.

6.1.2 Acid-metal Reaction with Na(s) [§0]

Test: Add a small piece of **Na(s)** to the sample in a test-tube.

Observations: [For **primary**, **secondary**, and **tertiary alcohols** (and **phenols**)]
Effervescence of H_2(g) which gives a ‘pop’ sound with a lighted splint.

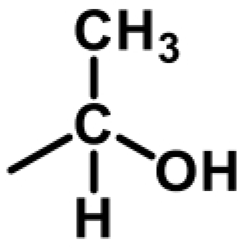
6.1.3 Oxidation with $K_2Cr_2O_7$ or $KMnO_4$ [§2.4.1, §2.4.2, §2.4.3]

Test: Add **$K_2Cr_2O_7$(aq)/$KMnO_4$(aq) and H_2SO_4(aq)** to the sample in a test-tube and **heat** using a hot water bath.

Observations: [For **primary**, and **secondary alcohols**]
orange $K_2Cr_2O_7$(aq) turns **green** / **purple** $KMnO_4$(aq) **decolourises**.
[For **tertiary alcohols**]
$K_2Cr_2O_7$(aq) **remains orange** / $KMnO_4$(aq) **remains purple**.

6.1.4 Tri-iodomethane Test / Iodoform Test [§2.4.4]

Test: Add **I_2(aq) and NaOH(aq)** to the sample in a test-tube and **heat** using a hot water bath.

Observations: [For alcohols with the  group]

Brown I_2 **decolourises**, and
Pale-yellow ppt. of CHI_3 is formed.

Test 6.1.1 (with $PC\ell_5$) and 6.1.2 (with Na) are not specific to alcohols. Carboxylic acids gives similar observations with $PC\ell_5$ and Na, while phenols react with Na as well.

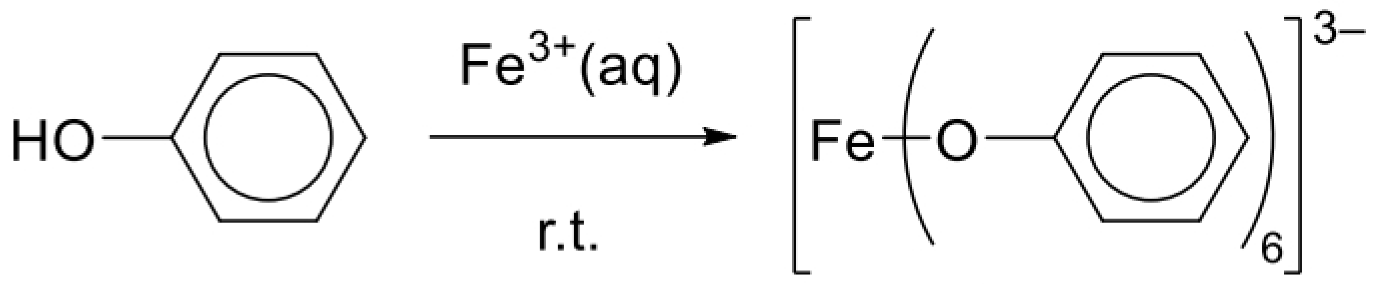
6.2 Identification Tests for Phenols

6.2.1 Electrophilic Substitution by Bromine [§4.3.2]

Test: Add **Br_2(aq)** to the sample in a test-tube at room temperature.
Observations: **Orange** Br_2(aq) **decolourises**, and
White ppt. of 2,4,6-tribromophenol formed upon addition of excess Br_2(aq).

6.2.2 Complex Formation using Neutral Iron(III) Chloride ($FeCl_3$)

Test: Add **neutral $FeCl_3$(aq)** to the sample in a test-tube at room temperature.
Observations: A **violet colouration** will be observed.



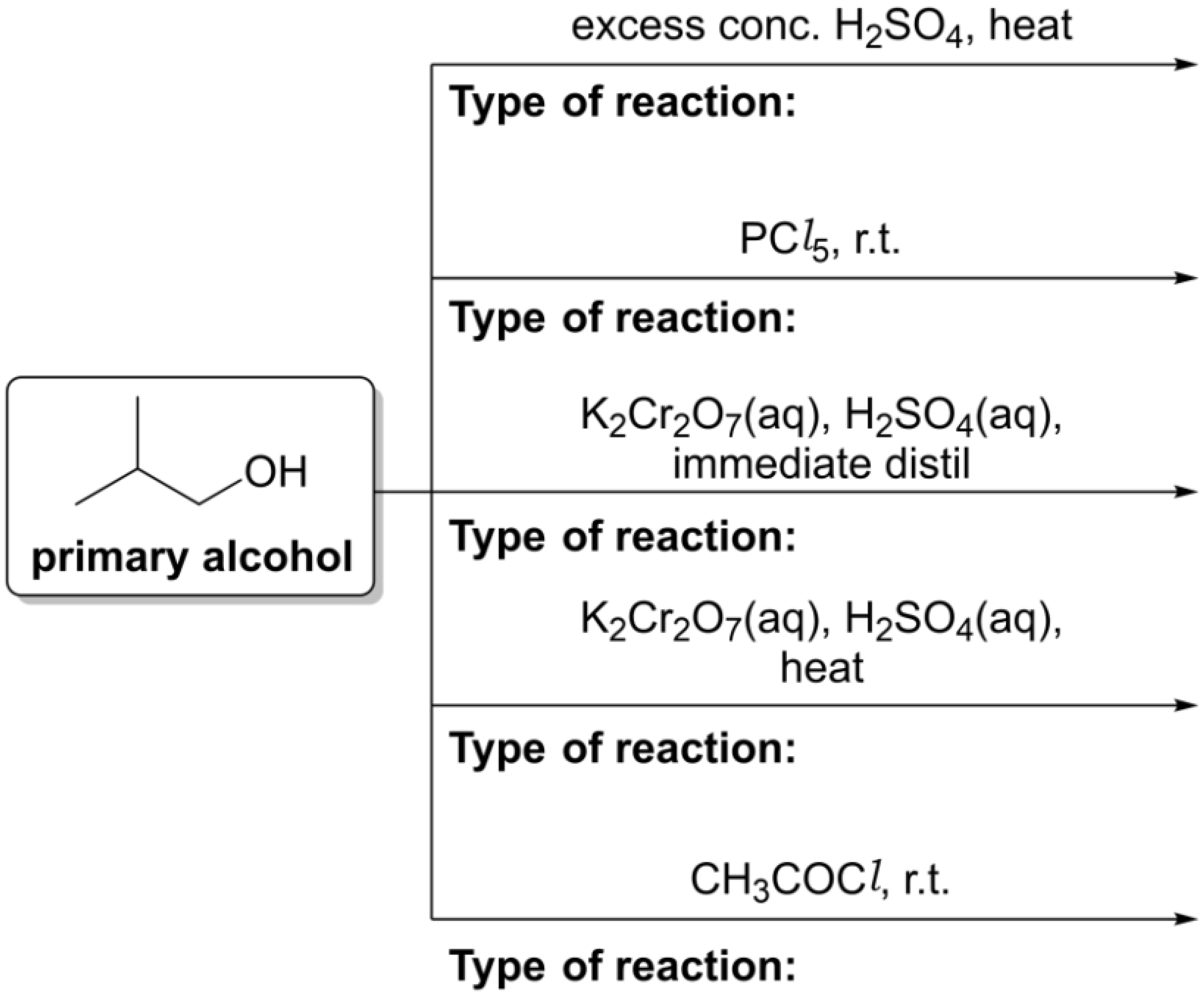
violet complex

Example 6A

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

A alkaline aqueous I_2
B aqueous $NaHCO_3$
C $K_2Cr_2O_7$ in dilute H_2SO_4
D Na

2 Draw the **skeletal formula** of the expected organic product and state the type of reaction involved in each step of the reaction scheme.



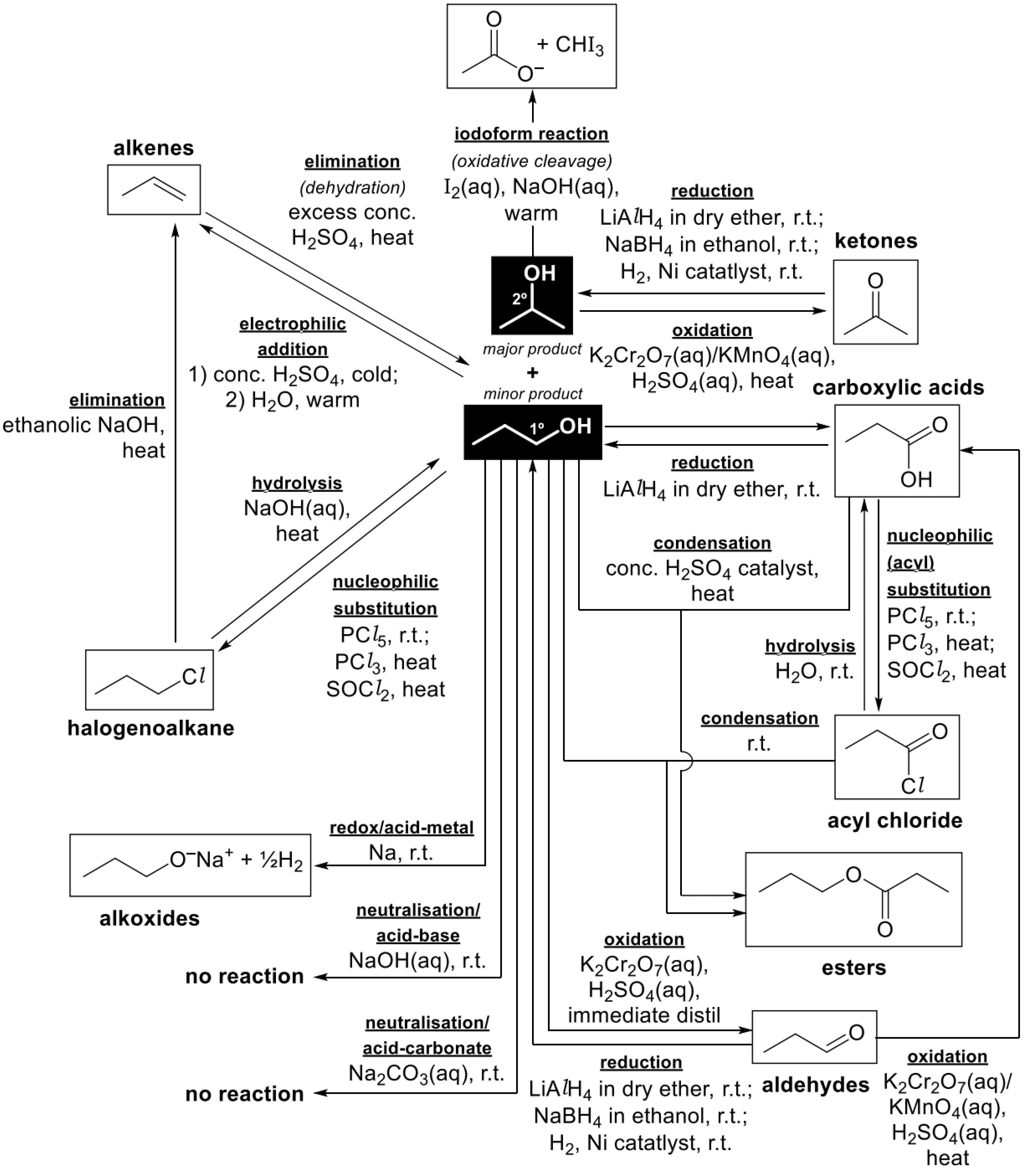
Checkpoint for §6

At the end of this section, you must be able to:

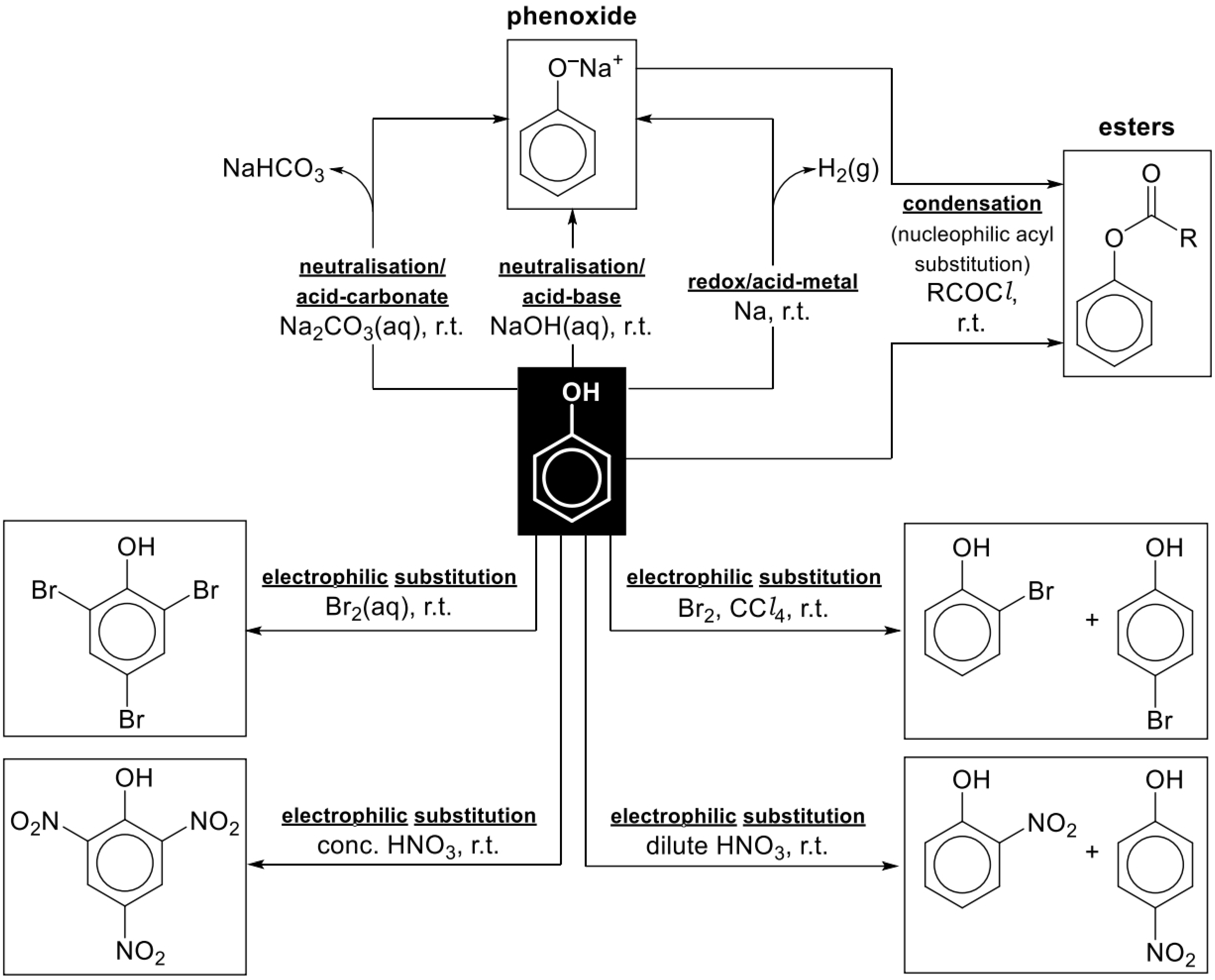
- deduce the presence of a OH– group in an alcohol from its reaction with
  - PCl_5
  - Na
  - $K_2Cr_2O_7$ or $KMnO_4$
- deduce the presence of a $CH_3CH(OH)–$ group in an alcohol from its reaction with alkaline aqueous iodine to form tri-iodomethane
- deduce the presence of a phenol from its reaction with
  - $Br_2(aq)$
  - neutral $FeCl_3$

7 Summary

7.1 Aliphatic Alcohols



7.2 Phenols

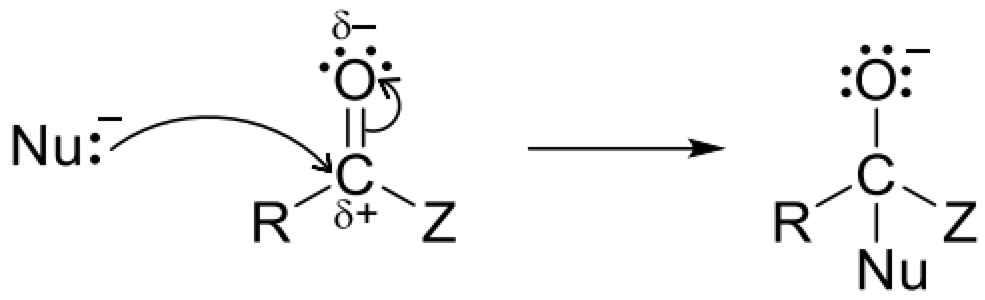

phenoxide
O⁻Na⁺
esters
NaHCO₃
H₂(g)
neutralisation/ acid-carbonate
Na₂CO₃(aq), r.t.
neutralisation/ acid-base
NaOH(aq), r.t.
redox/acid-metal
Na, r.t.
condensation
(nucleophilic acyl substitution)
RCOCl, r.t.
O
R
OH
electrophilic substitution
Br₂(aq), r.t.
Br
electrophilic substitution
Br₂, CCl₄, r.t.
+
electrophilic substitution
conc. HNO₃, r.t.
O₂N
NO₂
electrophilic substitution
dilute HNO₃, r.t.

8 Appendix

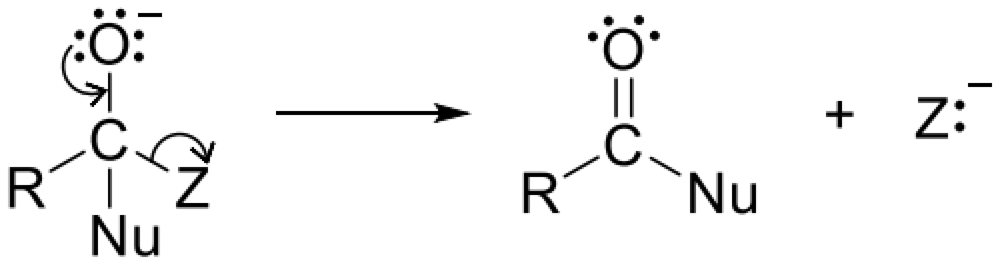
Appendix 1: Nucleophilic Acyl Substitution

Nucleophilic acyl substitution is often termed as an **addition-elimination** reaction as the mechanism involves the addition of the nucleophile first, before the elimination of the leaving group.

Step 1: addition of Nu^- to the δ+ C, the π bond in the C=O bond is broken



Step 2: expulsion of the leaving group, Z^-, with regeneration of the π bond

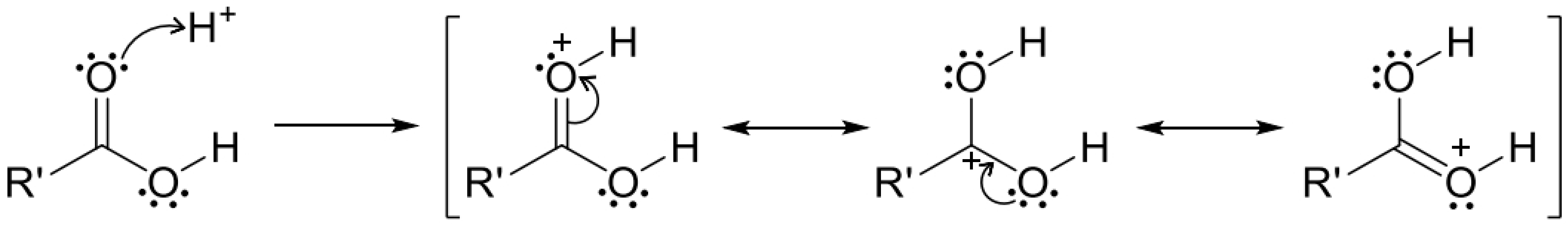


Hence, two factors govern the **ease/rate** of this reaction:

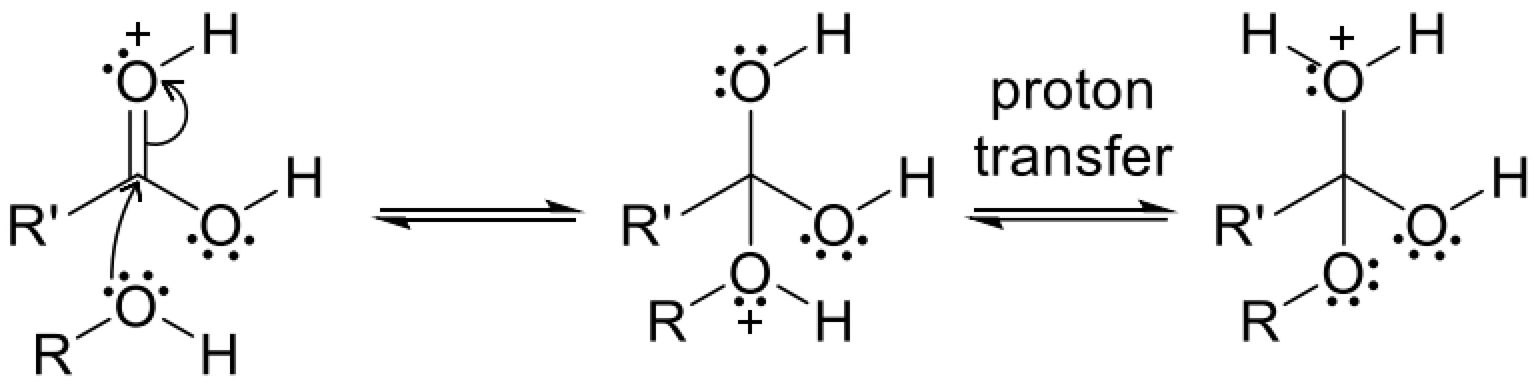
1. the strength of the nucleophile
2. the ease at which the leaving group will be eliminated

The following is the acid-catalysed mechanism for the **esterification of an alcohol**.

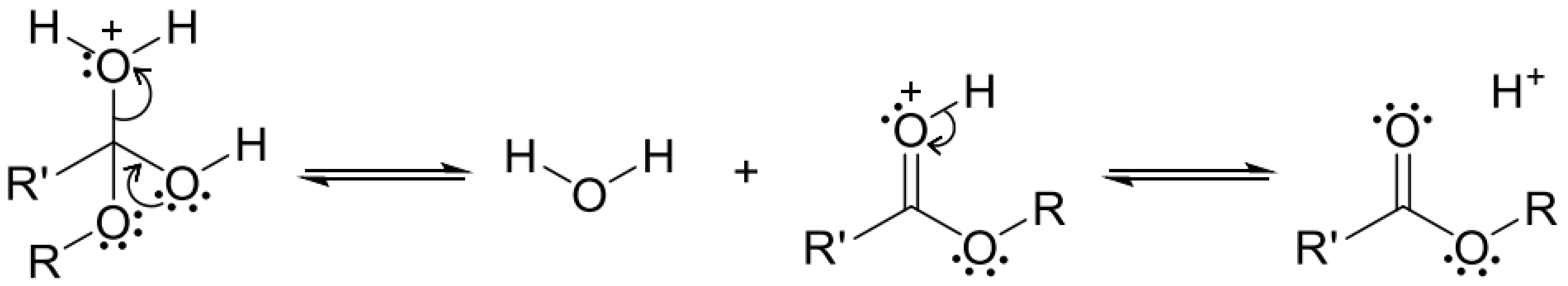
1. Protonation of carboxylic acid by the H_2SO_4 catalyst



2. Attack of alcohol on protonated acid **(Type of reaction: Nucleophilic Addition)**

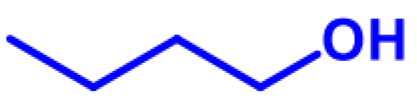


3. Removal of water **(Type of reaction: Elimination)** and deprotonation to give ester and regenerate of H^+ catalyst

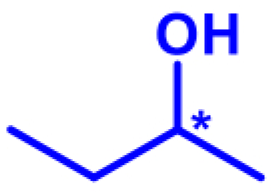


Self-Check Answers

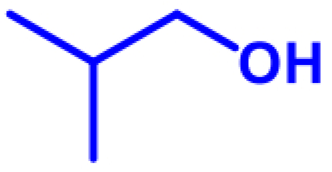
Self-Check 1A



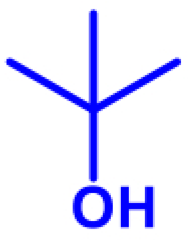
butan-1-ol
(primary)



butan-2-ol
(secondary)



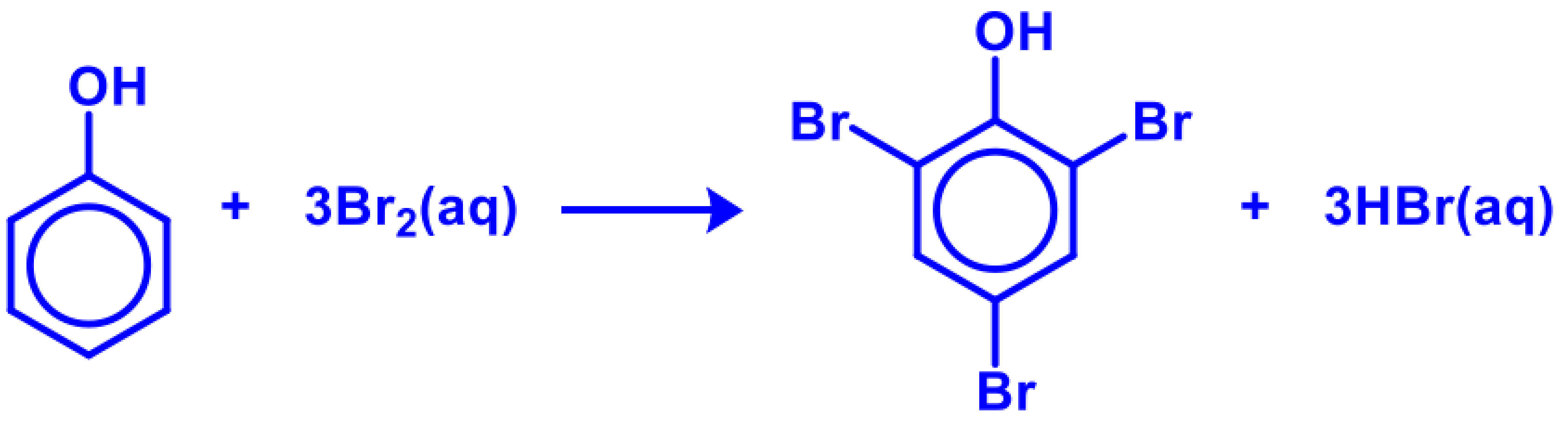
2-methylpropan-1-ol
(primary)



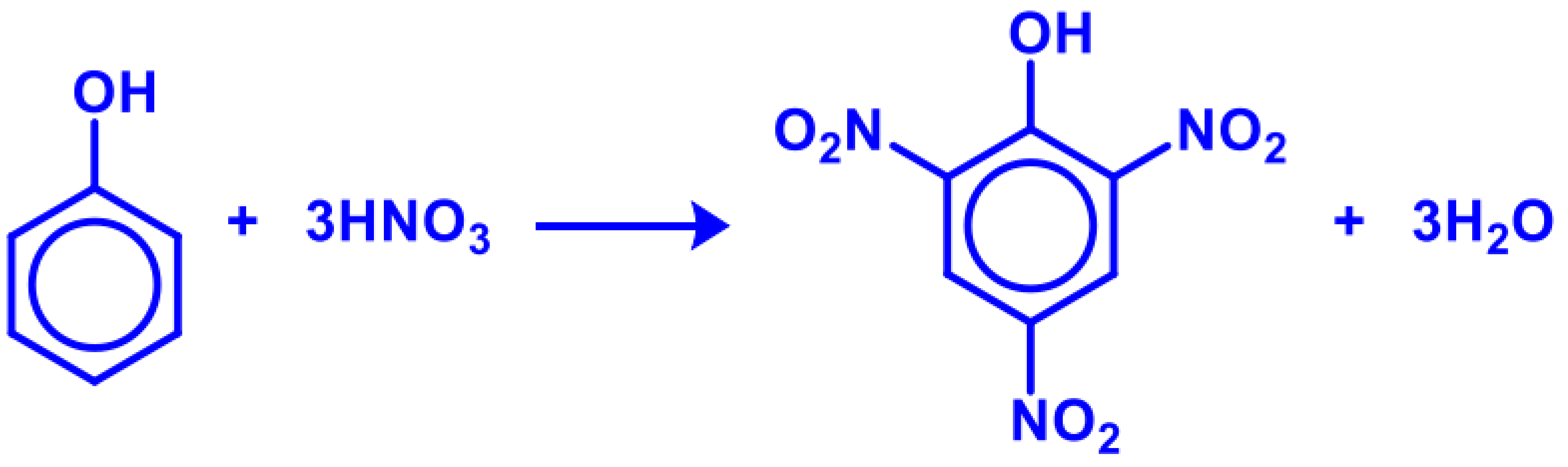
2-methylpropan-2-ol
(tertiary)

Self-Check 4A

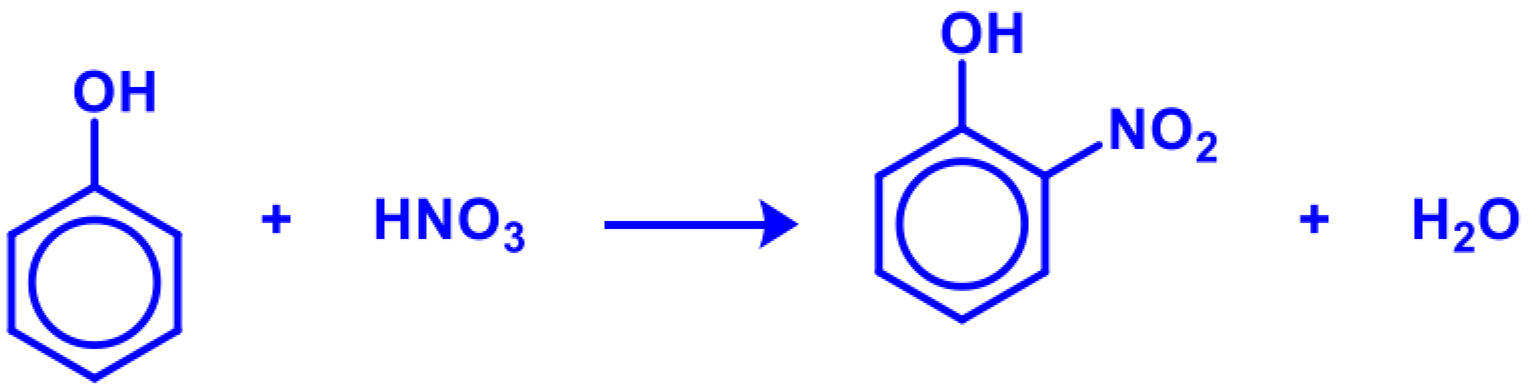
1 (a)



(b)



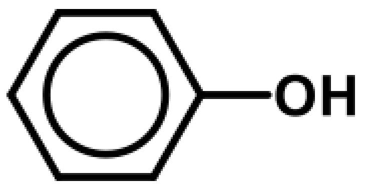
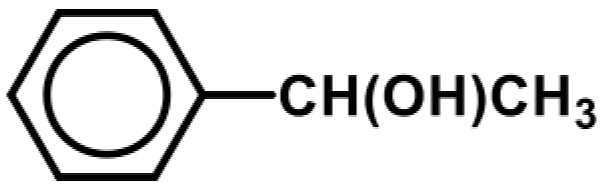
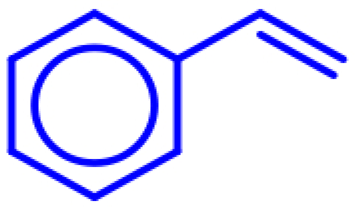
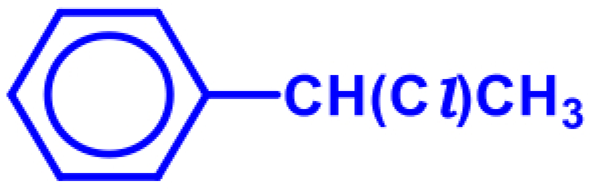
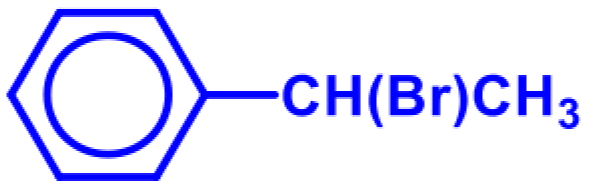
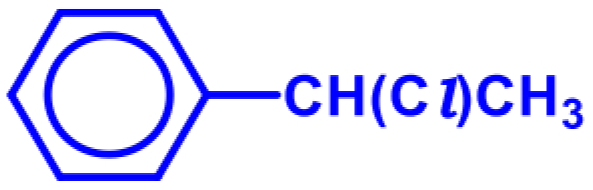
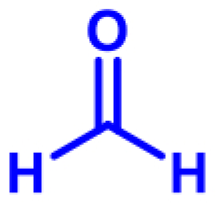
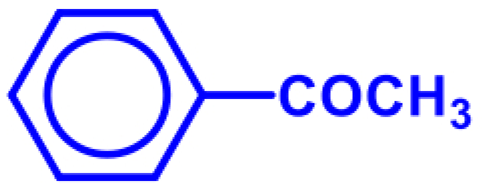
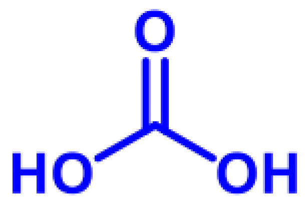
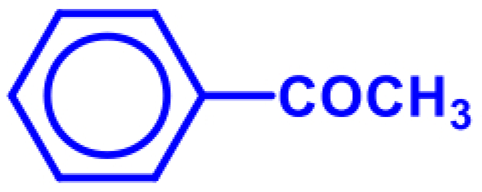
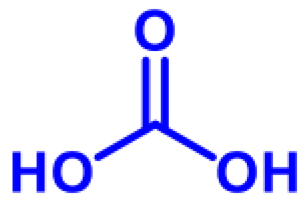
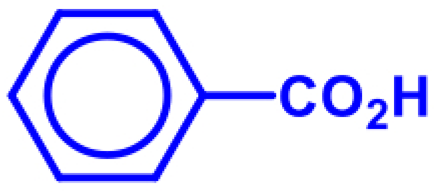
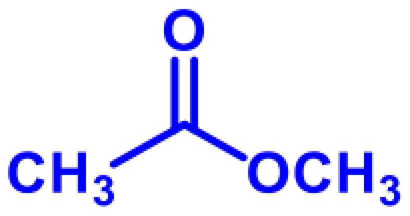
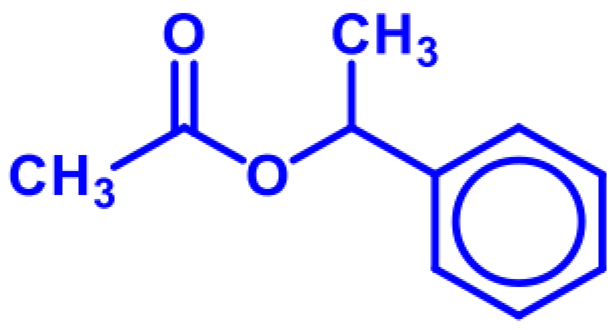
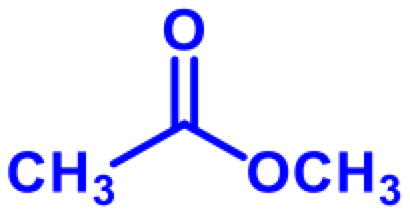
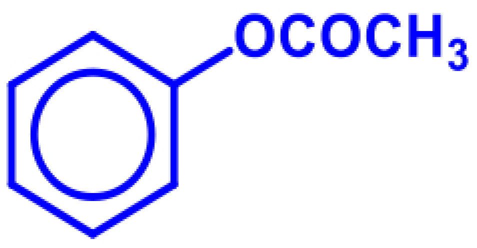
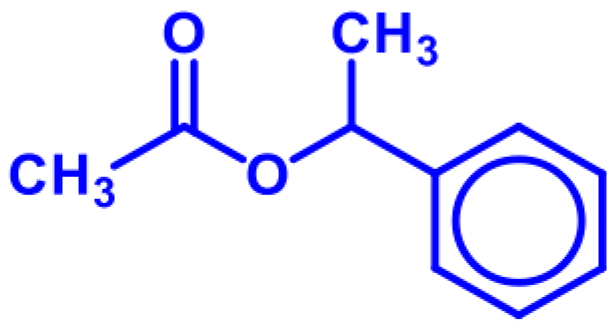
(c)



2 Orange Br_2(aq) is decolourised. White ppt observed.

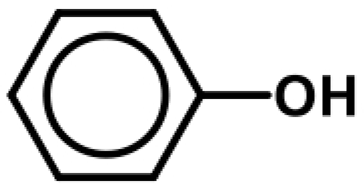
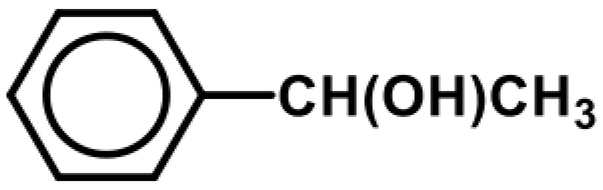
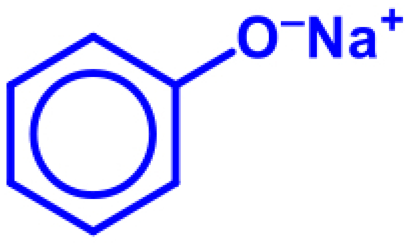
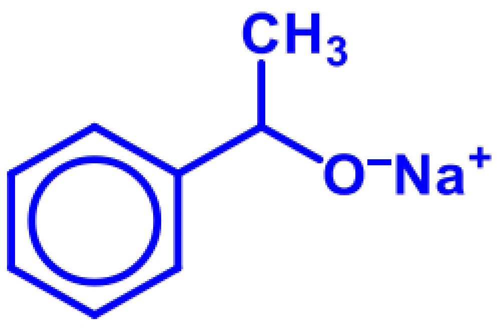
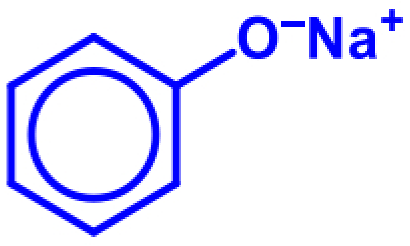
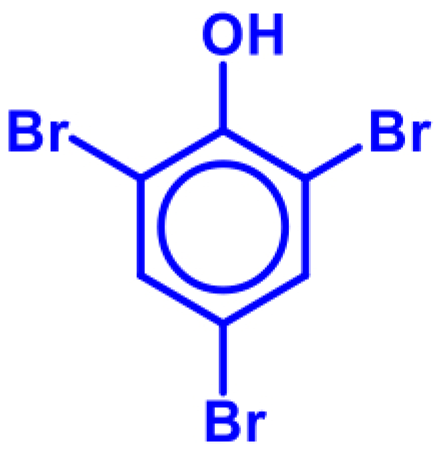
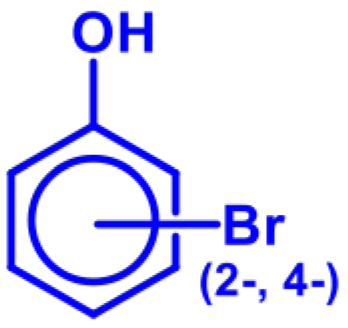
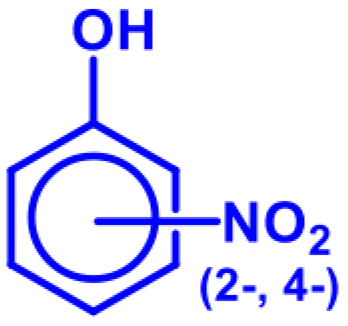
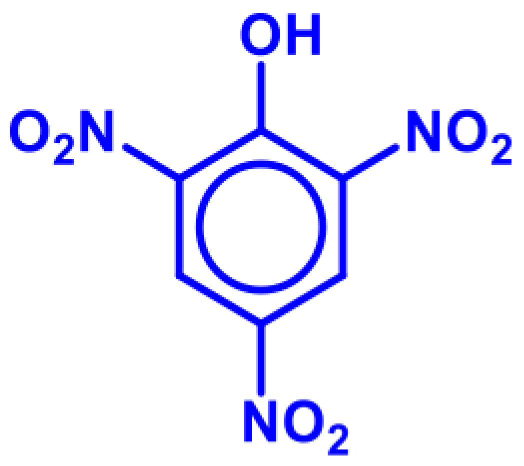
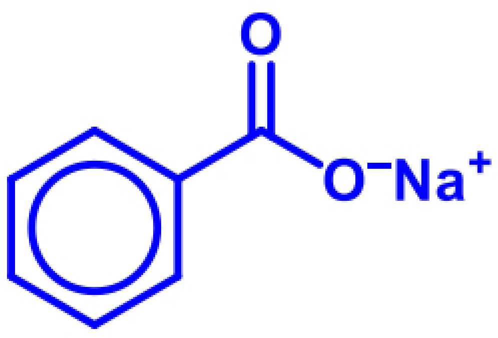
Self-Check 5A

1

reagent and conditions	**type of reaction**	**methanol, CH_3OH**	**phenol,** 	**1-phenylethanol,** 
excess conc. H_2SO_4, heat	*elimination*	**no reaction**	**no reaction**	
PCl_5(s), r.t.	*nucleophilic substitution*	**CH_3Cl**	**no reaction**	
HBr(g), r.t.		**CH_3Br**	**no reaction**	
$SOCl_2$, heat under reflux		**CH_3Cl**	**no reaction**	
$K_2Cr_2O_7$ (aq), H_2SO_4 (aq), distil immediately	*oxidation*		**no reaction**	
$K_2Cr_2O_7$ (aq), H_2SO_4 (aq), heat		 **→ $CO_2 + H_2O$**	**no reaction**	
$KMnO_4$ (aq), H_2SO_4 (aq), heat		 **→ $CO_2 + H_2O$**	**no reaction**	
CH_3COOH, conc. H_2SO_4, heat	*condensation (form ester)*		**no reaction**	
CH_3COCl, r.t.				

Self-Check 5A (cont'd)

1

reagent and conditions	**type of reaction**	**methanol, CH_3OH**	**phenol,**  	**1-phenylethanol,** 
Na(s), r.t.	*redox*	$CH_3O^-Na^+$	 	
NaOH (aq), r.t.	*acid-base*	no reaction	 	no reaction
Br_2(aq), r.t.	*electrophilic substitution*	no reaction	 	no reaction
Br_2 in CCl_4, r.t.		no reaction	 	no reaction
dilute HNO_3, r.t.		no reaction	 	no reaction
concentrated HNO_3, r.t.		no reaction	 	no reaction
I_2, aqueous NaOH, heat	*iodoform reaction / oxidation*	no reaction	no reaction	 CHI_3