15 Arenes

Compounds containing only carbon and hydrogen are called hydrocarbons. This class of compound can be subdivided into alkanes, alkenes and arenes.

15.4 Arenes ☐

ARENES

15.4 Arenes

a) describe the chemistry of arenes as exemplified by the following reactions of benzene and methylbenzene:
  - **(i) substitution reactions with chlorine and with bromine**
  - **(ii) nitration**
  - **(iii) Friedel-Crafts alkylation and acylation**
  - **(iv) complete oxidation of the side-chain to give a benzoic acid**
  - **(v) hydrogenation of the benzene ring to form a cyclohexane ring**

b) (i) describe the mechanism of electrophilic substitution in arenes, as exemplified by the formation of nitrobenzene and bromobenzene
  - **(ii) suggest the mechanism of other electrophilic substitution reactions, given data**
  - **(iii) describe the effect of the delocalisation of electrons in arenes in such reactions**

c) interpret the difference in reactivity between benzene and chlorobenzene

d) predict whether halogenation will occur in the side-chain or in the aromatic ring in arenes depending on reaction conditions

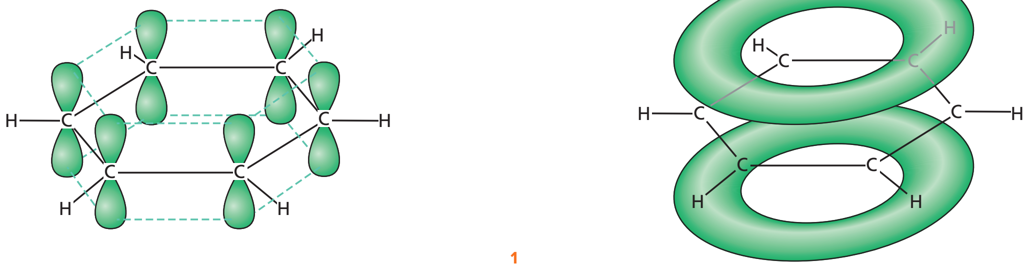
e) apply knowledge relating to position of substitution in the electrophilic substitution of arenes (see the *Data Booklet* Table 9)

STRUCTURE

Benzene 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.

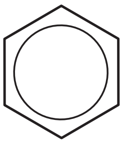
Each p orbital overlaps equally with both its neighbours, forming a delocalised six-centre molecular π orbital.



STRUCTURE

All carbon-carbon bonds are equal in length and strength, as are all carbon-hydrogen bonds, and the C—C—C and H—C—C angles are all 120°.

The benzene structure is normally represented by the skeletal formula



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.

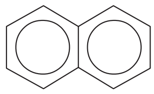
AROMATIC COMPOUNDS

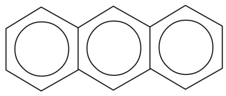
Compounds that contain rings of delocalised electrons are called aromatic compounds.

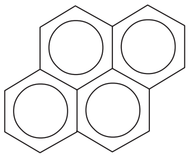
The name was originally applied to certain natural products that had strong, pleasant aromas, such as vanilla-bean oil, clove oil, almond oil, thyme oil and oil of wintergreen.

All of these oils contained compounds whose structures were found to include a benzene ring.

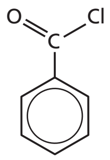
The term ‘aromatic’ eventually became associated with the presence of the ring itself, whether or not the compound had a pleasant aroma.


naphthalene

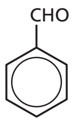

anthracene


pyrene

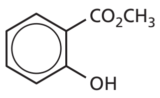
AROMATIC COMPOUNDS



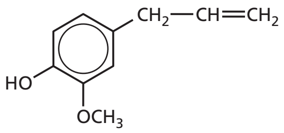
benzoyl chloride
(acidic and nauseating)



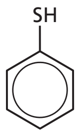
benzaldehyde
(oil of almonds)



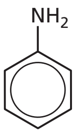
methyl salicylate
(oil of wintergreen)



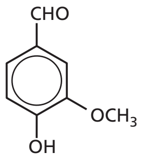
eugenol
(oil of cloves)



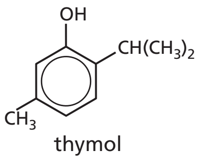
thiophenol
(burnt rubber)



phenylamine (aniline)
(musty, tar-like)



vanillin
(oil of vanilla bean)



thymol
(oil of thyme)

NAMING ARENES

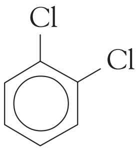
Arenes are hydrocarbons, such as benzene, methylbenzene and naphthalene. They are ring compounds in which there are delocalised electrons. The simplest arene is benzene.

The names and structures of some derivatives of benzene are shown below.

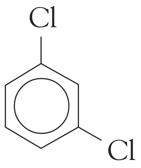
Systematic name	Substituent group	Structure
chlorobenzene	chloro, $-Cl$	C_6H_5-Cl
nitrobenzene	nitro, $-NO_2$	$C_6H_5-NO_2$
methylbenzene	methyl, $-CH_3$	$C_6H_5-CH_3$
phenol	hydroxy, $-OH$	C_6H_5-OH
phenylamine	amine, $-NH_2$	$C_6H_5-NH_2$

NAMING ARENES

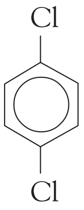
Aromatic compounds with more than one substituent on the benzene ring can exist as positional isomers. There are three dichlorobenzenes:



1,2-dichlorobenzene



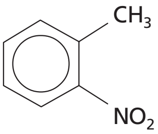
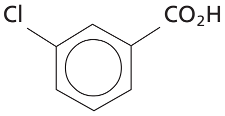
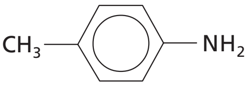
1,3-dichlorobenzene



1,4-dichlorobenzene

NAMING ARENES

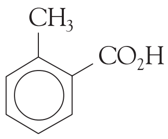
The terms ortho-, meta- and para- are sometimes used as prefixes to represent the relative orientations of the groups.

Orientation	Prefix	Abbreviation	Example
1,2-	*ortho-*	*o-*	
1,3-	*meta-*	*m-*	
1,4-	*para-*	*p-*	

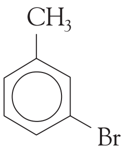
NAMING ARENES

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

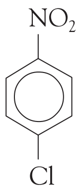
$—CO_2H$ > $—OH$ > $—CH_3$ > —halogen > $—NO_2$ (NO_2 is called the nitro group)



is 2-methylbenzoic acid

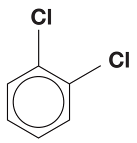


is 3-bromomethylbenzene

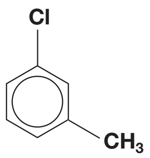


is 4-nitrochlorobenzene.

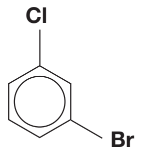
NAMING ARENES



1,2-dichlorobenzene

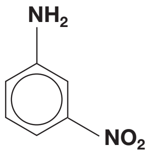


1-chloro-3-methylbenzene

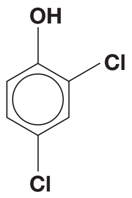


1-bromo-3-chlorobenzene

In phenyl compounds, such as phenol and phenylamine, the −OH and −NH2 groups are assumed to occupy the ‘1’ position.

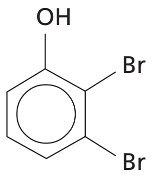


3-nitrophenylamine

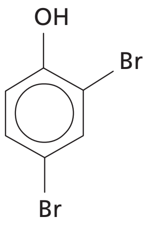


2,4-dichlorophenol

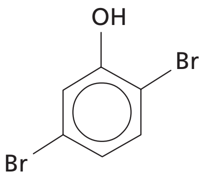
ISOMERS OF $C_6H_3Br_2OH$



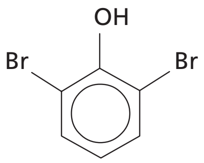
2,3-dibromophenol



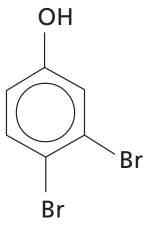
2,4-dibromophenol



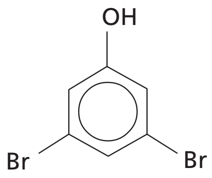
2,5-dibromophenol



2,6-dibromophenol



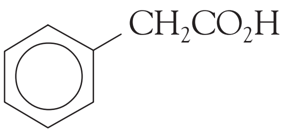
3,4-dibromophenol



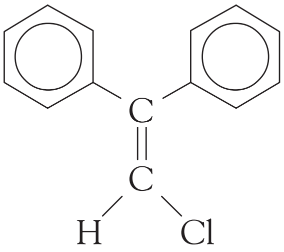
3,5-dibromophenol

NAMING

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



phenylethanoic acid



2,2-diphenylchloroethene

PROPERTIES

Benzene and most alkylbenzenes are strongly oily-smelling colourless liquids.

They do not mix with water, but they do mix with non-polar solvents such as cyclohexane.

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, and increase steadily with relative molecular mass as expected.

Benzene and methylbenzene are liquids at room temperature, while naphthalene is a solid.

REACTIVITY

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.

REACTIVITY

The electrophiles that react with benzene are all positively charged, with a strong electron-attracting tendency.

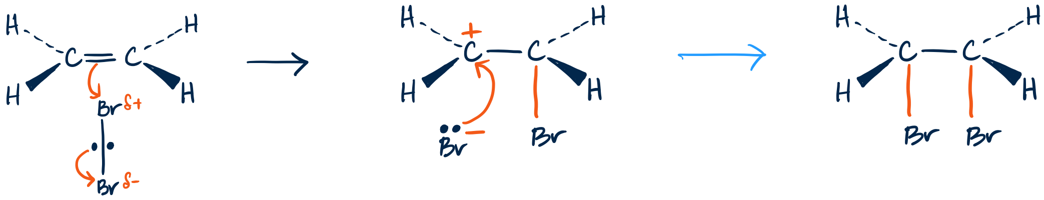
The other major difference between benzene and alkenes is what happens after the electrophile has attacked the π bond.

In alkenes, an anion ‘adds on’ to the carbocation intermediate.

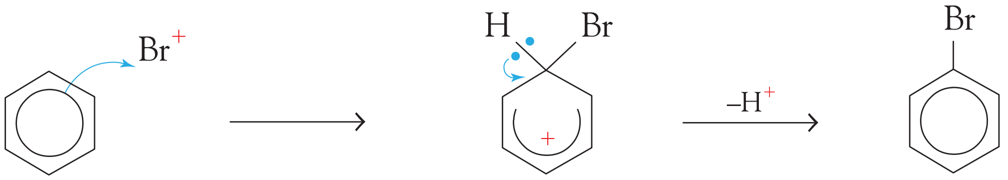
In benzene, on the other hand, the carbocation intermediate loses a proton, so as to re-form the ring of π electrons.

This demonstrates how stable the delocalised system is.

ELECTROPHILIC MECHANISMS



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



carbocation
intermediate

BROMINATION

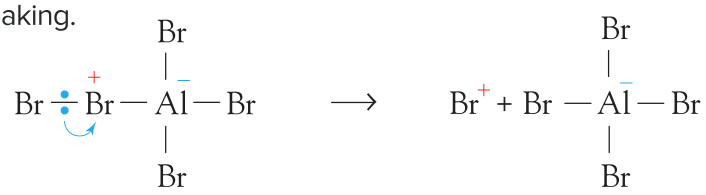
Benzene will react with non-aqueous bromine on warming in the presence of anhydrous aluminium chloride or aluminium bromide, or iron(III) chloride.

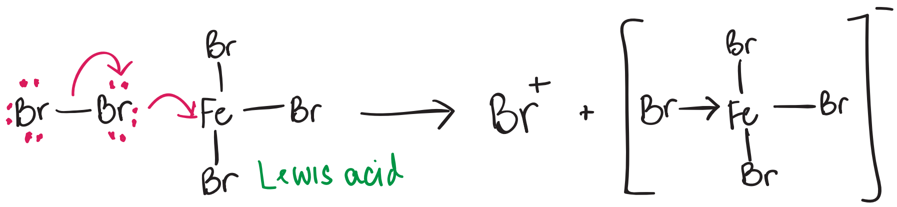
Anhydrous aluminium or iron(III) halides contain electron-deficient atoms.

They can react with the bromine molecule by accepting one of the lone pairs of electrons on bromine.

BROMINATION

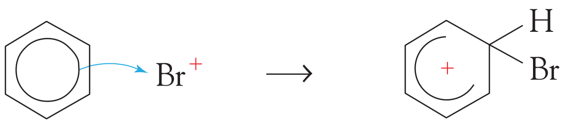
This causes strong polarisation of the Br—Br bond, weakening it, and eventually leading to its heterolytic breaking.





INTERMEDIATE

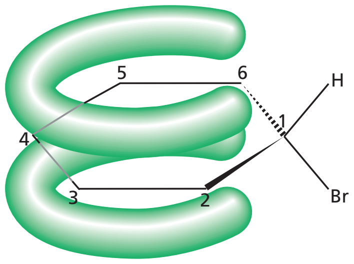
The bromine cation that is formed is a powerful electrophile. It becomes attracted to the π bond of benzene. It eventually breaks the ring of electrons and forms a σ bond to one of the carbon atoms of the ring:



INTERMEDIATE

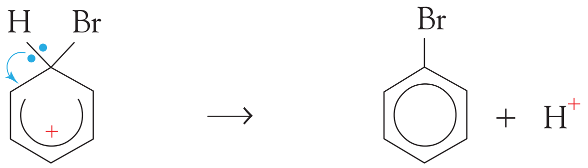
Two of the six π electrons are used to form the (dative) bond to the bromine atom.

The other four π electrons are spread over the remaining five carbon atoms of the ring, in a five-centre delocalised orbital.



BROMINATION

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

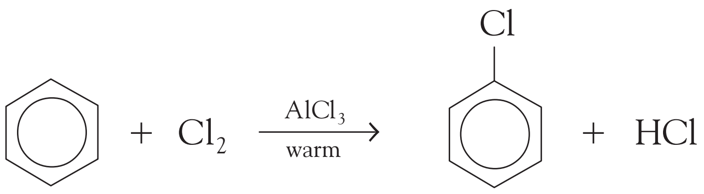


The final stage regenerates the catalyst, by the reaction between the proton (H^+) formed in the above step with the $[AlBr_4]^-$.

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

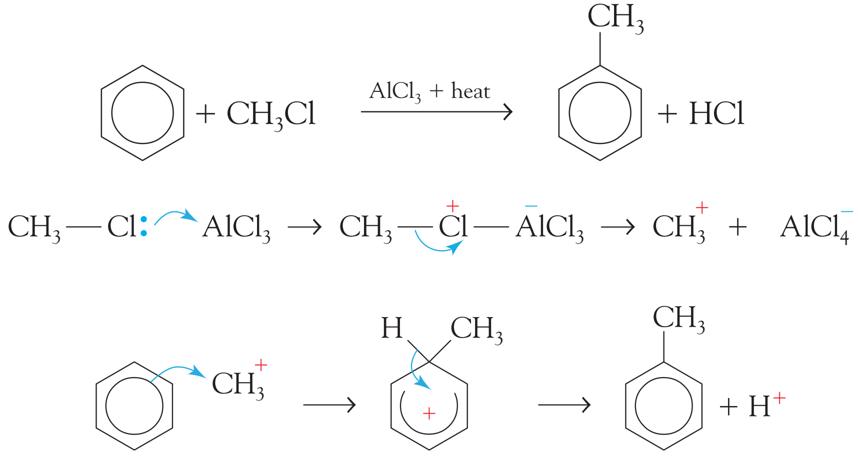
CHLORINATION

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



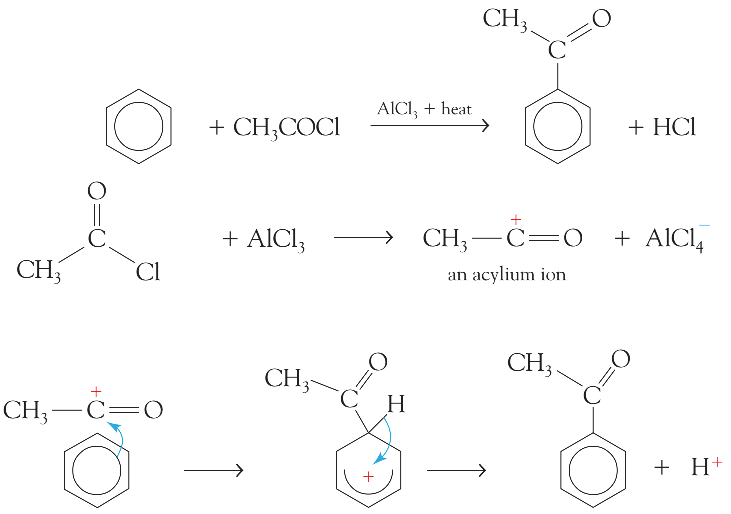
ALKYLATION

when benzene is heated with a chloroalkane in the presence of aluminium chloride, the alkyl group attaches to the benzene ring.



ACYLATION

If an acyl chloride is used instead of a chloroalkane, a phenylketone is produced.



SKILL CHECK 1

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

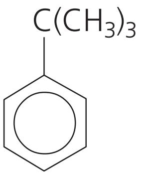
(a) CH_3CH_2Cl

(b) $(CH_3)_2CHCOCl$.

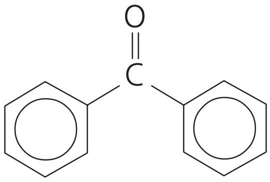
SKILL CHECK 2

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

1

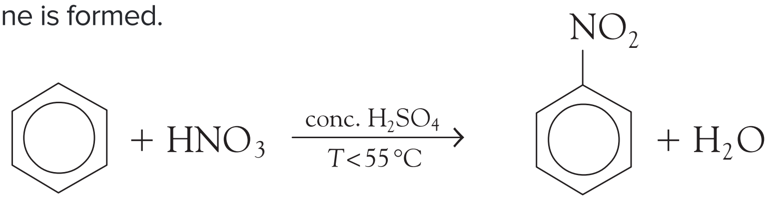


2



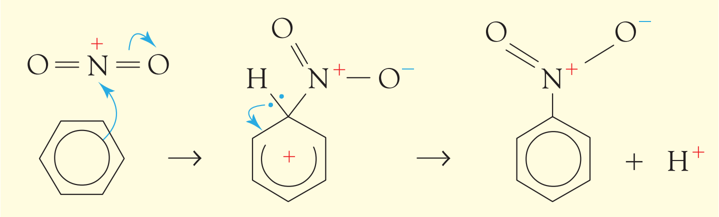
NITRATION

When benzene is treated with a mixture of concentrated nitric and sulphuric acid at around 55ºC nitrobenzene is formed.

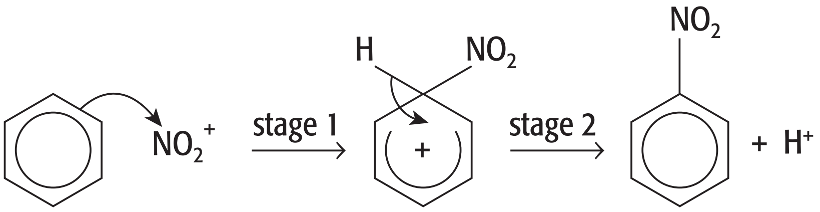


$$C_6H_6 + HNO_3 \xrightarrow[T<55\,°C]{\text{conc. } H_2SO_4} C_6H_5NO_2 + H_2O$$

nitrobenzene



NITRATION



Formation of the electrophile occurs in 3 steps @ 55 °C

$$HNO_3 \longrightarrow NO^{+}_{2} + OH^{-}$$

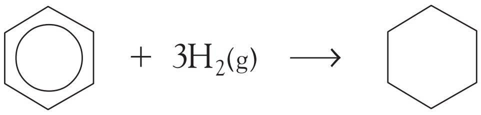
$$OH^{-} + H_2SO_4 \longrightarrow HSO_4^{-} + H_2O$$

$$H_2O + H_2SO_4 \longrightarrow HSO_4^{-} + H_3O^{+}$$

$$2\,H_2SO_4 + HNO_3 \longrightarrow 2\,HSO_4^{-} + H_3O^{+} + NO^{+}_{2}$$

HYDROGENATION

Benzene reacts with hydrogen gas and nickel catalyst at 200 °C to form cyclohexane.



$$\Delta H^{\ominus}_{\text{hydrogenation}} = -205 \text{ kJ mol}^{-1}$$

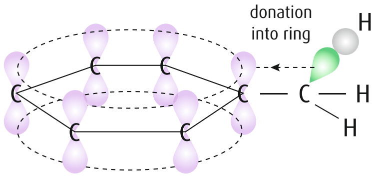
REACTIONS OF METHYL BENZENE

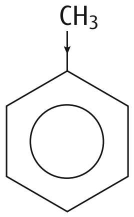
Methylbenzene reacts in the same way as benzene, via an electrophilic- substitution mechanism.

The conditions for the reactions of methylbenzene are slightly milder than those for the reactions of benzene as the methyl group is an activating group.

The methyl group donates electron density into the benzene ring (positive inductive effect).

This increases the amount of electron density in the ring so that it is more attractive to electrophiles and reacts more readily.



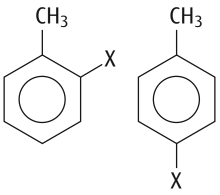


REACTIONS OF METHYL BENZENE

Methylbenzene reacts more readily than benzene due to the electron-releasing effect of the –CH_3 group (positive inductive effect).The methyl group activates the ring towards electrophilic substitution by donating electron density into the ring.

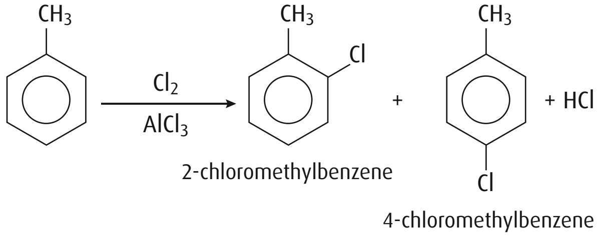
This makes the ring more negative, i.e. more attractive towards electrophiles and the reaction occurs more quickly than with benzene.

The methyl group is a 2,4-directing group and so the major products of substitution are:



CHLORINATION OF METHYL BENZENE

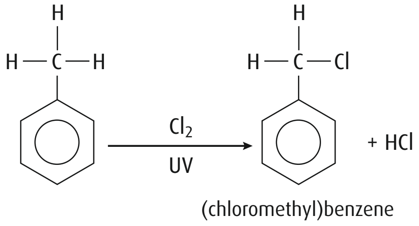
If methylbenzene is reacted with chlorine in the presence of a halogen carrier catalyst ($AlCl_3$) at room temperature 2-chloromethylbenzene and 4-chloromethylbenzene are formed.



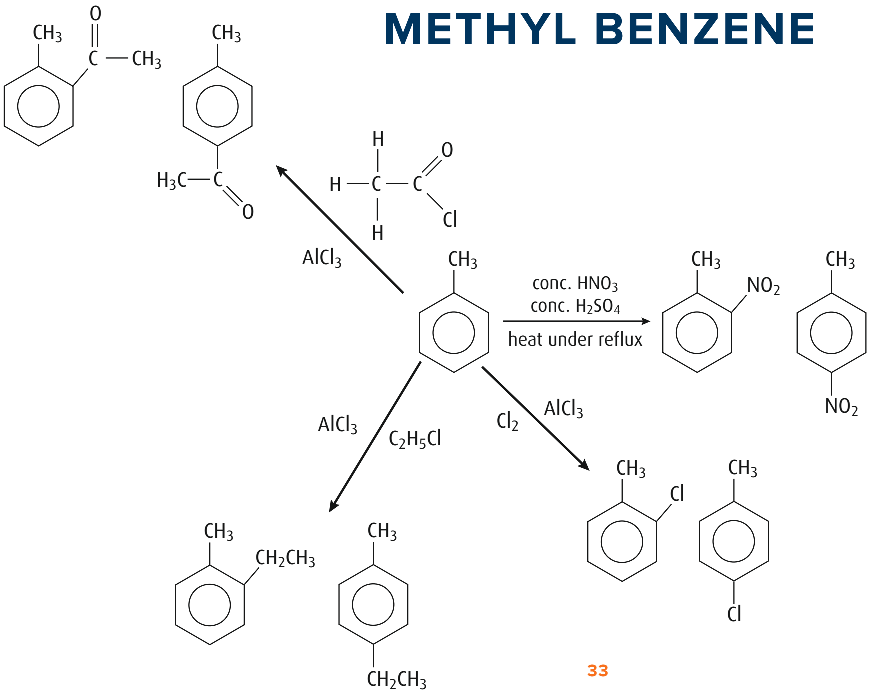
CHLORINATION OF METHYL BENZENE

If methylbenzene is reacted with chlorine in the presence of UV light then side-chain substitution occurs where a hydrogen atom in the methyl group is substituted by a Cl atom.

This involves a free radical substitution mechanism as for alkanes.

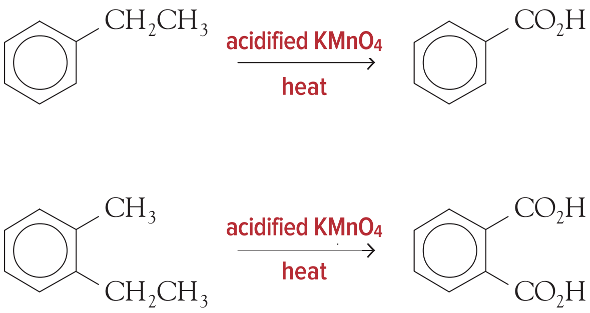


METHYL BENZENE



OXIDATION OF THE SIDE CHAIN

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

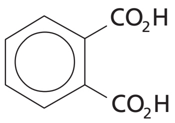


SKILL CHECK 3

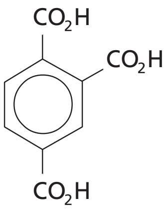
Three hydrocarbons A, B and C with the formula C_9H_{12} were oxidised by hot potassium manganate(VII).

Hydrocarbon A gave benzoic acid, $C_6H_5CO_2H$.

Hydrocarbon B gave benzene-1,2-dioic acid:



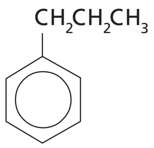
Hydrocarbon C gave benzene-1,2,4-trioic acid:



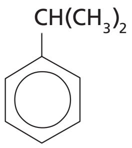
Suggest the structures of A, B and C.

ANSWER

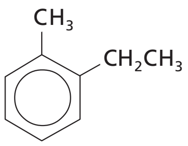
A is:



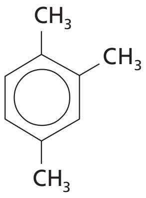
or



B is:

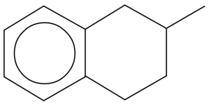


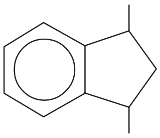
C is:

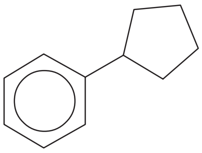


SKILL CHECK 4

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 $C_{11}H_{14}$.)

1


2


3


REACTIONS OF SUBSTITUTED BENZENE RINGS

Substituted benzene rings undergo basically the same reactions as a benzene ring, i.e. electrophilic substitution.

The nature of the substituent determines the position of further substitution and the rate of the reaction relative to unsubstituted benzene.

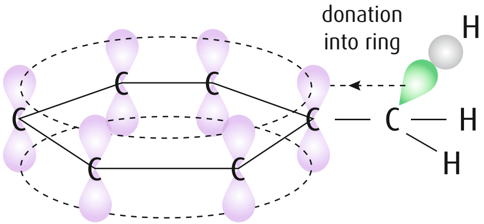
Substituents on a benzene ring may be divided into two groups: those which cause substitution predominantly at positions **2 and 4** (and 6) (**ortho** and **para** positions) and those that cause substitution at position **3** (and 5) (the **meta** position).

The orientation of the incoming group (NO_2 or Br) depends on the substituent already in the ring, and not on the electrophile.

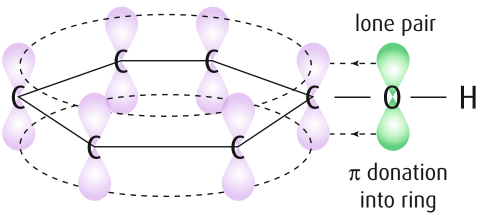
2,4-DIRECTING

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.

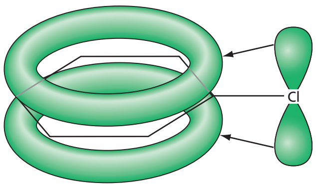


methylbenzene

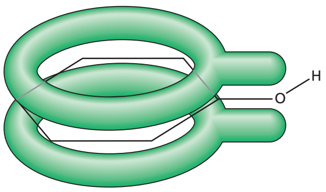


phenol

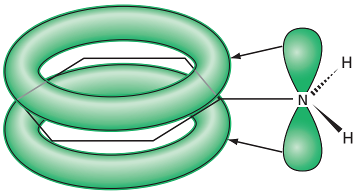
2,4-DIRECTING



chlorobenzene



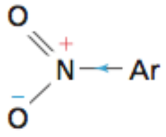
phenol

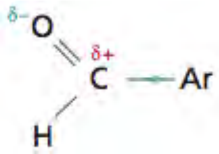


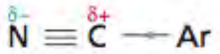
phenyl amine

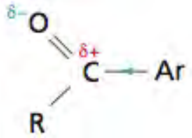
3-DIRECTING

On the other hand, all those substituents that favour 3-substitution have a δ+ atom joined directly to the ring.

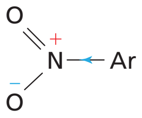
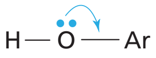
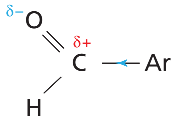
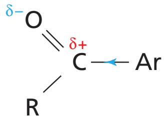








DIRECTING GROUPS

2- and 4-directing substituents	3-directing substituents
$CH_3 \rightarrow Ar$	
	
	$\overset{\delta-}{N} \equiv \overset{\delta+}{C} \leftarrow Ar$
	

DIRECTING GROUPS

One explanation is that an electron-releasing group stabilises the intermediate by electron donation into the ring.

This stabilisation is only possible when substitution occurs at positions 2, 4 and 6.

An electron-withdrawing group destabilises the intermediate by withdrawing electron density from the ring.

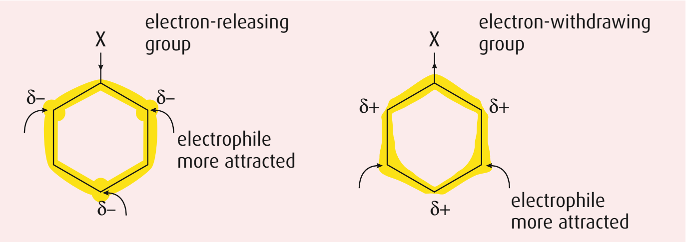
This destabilisation is greatest when substitution occurs at positions 2, 4 and 6, therefore substitution at position 3 is preferred.

DIRECTING GROUPS

An alternative way of explaining the directing effect of substituent groups (not for examinations) is in terms of the charge distribution in the initial compound.

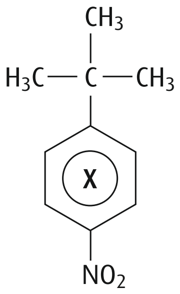
An electron-releasing group will increase the electron density at positions 2, 4 and 6 and therefore the electrophile is more attracted to these positions.

An electron-withdrawing group withdraws electron density from positions 2, 4 and 6 and, therefore, there is more electron density at positions 3 and 5 and an electrophile is attracted to these positions.



SKILL CHECK 5

Compound X, shown below, can be formed from benzene in a two-step reaction sequence. Design a reaction pathway showing all reagents and conditions and the intermediate compound for the conversion of benzene to X.



RATE

2,4-directing groups usually cause substitution faster than benzene and 3-directing group normally cause electrophilic substitution to occur more slowly than benzene (chlorine as a substituent is an exception to this – it is a 2,4-directing group and chlorobenzene reacts more slowly than benzene).

Substituents that cause substitution faster than with benzene are called activating groups (2,4-directing groups except for chlorobenzene) and those that cause substitution to occur more slowly than with benzene are called deactivating group (3-directing group).

RATE OF ELECTROPHILIC SUBSTITUTION

The rate-determining step in the reaction is the attack of the electrophile on the ring.

When an activating group is present this step occurs more quickly as there is more electron density in the ring so that an electrophile is attracted more strongly.

When the ring is deactivated by the withdrawal of electron density, the electrophile is attracted less strongly and the reaction occurs more slowly.

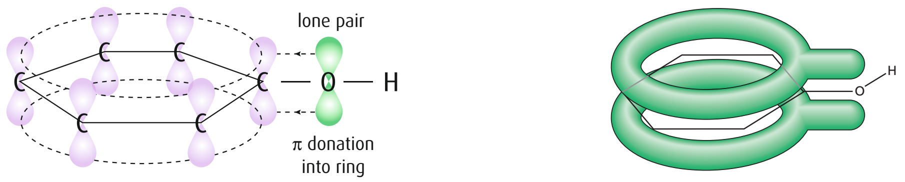
Activating groups donate electron density into the ring. This makes the ring **more negative**, i.e. **more attractive towards electrophiles** and the reaction occurs more quickly than with benzene.

PHENOL FASTER THAN BENZENE

At first sight we might expect the –OH group to be electron-withdrawing due to the high electronegativity of O. However, the –OH group also possesses a lone pair of electrons and overlap of this lone pair into the ring activates the benzene ring.

This π donation into the ring is a bigger effect than the electron withdrawing effect (due to the electronegativity of O).

Therefore there is net donation of electron density into the ring and the ring will attract electrophiles more strongly.

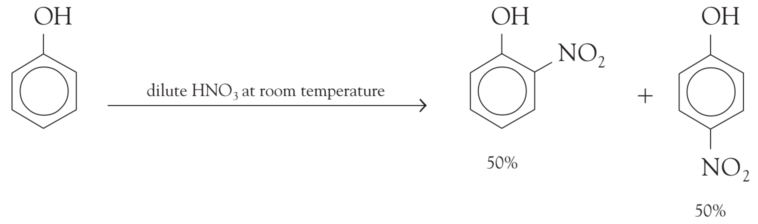


RING REACTIONS WITH PHENOLS

Phenols are more susceptible to electrophilic attack than benzene, owing to the delocalisation of the lone pair of electrons on oxygen.

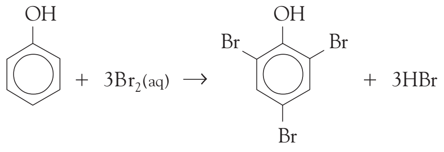
This allows phenol to react with reagents that are more dilute, and also to undergo multiple substitution with ease.

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

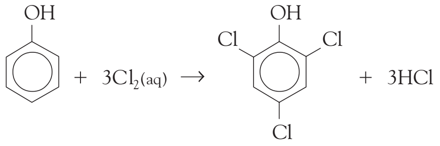


BROMINATION

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.

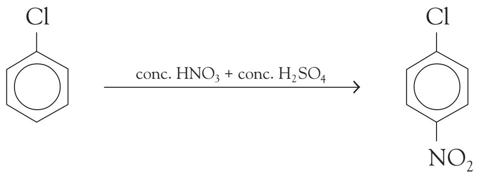


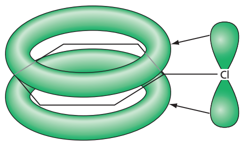
A similar product is formed by the action of chlorine water on phenol.



CHLOROBENZENE

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, due to an overlap of p electrons similar to that in phenol.

The p orbitals from the Cl atom tend to overlap with the delocalised p electrons in the benzene ring. This causes the C—Cl bond to be stronger, and hydrolysis does not occur.

ELECTROPHILIC SUBSTITUTION ON CHLOROBENZENE

Chlorobenzene reacts with electrophiles more slowly than benzene does. The chlorine is a deactivating group.

Chlorine is more electronegative than carbon, and so pulls the electrons in the ring towards itself.

That makes the electron density around the ring rather less in chlorobenzene.

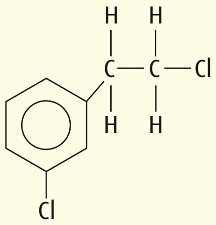
It becomes less attractive for electrophiles, and so the reaction is slower.

Halogenobenzenes are deactivating, yet are 2,4-directors. (The exception to the rule).

SKILL CHECK 6

Give the structure of the organic products formed when the following molecules are heated with excess aqueous sodium hydroxide:

a



b