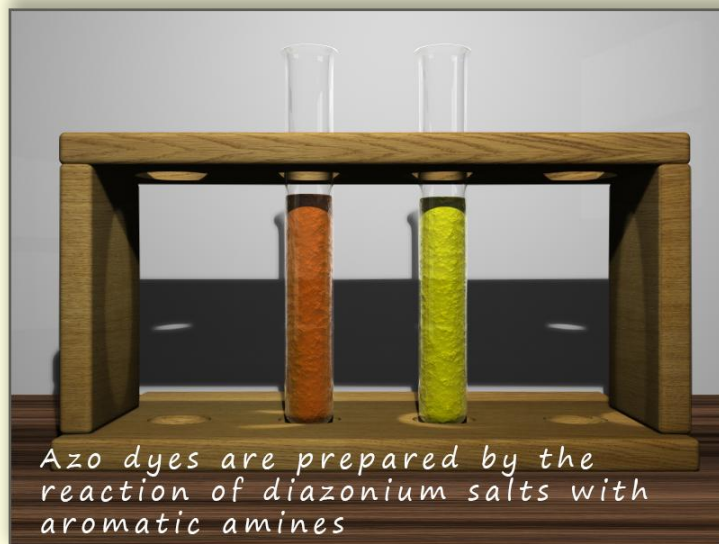


AZO Dyes

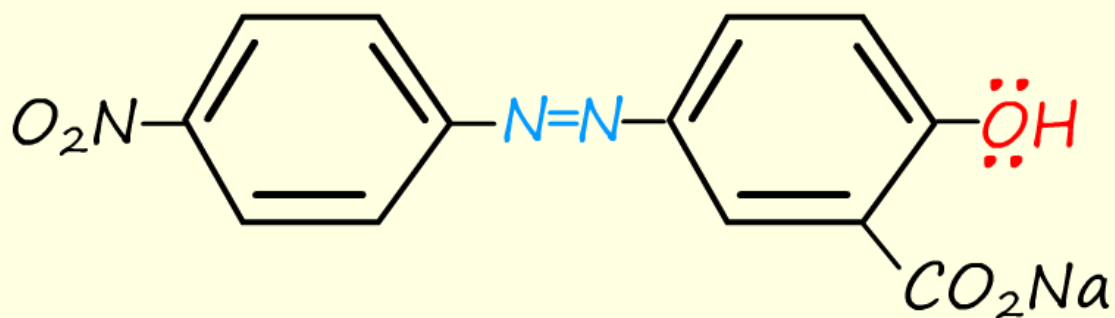
Answer all the questions below as fully as you can then check your answers

1. Why are azo dyes good dyes?
2. Write an equation to show how nitrous acid is prepared from sodium nitrite and acid.
3. What is formed when nitrous acid reacts with primary aryl amines?
 - a. Draw the functional group for an arenediazonium salt.
 - b. What are arenediazonium salts more stable than alkyl diazonium salts?
 - c. Why are diazonium salts unstable? Why should solid diazonium salts not be prepared dry in the lab?
 - d. What is a diazotisation reaction?
4. The image opposite shows two azo dyes.
 - a. The orange dye was prepared by the reaction of benzenediazonium chloride with phenol and the yellow solid dye was prepared by the reaction of benzenediazonium chloride with N,N-dimethylphenylamine.



Azo dyes are prepared by the reaction of diazonium salts with aromatic amines

- i. Write equations to show how both of these two azo dyes are made.
- ii. What is responsible for azo dyes being coloured compounds?
6. The azo dye shown below is called alizarin yellow, it is widely used to dye cloth.



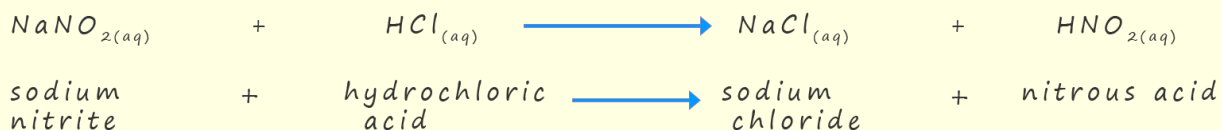
- a. Draw the structures of two compounds which could undergo a coupling reaction to form alizarin yellow dye.
- b. Draw a mechanism using your two structures from part a to show how alizarin yellow is formed.

Answers

1. Why are azo dyes good dyes?

They are available in a wide range of vibrant colours and are colourfast (not easily washed out of the fabric)

2. Write an equation to show how nitrous acid is prepared from sodium nitrite and acid.

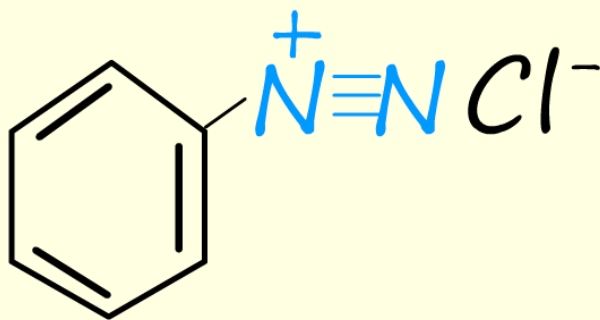


3. What is formed when nitrous acid reacts with primary aryl amines?

primary aromatic amines react with nitrous acid to form salts called arenediazonium salts.

a. Draw the functional group for an arenediazonium salt.

The functional group is shown below, recall that alkyl diazonium salts are unstable and decompose to release nitrogen gas.



benzenediazonium chloride
 ArN_2^+ is an aryl diazonium group.

b. What are arenediazonium salts more stable than alkyl diazonium salts?

The positive charge on the nitrogen atom can be delocalised through the aromatic ring in an arenediazonium salt. This simply involves the overlap of the p-orbitals on the nitrogen atoms with the p-orbitals on the carbon atoms in the aromatic ring. This obviously cannot happen with alkyl diazonium salts. The alkyl group may have a positive inductive effect and push electron density into the N_2^+ ion but it is not sufficient enough to stabilise it.

c. Why are diazonium salts unstable? Why should solid diazonium salts not be prepared dry in the lab?

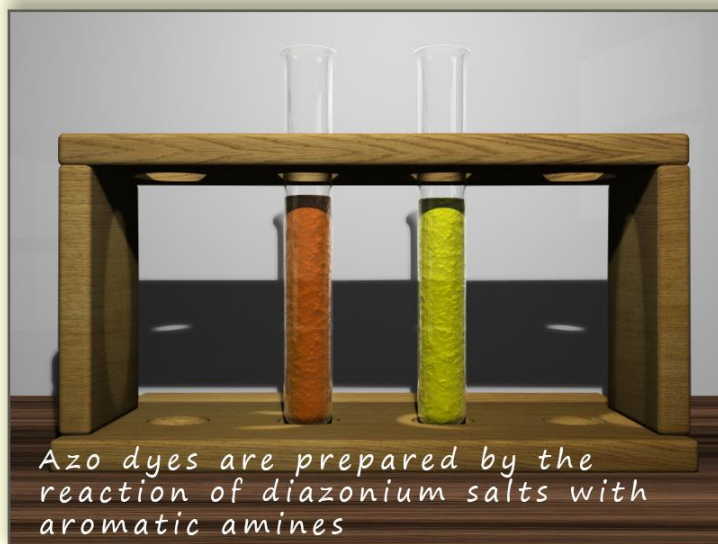
Nitrogen is a very electronegative element and will not be particularly "happy" about having a positive charge. The nitrogen molecule N_2 is also a very stable molecule. So diazonium salts are unstable because they possess an excellent leaving group, nitrogen gas (N_2).

d. What is a diazotisation reaction?

The reaction of primary aromatic amines with nitrous acid to form salts called arenediazonium salts is called diazotisation

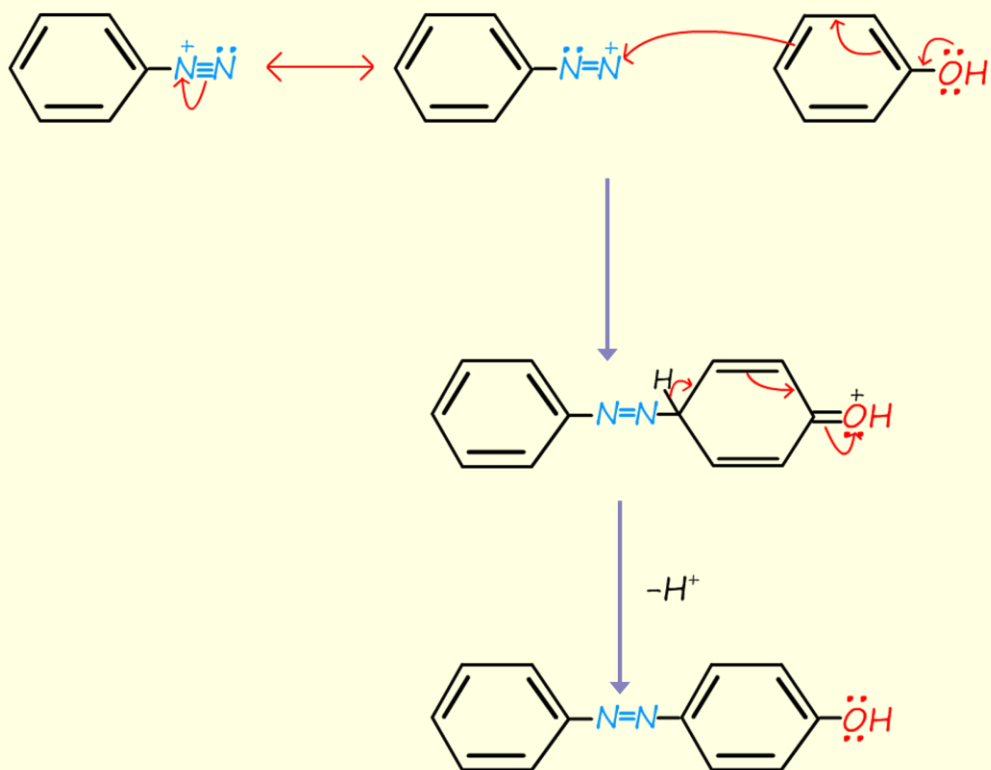
4. The image opposite shows two azo dyes.

a. The orange dye was prepared by the reaction of benzenediazonium chloride with phenol and the yellow solid dye was prepared by the reaction of benzenediazonium chloride with N,N-dimethylphenylamine.

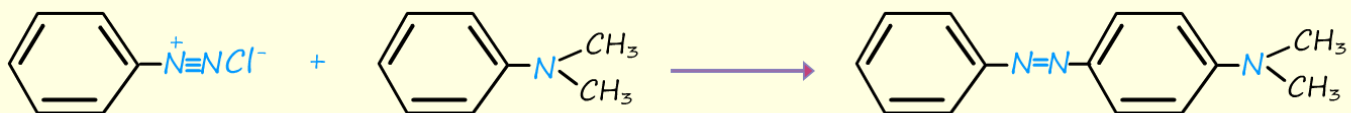


Azo dyes are prepared by the reaction of diazonium salts with aromatic amines

i. Write equations to show how both of these two azo dyes are made.



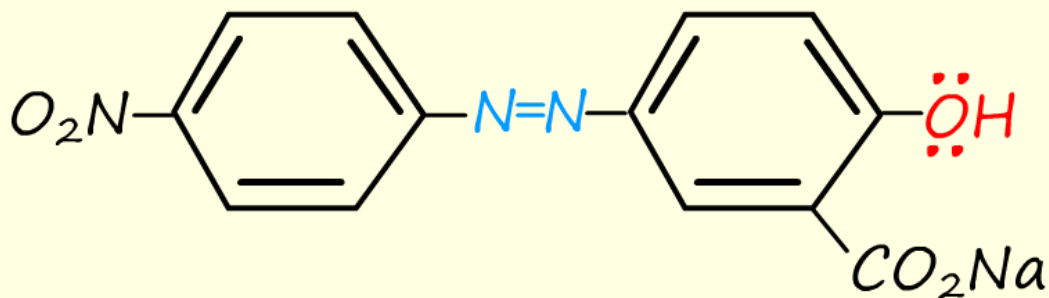
And for the yellow azo compound we have:



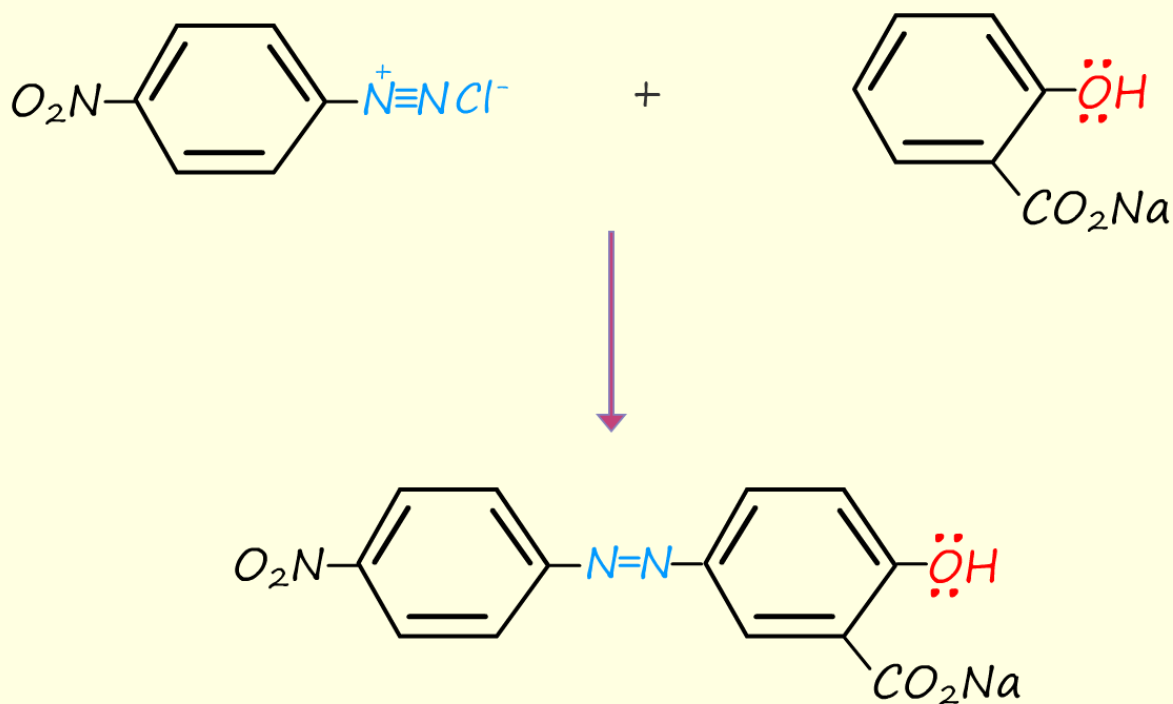
ii. What is responsible for azo dyes being coloured compounds?

The extended conjugated system, that is the alternate single and double $\text{C}=\text{C}$ and $\text{C}-\text{C}$ bonds is responsible for the colour of the azo dye.

6. The azo dye shown below is called alizarin yellow, it is widely used to dye cloth.



- a. Draw the structures of two compounds which could undergo a coupling reaction to form alizarin yellow dye.



- b. Draw a mechanism using your two structures from part a to show how alizarin yellow is formed.

The mechanism will be similar to that in 4a, only the attached groups are different!