

Extension 20: Diazonium Salts

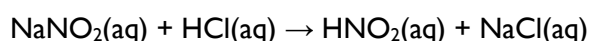
1. Prerequisites

The concepts required to understand this section are:

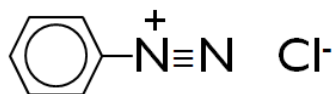
Topic	Book page
Curly arrows	363
S _N I reactions	370

2. Aryl diazonium salts

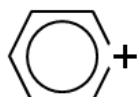
One useful method of putting different substituents onto a benzene ring involves using aryl diazonium salts as intermediates. Diazonium salts are made by reacting aromatic amines with sodium nitrite and hydrochloric acid at 0°C. Phenylamine, as an example, is first dissolved in hydrochloric acid, and then a solution of sodium or potassium nitrite added. The reaction between the hydrochloric acid and the nitrite ions produces nitrous acid:



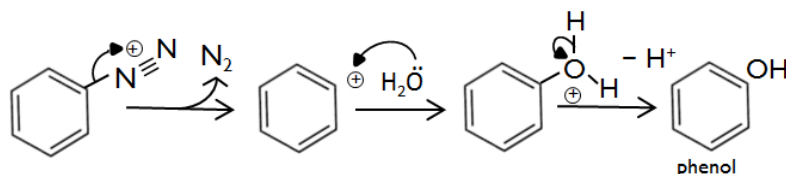
The nitrous acid is made this way (in the reaction mixture) because it decomposes very readily. In these conditions, it produces the NO⁺ ion which reacts with the amine to form a diazo ion. This positive ion, contains the -N₂⁺ group -"azo" refers to nitrogen. The solution contains benzenediazonium chloride:



These ions are unstable and, on warming to room temperature, they lose nitrogen leaving an unstable cation:

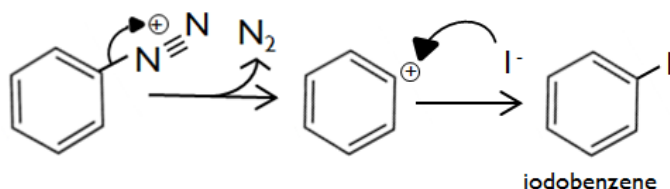


The cation will react with nucleophiles in an S_NI reaction and can be used to substitute atoms or groups that are otherwise difficult to attach to a benzene ring. Reaction with water introduces -OH into the ring making a phenol, for example. This happens if your preparation solution is warmed.



3. Substituting an iodine atom

If potassium iodide solution is added to the benzenediazonium chloride solution at a low temperature, iodobenzene is formed.

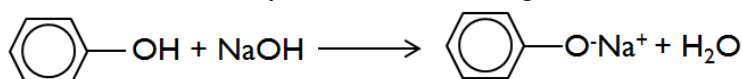


4. Coupling reactions of diazonium ions

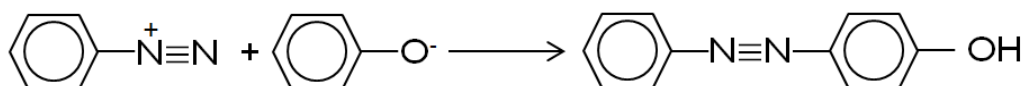
In these reactions, the nitrogen is not lost, but used to make a bridge between two benzene rings.

(i) With phenol:

Phenol is dissolved in sodium hydroxide solution to give a solution of sodium phenoxide.

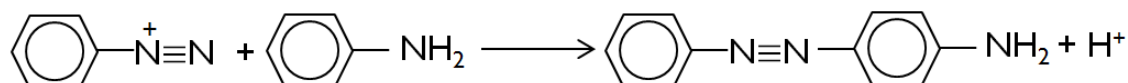


The solution is cooled in ice, and cold benzenediazonium chloride solution is added. A yellow-orange solution or precipitate is formed. The product is one of what are known as azo compounds, in which two benzene rings are linked by a nitrogen bridge. The mechanism is too complicated to include here, but there are some questions asked at the end of this account that you might like to think about.



(ii) With phenylamine (aniline)

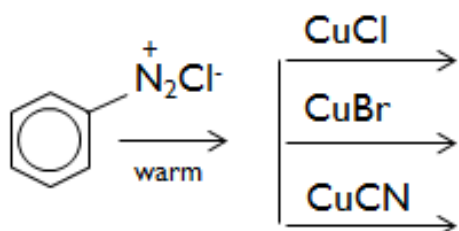
When liquid phenylamine is added to a cold solution of benzenediazonium chloride, a yellow solid is produced:



These strongly coloured azo compounds are frequently used as dyes known as **azo dyes**. There are many examples – the indicator, methyl orange is one.

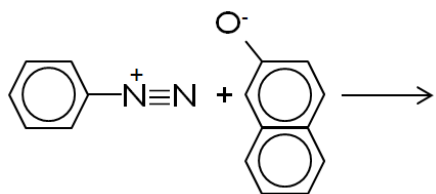
Revision questions

1. Why are diazonium salts generally soluble in water?
2. What do you think would be the products of these three reactions?



3. In the coupling reaction of phenol with another diazo salt, phenol is an ortho/para directing group. Why does the diazo salt prefer to couple in the para position?

4. What do you think is the product of the following reaction? (Hint: it is an intense orange-red colour.)

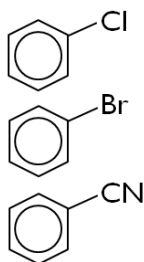


ion formed from the
reaction of sodium
hydroxide with
naphthalene-2-ol

Answers

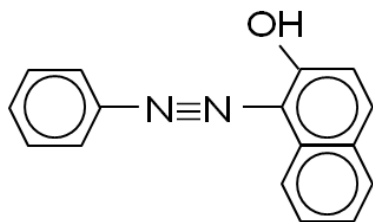
1. They are ionic.

2.



3. The para position is less sterically hindered.

4.



Notice, that this time, the para position from -OH is not available.