

31 HALOGEN COMPOUNDS

Learning outcomes

Candidates should be able to:

1. recall the reactions by which halogenoarenes can be produced: substitution of an arene with Cl_2 or Br_2 in the presence of a catalyst, $AlCl_3$ or $AlBr_3$ to form a halogenoarene, exemplified by benzene to form chlorobenzene and methylbenzene to form 2-chloromethylbenzene and 4-chloromethylbenzene
2. explain the difference in reactivity between a halogenoalkane and a halogenoarene as exemplified by chloroethane and chlorobenzene

Difference in reactivity between a halogenoalkane and a halogenoarene

Unlike halogenoalkanes, halogenoarenes cannot be hydrolysed, even by boiling in aqueous sodium hydroxide. The carbon-halogen bond is stronger in halogenoarenes than in halogenoalkanes, possibly due to p-electron overlap, similar to that in phenol.

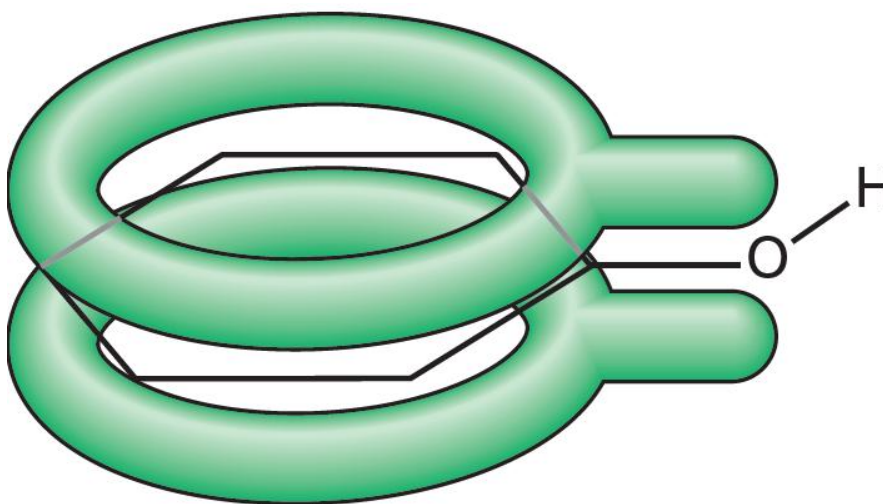


Figure: Delocalisation of the lone pair in phenol

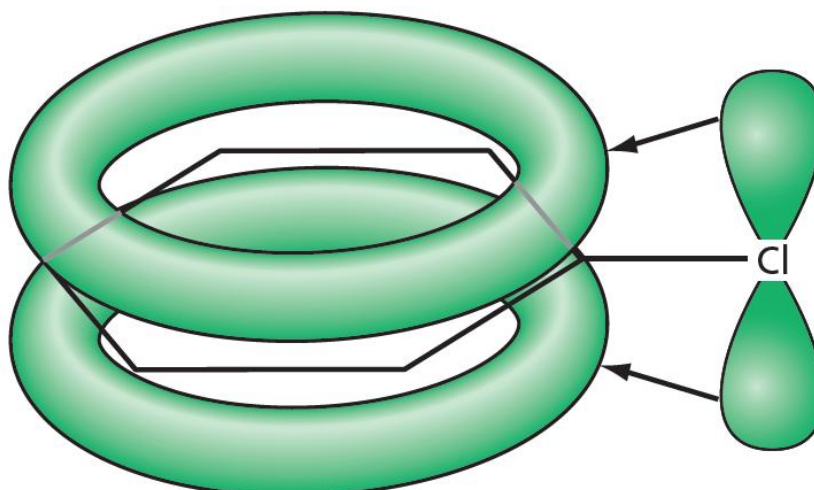


Figure: Delocalisation of the lone pair in chlorobenzene

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 p cloud of the ring. This means that halogenoarenes are inert to all nucleophiles.

1. A three-step synthesis of phenylethanoic acid from methylbenzene is shown.



- (i) State reagents and conditions for step 1.

..... [1]

- (ii) Draw the structure of an organic by-product that forms in step 1.

[1]

2. Chlorobutane and chlorobenzene are added separately to samples of warm aqueous AgNO_3 . One of the chloro-compounds reacts slowly, and the other does not react.

- (i) Identify the chloro-compound that reacts and describe any observations.

.....
 [1]

- (ii) Write two equations to explain any observations in (i).

.....
 [2]

- (iii) Explain the difference in reactivity of chlorobutane and chlorobenzene with warm aqueous AgNO_3 .

.....

 [2]

3. Chloroethane reacts with NaOH(aq) . Chlorobenzene does not.

- (i) Name the mechanism of the reaction that chloroethane undergoes with NaOH(aq) , and identify the major organic product that is formed.

mechanism

major organic product

[1]

(ii) Explain the difference in reactivity of chloroethane and chlorobenzene when treated with NaOH(aq).

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.....
..... [2]

4. Describe the difference in reactivity between chloroethane and chlorobenzene with OH⁻(aq).
Explain your answer.

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.....
.....
..... [2]

5. Explain the difference in the reactivities of chlorobenzene and chloroethane in nucleophilic substitution reactions.

.....
..... [1]

6. Chlorobenzene and chloroethane have different reactivities in nucleophilic substitution reactions.

(i) Identify a suitable reagent to illustrate this difference in reactivity.
The reagent chosen should give **visibly** different results with chlorobenzene and chloroethane.

..... [1]

(ii) Write equations to describe any reactions that occur.

[1]

7. Separate samples of C₆H₅Br and C₆H₅CH₂Br are added to warm AgNO₃(aq).
State the expected observations, if any. Explain your answer.

C₆H₅Br with AgNO₃(aq)

C₆H₅CH₂Br with AgNO₃(aq)

explanation

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.....
..... [3]

***This is not a complete note. It is to guide you. It is recommended to study the prescribed textbooks along with this material. ***