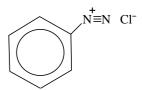
## BENZENE DIAZONIUM CHLORIDE

Structure

- has the formula  $C_6H_5N_2+CI^-$
- a diazonium group is attached to the benzene ring
- the aromatic ring helps stabilise the ion



Preparation

From phenylamine (which can be made by reduction of nitrobenzene)

reagents nitrous acid\* and hydrochloric acid

conditions keep below 10°C

equation  $C_6H_5NH_2 + HNO_2 + HCl \longrightarrow C_6H_5N_2 + Cl + 2H_2O$ 

$$NH_2$$
 +  $HC1$   $< 10^{\circ}C$  +  $2H_2O$ 

\* notes nitrous acid is unstable and is made in situ from sodium nitrite

 $C_6H_5NH_2 + NaNO_2 + 2HCl \longrightarrow C_6H_5N_2^+Cl^- + NaCl + 2H_2O$ 

$$NH_2$$
  
+  $NaNO_2$  +  $2HCl$   $< 10^{\circ}C$   
+  $NaCl$  +  $2H_2O$ 

the solution is kept cold to slow down decomposition of the diazonium salt

 $C_6H_5N_2^+ Cl^- + H_2O \longrightarrow C_6H_5OH + HCl + N_2$ 

$$N_2^+Cl^-$$
 +  $H_2O$   $>10^\circ C$  +  $HCl$  +  $N_2$ 

Reactions

Benzene diazonium chloride undergoes two main types of reaction

SUBSTITUTION OF THE DIAZONIUM GROUP

nitrogen expelled

COUPLING REACTIONS

nitrogen atoms retained

## **SUBSTITUTION**

**OH** reagents

reagents water (hydrolysis) conditions warm above 10°C

equation

**...** 

$$N_2^+Cl^-$$
+  $H_2O$   $>10^{\circ}C$  +  $HCl$  +  $N_2$ 

Diazonium salts

use

- the only reasonably simple way to substitute OH
- phenol is an antiseptic and is used to make polymers

## **COUPLING**

Phenols reagents phenol and sodium hydroxide

conditions alkaline solution below 10°C

equation

 $C_6H_5N_2^+$   $Cl^-$  +  $C_6H_5OH$  + NaOH —>  $C_6H_5-N=N-C_6H_4OH$  + NaCl + H<sub>2</sub>O

$$N_2^+Cl^-$$
 + NaOH - N=N-OH + NaCl + H<sub>2</sub>O

(4-hydroxyphenol)azobenzene

**YELLOW** 

use making azo dyes

the **-N=N-** is the AZO functional group

Q.1 Outline a scheme, listing reagents and conditions, for the synthesis of 1,3-diiodobenzene. (n.b. iodine directs to the 2,4,and 6 positions)