30 Hydrocarbons

Arenes

Arenes are organic compounds that contain a benzene ring made up of six carbons.

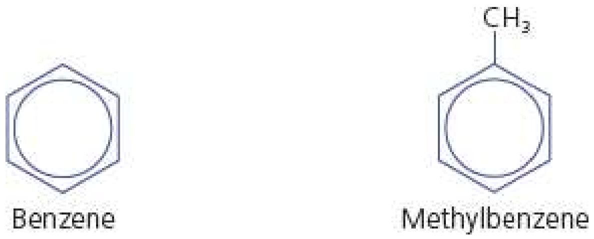
- In a benzene ring the carbon atoms are numbered clockwise from the uppermost atom. You only need to use this numbering system if there is more than one group attached to the ring.
- The structure of the benzene ring gives **aryl** compounds particular properties which differ from those of alkenes.

KEY TERM

Aryl compounds contain at least one benzene ring as part of their structure.

As we saw in Chapter 29, as well as σ bonds between the carbon atoms in the ring and with the hydrogen atoms, there is a ‘ring’ of electrons which are not held by any particular carbon atom. These are called **delocalised** electrons and explain why arenes undergo substitution rather than addition reactions.

- You need to know about two arenes – benzene and methylbenzene (Figure 30.1).



Benzene

Methylbenzene

Figure 30.1

- Although you might not think these molecules are very different, the presence of a side chain in methylbenzene means that it is able to undergo an additional set of reactions compared to benzene.

Substitution reaction: halogenation

Benzene

Benzene reacts at room temperature with chlorine or bromine in the presence of a catalyst. One of the hydrogen atoms in the ring is replaced by a chlorine atom or a bromine atom. A typical catalyst is the aluminium halide of the halogen being substituted, or iron (which reacts with the halogen to form iron(III) halide, which then acts as the catalyst):

$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$

$C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr$

In the case of aluminium bromide, it reacts with the bromine molecule accepting one of the lone pairs of electrons to form the intermediate shown in Figure 30.2(a). This then breaks the Br–Br bond forming a powerful electrophile (Figure 30.2(b)).

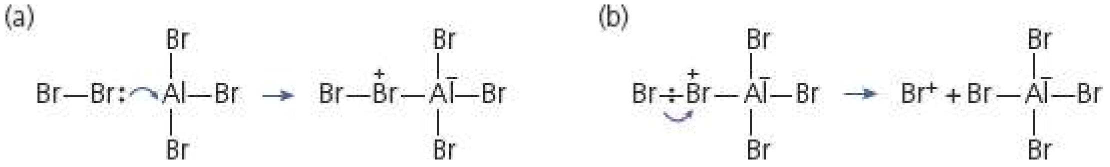


Figure 30.2

The electrophile is attracted to the π electrons of the benzene ring, breaking the ring of electrons to form a σ dative bond to one of the carbon atoms in the ring (Figure 30.4(a)). This intermediate then loses a proton and the π electron ring is reformed (Figure 30.3(b)).

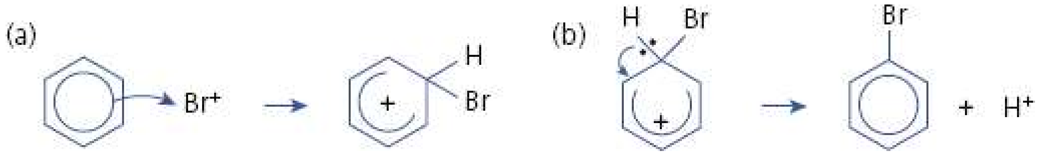


Figure 30.3

Note that in the presence of ultraviolet light (or sunlight), but without a catalyst, benzene undergoes addition reactions with both chlorine and bromine, with six halogen atoms being added to the ring (Figure 30.4).

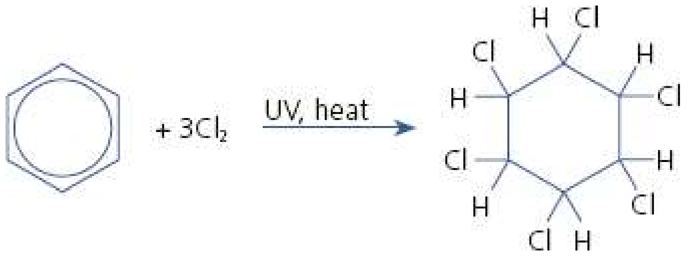


Figure 30.4

As you might expect, the reaction is faster with chlorine than with bromine.

NOW TEST YOURSELF

1 Suggest why benzene undergoes a substitution reaction rather than an addition reaction with chlorine.

Methylbenzene

- With methylbenzene there are two different types of substitution, depending on whether a ring hydrogen or a methyl hydrogen is substituted.
- As with benzene, substitution of a ring hydrogen occurs at room temperature in the presence of an aluminium halide or iron catalyst.
- There is an additional complication of where the halogen atom goes in relation to the methyl group. Methyl groups direct further substitution to the 2- or 4- positions in the ring (the 1-position is that occupied by the methyl group). The reaction with either chlorine or bromine under these conditions results in the formation of a mixture of 2-halo- and 4-halomethylbenzene (Figure 30.5).

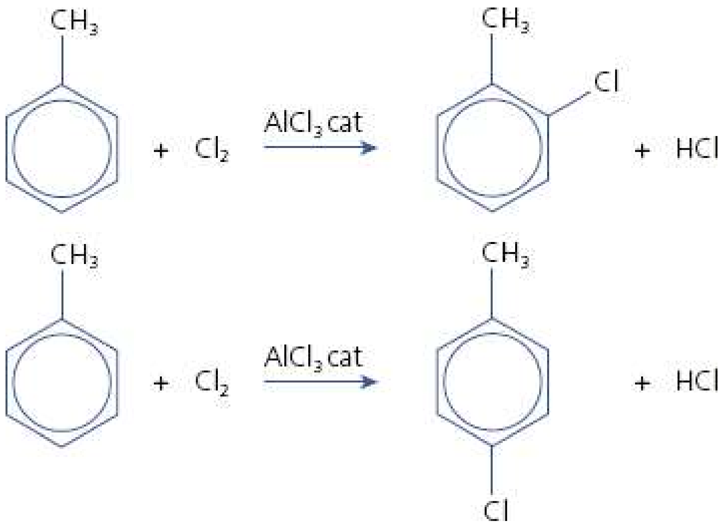


Figure 30.5

- When boiling methylbenzene is reacted with chlorine or bromine in the presence of ultraviolet light, the methyl hydrogen atoms are substituted (Figure 30.6). Provided sufficient halogen is present, all three hydrogen atoms are eventually substituted.

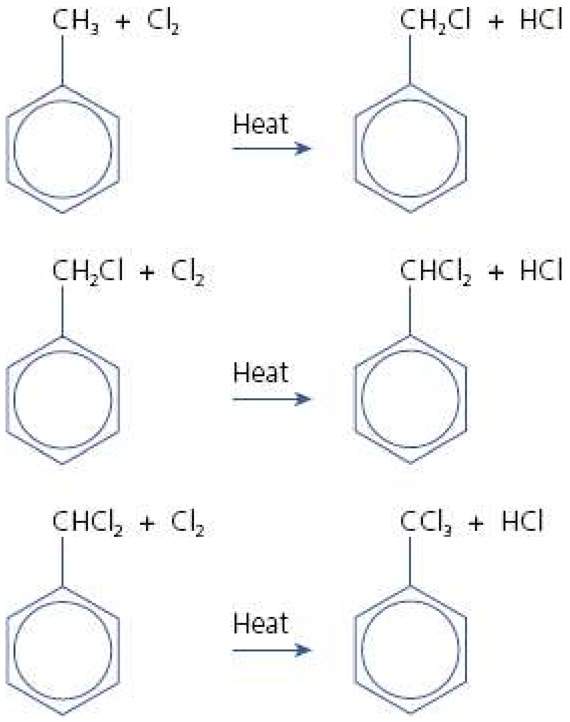
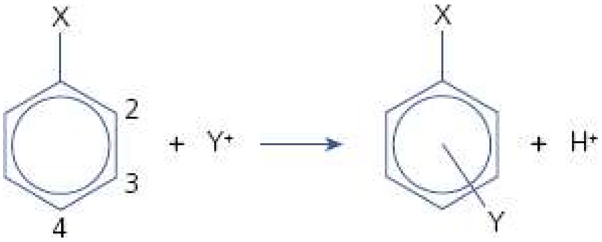


Figure 30.6

Orientating effects of groups in aromatic substitution

You also need to be able to predict the positions of substituents in arenes that have already undergone substitution (Table 30.1).

Table 30.1 The orientating effect of groups in aromatic substitution reactions

	
X groups that direct the incoming Y group to the 2- or 4-positions	**X groups that direct the incoming Y group to the 3-position**
$–NH_2$, –NHR or $–NR_2$	$–NO_2$
–OH or –OR	$–NH_3$
–NHCOR	–CN
$–CH_3$, –alkyl	–CHO, –COR
–Cl	$–CO_2H$, $–CO_2R$

NOW TEST YOURSELF

2 If chlorobenzene is reacted with concentrated nitric acid where, in relation to the chlorine atom, will the nitro group go in the ring?

Substitution reaction: nitration

Benzene

When benzene is treated with a mixture of concentrated nitric acid and concentrated sulfuric acid at a temperature lower than 50°C, yellow nitrobenzene is gradually formed. The sulfuric acid acts as a catalyst:

$$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$$

At higher temperatures, or with prolonged reaction even at 50°C, further nitration occurs (Figure 30.7) with a second nitro group being substituted into the ring. The second nitro group goes into the 3-position:

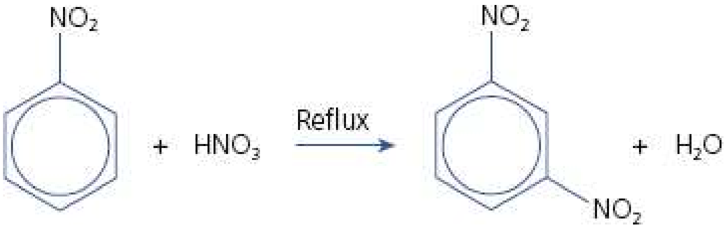


Figure 30.7

Compare this with the methyl group in methylbenzene (below). It *is* possible to get a further nitro group in the 5-position, but the presence of a nitro group ‘deactivates’ the benzene ring, making it much less likely to react.

The mechanism for the mononitration of benzene is an example of electrophilic substitution. The nitrating mixture of concentrated nitric acid and concentrated sulfuric acid produces the electrophile – the nitronium ion, NO_2^+:

$$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$$

The NO_2^+ ion approaches delocalised electrons in benzene and two of these form a bond with the positive charge (Figure 30.8(a)), now spread over the rest of the atoms in the ring. The HSO_4^- ion produced in the nitrating mixture now removes a hydrogen atom (Figure 30.8(b)), re-forming the sulfuric acid catalyst.

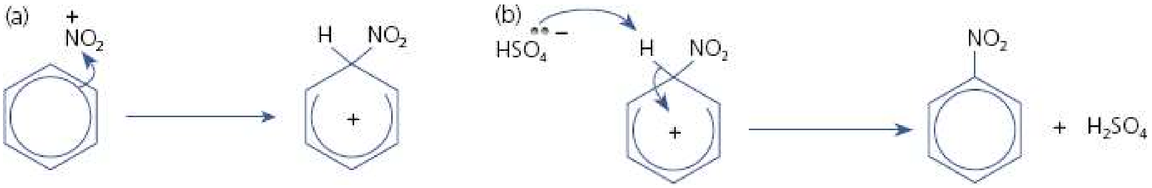


Figure 30.8

Methylbenzene

- In nitration, methylbenzene reacts about 25 times faster than benzene. This means that a lower temperature (around 30°C rather than 50°C) has to be used to prevent more than one nitro group being substituted.
- Apart from that, the reaction is the same, and the same nitrating mixture of concentrated sulfuric acid and nitric acid is used.
- As with the halogens, a mixture of the 2- and 4-nitro substituted arenes (Figure 30.9) is formed.

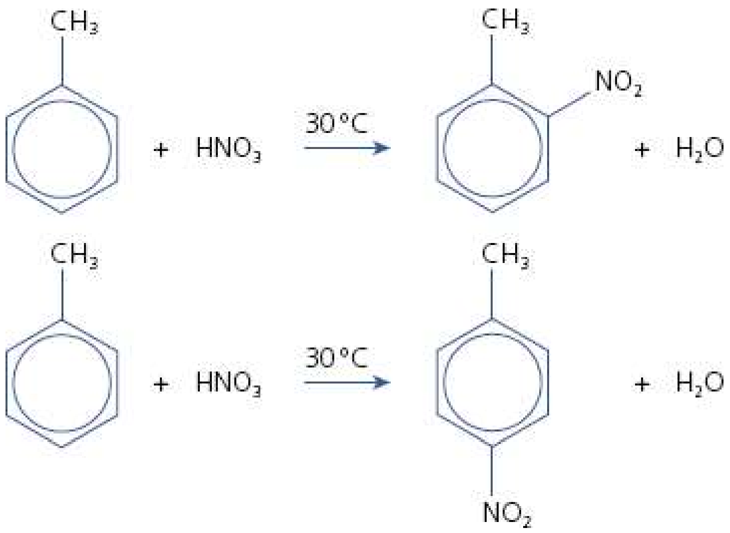


Figure 30.9

Alkylation and acylation

- Using alkyl halides you can substitute an alkyl group into a benzene ring, and using an acyl halide you can substitute an acyl, RCO– group. These are known as Friedel–Crafts reactions.
- Benzene can be **alkylated** by reaction with a halogenoalkane (Figure 30.10), such as chloromethane, in the presence of an aluminium chloride catalyst to form methylbenzene.

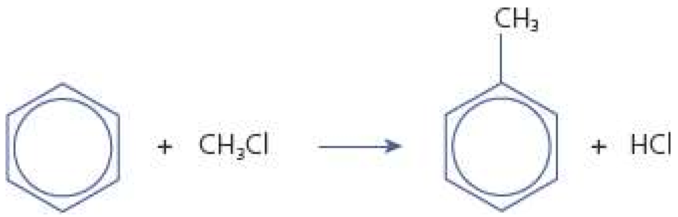


Figure 30.10

- Benzene can also be **acylated** by reaction with an acyl halide (Figure 30.11) such as ethanoyl chloride in the presence of an aluminium chloride catalyst to form phenylethanone.

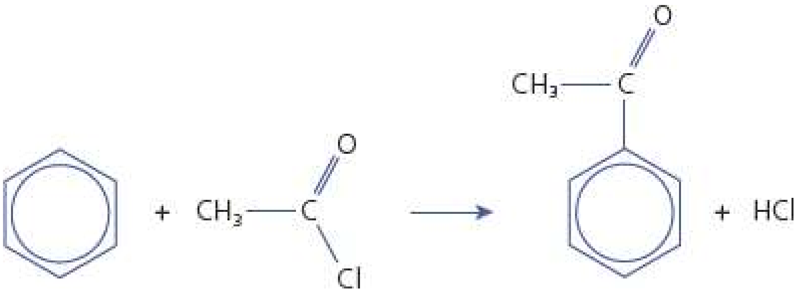


Figure 30.11

KEY TERMS

Alkylation is the substitution of an alkyl group, RC–, to a benzene ring. This substitution was discovered by Charles Friedel and James Crafts, who heated benzene with a chloroalkane and an aluminium chloride catalyst. They found that the alkyl group from the chloroalkane attached to the benzene ring.

Acylation is the addition of an acyl group, RCO–, to a benzene ring forming a phenylketone.

NOW TEST YOURSELF

3 What organic compounds would you form if benzene is reacted under suitable conditions with:

a CH_3CH_2Cl

b C_3H_7COCl?

Side-chain oxidation

This applies only to methylbenzene (and other arenes with alkyl side chains). Alkyl groups in alkanes are usually fairly unreactive towards oxidising agents. However, when attached to a benzene ring they are relatively easily oxidised (Figure 30.12). Heating methylbenzene (or any alkylbenzene) with alkaline potassium manganate(VII) solution, followed by acidification with dilute sulfuric acid, gives benzoic acid (Figure 30.12).

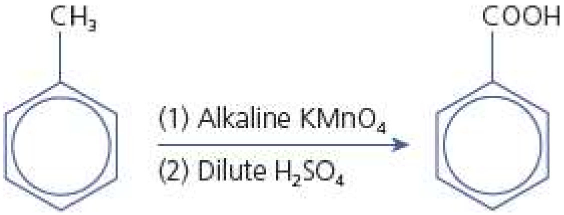


Figure 30.12

Hydrogenation

It is possible to completely hydrogenate a benzene ring to form cyclohexane (Figure 30.13). This is usually done using a nickel catalyst. The aromatic nature of the ring means that this requires more vigorous conditions than the hydrogenation of ethene.

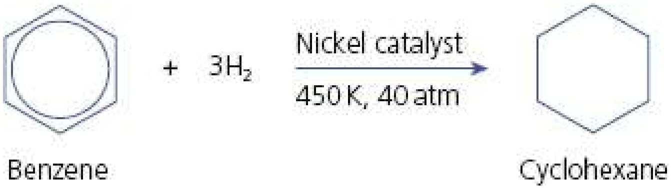


Figure 30.13

REVISION ACTIVITY

a Give a typical reaction of benzene that indicates it does not contain carbon–carbon double bonds.

b Outline two different reactions that methylbenzene can undergo with bromine.

c What chloro- compound would you use to form:

- **i** $(CH_3)_2CH{-}C_6H_5$
- **ii** diphenylketone?

END OF CHAPTER CHECK

By now you should be able to:

- describe the chemistry of arenes exemplified by reactions of benzene and methylbenzene:
  - substitution with Cl_2 or Br_2 in the presence of $AlCl_3$ or $AlBr_3$
  - nitration with concentrated HNO_3 and concentrated H_2SO_4
  - Friedel–Crafts alkylation
  - Friedel–Crafts acylation
  - complete oxidation of a side chain using hot alkaline $KMnO_4$
  - hydrogenation of the benzene ring using H_2 and a Pt or Ni catalyst
- describe the mechanism of electrophilic substitution to form nitrobenzene or bromobenzene; discuss the effects of delocalisation to explain the predominance of substitution over addition
- predict whether halogenation will occur in the side chain or ring in arenes depending on conditions
- describe the different directing effects of different substituents on the benzene ring: $–NH_2$, –OH, –R, $–NO_2$, –COOH, –COR