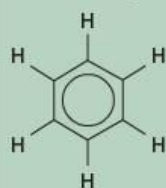


25 Arenes and phenols

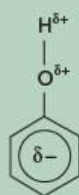
Functional groups:



arenes



X = Cl, Br, I
halogenoarenes



phenols

The arenes are a group of hydrocarbons whose molecules contain the benzene ring. Although they are unsaturated, they do not show the typical reactions of alkenes. Their characteristic reaction is electrophilic substitution. Phenols contain a hydroxy group (—OH) joined directly to a benzene ring. The presence of the ring modifies the typical alcohol-like reactions of the —OH group. Likewise, the presence of the —OH group modifies the typical arene-like reactions of the benzene ring. The presence of the benzene ring severely reduces the reactivity of the carbon-halogen bond in halogenoarenes.

Learning outcomes

By the end of this topic you should be able to:

- 14.1a)** interpret and use the general, structural, displayed and skeletal formulae of the following classes of compound: arenes, halogenoarenes and phenols (part, see also Topic 12)
- 14.1c)** understand and use systematic nomenclature of simple aromatic molecules with one benzene ring and one or more simple substituents
- 14.3a)** describe and explain the shape of, and bond angles in, benzene molecules in terms of σ and π bonds
- 15.4a)** describe the chemistry of arenes as exemplified by the following reactions of benzene and methylbenzene: substitution reactions with chlorine and with bromine, nitration, Friedel-Crafts alkylation and acylation, complete oxidation of the side-chain to give a benzoic acid, and hydrogenation of the benzene ring to form a cyclohexane ring
- 15.4b)** describe the mechanism of electrophilic substitution in arenes, as exemplified by the formation of nitrobenzene and bromobenzene, suggest the mechanism of other electrophilic substitution reactions, given data, and describe the effect of the delocalisation of electrons in arenes in such reactions
- 15.4c)** interpret the difference in reactivity between halogenoalkanes and chlorobenzene
- 15.4d)** predict whether halogenation will occur in the side-chain or in the aromatic ring in arenes depending on reaction conditions
- 15.4e)** apply knowledge relating to position of substitution in the electrophilic substitution of arenes
- 17.2a)** recall the chemistry of phenol, as exemplified by the following reactions: with bases, with sodium, with diazonium salts (see also Topic 27), and nitration of, and bromination of, the aromatic ring
- 17.2b)** describe and explain the relative acidities of water, phenol and ethanol.



25.1 Introduction

The structure of the benzene ring

Arenes are hydrocarbons that contain one or more benzene rings. Benzene was first isolated and identified by the English chemist Michael Faraday in 1825. Its structure posed a problem for nineteenth-century chemists. Comparing its molecular formula,

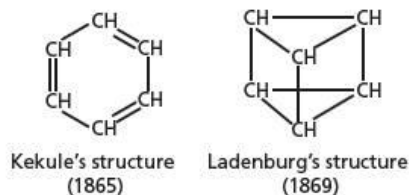


Figure 25.1 Two structures that were proposed for benzene in the nineteenth century

C_6H_6 , to that of the alkane hexane, C_6H_{14} , it can be seen that benzene is highly deficient in hydrogen. Other compounds with very low hydrogen-to-carbon ratios were all known to be highly unsaturated, containing many $C=C$ double bonds: they readily decolorise $KMnO_4(aq)$ and $Br_2(aq)$, and react with HBr , and with H_2O in the presence of acids. Benzene showed none of these reactions. Furthermore, it was apparent that all six hydrogen atoms in benzene were equivalent to each other, in that only one isomer of chlorobenzene, C_6H_5Cl , could be made. There were three isomers of dichlorobenzene, $C_6H_4Cl_2$, however. No open-chain structure would show these properties, but several structures containing rings were suggested in the 1860s. Those proposed by the German chemists Albert Ladenburg and August Kekulé are shown in Figure 25.1.

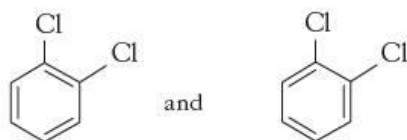
Now try this

- 1 Draw the structural formulae of all possible isomers of $C_6H_4Cl_2$ using the Ladenburg structure, and thus show that there are only three of them.
- 2 Draw the structural formulae of all possible isomers of $C_6H_4Cl_2$ using the Kekulé structure, and thus show that there are four of them.

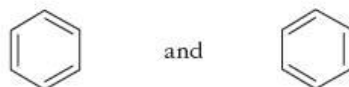


Figure 25.2 The German chemist Friedrich August Kekulé von Stradonitz (1829–96) was the first to suggest that benzene had a ring structure.

If two hydrogens are replaced by chlorines, to form dichlorobenzene, it is found that three (and only three) isomers of $C_6H_4Cl_2$ can be made (see section 25.2). Although this fitted with Ladenburg's structure, Kekulé's structure did not quite account for this observation; his proposed structure implied that there should be two isomers of 1,2-dichlorobenzene:



In fact, there is only one 1,2-dichlorobenzene. To overcome this disagreement with his structure, Kekulé proposed that the bonding in the benzene ring alternated between two equivalent structures:



Now that we accept that π electrons can become delocalised in many-atom π orbitals, formed by the overlapping of p orbitals on adjacent atoms, we have no need to postulate this alternation between the two Kekulé forms. The true bonding in benzene has sometimes been described as being in between the two extremes represented by the two Kekulé forms. We represent this 'in-between' state by a *double-headed arrow* joining the two formulae:



It is important to understand the meaning of the double-headed arrow, \leftrightarrow . This states that there is *only one* structure, which is in between the two 'classical' structures drawn either side of the arrow. The existence of a structure which cannot be represented by a single 'classical' structure, but which is intermediate between several of them, is known as **mesomerism** (from the Latin/Greek word *meso*, meaning 'middle'). The classical structures are called mesomers.

An early representation of the mesomeric structure of benzene was proposed by the German chemist Johannes Thiele in 1899 (see Figure 25.3); this is very similar to the delocalised structure we draw today.

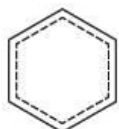


Figure 25.3 The representation of the benzene molecule proposed by Thiele in 1899

The structure of benzene was described in detail in section 3.16. It consists of six carbon atoms arranged in a regular hexagon, each joined to a hydrogen atom and to its neighbours by σ bonds. There are six spare p orbitals, one on each carbon atom, all parallel to each other and perpendicular to the plane of the ring. Each p orbital overlaps equally with both its neighbours, forming a delocalised six-centre molecular π orbital (see Figure 25.4).

Figure 25.4 The delocalised π bond in benzene

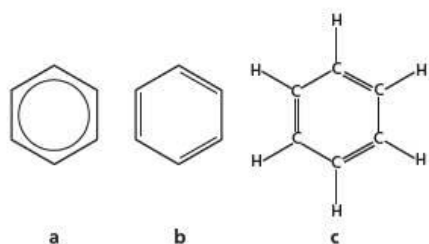
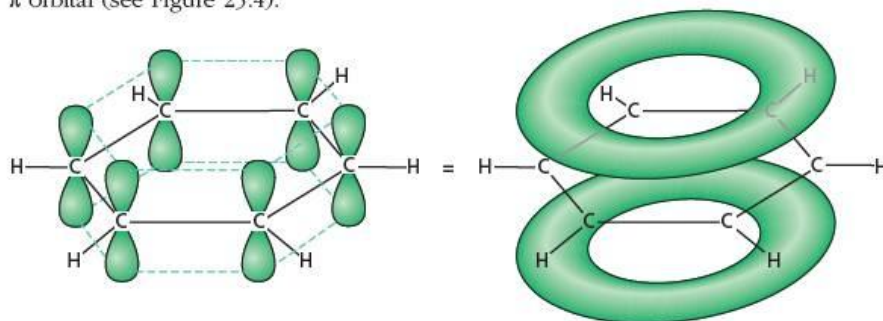
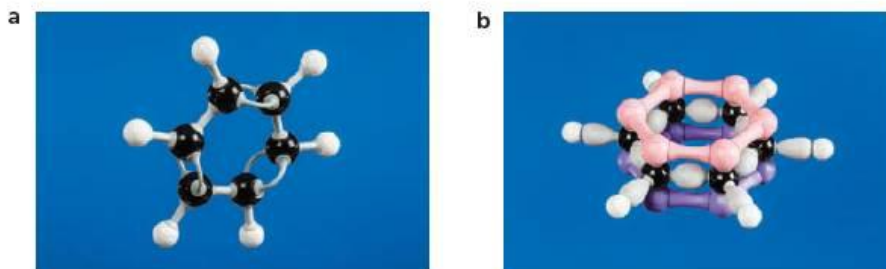


Figure 25.5 Three representations of the benzene molecule: **a** the Thiele skeletal formula, **b** the Kekulé skeletal formula, **c** the structural formula for benzene

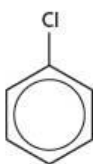
All the bond angles in benzene are 120° . All the C—C bonds have the same length, 0.139 nm. This is intermediate between the length of the C—C bond in an alkane (0.154 nm) and the C=C double bond in an alkene (0.134 nm).

The usual representation used for benzene is either the symmetrical skeletal formula (derived from the Thiele structure) or the Kekulé structure, either skeletal or structural. Figure 25.5 shows these representations. The benzene structure is normally represented by the skeletal formula, as in Figure 25.5a. When we want to show in detail how the π electrons move during reactions, however, we may sometimes use a Kekulé structure, as in Figure 25.5b or 25.5c. Figure 25.6 shows models of the Kekulé and Thiele structures.

Figure 25.6 **a** Ball-and-stick and **b** electron-density molecular models of benzene



In the skeletal formula, each corner of the hexagon is assumed to contain a carbon atom, to which is attached a hydrogen atom, unless otherwise stated. For example, chlorobenzene can be written as follows:

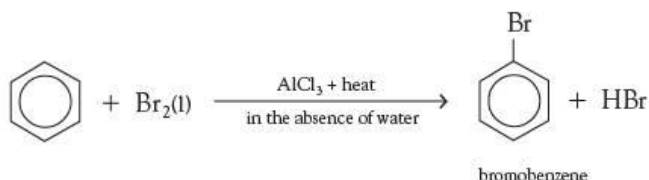


The Kekulé structure fitted in with the chemical bonding ideas of the 1860s, but was clearly incorrect in one important respect. It predicts that benzene is highly unsaturated – the formula suggests that the molecule contains three double bonds. It ought to undergo addition reactions readily, just like an alkene. In fact, benzene is inert to most reagents that readily add on to alkenes (see Table 25.1).

Table 25.1 A comparison of some reactions of benzene and cyclohexene

Reagent	Benzene	Cyclohexene
shaking with $\text{KMnO}_4(\text{aq})$	no reaction	immediate decolorisation
shaking with $\text{Br}_2(\text{aq})$	no reaction	immediate decolorisation
$\text{H}_2(\text{g})$ in the presence of nickel	very slow reaction at 100°C and 100 atm	rapid reaction at 20°C and 1 atm

Under more severe conditions, benzene can be made to react with one of these reagents, bromine. But now the reaction follows a different course – a substitution reaction occurs, rather than addition, and the necessary reaction conditions are much more extreme.



The stability of benzene

The six-centre delocalised π bond is responsible for the following physical and chemical properties of benzene.

- It causes all C—C bond lengths to be equal, creating a planar, regular hexagonal shape.
- It prevents benzene undergoing any of the normal addition reactions that alkenes show.

The π bond also makes benzene more stable than expected. Not only is benzene much less reactive than cyclohexene, it is also thermodynamically more stable. We can demonstrate this by comparing the actual and the 'calculated' enthalpy changes of hydrogenation. The hydrogenation of alkenes is an exothermic process:

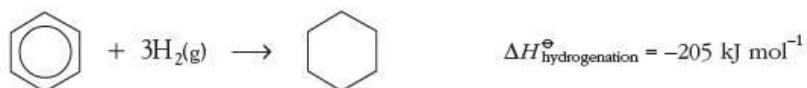


For many higher alkenes, the enthalpy changes of hydrogenation are very similar to each other, and average about 118 kJ mol^{-1} . Furthermore, for dienes and trienes (containing two and three double bonds, respectively), the enthalpy changes of hydrogenation are simple multiples of this value (see Table 25.2). So we might expect benzene to follow the same trend.

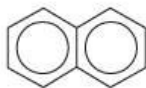
Table 25.2 Enthalpy changes of hydrogenation of some alkenes

Alkene	Formula	$\Delta H^\ominus_{\text{hydrogenation}} / \text{kJ mol}^{-1}$	ΔH^\ominus per C=C
cis-but-2-ene	$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$	-119	-119
cyclohexene		-118	-118
butadiene	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	-236	-118
cyclohexadiene		-232	-116
'cyclohexatriene'		[-354] (predicted)	[-118] (assumed)

If we measure the experimental enthalpy change of hydrogenation of benzene, we find that it is far less exothermic than that predicted for 'cyclohexatriene' in Table 25.2:



Or the two rings could share two carbon atoms in common (with their π electrons), as in naphthalene:



More rings can fuse together, giving such compounds as anthracene and pyrene:



anthracene



pyrene

Notice that with each successive ring fused together, the hydrogen-to-carbon ratio decreases, from 1:1 in benzene to 5:8 in pyrene. Eventually, as many more rings fuse together, a sheet of the graphite lattice (graphene) would result (see Topic 4).

Many of the multiple-ring arenes, such as pyrene, are strongly carcinogenic (cancer producing). Even benzene itself is a highly dangerous substance, causing anaemia and cancer on prolonged exposure to its vapour. In the past it was used as a laboratory solvent, but its use is now severely restricted, although it is still added to some brands of unleaded petrol to increase their anti-knock rating.

Physical properties of arenes

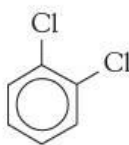
Benzene and most alkylbenzenes are strongly oily-smelling colourless liquids, immiscible with, and less dense than, water. They are non-polar, and the only intermolecular bonding is due to the induced dipoles of van der Waals' forces. Their boiling points are similar to those of the equivalent cycloalkanes (see Table 25.3), and increase steadily with relative molecular mass as expected.

Table 25.3 Boiling points of some cyclohexanes and arenes

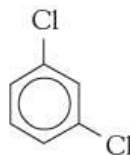
Compound	Formula	Boiling point/ $^{\circ}\text{C}$	Compound	Formula	Boiling point/ $^{\circ}\text{C}$
cyclohexane	C_6H_{12}	81	benzene	C_6H_6	80
methylcyclohexane	C_7H_{14}	100	methylbenzene	C_7H_8	111
			ethylbenzene	C_8H_{10}	136
			propylbenzene	C_9H_{12}	159

25.2 Isomerism and nomenclature

Aromatic compounds with more than one substituent on the benzene ring can exist as positional isomers. There are three dichlorobenzenes:



1,2-dichlorobenzene



1,3-dichlorobenzene



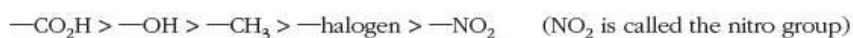
1,4-dichlorobenzene

The terms *ortho*-, *meta*- and *para*- are sometimes used as prefixes to represent the relative orientations of the groups (see Table 25.4).

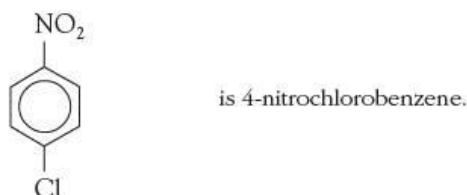
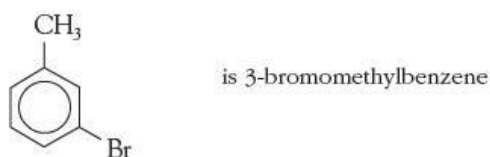
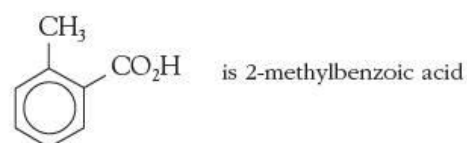
Table 25.4 Orientations of substituents on the benzene ring

Orientation	Prefix	Abbreviation	Example
1,2-	<i>ortho-</i>	<i>o-</i>	
1,3-	<i>meta-</i>	<i>m-</i>	
1,4-	<i>para-</i>	<i>p-</i>	

If the two substituents are different, one of them is defined as the 'root' group, in the following order of precedence



and the ring carbons numbered from the carbon atom holding that group. For example:

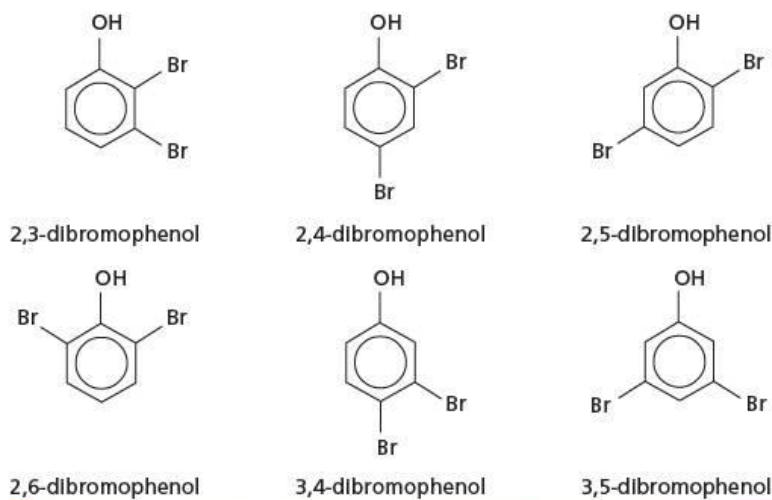


Worked example

Draw out all possible positional isomers of $\text{C}_6\text{H}_3\text{Br}_2\text{OH}$ and name them.

Answer

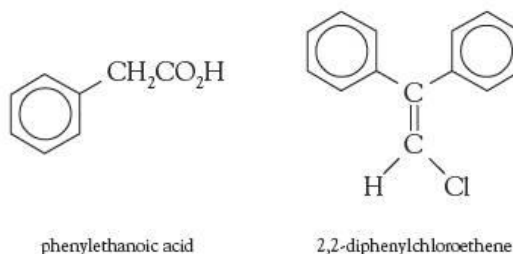
There are six isomers. Their names and formulae are as follows:



Now try this

How many isomers are there of trichloromethylbenzene, $\text{C}_6\text{H}_2\text{Cl}_3(\text{CH}_3)$? What are their names?

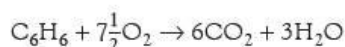
If the benzene ring is a 'substituent' on an alkyl or alkenyl chain, it is given the name **phenyl**:



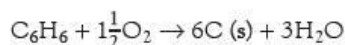
25.3 Reactions of arenes

Combustion

Benzene and methylbenzene (whose old name, toluene, is still in use) are components of many brands of unleaded petrol. In sufficient oxygen, they burn completely to carbon dioxide and steam:



If liquid arenes are set alight in the laboratory, they burn with very smoky flames. Much soot is produced because there is insufficient oxygen for complete combustion. A smoky flame is an indication of a compound with a high C:H ratio.

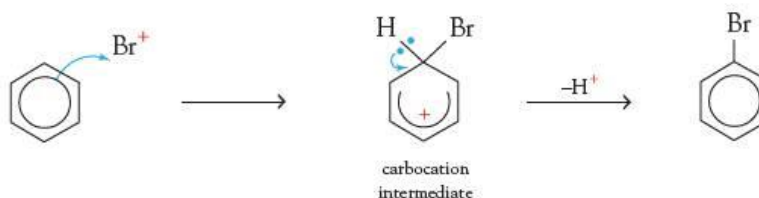
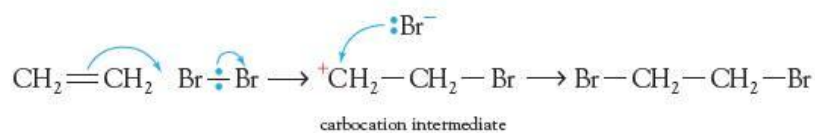


Just as with hydrogenation, the enthalpy of combustion of benzene is less exothermic than expected, because of the stability due to the six delocalised π electrons.

Electrophilic substitution in benzene

In a similar way to the π bond in alkenes, the delocalised π bond in benzene is an area of high electron density, above and below the six-membered ring. Benzene therefore reacts with electrophiles. Because of the extra stability of the delocalised electrons, however, the species that react with benzene have to be much more powerful electrophiles than those that react with ethene. Bromine water and aqueous acids have no effect on benzene.

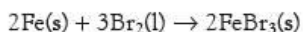
The electrophiles that react with benzene are all positively charged, with a strong electron-attracting tendency. The other major difference between benzene and alkenes is what happens after the electrophile has attacked the π bond. In alkenes, an anion 'adds on' to the carbocation intermediate. In benzene, on the other hand, the carbocation intermediate loses a proton, so as to re-form the ring of π electrons. This demonstrates how stable the delocalised system is.



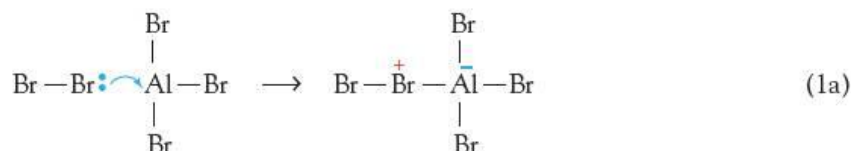
Alkenes react by **electrophilic addition**.
Arenes react by **electrophilic substitution**.

Bromination

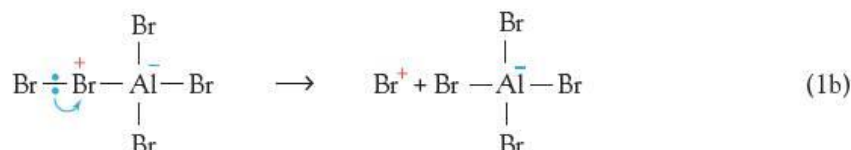
Benzene will react with non-aqueous bromine on warming in the presence of anhydrous aluminium chloride or aluminium bromide, or iron(III) chloride, or even just iron metal. In the latter case, an initial reaction between iron and bromine provides the iron(III) bromide catalyst:



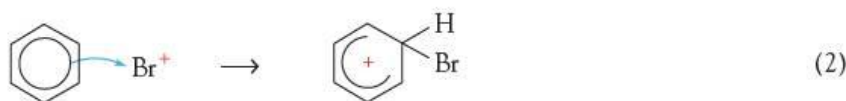
Anhydrous aluminium or iron(III) halides contain electron-deficient atoms. They can react with the bromine molecule by accepting one of the lone pairs of electrons on bromine:



This causes strong polarisation of the Br—Br bond, weakening it, and eventually leading to its heterolytic breaking:

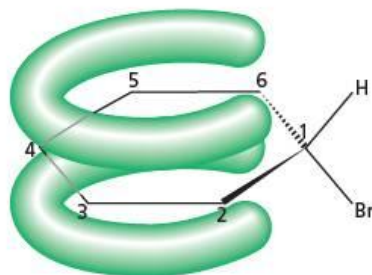


The bromine cation that is formed is a powerful electrophile. It becomes attracted to the π bond of benzene. It eventually breaks the ring of electrons and forms a σ bond to one of the carbon atoms of the ring:

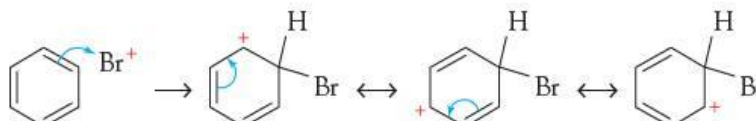


Two of the six π electrons are used to form the (dative) bond to the bromine atom. The other four π electrons are spread over the remaining five carbon atoms of the ring, in a five-centre delocalised orbital (see Figure 25.10).

Figure 25.10 The four π electrons are delocalised over five carbons.

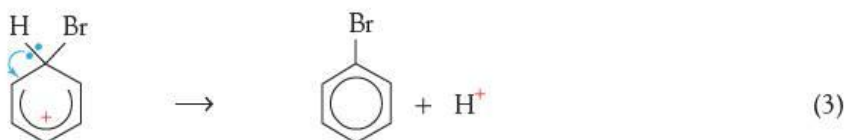


The distribution of the four π electrons is not even. They are associated more with carbon atoms 3 and 5 than with atoms 2, 4 and 6. The positive charge is therefore distributed over atoms 2, 4 and 6. This is best represented by the following classical mesomers:

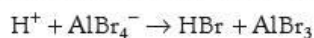


We shall return to this feature of the intermediate carbocation when we look at orientation effects on page 427.

The intermediate carbocation then loses a proton, to re-form the sextet of π electrons:



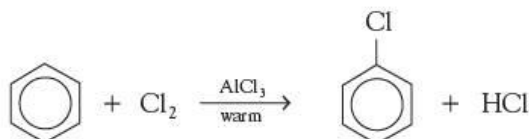
The final stage regenerates the catalyst, by the reaction between the proton formed in step (3) with the $[\text{AlBr}_4]^-$ formed in step (1b):



Further substitution can occur with an excess of bromine, to form dibromobenzene, and even tribromobenzene. For the reactions of bromobenzene, see section 25.4.

Chlorination

Just as with bromine, chlorine in the presence of an electron-acceptor such as aluminium chloride will substitute into the benzene ring:



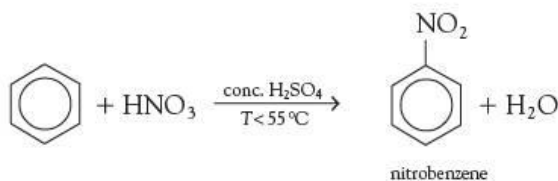
The properties and reactions of chlorobenzene are discussed in section 25.4.

Now try this

Suggest a mechanism for the chlorination of benzene.

Nitration

Benzene does not react with nitric acid, even when the acid is concentrated. But a mixture of concentrated nitric and concentrated sulfuric acids produces nitrobenzene:

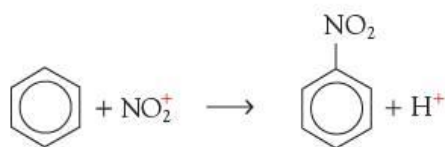


Further nitration to dinitrobenzene (and also some oxidation) can occur unless the temperature is controlled to be below about 55°C .

The role of the concentrated sulfuric acid in this reaction is to produce the powerful electrophile needed to nitrate the benzene ring. By analogy with bromination:



we might expect the electrophile for nitration to be NO_2^+ :

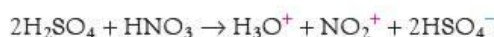


and this indeed seems to be the case.

Over the years, various pieces of evidence have been collected to substantiate the claim of NO_2^+ (known as the nitryl cation or nitronium ion) to be the electrophile.

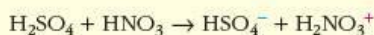
- Stable salts containing the nitryl cation exist, for example nitryl chlorate(VII), $\text{NO}_2^+\text{ClO}_4^-$, and nitryl tetrafluoroborate(III), $\text{NO}_2^+\text{BF}_4^-$. Each of these, when dissolved in an inert solvent, nitrates benzene smoothly and in high yield to give nitrobenzene.
- The infrared spectrum of a compound tells us about the types of bonds in the compound, and its shape. The infrared spectrum of a solution of nitric acid in sulfuric acid shows a strong absorbance at 2350 cm^{-1} . This absorbance is also present in the spectra of nitryl salts, but is not present in that of nitric acid in the absence of sulfuric acid. It is almost identical to a similar absorbance in the spectrum of carbon dioxide. CO_2 and NO_2^+ are isoelectronic linear molecules (see section 3.13), and so would be expected to have similar infrared spectra.
- Various physico-chemical data (for example, the depression of freezing point) show that when one molecule of HNO_3 is dissolved in concentrated sulfuric acid, *four* particles are formed. (The freezing point of a liquid is lowered if substances are dissolved in it, and the amount of the depression depends upon the mole ratio of solute to solvent.)

These three pieces of evidence suggest that the following reaction occurs when the two acids are mixed:

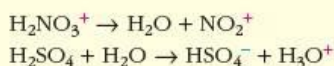


The mechanism of the nitration of benzene

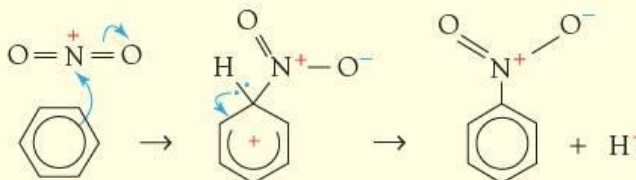
Sulfuric acid is a stronger acid than nitric acid. It is so strong that it donates a proton to nitric acid. In this reaction, nitric acid is acting as a base!



The protonated nitric acid then loses a water molecule, and this is then protonated by another molecule of sulfuric acid:

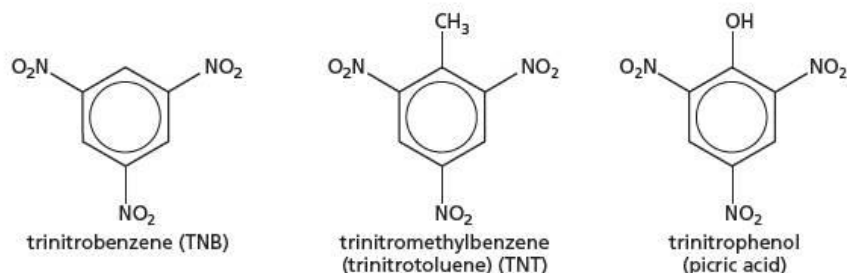


The nitronium ion then attacks the benzene ring in the usual way, forming the carbocation intermediate, which subsequently loses a proton:

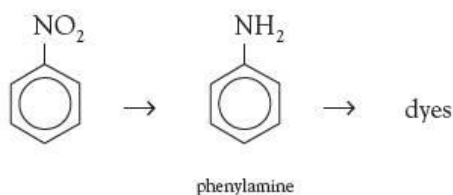


The nitration of benzene and other arenes is an important reaction in the production of explosives (see Figure 25.11)

Figure 25.11 Three powerful explosives that are poly-nitro compounds

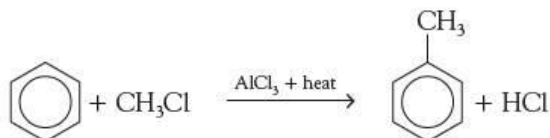


Also, via subsequent reduction, nitration is an important route to aromatic amines, which are used to make a variety of dyes (see Topic 27).



Alkylation (the Friedel–Crafts reaction)

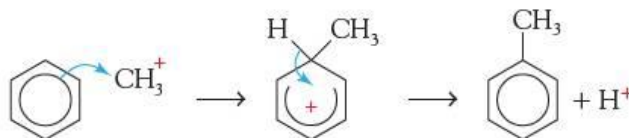
In 1877 the French chemist Charles Friedel and his co-worker, American chemist James Crafts, discovered that when benzene is heated with a chloroalkane in the presence of aluminium chloride, the alkyl group attaches to the benzene ring.



The reaction goes via the formation of an intermediate carbocation.

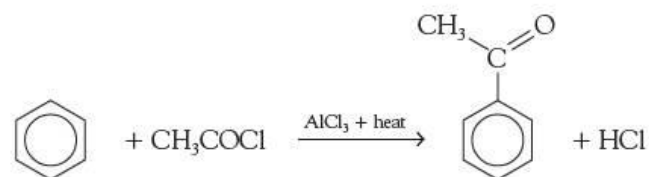


The carbocation is the electrophile.

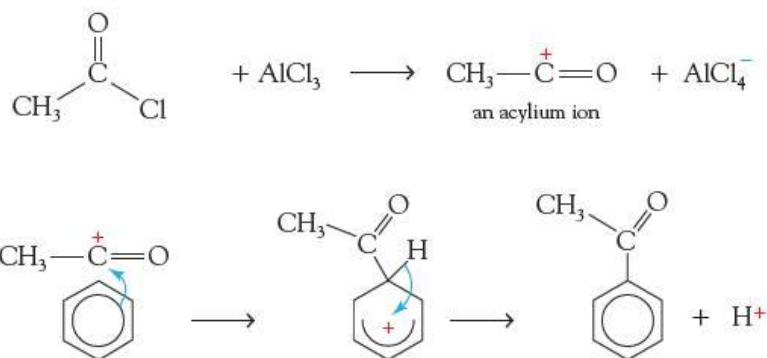


Acylation (Friedel–Crafts acylation)

If an acyl chloride (see section 26.3, page 442) is used instead of a chloroalkane in the Friedel–Crafts reaction, a phenylketone is produced.



The reaction between an acyl chloride and aluminium chloride produces the acylium ion. The intermediate is formed from the attack of the acylium ion on the benzene ring.

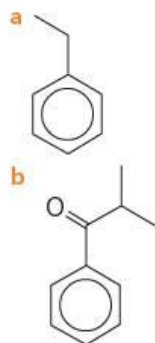


Worked example

Draw the structural formulae of the products you would expect from the reaction of benzene and aluminium chloride with

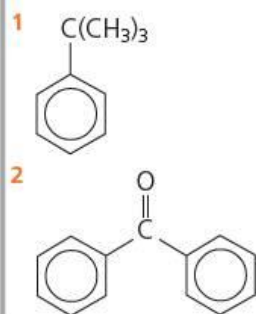
- a $\text{CH}_3\text{CH}_2\text{Cl}$
 b $(\text{CH}_3)_2\text{CHCOCl}$

Answer



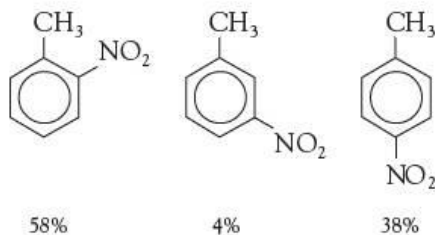
Now try this

What organochlorine compounds are needed to synthesise the following compounds from benzene?



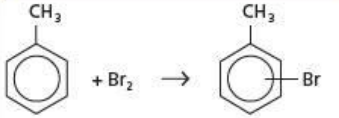
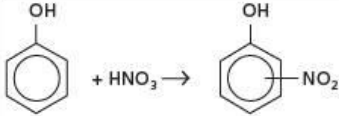
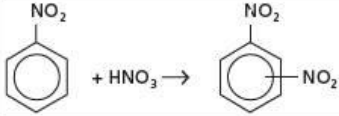
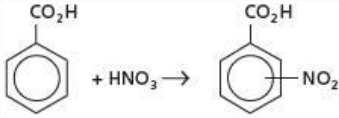
Electrophilic substitution in substituted arenes – the orientation of the incoming group

When methylbenzene is treated with nitric and sulfuric acids, the three possible mono-nitro compounds are formed in the following ratios:



If the NO_2^+ electrophile had attacked the ring in a purely random way, the distribution should have been 40:40:20 (there being two 2-positions and two 3-positions, but only one 4-position). This non-random attack is seen in other reactions too (see Table 25.5).

Table 25.5 Orientation in some electrophilic substitution reactions

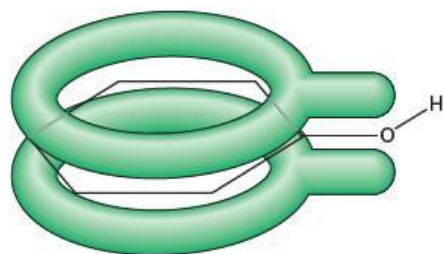
Reaction	Percentage of product			Ratio (ortho + para) meta
	ortho (1,2)	meta (1,3)	para (1,4)	
	33	1	66	99:1
	50	1	49	99:1
	6	93.5	0.5	1:14
	19	80	1	1:4

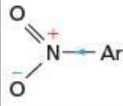

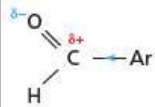

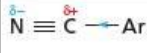
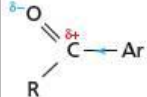
The data in Table 25.5 can be interpreted as follows.

- The orientation of the incoming group (NO_2 or Br) depends on the substituent *already in the ring*, and not on the electrophile.
- Some substituents favour both 2- and 4-substitution, whereas other substituents favour 3-substitution, at the expense of both 2- and 4-substitution.

If we look closely at the types of substituents that are 2,4-directing, we find that either they are capable of donating electrons to the ring by the inductive effect, or they have a lone pair of electrons on the atom joined to the ring. This lone pair can be incorporated into the π system by sideways overlap of p orbitals (see Figure 25.12).

On the other hand, all those substituents that favour 3-substitution have a δ^+ atom joined directly to the ring (see Table 25.6).

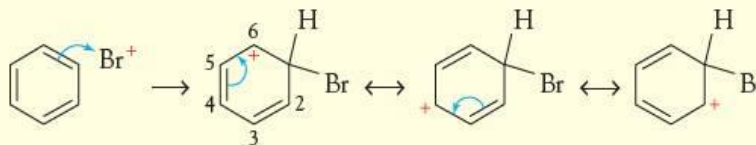
**Figure 25.12** Delocalisation of the lone pair in 2,4-directing substituents**Table 25.6** Substituents and their effects on the benzene ring

2- and 4-directing substituents	3-directing substituents
$\text{CH}_3 \rightarrow \text{Ar}$	
	
	
	

The orientation effects of different substituents

To explain why electron-donating substituents are 2,4-directing, and why electron-withdrawing groups are 3-directing, we need to return to the electron distribution in the carbocation intermediate, mentioned on page 423.

In the bromination of benzene, the intermediate can be represented as follows.

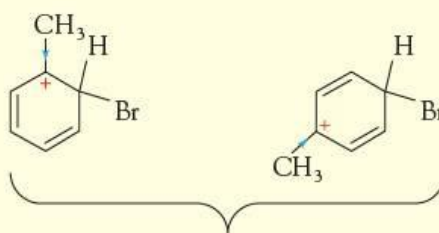


The $+$ charge (that is, the electron deficiency) is due to only four π electrons being spread over five carbon atoms. But the $+$ charge is not evenly spaced. As can be seen above, it is mainly on carbon atoms 2, 4 and 6.

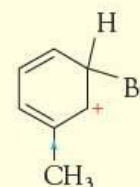
Electron-donating groups at these positions will therefore be more effective at stabilising the intermediate, by spreading out its charge, than if the electron-donating group were in position 3 or 5, one carbon removed from the $+$ charge:

Now try this

The bromination of nitrobenzene produces mainly 3-bromonitrobenzene. Draw out the mesomers of the intermediate carbocation and use a similar argument to the one above to explain why production of 3-bromonitrobenzene is favoured over that of 2- or 4-bromonitrobenzene.



If the methyl group is situated in the 2- or 4-position relative to the bromine atom, the intermediate is *much* more stable compared to the intermediate in the substitution of benzene.

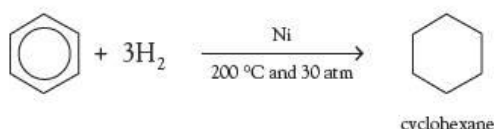


If the methyl group is situated in the 3-position relative to the bromine atom, the intermediate is only a *little* more stable compared to the intermediate in the substitution of benzene.

Addition reactions of the benzene ring

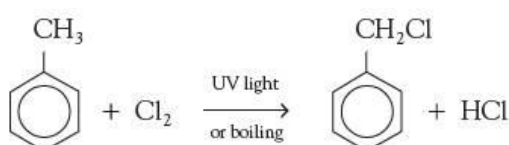
When it reacts with electrophiles, benzene always undergoes substitution. However, under some conditions it can be forced to undergo addition reactions. One of these is the addition of hydrogen.

Ethene adds on hydrogen over a nickel catalyst readily at room temperature and slight pressure. Benzene, being more stable, requires an elevated temperature and pressure:



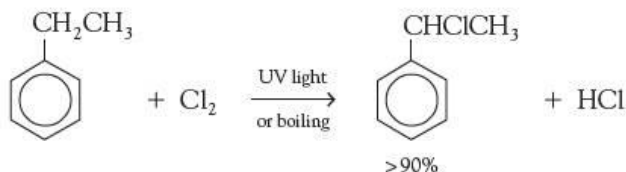
Substitution in the side chain

Methylbenzene and other alkylbenzenes very readily undergo radical substitution with chlorine or bromine in the presence of ultraviolet light (just like alkanes – see section 13.5), or by boiling in the absence of ultraviolet light.



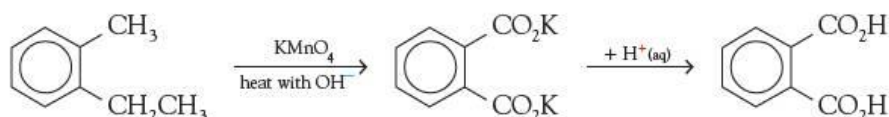
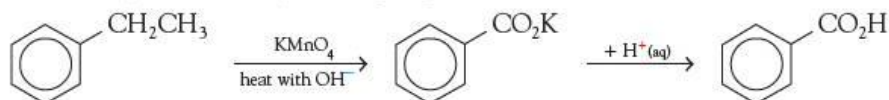
Just as with alkanes, more than one chlorine atom can be substituted. But substitution occurs only in the side chain during this reaction, not in the ring.

In ethylbenzene, the hydrogen atoms on the carbon atom adjacent to the benzene ring are substituted much more readily than the three hydrogens on the other carbon, so the following reaction gives a good yield of the product:



Oxidation of the side chain

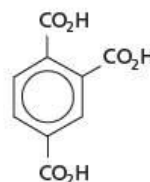
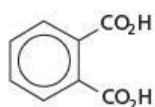
When alkylbenzenes are treated with hot alkaline potassium manganate(VII), oxidation of the whole side chain occurs, leaving the carbon atom closest to the ring as a carboxylate or carboxylic acid group:



Worked example

Three hydrocarbons **A**, **B** and **C** with the formula C_9H_{12} were oxidised by hot potassium manganate(VII).

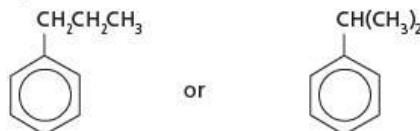
- Hydrocarbon **A** gave benzoic acid, $\text{C}_6\text{H}_5\text{CO}_2\text{H}$.
- Hydrocarbon **B** gave benzene-1,2-dioic acid:
- Hydrocarbon **C** gave benzene-1,2,4-trioic acid:



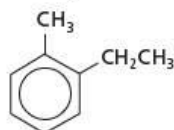
Suggest the structures of **A**, **B** and **C**.

Answer

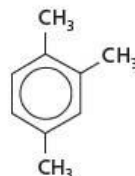
Since **A** gave benzoic acid, all three 'extra' carbon atoms must be in the same side chain. So **A** is:



Compound **B** must contain two side chains, since two carboxylic acid groups are left after oxidation. What is more, the chains must be on adjacent carbons in the ring, as a 1,2-dicarboxylic acid is formed. So **B** is:



By similar reasoning, **C** must be:



Now try this

Suggest structures for the aromatic carboxylic acids which will be produced when the following compounds are oxidised by hot potassium manganate(VII). (All these compounds are isomers with the molecular formula $\text{C}_{11}\text{H}_{14}$.)



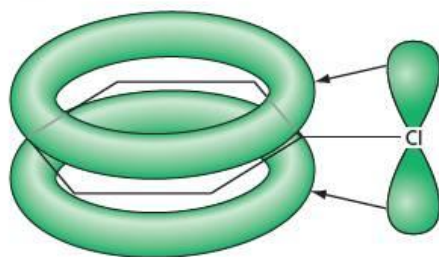
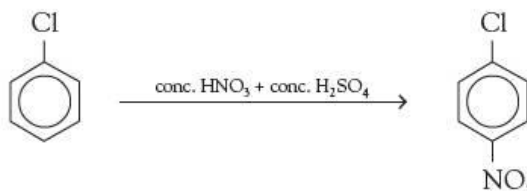


Figure 25.13 Delocalisation of the lone pair in chlorobenzene

25.4 Halogenoarenes

We saw on pages 423–424 how bromobenzene and chlorobenzene can be made from benzene. The reactions of the ring in halogenobenzenes are similar to those of benzene. Halogenoarenes undergo electrophilic substitution, and can be nitrated:



However, unlike halogenoalkanes, halogenoarenes cannot be hydrolysed, even by boiling in aqueous sodium hydroxide. The carbon–halogen bond is stronger in halogenoarenes than it is in halogenoalkanes, possibly due to an overlap of p electrons similar to that in phenol (see Figure 25.13, and compare it with Figure 25.12).

In addition to this, the carbon attached to the halogen is not accessible to the usual nucleophilic reagents that attack halogenoalkanes, since its δ^+ charge is shielded by the negative π cloud of the ring. This means that halogenoarenes are inert to all nucleophiles.

Certain halogenoarenes find important uses as insecticides and herbicides (see the panel below).

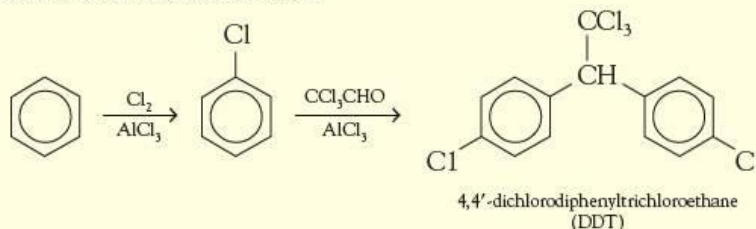
Organochlorine insecticides and herbicides

Insecticides



Figure 25.14 Malaria is caused by a microscopic parasite that is spread by the bite of the *Anopheles* mosquito. Malaria affects over 300 million people worldwide and kills around 3 million a year. DDT treatment of the *Anopheles* mosquito saves millions of human lives, so the environmental price is considered worth paying.

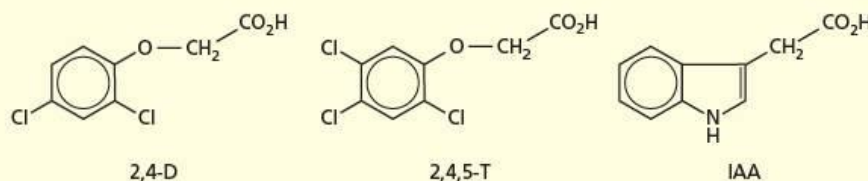
Chlorobenzene used to be made in large quantities as an intermediate in the production of the insecticide DDT:



The use of chlorinated insecticides is now banned in many countries. These compounds are quite inert to biodegradation, so they stay in the environment for many years. What is more, being non-hydrogen-bonded covalent substances, they are insoluble in water, but soluble in fats and oils. They tend to concentrate in the fatty tissue of animals, especially those higher up the food chain. Birds of prey were especially vulnerable. At one time, the shells of their eggs were so thin that they cracked during attempted incubation, with disastrous consequences for their populations. DDT may still be used in parts of Africa and Asia to control the malaria mosquito, as the advantages to human health are considered to outweigh the disadvantages to the environment.

Herbicides

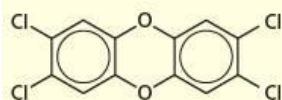
The compounds 2,4-dichlorophenoxyethanoic acid (2,4-D) and 2,4,5-trichlorophenoxyethanoic acid (2,4,5-T) have been successfully used for many years as selective weedkillers for broad-leaved weeds. They have little effect on narrow-leaved plants such as grass and cereals, and so can be used as lawn or field weedkillers. Their action mimics that of the natural plant growth hormone indole

Figure 25.15 The structures of some hormone weedkillers (herbicides)

2,4-D and 2,4,5-T were components of 'Agent Orange', sprayed as a jungle defoliant by the US army during the Vietnam war. It was during this large-scale use that an unforeseen problem came to light. During the manufacture of the intermediate chlorinated phenol, a small quantity of a highly toxic impurity, tetrachlorodibenzodioxin (or 'dioxin') was also produced (see Figure 25.16). The temperature of the reaction has to be controlled very carefully if the amount of dioxin is to be kept at a low level.

Unlike 2,4-D or 2,4,5-T, dioxin is not soluble in water. If ingested, or absorbed through the skin or lungs, it becomes concentrated in the fatty tissues of the body. It has now been discovered that dioxin is one of the most poisonous chemicals known – it is strongly carcinogenic (cancer producing), teratogenic (produces malformation of the foetus) and mutagenic (causes mutations). It causes skin burns and ulcers that heal only very slowly. Improved methods of production of 2,4-D and 2,4,5-T are now in place, but the risk of accidentally producing large quantities of dioxin is still present unless effective controls are in place. Other non-chlorine-containing hormone weedkillers are preferred – they are equally effective, but more expensive.

The use of chlorinated herbicides is now severely restricted, just as is the use of chlorinated insecticides.



tetrachlorodibenzo-1,4-dioxin
(TCDD, 'dioxin')

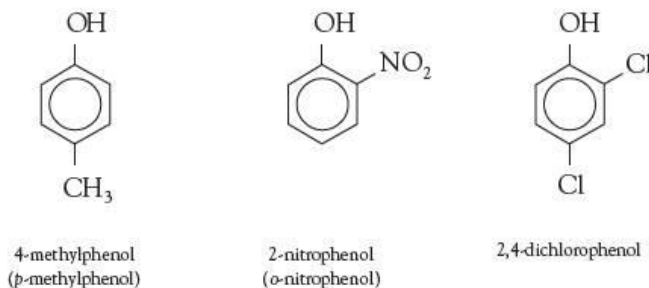
Figure 25.16 Dioxin – a highly toxic molecule

25.5 Phenols

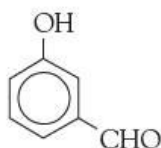
Phenols contain two functional groups – the —OH group of the alcohols, and the phenyl ring of the arenes. Their reactions are for the most part the sum of the two sets, but with significant modifications.

Nomenclature

Many of the compounds illustrated in Figure 25.8 (page 419) are phenols. If the only other groups on the benzene ring are halogen atoms, nitro, amino or alkyl groups, the compounds are named as derivatives of phenol itself:



If, however, the other group is an aldehyde, ketone or carboxylic acid group, the phenolic —OH becomes a 'hydroxy' substituent:



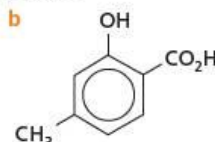
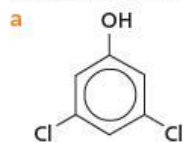
3-hydroxybenzaldehyde
(also known as
3-hydroxybenzenecarbaldehyde)



4-hydroxybenzoic acid
(also known as
4-hydroxybenzenecarboxylic acid)

Worked example

Name the following compounds:



Answer

a 3,5-dichlorophenol **b** 2-hydroxy-4-methylbenzoic acid

Now try this

Draw the structural formulae of the following compounds.

- 2,4,6-trimethylphenol
- 3,4,5-trihydroxybenzoic acid

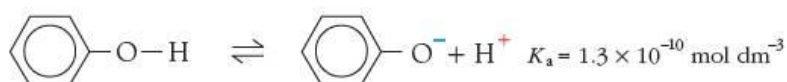
Reactions of the —OH group

The C—O bond in phenol is very strong, as a result of the delocalisation of the lone pair of electrons on oxygen over the arene ring. There are no reactions in which it breaks, unlike the situation with the alcohols (see section 16.3).

Reactions of the O—H bond

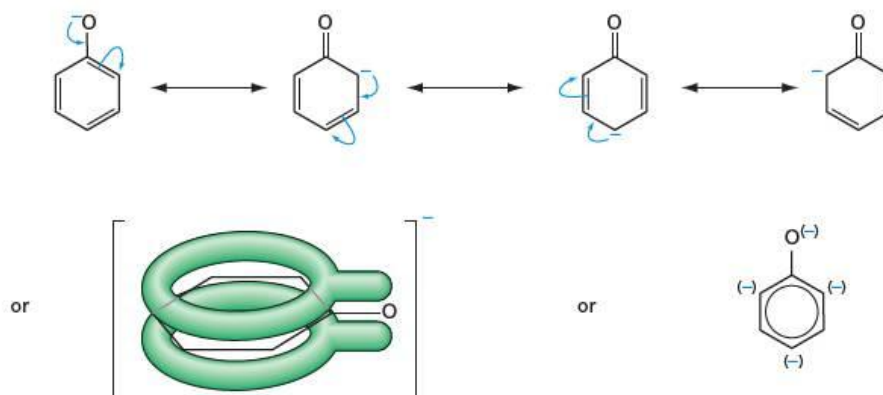
Acidity

Phenols are more acidic than alcohols:

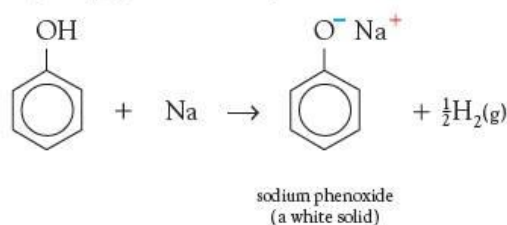


The negative charge of the anion can be delocalised over the benzene ring. Figure 25.17 shows various ways in which this can be represented.

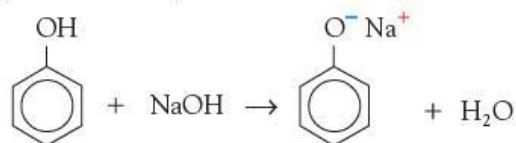
Figure 25.17 Representations of the phenol anion



Consequently, phenol not only reacts with sodium metal, giving off hydrogen gas:



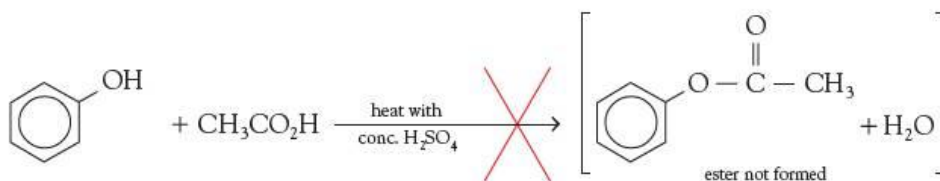
but, unlike alcohols, it also dissolves in aqueous sodium hydroxide:



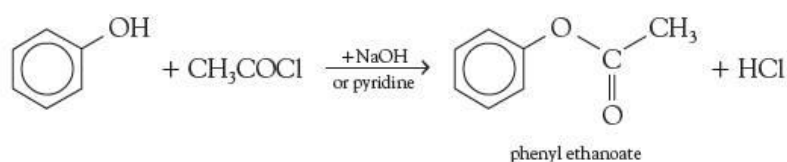
Phenol is visibly acidic: the pH of a 0.1 mol dm^{-3} solution in water is 5.4, so it will turn universal indicator solution yellow. An old name for phenol is carbolic acid (see section 25.6).

Esterification

Because of the delocalisation over the ring of the lone pair on the oxygen atom, phenol is not nucleophilic enough to undergo esterification in the usual way, that is, by heating with a carboxylic acid and a trace of concentrated sulfuric acid (for the mechanism of esterification, see section 18.3).



Phenol can, however, be esterified by adding an acyl chloride:



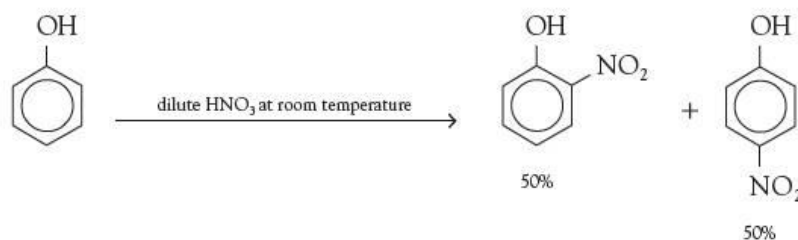
See section 26.3 for a fuller description of the conditions used for this reaction.

Substitution reactions of the benzene ring

As we mentioned on page 428, phenols are more susceptible to electrophilic attack than benzene, owing to the delocalisation of the lone pair of electrons on oxygen. This allows phenol to react with reagents that are more dilute, and also to undergo multiple substitution with ease.

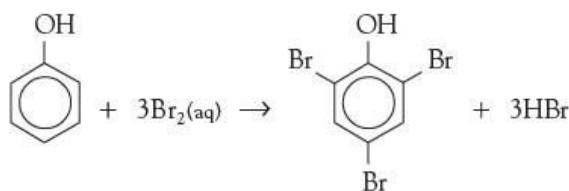
Nitration

When treated with *dilute* aqueous nitric acid (no sulfuric acid is needed) phenol gives a mixture of 2- and 4-nitrophenols:

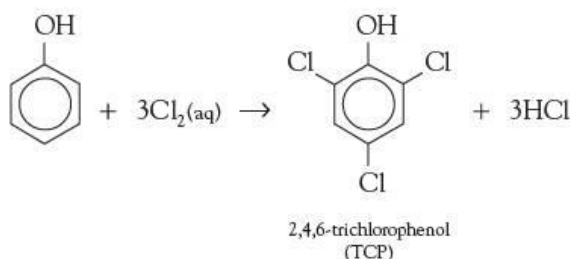


Bromination

Phenol decolorises a dilute solution of bromine in water at room temperature, giving a white precipitate of 2,4,6-tribromophenol. No aluminium bromide is needed. Contrast this with the conditions needed for the bromination of benzene on page 423.

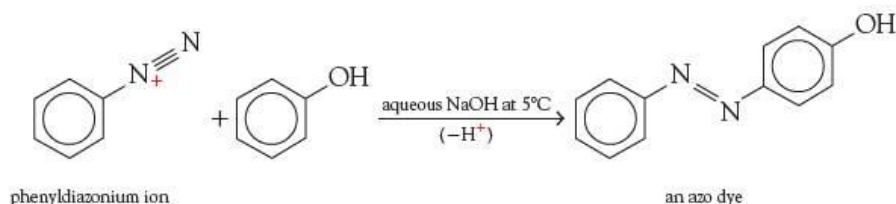


A similar product, formed by the action of chlorine water on phenol, is used in dilute solution as the antiseptic TCP (see page 436).



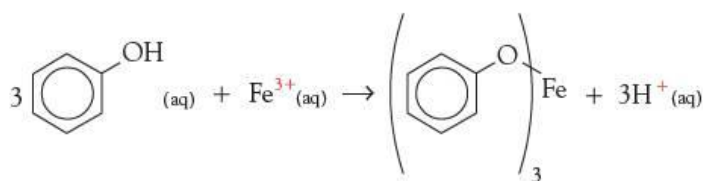
Coupling

Phenols couple with diazonium salts (see section 27.3) to form azo dyes:



A specific test for phenols

When a dilute solution of iron(III) chloride is added to a dilute solution of a phenol, a coloured complex is formed. The colour depends on the substituents on the ring. With phenol itself, a purple coloration is observed:



25.6 Some important phenols

Antiseptics

A dilute solution of phenol in water (known as carbolic acid) was one of the first disinfectants to be used in medicine, by Joseph Lister in Glasgow, Scotland, in 1867. Phenol itself is unfortunately too corrosive to be of general use as an antiseptic. Many chloro derivatives have been found to be more potent antiseptics than phenol itself. They can be used in much lower concentrations, which reduces their corrosive effect. Two of the most common are trichlorophenol (TCP) and chloroxylenol (see Figure 25.19). Thymol occurs in oil of thyme, and is an excellent non-toxic antiseptic, as well as being a fungicide.

Figure 25.18 The Scottish doctor Joseph Lister (1827–1912) was the first to use phenol as an antiseptic during surgery. Deaths from infections following operations were much reduced as a result, though the corrosive nature of phenol did not help the skin to heal.

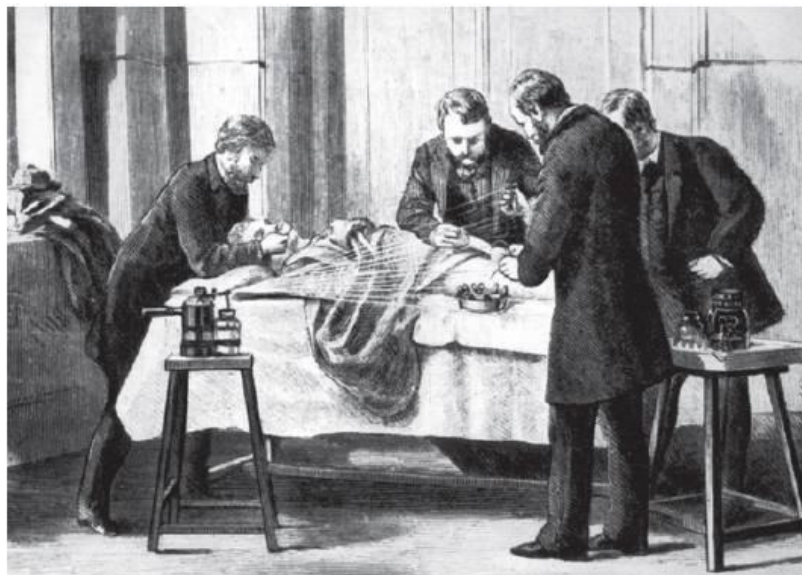
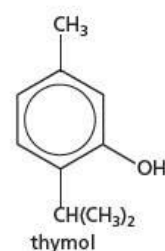
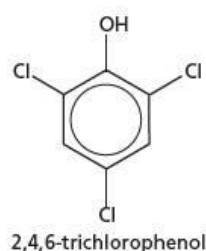
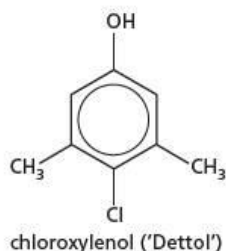


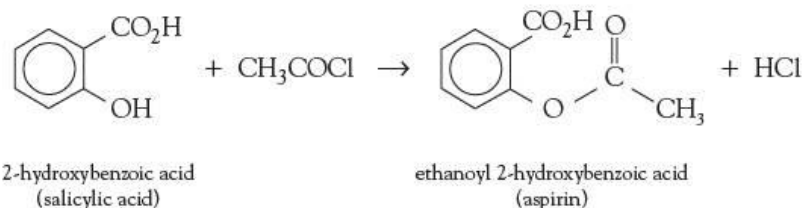
Figure 25.19 Three antiseptics that are derivatives of phenol



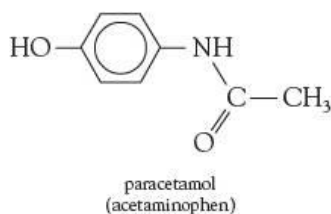
Analgesics

A significant number of pharmaceutical drugs contain phenolic groups, or are derived from phenols.

The painkilling and fever-reducing properties of an extract of willow bark have been known in many countries since at least the sixteenth century. In the nineteenth century, the active ingredient, salicylic acid (2-hydroxybenzoic acid), was isolated and purified (the name 'salicylic' derives from the Latin name for willow, *Salix*). The therapeutic use of salicylic acid was limited, however, because it caused vomiting and bleeding of the stomach. In 1893 an ester derived from salicylic acid and ethanoic acid was found to have far fewer side-effects:

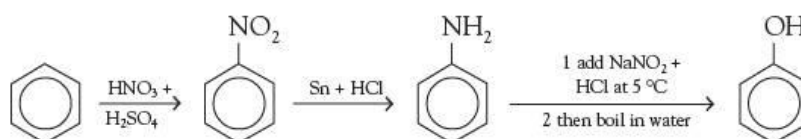


Aspirin is the most widely used of all analgesics. However, it still retains some of the stomach-irritating effects of salicylic acid. A less problematic painkiller is paracetamol, which is another phenol.



25.7 Preparing arenes and phenols

- Benzene and methylbenzene are formed during the cracking and re-forming of fractions from the distillation of crude oil (see section 13.3).
- The —OH group of phenols can be introduced onto an arene ring by the following sequence (see section 27.3 for details):

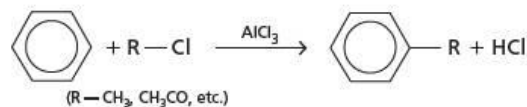
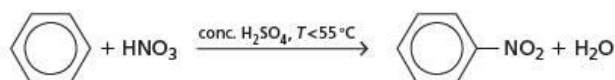
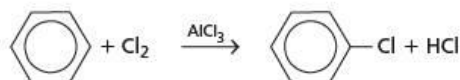
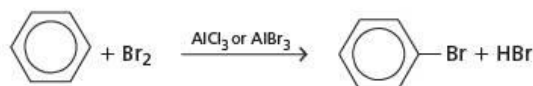


Summary

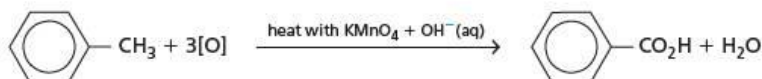
- **Arenes** are hydrocarbons that contain one or more benzene rings.
- The benzene ring contains a delocalised group of six π electrons. This confers great stability on the system.
- Despite their unsaturation, arenes do not undergo the usual addition reactions associated with alkenes. Their preferred reaction type is **electrophilic substitution**.
- **Aromatic** compounds can be halogenated in either the ring or the side chain, depending on the conditions used.
- Aromatic compounds with alkyl side chains can be oxidised by potassium manganate(VII) to benzenecarboxylic acids.
- Under forcing conditions with hydrogen, the benzene ring can undergo addition rather than substitution.
- **Phenols** are more acidic than alcohols, and can only be esterified by using acyl chlorides.
- The C—O bond in phenols is very strong, and no reactions occur in which it breaks.
- The benzene ring in phenol is much more susceptible to electrophilic attack than is the ring in benzene itself.
- Like alcohols and carboxylic acids, phenol reacts with sodium. Unlike alcohols, it reacts with sodium hydroxide; unlike carboxylic acids, it does *not* react with carbonates.

Key reactions you should know

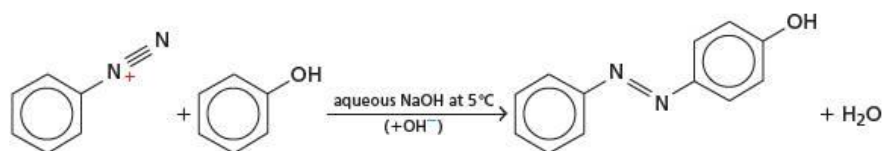
- Electrophilic substitutions:



- Side-chain reactions:



• Reactions of phenols:



Examination practice questions

Please see the data section of the CD for any A_r values you may need.

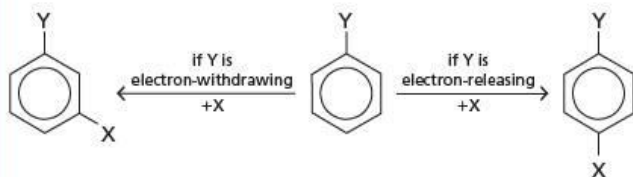
1 The substituted benzene compound



can be further substituted.

If Y is an electron-withdrawing group, the next substitution will be in position 3.

If Y is an electron-releasing group, the next substitution will be mostly in position 4.

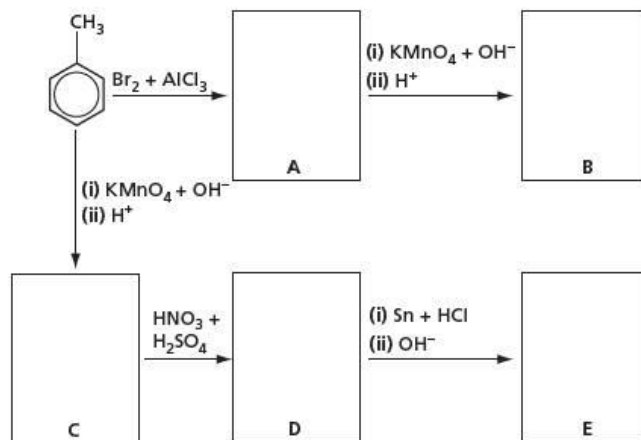


The following table lists some electron-withdrawing and electron-releasing substituents.

Electron-withdrawing groups	Electron-releasing groups
$-\text{NO}_2$	$-\text{CH}_3$
$-\text{COCH}_3$	$-\text{CH}_2\text{Br}$
$-\text{CO}_2\text{H}$	$-\text{NH}_2$

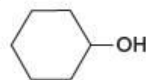
Use the above information to draw relevant structural formulae.

[5]

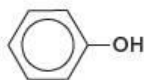


[Cambridge International AS & A Level Chemistry 9701, Paper 4 Q6 June 2008]

- 2 Cyclohexanol and phenol are both solids with low melting points that are fairly soluble in water.



cyclohexanol



phenol

- a Explain why these compounds are more soluble in water than their parent hydrocarbons cyclohexane and benzene. [2]
- b Explain why phenol is more acidic than cyclohexanol. [2]
- c For **each** of the following reagents, draw the structural formula of the product obtained for **each** of the two compounds. If no reaction occurs write **no reaction**. [7]

Reagent
Na(s)
NaOH(aq)
Br ₂ (aq)
I ₂ (aq) + OH ⁻ (aq)
an excess of acidified Cr ₂ O ₇ ²⁻ (aq)

- d Choose **one** of the five reagents that could be used to distinguish between cyclohexanol and phenol. Describe the observations you would make with each compound. [2]

[Cambridge International AS & A Level Chemistry 9701, Paper 41 Q4 November 2009]