

4. Diels-Alder Reactions: Triptycene

M. Jones: Benzyne, 14.14, pgs 733-735, Problem 14.65 p 745

This procedure has been adapted from the microscale procedure described in the third edition of *Macroscale and Microscale Organic Experiments* by Kenneth L. Williamson (Houghton Mifflin, Boston, 1999).

Background

Benzyne. In this laboratory, you will be using anthranilic acid as the starting material for the formation of triptycene (Figure 1). Treatment of anthranilic acid with isoamyl nitrite produces benzyne, which adds to anthracene to form triptycene.

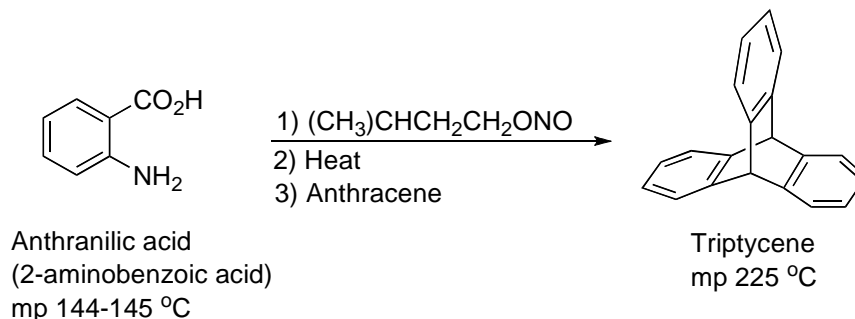


Figure 1. The overall reaction for the synthesis of triptycene.

Upon closer examination, there are few intermediate steps along the way worth noting. The first step is the diazotization of anthranilic acid to give an equilibrium mixture of **A** and **B** (shown below), both of which are precursors for benzyne. They cannot be isolated at room temperature and are considered to be explosive. The key to the first step is not to have the anthranilic acid and the isoamyl nitrite together in the same solution because there will be side products formed.

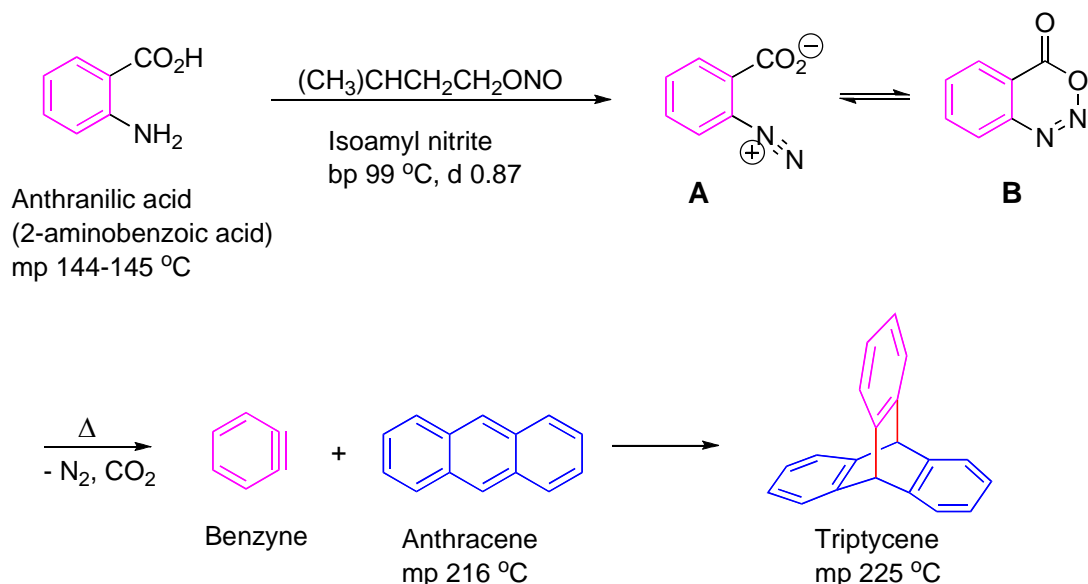


Figure 2. The overall reaction including intermediates **A** and **B**.

Normally, it is preferred to run the reaction for a longer period of time. For this reaction, it has been run using dichloromethane (methylene chloride, CH_2Cl_2 , bp 41 °C) over a multiple hour period. You will be using a higher boiling point solvent, 1,2-dimethoxyethane (ethylene glycol dimethyl ether or monoglyme, bp 85 °C) so as to bring the reaction time into the lab period timeframe.

For this reaction, record the starting amounts of your reactants, observations, amount of product, calculate the % yield, and record the melting point. Do not report any experimental data that you did not measure or take yourself.

Cautions:

- Take extra care when handling these compounds.
- Make sure to use a clean spatula and reaction tube. The reaction tubes should be cleaned with soap, water and a brush first, rinse thoroughly, and dry (if needed rinse with acetone).
- Make sure to return the top to the bottles.
- Do not put hot glassware directly into an ice bath without cooling it to room temperature first.

Experiment

Add 400 mg of anthracene, 0.4 mL of isoamyl nitrite, 4 mL of glyme (1,2-dimethoxyethane), and a boiling chip to a large reaction tube. Heat the tube to a gentle reflux using a sand bath. Dissolve 520 mg of anthranilic acid into 2 mL of glyme (1,2-dimethoxyethane). Add the anthranilic acid solution dropwise over a 20-minute period through a septum. When the addition is complete, add 0.4 mL of isoamyl nitrite to the reaction mixture. When the second addition is complete, reflux for an additional 10 minutes. Let the reaction cool, and then add 5 mL of ethanol, followed by 10 mL of a 3 M sodium hydroxide solution. Filter the mixture and rinse the solid with cold ethanol followed by cold water to remove the brown color. Weight the crude product. Place the solid into a 25 mL round-bottomed flask; add 200 mg of maleic anhydride and 4 mL of triglyme. Fit with a reflux condenser and reflux the mixture in a sand bath for five minutes. Let the solution cool; again, add 2 mL of ethanol, followed by 6 mL of the 3 M sodium hydroxide solution. Filter the mixture and rinse the solid with a cold ethanol followed by cold water to remove the brown color. Recrystallize the solid in methanol. Filter the solid, dry and weigh the final product.