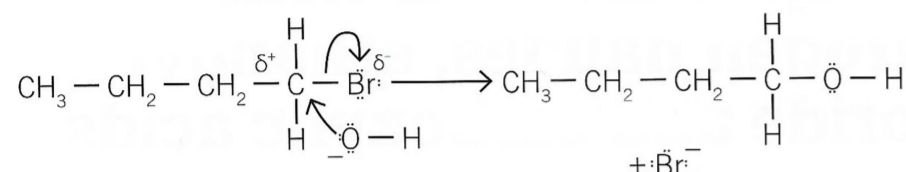


## 4.3 Alcohols and phenols

## Formation of alcohols

## 1. From halogenoalkanes

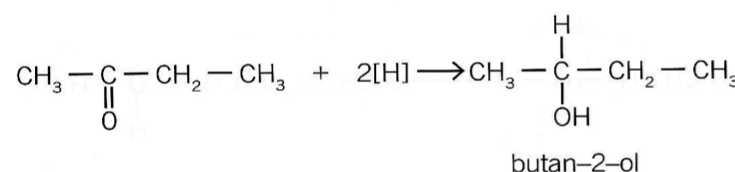
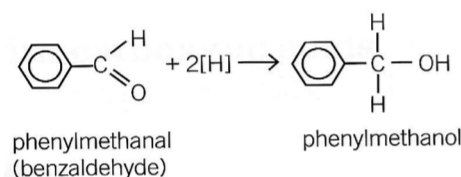
This is a nucleophilic substitution reaction. Reflux halogenoalkane with an aqueous solution of alkali (usually NaOH). For example:



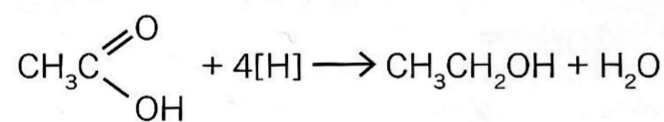
## 2. From carbonyl compounds

This is a reduction reaction. It is the reverse reaction of oxidation of alcohols studied in Unit 2.

Aldehydes and ketones are reduced using  $\text{NaBH}_4$ , sodium tetrahydridoborate(III), dissolved in water. The reducing agent is represented as  $[\text{H}]$  in an equation. Aldehydes produce  $1^\circ$  alcohols and ketones produce  $2^\circ$  alcohols.



$\text{NaBH}_4$  is not powerful enough to reduce carboxylic acids.  $\text{LiAlH}_4$ , lithium tetrahydridoaluminate(III), dissolved in ethoxyethane, a stronger reducing agent, is used instead.



Reduction using  $\text{NaBH}_4$  is safer due to the nature of the reducing agent and its solvent.

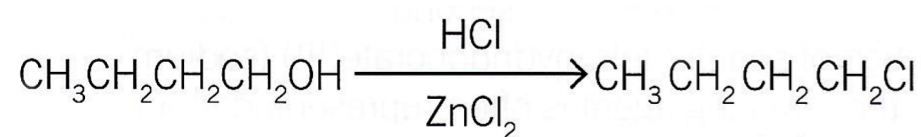
## Reactions of alcohols

## 1. With hydrogen halides

Slow and reversible reactions with poor yields.

The method depends on the halogen.

To produce a **chloroalkane**, pass HCl gas through alcohol with dry  $\text{ZnCl}_2$  as a catalyst.



Chloroalkanes can also be produced using phosphorus pentachloride,  $\text{PCl}_5$ . Phosphorus(V) oxide trichloride,  $\text{POCl}_3$ , and hydrogen chloride also form in the reaction. Separation can be difficult if the halogenoalkane produced has a similar boiling temperature to  $\text{POCl}_3$ .

Another method is to use sulfur(VI) oxide dichloride,  $\text{SOCl}_2$ . The co-products,  $\text{SO}_2$  and  $\text{HCl}$  are gaseous, so are easily lost from the reaction mixture.

To produce a **bromoalkene**, carry out an 'in situ' reaction. Heat a mixture of the alcohol,  $\text{KBr}$  and 50%  $\text{H}_2\text{SO}_4$ .

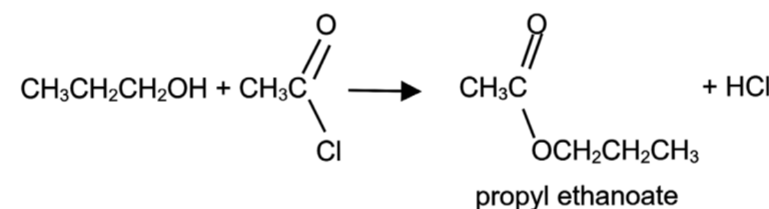


To produce an **iodoalkane**, use warm damp red phosphorus and iodine which forms phosphorus(III) iodide,  $\text{PI}_3$ .

## 2. With ethanoyl chloride

An alcohol reacts rapidly with ethanoyl chloride,  $\text{CH}_3\text{COCl}$ , forming an **ester**, and misty fumes of  $\text{HCl}$  are given off.

This method gives a better yield of ester than by using carboxylic acid as it's not a reversible reaction. However, it is not cost effective in industry, as acid chlorides are expensive.

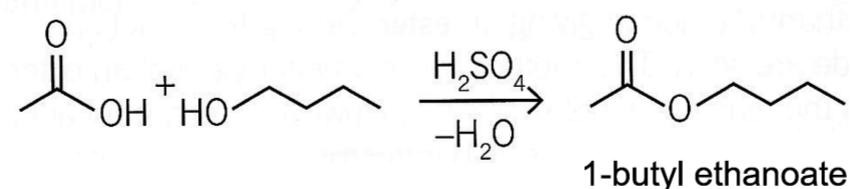


## 3. With carboxylic acids

The reactants are refluxed together with a concentrated  $\text{H}_2\text{SO}_4$  catalyst. The products are distilled, and the ester collected at its boiling temperature.

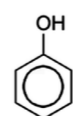
The immiscible ester layer is removed using a separating funnel and  $\text{NaHCO}_3$  (aq) is added to neutralise any remaining carboxylic acid.

The ester is dried with anhydrous  $\text{CaCl}_2$ , which reacts with any remaining alcohol. The ester can then be redistilled to give a pure product.

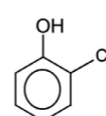


## Naming phenols

Phenol is an aromatic compound with an  $-\text{OH}$  group bonded directly to a benzene ring. If other groups are bonded to the benzene ring, the compound is named according to the position of the substituted group, with the phenol group bonded to carbon 1



phenol

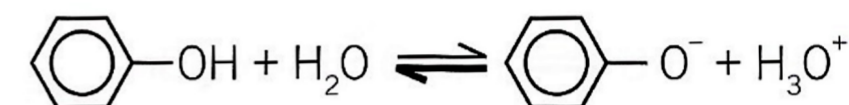


2-chlorophenol

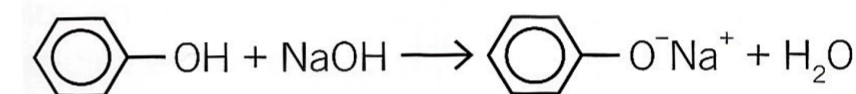
## Acidity of phenol

Phenol is weakly acidic. It is more acidic than alcohols but less than carboxylic acids.

In phenol a lone pair on the oxygen atom overlaps with the  $\pi$  electron system of the ring. This makes the  $\text{C}-\text{O}$  bond stronger than in an alcohol and causes the  $\text{H}^+$  ion to be lost more easily, forming the phenoxide ion,  $\text{C}_6\text{H}_5\text{O}^-$ .



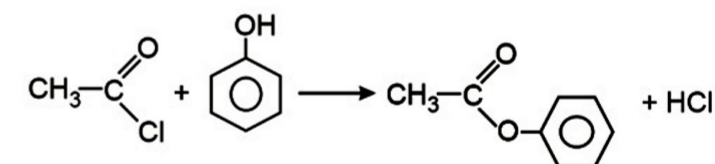
The phenoxide ion is more stable than expected due to the delocalisation of the negative charge on this ion. Phenol is not soluble in water because of the large hydrocarbon part of the molecule. It will dissolve readily in sodium hydroxide, however, as the  $\text{H}^+$  ion reacts with the  $\text{OH}^-$  from the hydroxide. This shows its acidic properties.



A test to distinguish between a carboxylic acid and a phenol is to add sodium carbonate solution. Carboxylic acids will react to produce bubbles of  $\text{CO}_2$ , but phenols won't as they are not acidic enough.

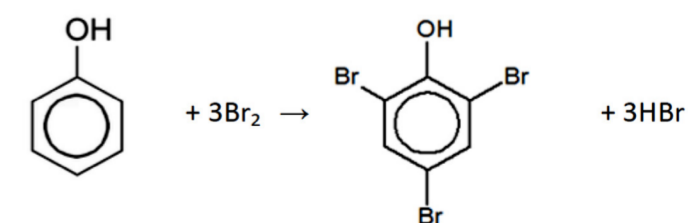
## Reaction of phenol with ethanoyl chloride

Phenols will not react with carboxylic acids to make esters, but they will react with ethanoyl chloride to form esters such as phenyl ethanoate. It is, however, a slow reaction at room temperature.



## Reaction of phenol with bromine

Phenol reacts with bromine water to produce a white precipitate of 2,4,6-tribromophenol and the orange bromine water is decolourised.



## Test for phenol

Aqueous iron(III) chloride (pale yellow) added to phenol will give a purple colour.

In fact, any compound that has an  $-\text{OH}$  group bonded directly to a benzene ring will give a positive test with iron(III) chloride.