Ring Aromatization through an Elimination Reaction

CHEM HELP *ASAP*

experiment video: https://youtu.be/sjDmTf_JRjQ

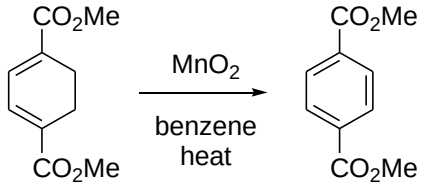
Purpose

The purpose of this experiment is to use sequential elimination reactions to form an aromatic ring. The crude product will be isolated by simple filtration and is pure enough be analyzed without purification.

Background

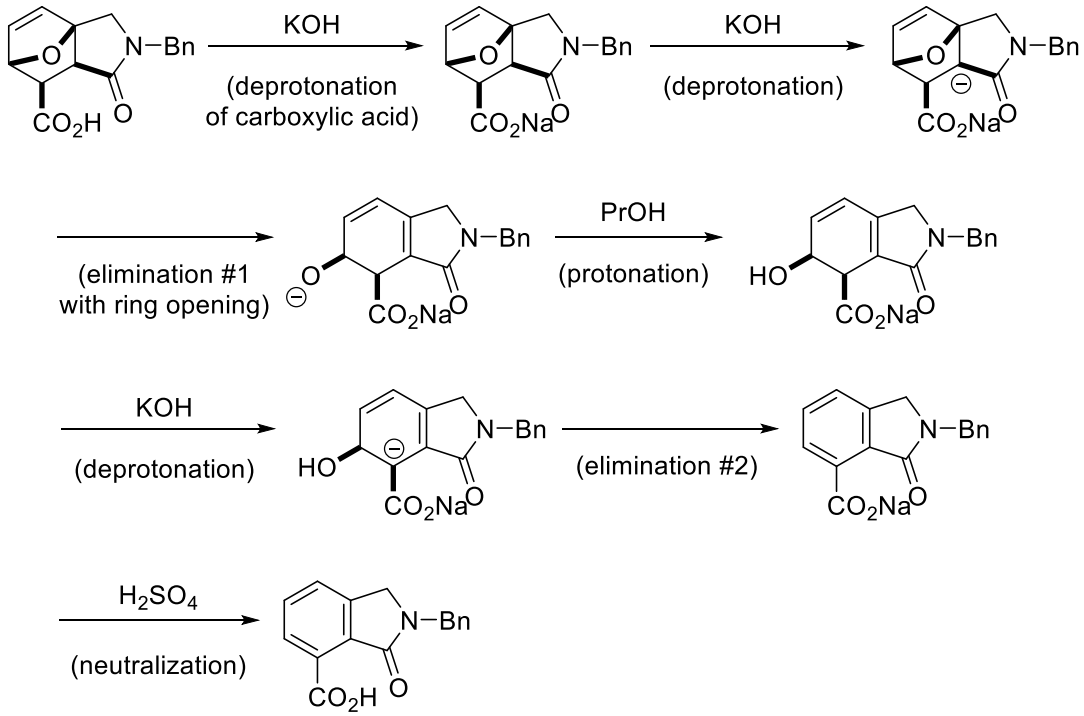
Aromatization reactions involve the conversion of a non-aromatic ring into an aromatic one. These reactions involve creating new π-bonds so that a ring can satisfy all of Huckel's rules and become aromatic. The driving force behind aromatization reactions is the aromatic stability of the final products.

Many aromatization reactions require an oxidation and removal of H_2 to form a new π-bond and aromatic ring. One example is the MnO_2 oxidation of cyclohexadienes (Scheme 1). While this particular reaction works well, the conditions can be harsh for these types of oxidative processes.



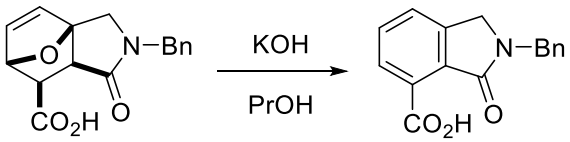
Scheme 1. Oxidative aromatization of a cyclohexadiene

Some aromatizations involve E2 or E1-type eliminations to install new π-bonds. The starting molecule below (Scheme 2) combines the potential to form an aromatic ring with inherent ring strain. The overall transformation involves loss of water. This type of elimination can be catalyzed either with acid or base. The mechanism requires multiple steps with several deprotonations and two eliminations.



Scheme 2. Aromatization of cycloadduct under basic conditions

The reaction itself is easy to perform. The cycloadduct is added to a hot solution of 15% KOH in propanol. After 15 minutes, the reaction is cooled and then diluted in water. At this point, the product has been formed but the carboxylic acid is deprotonated under the basic conditions. The deprotonated acid gives the molecule a negative charge and allows the structure to stay dissolved in the reaction solution. The reaction is then acidified with H_2SO_4. This step neutralizes the deprotonated carboxylic acid to give a solid product for filtration.



Scheme 3. Today's reaction scheme

Procedure – 2,3-dihydro-3-oxo-2-(phenylmethyl)-1*H*-isoindole-4-carboxylic acid

modified from Zubkov, F. I.; Airiyan, I. K.; Ershova, J. D.; Galeev, T. R.; Zaytsev, V. P.; Nikitina, E. V.; Varlamov, A. V. *RSC Adv.* **2012,** *2,* 4103-4109.

Based on the number of mmol of the cycloadduct, add 10 equivalents of KOH in a 20 mL scintillation vial and dilute the KOH in enough propanol to make a 15% (w/v) solution. *Loosely* cap the vial and warm the mixture on a sand bath to around 100 °C to fully dissolve the KOH. (CAUTION: Remember that a sealed system can explode when heated.) Add the solid cycloadduct, replace the cap, and heat the mixture for 15 minutes. Once the heating is complete, allow the reaction to cool to room temperature. Pour the solution into a 100 mL beaker and add approximately 30 mL of water to dilute the reaction. Use small amounts of water to completely rinse the vial. Add 6 M H_2SO_4 dropwise to the beaker to acidify the mixture. Swirl or stir the beaker while adding the acid. Once the addition of acid no longer causes more product to precipitate, check the pH of the solution with pH paper to make sure the pH is 2 or less. Check the pH by sampling the beaker with a pipet. Do **not** dip the pH paper into your beaker. Filter the acidified reaction with a Buchner funnel and a 125-mL side-arm flask, rinse the collected solid with 10-20 mL of water, and spread the solid on a watch glass to dry. Determine the mass of the recovered product, calculate the percent yield, take a melting point, record a TLC (mobile phase: EtOAc), and interpret the NMR spectrum.