Practical 5.13 The reactions of the phenolic functional group

There is a microscale alternative to this experiment – Practical MS5.13

Purpose

To carry out the reaction of a phenol with bromine water and dilute nitric acid and use these results to illustrate the activation of the benzene ring [5.4.1e]

Safety

Wear eye protection. Full-range indicator is flammable. Ethanol is highly flammable and harmful. 2 M ethanoic acid is an irritant. Metallic sodium is corrosive and highly flammable. 2 M sodium hydroxide is corrosive. Concentrated hydrochloric acid is corrosive. Ethanoic anhydride is corrosive and must be used in a fume cupboard wearing protective gloves; it causes severe burns and severely irritates all tissues. 0.05 M bromine solution is harmful. 2 M nitric acid is corrosive. Phenol is corrosive and toxic, wear gloves when using phenol. Methyl 4-hydroxybenzoate is an irritant.

Each group of students will need:

Eye protection
Gloves (nitrile)
Test tubes and rack
Combustion spoon, or equivalent
Dropping pipettes

Access to:

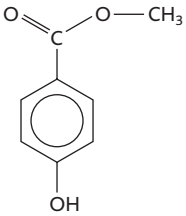
0.05 M bromine water, 5 cm^3 HARMFUL, IRRITANT
(bromine water VERY TOXIC, CORROSIVE)
2 M ethanoic acid, 2 cm^3 IRRITANT
Ethanoic anhydride, 1 cm^3 CORROSIVE, HARMFUL
Ethanol, 2 cm^3 HIGHLY FLAMMABLE, HARMFUL
Full-range indicator
Phenol CORROSIVE, TOXIC
Methyl 4-hydroxybenzoate IRRITANT
1 M nitric acid, 5 cm^3 CORROSIVE
1 M hydrochloric acid IRRITANT
Sodium, a small cube (2–3 mm side) CORROSIVE, HIGHLY FLAMMABLE
1 M sodium carbonate, 5 cm^3
2 M sodium hydroxide, 10 cm^3 CORROSIVE

Background

In these experiments, your objective is to find out how the properties of the —OH group are modified by being attached to a benzene ring. You will see some of the characteristic features of the chemistry of phenol or phenolic compounds.

Because of the toxic and corrosive nature of many phenols, methyl 4-hydroxybenzoate can be used as an example of a phenolic compound.

phenol



methyl 4-hydroxybenzoate

Method

1 Solubility in water

Put about 5 cm^3 of water in a test tube, and add a small quantity of phenol or methyl 4-hydroxybenzoate. Heat to boiling and allow to cool slowly. Test the final solution with full-range indicator.

a Describe your observations.

Edexcel practical materials adapted from Nuffield Advanced Chemistry materials

Practical 5.13 (cont.) The reactions of the phenolic functional group

b Compare your results with the effects that an ethanol–water and an ethanoic acid–water mixture have on full-range indicator.

2 Phenolic compounds as acids

A Reaction with sodium

Put a small amount of phenol or methyl 4-hydroxybenzoate in a *dry* test tube and warm until molten. Add a small cube (2–3 mm side) of sodium (take care: wear eye protection) and watch carefully. *Do not heat the tube continuously*. Dispose of the contents with care – do *not* pour down the sink in case some sodium remains: carefully add 1–2 cm^3 of ethanol to the *cool* test tube, wait until all bubbling has ceased, and then pour away.

c Describe your observations.

d What bond has been broken in your phenolic compound, a C—H bond, a C—O bond or an O—H bond?

e Compare your results with those that would be obtained if ethanol was used instead of your phenolic compound.

B Reaction with sodium hydroxide

Put about 5 cm^3 of 2 M sodium hydroxide solution in a test tube, and add a small amount of phenol or methyl 4-hydroxybenzoate and warm. Now add about 2 cm^3 of concentrated hydrochloric acid.

f Describe your observations.

g Compare the solubility of your phenolic compound in alkali with its solubility in water.

h Compare this reaction with that of ethanoic acid with sodium hydroxide.

Practical 5.13 (cont.) The reactions of the phenolic functional group

C Reaction with sodium carbonate

Put about 5 cm^3 of 1 M sodium carbonate solution in a test tube, and add a small amount of phenol or methyl 4-hydroxybenzoate.

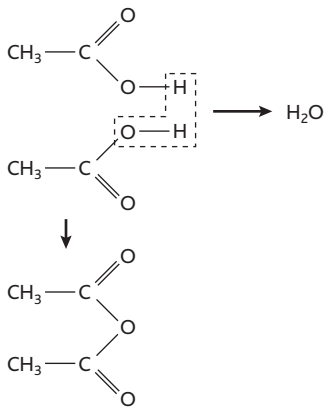
i Describe your observations.

j Does this suggest that phenol or your phenolic compound is a strong or a weak acid?

3 Reaction with an organic acid

Organic acids react with alcohols to make compounds known as *esters*, which you will study later. Organic acids also react with phenol, but the rate of the reaction is extremely slow. So in this experiment you will use ethanoic anhydride, which is more reactive and forms the same product. One molecule of ethanoic anhydride, $(CH_3CO)_2O$, is formed from two molecules of ethanoic acid, CH_3COOH, by the loss of a water molecule.

2 molecules of ethanoic acid:



1 molecule of ethanoic anhydride

The reaction between inorganic acids and bases (hydroxides), which are ionic and water soluble …

acid + base → salt + water

… is comparable to the reaction between organic acids and alcohols, which are covalent and mostly insoluble in water:

acid + alcohol → ester + water

Put about 0.5 g of phenol or methyl 4-hydroxybenzoate in a test tube, and, in a fume cupboard, add 4 cm^3 of 2 M sodium hydroxide to dissolve the phenolic compound. Add 1 cm^3 of ethanoic anhydride, cork the test tube, and shake it for a few minutes. An emulsion of the product should form – cool in an ice bath to obtain the crystalline product.

Practical 5.13 (cont.) The reactions of the phenolic functional group

4 Properties of the benzene ring

A Reaction on combustion

Set fire to a small amount of phenol or methyl 4-hydroxybenzoate on a combustion spoon.

k What sort of flame do you see?

_____

l Is a similar flame obtained when ethanol and ethanoic acid are burnt?

_____

m Compare these results with your results for the combustion of alkanes and arenes. Does the presence of a hydroxyl group alter the result?

_____

_____

B Reaction with bromine

Shake a small amount of phenol or methyl 4-hydroxybenzoate with 5 cm^3 of water and add bromine water.

n How readily does a reaction occur?

_____

C Reaction with nitric acid

To a small amount (0.04 g) of phenol or methyl 4-hydroxybenzoate add 4 cm^3 of 2 M nitric acid. Heat to boiling, allow to cool, then chill rapidly in an ice bath.

o How readily do coloured products appear?

_____

p Compare the conditions you have used with those normally required for the bromination and nitration of an arene ring.

_____

_____

q What type of reactions are these?

_____

The product from **4C** can be examined by chromatography in 1 : 1 hexane/ethoxyethane (hexane is highly flammable and harmful, ethoxyethane is extremely flammable) on a silica thin layer; view the result in ultraviolet light. Make a Risk Assessment if you attempt this experiment.