Experiment 9 - Arenediazonium Salts

OBJECTIVE

In this experiment, the use of one of the more specialized aromatic reactions, diazonium salts, is examined.

INTRODUCTION

During the study of the chemistry of aromatic compounds, several reactions are encountered that allow for halogenation (**Cl and Br only**), nitration, alkylation, and acylation of the aromatic ring. Also, one is introduced to the influence of substituents on the ring, i.e., groups that are ortho-para directors, or meta directors. However, as one looks through the lecture text, it is apparent that various other substituents are seen in aromatic systems (**OH, CN, I, etc.**) and substitution patterns that do not fit the norm also are observed. These groups are usually added to the aromatic ring via more specific types of reactions.

Arenediazonium salts are generated by the reaction of a primary amine with nitrous acid (produced from sodium nitrite) as shown below. The aromatic amines (anilines) are generated by the reduction of the corresponding nitro compound, which is easily prepared via electrophilic nitration of the ring (see **nitration of methyl benzoate**). The diazonium salts are unstable at temperatures above 5 - 10°C and some explode if allowed to dry. The aliphatic counterpart can be prepared in the same way; however, even at low temperature it is more unstable and can spontaneously decompose by loss of nitrogen to produce carbocation.

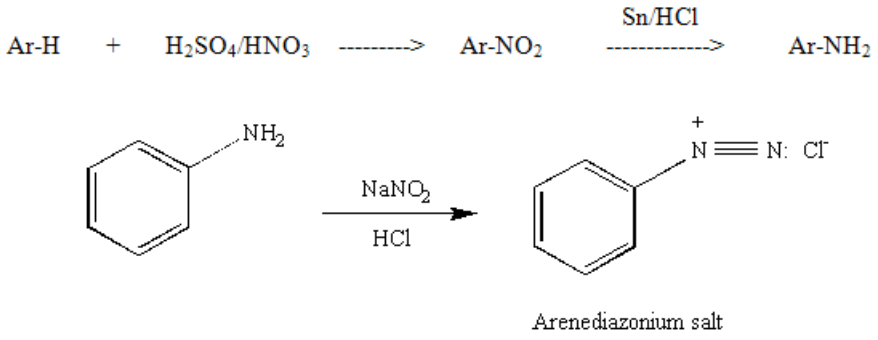


Figure 1

Arenediazonium salts are useful intermediates in the synthesis of aromatic compounds. The diazonium group is readily replaced by a variety of functional groups, thus providing a way to introduce groups that cannot be directly substituted onto the aromatic ring, such as –I, –OH, –F, –CN, –H. Also, one can produce substitution patterns that are contrary to the normal patterns (i.e., preparation of 1,3-dihalosubstituted benzenes). Most of these substitutions do not involve isolation of the diazonium salt.

One simply adds the desired reagent to a solution (aqueous in most cases) of the diazonium salt at 0 - 5°C and allows the solution to slowly warm to room temperature or higher if necessary.

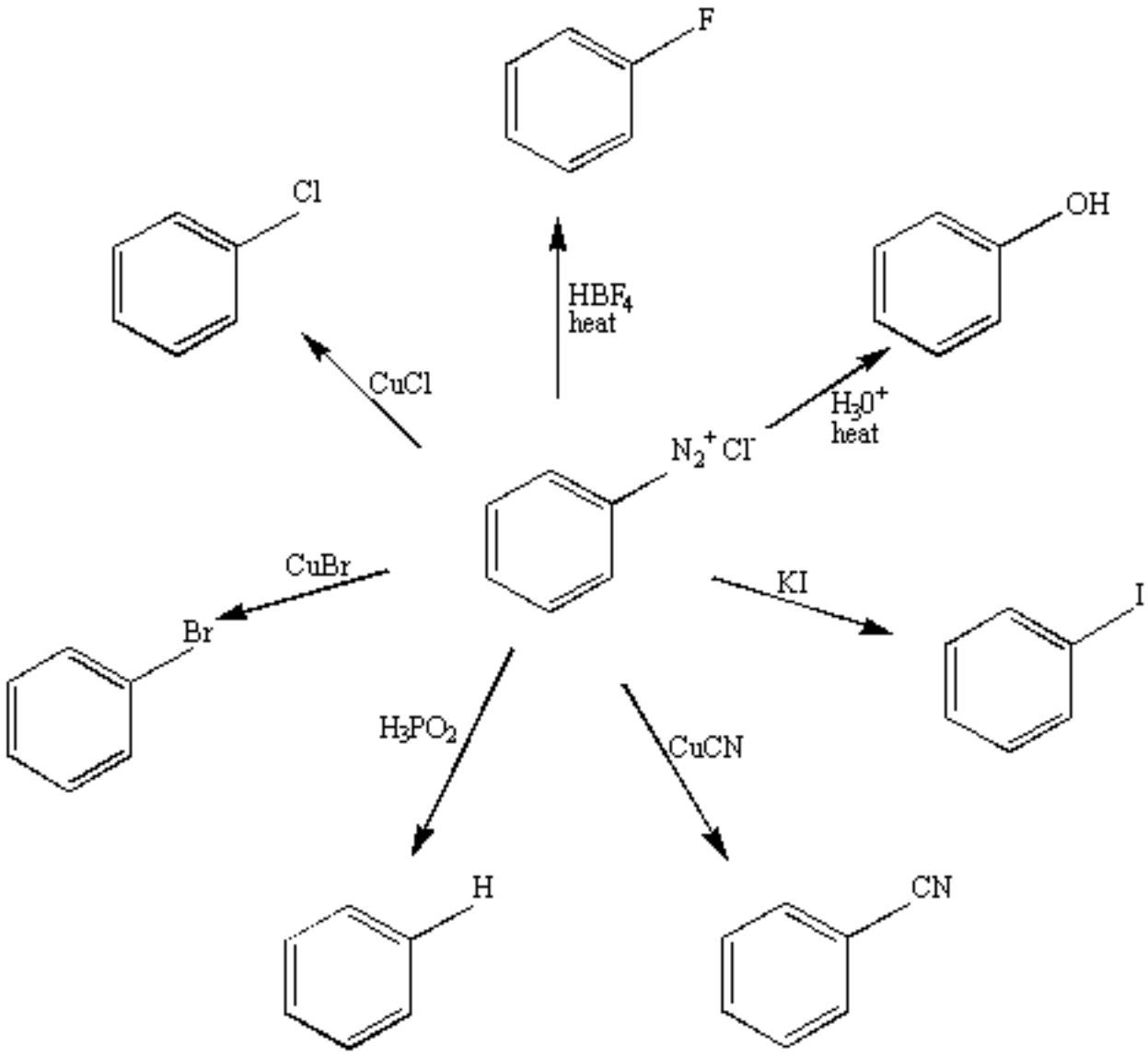
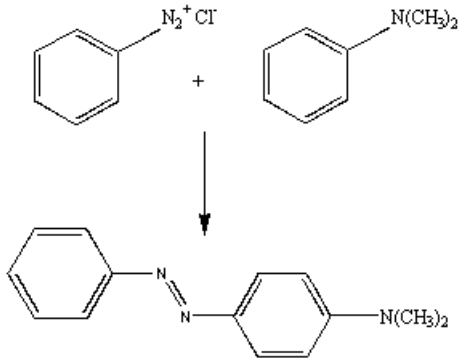


Figure 2

Another useful reaction of diazonium ions is their use as electrophiles in electrophilic aromatic substitution reactions. They will react with highly activated aromatic systems (phenols, arylamines) to yield azo compounds (diazo coupling reaction). Due to the extended system of delocalized pi electrons, azo compounds are usually colored and therefore have found use as dyes.



BUTTER YELLOW

Figure 3

Aromatic iodides have limited stability; therefore, they are not stored for long periods of time. Diazonium salts provide a useful method to prepare the compound just prior to its use. In this experiment, an aryl iodide will be prepared from the corresponding amine by first producing the diazonium salt, then reacting with potassium iodide.

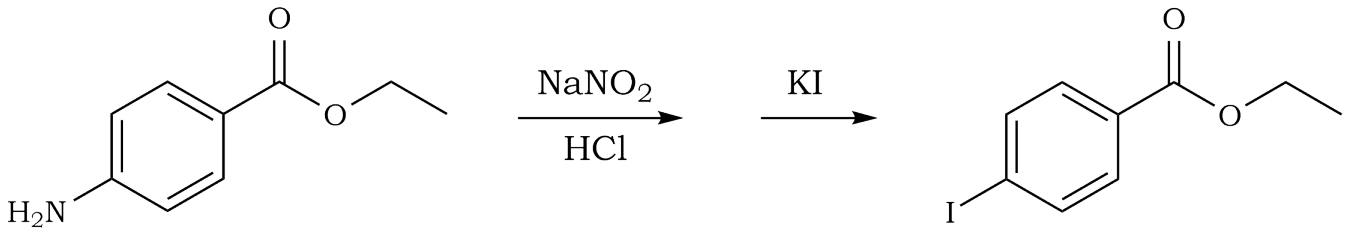


Figure 4

PRE-LAB

Complete the pre-lab assignment in WebAssign.

PROCEDURE

In a 50 mL Erlenmeyer flask, 0.5 g of ethyl 4-aminobenzoate (benzocaine) is dissolved in 8 mL of water containing 2 mL of 6 M HCl. Heating may be required for complete solution formation. The solution is cooled to 0 - 5°C in an ice bath and a solution of 0.23 g of sodium nitrite in 2 mL of water is slowly added. Keep the resulting solution cold and swirl the contents intermittently for a period of 5 - 10 minutes.

Prepare a solution of 1 g of potassium iodide in 2 mL of water. Cool this solution in an ice bath then slowly add it, with swirling, to the cold solution of the diazonium salt. Allow the reaction mixture to slowly warm to room temperature (swirl occasionally) over a period of 10 - 15 minutes. Pour the aqueous reaction mixture into a separatory funnel and extract with 20 mL of diethyl ether. The aqueous layer is removed and the organic layer is washed successively (remove the aqueous layer each time) with 15 mL of 10% HCl, 15 mL of saturated sodium bicarbonate, and 15 mL of saturated sodium thiosulfate.

Transfer the organic layer (yellow to orange in color) to a clean 50 mL Erlenmeyer flask and add a small amount of anhydrous sodium sulfate (cover the bottom of the flask) to dry the organic solution. Allow the solution to dry for 5 minutes, filter (or decant) the ether solution to remove the drying agent (you may use a small amount of ether, ∼5 mL, to rinse the drying agent), and concentrate to yield the product.

Prior to concentrating, check for purity of the product by TLC analysis using hexane:acetone, 7:3. Spot both the product solution and a solution of the starting material on the TLC plate and compare the R_f value of your product with that of the starting material. Determine the yield and percentage yield of the reaction. Perform an infrared analysis on your product and compare the spectrum to that of the starting material.

IN-LAB QUESTIONS

Download and print the following worksheet. You will use this worksheet to record your answers to the In-Lab questions.

Questions

Record the following data.

Question 1: Amount of ethyl 4-aminobenzoate used _____ g, _____ mol

Question 2: Amount of sodium nitrite used _____ g, _____ mol

Question 3: Amount of potassium iodide used _____ g, _____ mol

Question 4: Amount of ethyl 4-iodobenzoate produced _____ g, _____ mol

Question 5: Theoretical yield of ethyl 4-iodobenzoate _____ mol, _____ g

Question 6: Percentage Yield _____

Question 7: Record your calculations.

Question 8: What was the R_f value of the starting material? Of the product? Which one is the more polar?

Question 9: You used infrared spectroscopy as a means to determine the absence of any starting material in the product. What infrared stretches were used?

