Edexcel

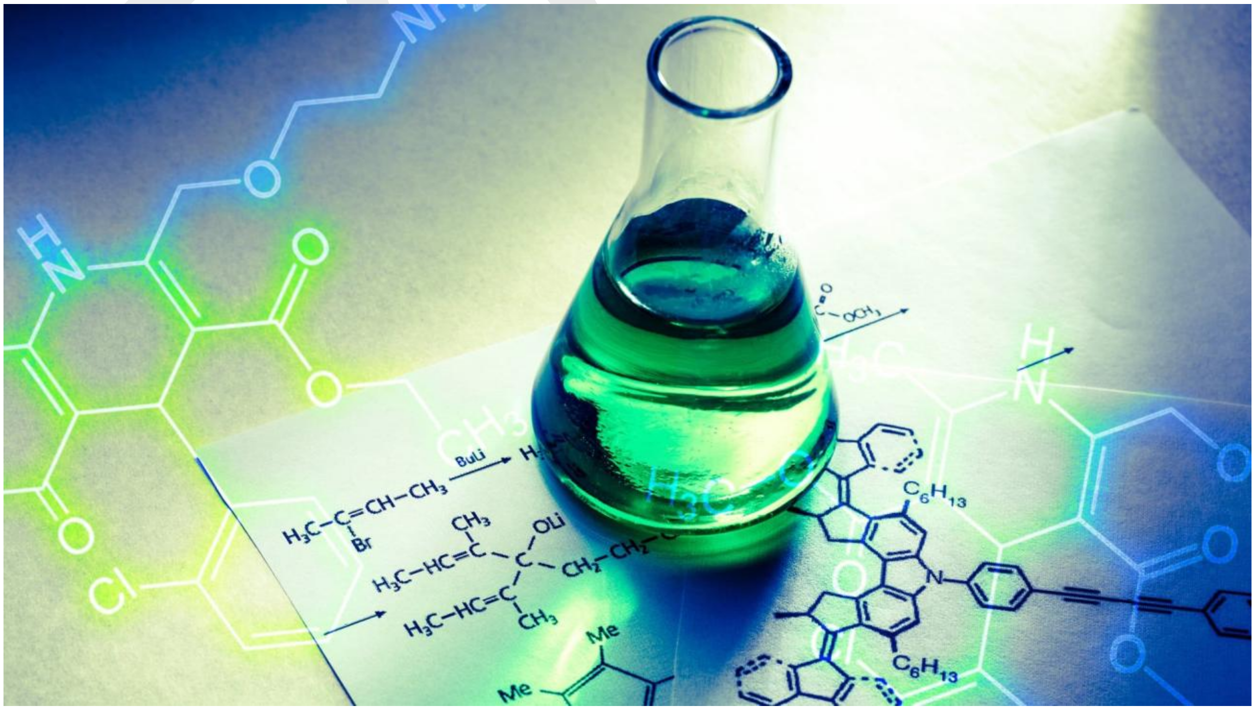
A - Level

Chemistry

CODE: (WCH11)

Topic 18

Organic chemistry – Arenes



18A 1 Benzene: Module with two models

WHAT ARE AROMATIC COMPOUNDS?

The sections in Topic 18 deal with compounds containing a benzene ring. You have already seen benzene rings in previous sections. However, no detail was given about them.

▲ **fig A** Many brightly coloured dyes are made from aromatic compounds.

ORIGIN OF THE TERM

The word 'aromatic' in everyday language refers to smells, usually pleasant. Some herbs used in cooking are often described as aromatic.

ALIPHATIC AND AROMATIC

With a few exceptions, almost all the organic compounds you have seen so far in this course could have been described as 'aliphatic', although this is a term we did not use to describe them because there was no point. You can regard aliphatic compounds as all those that are not aromatic!

BENZENE

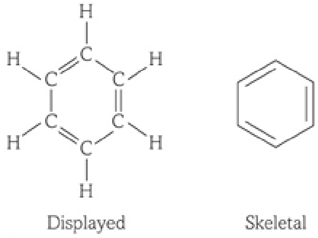
The compound benzene is at the heart of every aromatic compound. So, the first thing we must do is understand what is special about benzene. Benzene can be described as an arene, as can many of its derivatives. You already know that -ene indicates the presence of a C=C double bond in a molecule (as in ethene). Therefore, you would expect that an arene also contains C=C double bonds. The answer is - yes and no.

PHYSICAL PROPERTIES OF BENZENE

Benzene, a colorless liquid with a boiling temperature of 80°C, is present in crude oil and fuels, including petrol tanks. It was first isolated by Michael Faraday in 1825 and its molecular formula is C_6H_6, indicating it is highly unsaturated. Finding a structural formula was challenging due to its chemical reactions.

THE KEKULÉ STRUCTURE

One of the better-known stories in the history of chemistry is how the German chemist Friedrich August Kekulé came to suggest the structure of benzene that still bears his name. The story goes like this... Kekulé was sleeping in an armchair in front of a fire. In the flames he imagined some snake-like molecules dancing, one of which held its own tail and whirled around in the flames. Inspired by this dream about snakes, in 1865 he proposed a cyclic or ring structure for benzene. Fig B shows the displayed and skeletal forms of this structure.



▲ **fig B** Kekulé structure of benzene.

PROBLEMS WITH THE KEKULÉ STRUCTURE

We still use the original skeletal structure to represent benzene today. However, since it was first used, there has been mounting experimental evidence that does not fit with the structure. Several problems arose in the 19th century, although more became apparent in the 20th century.

PROBLEM 1

If benzene contains three C=C double bonds, it should readily decolourise bromine water in an addition reaction. However, it does not decolourise bromine water. When bromine does react with benzene, a substitution reaction occurs (see Section 18A.2). This evidence suggests that there are no C=C double bonds. Fig C shows the results of shaking bromine water with a liquid alkane, benzene and a liquid alkene in separate test tubes.

fig C The yellow colour is caused by unreacted bromine.

PROBLEM 2

As more compounds containing the benzene ring were discovered, including those such as dibromobenzene ($C4H_4Br_2$), another
problem arose. If the Kekulé structure is correct, there should be four isomers with this molecular formula:

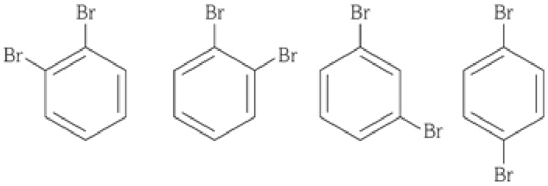
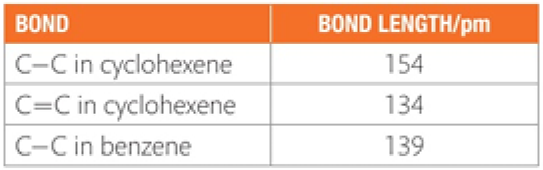


fig D These are the four isomers of $C_6H_4Br_2$, assuming that the Kekulé structure is correct.

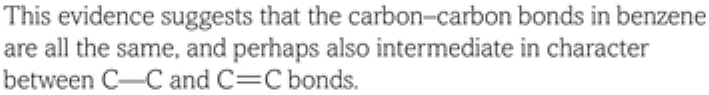
PROBLEM 3

When data from X-ray diffraction about the lengths of covalent bonds in molecules became available, there was another problem. Table A shows the bond lengths in benzene and cyclohexene (a cyclic alkene with five C-C single bonds and one C=C double bond) in picometres.



BOND	BOND LENGTH/pm
C–C in cyclohexene	154
C=C in cyclohexene	134
C–C in benzene	139

table A



This evidence suggests that the carbon–carbon bonds in benzene are all the same, and perhaps also intermediate in character between C—C and C=C bonds.

PROBLEM 4

When thermochemical data about enthalpy changes of hydrogenation became available, there was yet another problem. Table B shows these enthalpy changes for three relevant compounds.

COMPOUND	ENTHALPY CHANGE OF HYDROGENATION/kJ mol^{-1}
cyclohexene	−120
cyclohexa-1,4-diene	−239
cyclohexa-1,3,5-triene (theoretical)	−360
benzene (actual)	−208

table B

All of these hydrogenation reactions form the cyclic alkane cyclohexane. This evidence suggests the following.

- The first two values indicate that the enthalpy change for adding 1 mol of H_2 to 1 mol of C=C bonds is around −120 kJ mol^{-1} (the value for cyclohexa-1,4-diene is double that of cyclohexene because there are twice as many C=C bonds).
- The Kekulé structure could be named cyclohexa-1,3,5-triene, for which the value should be treble that of cyclohexene.
- The actual benzene has a value very much lower (152 kJ mol^{-1} lower) than a theoretical structure with three C=C double bonds would have.

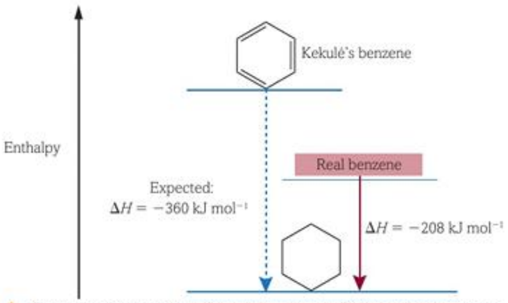


fig E This diagram shows the enthalpy changes for Kekulé's benzene and real benzene.

PROBLEM 5

Fig F shows a comparison of the infrared spectra of cyclohexene and benzene.

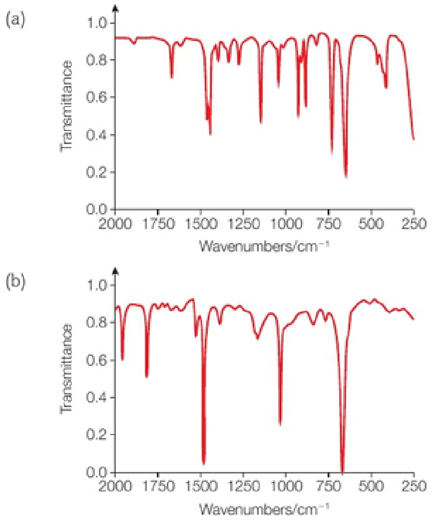


fig F Comparison of the infrared spectra of (a) cyclohexene and (b) benzene.

A NEW MEANING OF 'AROMATIC'

Now we can use the old word 'aromatic' in a new way - it refers to a hydrocarbon ring containing delocalised electrons. The traditional skeletal formula for benzene can now be replaced by this:

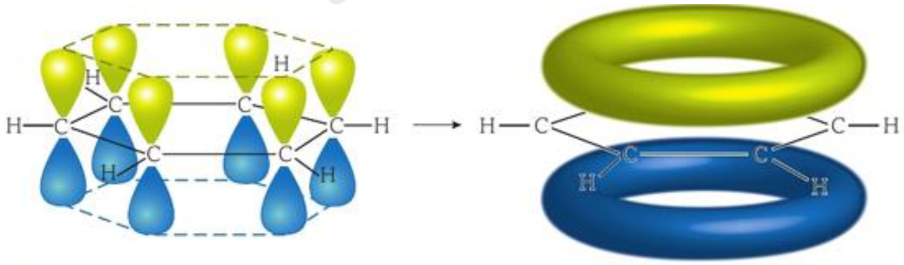
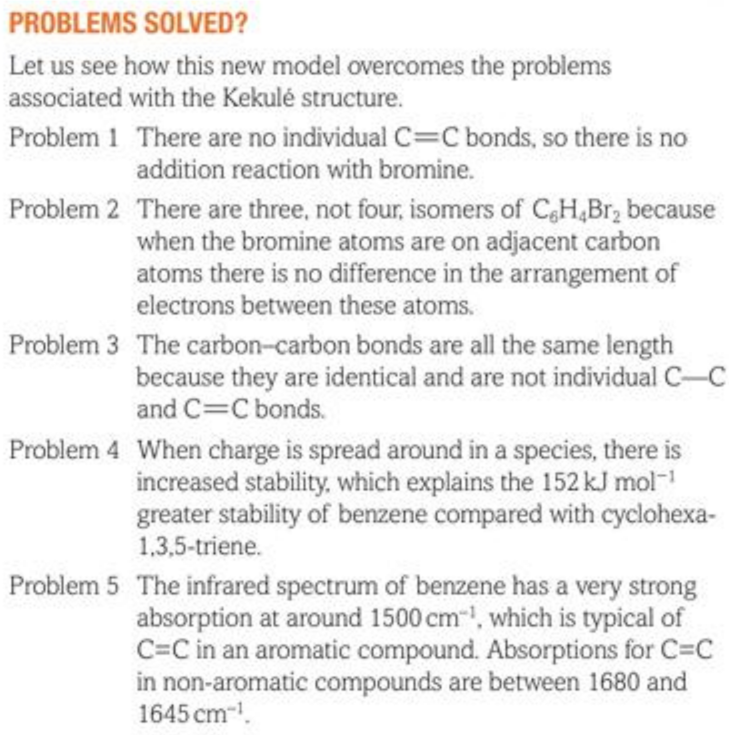


fig G The delocalised structure of benzene forms when the p-orbitals overlap sideways forming a π-electron cloud above and below the plane of the carbon atoms. Each carbon atom contributes one electron to the cloud, giving a delocalised system of six electrons in total.



PROBLEMS SOLVED?

Let us see how this new model overcomes the problems associated with the Kekulé structure.

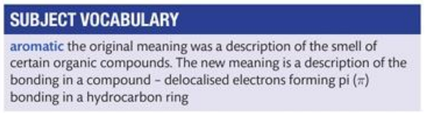
Problem 1 There are no individual $C{=}C$ bonds, so there is no addition reaction with bromine.

Problem 2 There are three, not four, isomers of $C_6H_4Br_2$ because when the bromine atoms are on adjacent carbon atoms there is no difference in the arrangement of electrons between these atoms.

Problem 3 The carbon–carbon bonds are all the same length because they are identical and are not individual $C{-}C$ and $C{=}C$ bonds.

Problem 4 When charge is spread around in a species, there is increased stability, which explains the 152 kJ mol^{-1} greater stability of benzene compared with cyclohexa-1,3,5-triene.

Problem 5 The infrared spectrum of benzene has a very strong absorption at around 1500 cm^{-1}, which is typical of $C{=}C$ in an aromatic compound. Absorptions for $C{=}C$ in non-aromatic compounds are between 1680 and 1645 cm^{-1}.



SUBJECT VOCABULARY

aromatic the original meaning was a description of the smell of certain organic compounds. The new meaning is a description of the bonding in a compound – delocalised electrons forming pi (π) bonding in a hydrocarbon ring

A NEW MEANING OF 'AROMATIC'

Now we can use the old word 'aromatic' in a new way - it refers to a hydrocarbon ring containing delocalised electrons. The traditional skeletal formula for benzene can now be replaced by this:

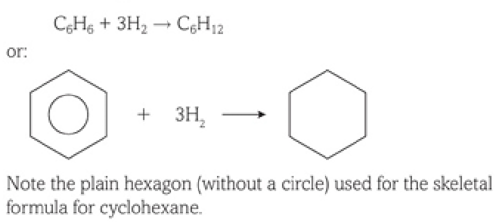
18A 2 Some reactions of benzene

REACTIONS AS A HYDROCARBON

In Section 18A.1, hydrogenation was mentioned. This reaction occurs in the same way with benzene as with alkenes. The same is true for combustion.

HYDROGENATION

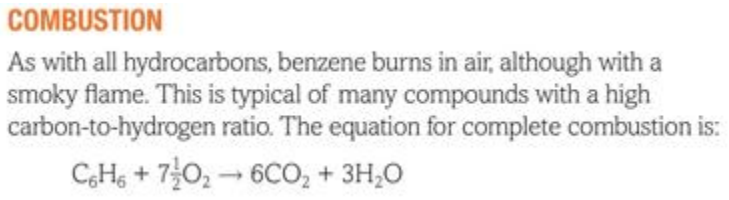
This is done by mixing benzene with hydrogen and heating under pressure with a nickel catalyst. The equation for the reaction can be shown using molecular or skeletal formulae:



$C_6H_6 + 3H_2 \rightarrow C_6H_{12}$

or:

Note the plain hexagon (without a circle) used for the skeletal formula for cyclohexane.



COMBUSTION

As with all hydrocarbons, benzene burns in air, although with a smoky flame. This is typical of many compounds with a high carbon-to-hydrogen ratio. The equation for complete combustion is:

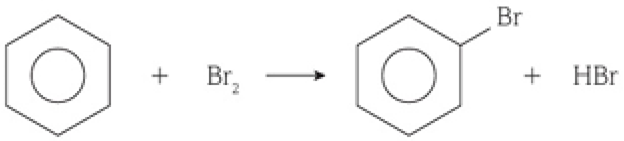
$$C_6H_6 + 7\tfrac{1}{2}O_2 \rightarrow 6CO_2 + 3H_2O$$

REACTIONS AS AN ARENE

The most important reactions of benzene are substitution reactions, in which the products are also aromatic. We will consider the mechanisms of these reactions in the next section (Section 18A.3).

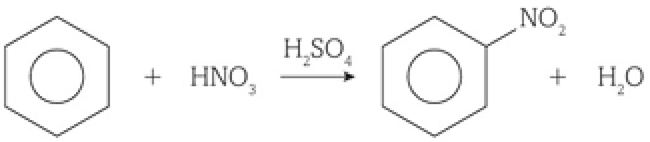
BROMINATION

Benzene and bromine are heated under reflux, in the presence of a catalyst called a **halogen carrier**. Halogen carriers are usually metal-halogen compounds such as aluminium chloride, aluminium bromide or iron(III) bromide. For bromination, it is enough to add iron filings because they react with some of the bromine to form iron(III) bromide. The products are bromobenzene and hydrogen bromide. The equation for the reaction is:



NITRATION

This refers to the replacement of a hydrogen atom by a nitro group. The nitro group has the formula NO_2 and should not be confused with the gas nitrogen dioxide. The reaction is carried out by warming benzene with a mixture of concentrated nitric and sulfuric acids. The nitric acid can be considered as the source of the NO_2 group and the sulfuric acid as a catalyst. The products are nitrobenzene and water. The equation for the reaction is:



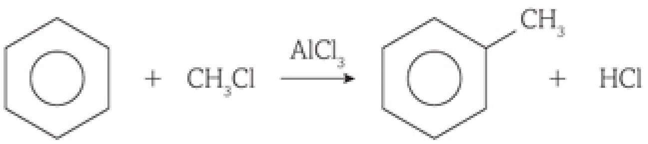
FRIEDEL-CRAFTS REACTIONS

Reactions with this name were developed by Charles Friedel (a French chemist) and James Crafts (an American chemist). There are several types of reaction bearing their names, but we will consider only two of them: alkylation and acylation. They both have these features in common:

- using a reagent represented by XY, one of the hydrogen atoms in benzene is substituted by Y, and the other product is HX
- a catalyst is needed - often aluminium chloride, although other halogen carriers such as iron(III) chloride and iron(III) bromide also work
- anhydrous conditions are needed because water would react with the catalyst and sometimes also with the organic product.

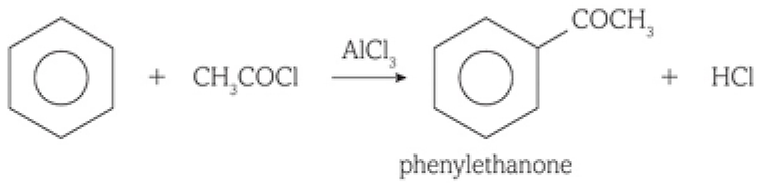
FRIEDEL-CRAFTS ALKYLATION REACTIONS

Alkylation means the substitution of one of the hydrogen atoms of benzene by an alkyl group. The reagent is a halogenoalkane, and the products are an alkylbenzene (methylbenzene) and hydrogen chloride. The equation for the reaction with chloromethane is:



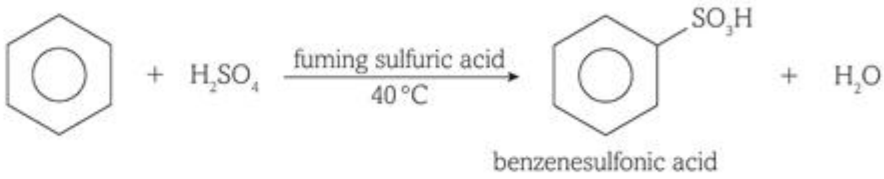
FRIEDEL-CRAFTS ACYLATION REACTIONS

Acylation means the substitution of one of the hydrogen atoms in benzene by an acyl group. The reagent is an acyl chloride, and the products are a ketone (phenylethanone) and hydrogen chloride. The equation for the reaction with ethanoyl chloride is:



SULFONATION

Sulfonation refers to the replacement of a hydrogen atom by a $-SO_3H$ group. The reaction is carried out by warming benzene with fuming sulfuric acid at 40 °C for 20 to 30 minutes.



The product is benzenesulfonic acid.

Fuming sulfuric acid is made by dissolving sulfur(VI) oxide (sulfur trioxide, SO_3) in concentrated sulfuric acid.

NAMING AROMATIC COMPOUNDS

The rules for naming aromatic compounds are similar to those for aliphatic compounds, using prefixes, locants, hyphens, commas, and multiplying prefixes. Some names use 'phen' or 'phenyl' to represent the benzene ring when attached to another functional group, but 'benzyl' is not used.

18A 3Electrophilic substitution mechanisms

ELECTROPHILIC SUBSTITUTION

Although you have not seen this mechanism before, you have studied substitution reactions in Topics 4 and 10 (Book 1: IAS), and electrophilic addition reactions in Topic 5 (Book 1: IAS).
Before we consider the mechanisms of the individual reactions, it is worth considering what they all have in common:

- The benzene ring is electron-rich. Although it is electrically neutral, the delocalised electrons in the pi (π) bond above and below the atoms mean that the molecule attracts electrophiles - species attracted to negative charge.

- Using Y^+ to represent the electrophile, as Y^+ approaches the delocalised π-bond, it attracts two of the six electrons, which form a covalent bond with it.

- This intermediate species lacks the stability of an aromatic compound (because the circle is broken), so in the next step the H leaves as H^+ and the two electrons in the C-H bond join the remaining four to restore the delocalised π-bond (with its relatively high stability).

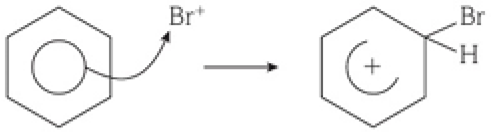
BROMINATION

Step 1: formation of the electrophile

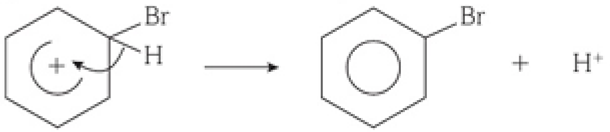
Bromine reacts with the catalyst to form Br^+:

$$AlBr_3 + Br_2 \rightarrow Br^+ + AlBr_4^-$$

Step 2: electrophilic attack



Step 3: formation of the aromatic product



Step 4: regeneration of the catalyst

$$AlBr_4^- + H^+ \rightarrow AlBr_3 + HBr$$

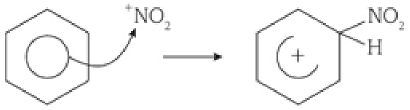
NITRATION

Step 1: formation of the electrophile

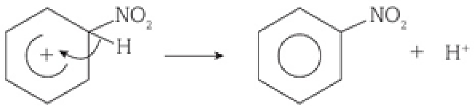
Nitric acid and sulfuric acid react to form NO_2^+ (the nitryl ion or nitronium ion):

$$HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$$

Step 2: electrophilic attack



Step 3: formation of the aromatic product



Step 4: regeneration of the catalyst

$$HSO_4^- + H^+ \rightarrow H_2SO_4$$

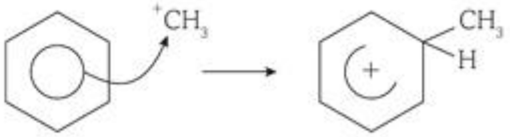
ALKYLATION

Step 1: formation of the electrophile

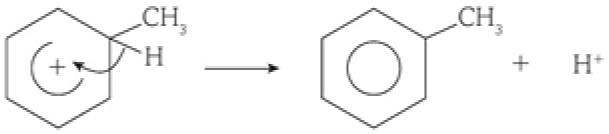
Chloromethane reacts with the catalyst to form CH_3^+:

$$AlCl_3 + CH_3Cl \rightarrow CH_3^+ + AlCl_4^-$$

Step 2: electrophilic attack



Step 3: formation of the aromatic product



Step 4: regeneration of the catalyst

$AlCl_4^- + H^+ \rightarrow AlCl_3 + HCl$

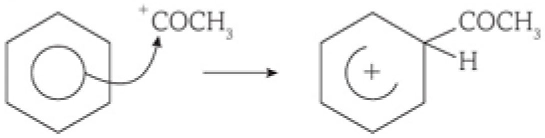
ACYLATION

Step 1: formation of the electrophile

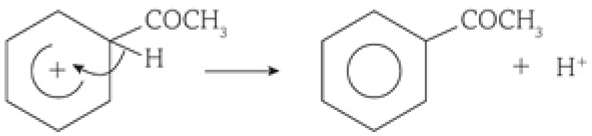
Ethanoyl chloride reacts with the catalyst to form CH_3CO^+:

$AlCl_3 + CH_3COCl \rightarrow CH_3CO^+ + AlCl_4^-$

Step 2: electrophilic attack



Step 3: formation of the aromatic product



Step 4: regeneration of the catalyst

$AlCl_4^- + H^+ \rightarrow AlCl_3 + HCl$

SUBJECT VOCABULARY

substitution a reaction in which an atom, or group of atoms, in a molecule is replaced by another atom, or group of atoms

electrophilic a reaction mechanism in which the attacking species is an electrophile

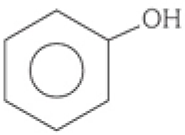
electrophile an atom, molecule or ion that can accept a pair of electrons

18A 4Phenol

WHAT IS PHENOL?

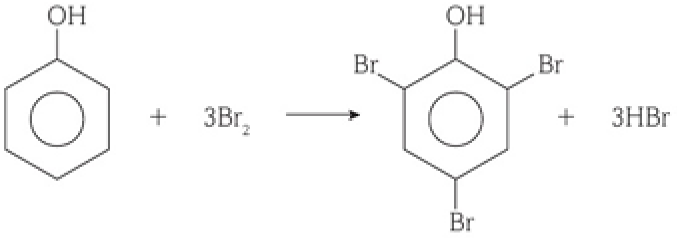
This section explores an aromatic compound with a benzene ring and aliphatic part, the hydroxyl (OH) group, following important reactions of the benzene ring and aliphatic compounds.

Phenol consists of a hydroxyl group joined to a benzene ring. It has some properties similar to an aliphatic alcohol such as ethanol, and you would expect it to undergo electrophilic substitution reactions because it contains a benzene ring. Its structure is:



BROMINATION OF PHENOL

You will remember from Section 18A.2 that benzene undergoes bromination, but the reaction needs a catalyst and the reaction mixture has to be heated under reflux. In contrast, the bromination of phenol occurs at room temperature without a catalyst, and works with bromine water. The bromine water is decolourised during the reaction, and the organic product forms as a white precipitate. The equation for the reaction is:



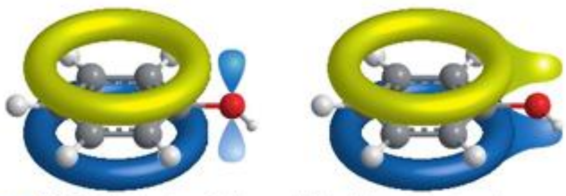
The substitution reaction in benzene and phenol is more prevalent with phenol due to the presence of three bromine atoms, which are joined to carbons 2, 4, and 6, making it more readily occurring than benzene. This is a key difference in the organic product.

- The lone pair of electrons in the p2-orbital on the oxygen atom of the OH group interacts with the delocalised pi (7) electrons in the ring (fig A).

- The electron density above and below the ring of atoms is increased, a process sometimes referred to as 'activation' because the molecule is now much more reactive towards electrophiles.

- Bromine molecules, although originally non-polar, are polarised as they approach the benzene ring. Eventually, the Br-Br bond breaks and the Br* electrophile attacks the benzene ring.

Fig A shows how the delocalised electrons in the π-bond change because of the presence of the oxygen.



▲ **fig A** The electrons in the p_z-orbital of the oxygen atom become part of the delocalised electron system. This increases the electron density above and below the ring and makes the molecule more attractive to electrophiles such as Br^+.

USES OF PHENOL AND ITS DERIVATIVES

One of the earliest and best known uses of phenol was in antiseptic surgery, especially by the surgeon Joseph Lister. Since then, other antiseptics have been developed from phenol. One of the most familiar of these is the product of the chlorination of phenol - this is 2,4,6-trichlorophenol, better known as the antiseptic TCP. Nowadays, phenol is widely used in many industries, notably in the manufacture of polymers and pharmaceuticals.