



4-[(E)-2-(2-hydroxynaphthalen-1-yl)diazen-1-yl]benzoic acid

4-[(E)-2-(2-hydroxynaphthalen-1-yl)diazenen-1-yl]benzoic acid is a solvatochromic diazo dye.

Solvatochromic dyes change color in solution depending on the polarity of the solvent, making them useful to measure solvent polarity.

We will be synthesizing this dye in a three step sequence, all of which are common reactions covered in organic classes,

starting with p-nitrotoluene.

Each product will be characterized by MP, TLC, FTIR & HNMR.

Summary of steps: p-nitrotoluene → p-nitrobenzoic acid → p-aminobenzoic acid → diazo dye

You only need info for the first reaction for next week. (MP, MWt, Hazards, MSDS, FTIR, HNMR)

You should determine the structures and balanced reactions for all of the compounds given above as we proceed. You will also need to acquire reference FTIR and HNMR spectra for your products.

Locate and print the procedure for preparation of o-chlorobenzoic acid in "Vogel's Textbook of Practical Organic Chemistry, 5<sup>th</sup> ed." (exp. 6.150, p. 1058) via the online link on the 228 web page, in hardcopy at the MST library circulation desk or via Google search.

We will be modifying the Vogel procedure to start with p-nitrotoluene rather than o-chlorotoluene.

We will work on a 0.050 mole scale, starting with 6.85 g of p-nitrotoluene.

**For next week, wed., 10/19/16, have your step 1 oxidation reaction prelab property/hazard table in your lab book and a general idea of what is to be done in the first step.**

**Nitrile gloves are recommended for all steps.**

MSDS List for step 1:

KMnO<sub>4</sub> MnO<sub>2</sub> p-nitrotoluene 3M HCl NaOH p-nitrobenzoic acid Ethanol Celite NaHSO<sub>3</sub>

The following week, we will isolate the product and eventually characterize the product by MP, TLC, FTIR and NMR. There will be a quiz over the first step, 10/26/16.

Step 1. Procedure: We will make any necessary procedural modifications as we proceed.

Place ~220 ml of distilled water and a stir bar in a 600 ml beaker on a hotplate. Cover with a watch glass to minimize evaporation. Set the hotplate to ~250 °C until the water is boiling, then decrease heat if necessary. Add ~0.89 g of NaOH and 6.85 g p-nitrotoluene to the beaker.

Weigh 17.38 g  $\text{KMnO}_4$  and add a small amount once the solution is at ~95 °C. Continue to add in small increments over ~30 min. Once all of the  $\text{KMnO}_4$  is in, continue reflux for a total of ~2hr.

Then add ~1ml of EtOH to remove excess  $\text{KMnO}_4$ . If the purple color is gone, enough has been added, if not, add more until the mixture is brown with no purple. *This is a possible stopping point.*

Cool the mixture to RT and prepare a vacuum filtration setup using a 500 ml filter flask and 70 mm Buchner with Whatman #1 paper. Prepare a slurry of ~5 g Celite in 50 ml water. Dump this rapidly into the Buchner under vacuum to create a pad on the filter paper. Filter your brown reaction mixture through this to give a clear pale yellow filtrate. *This is another possible stopping point.*

If the filtrate smells of p-nitrotoluene, transfer to a beaker and evaporate down to ~100 ml in a hood. Cool and acidify with 6M HCl to pH ~2 via pH paper. Place in an ice bath and allow crystals to form. Vacuum filter the precipitate through a clean sheet of whatman #1 and wash crystals with a small amount of ice cold water. Allow to dry. Weigh, calculate % yield, run MP, TLC, FTIR and NMR.

### Prelab questions (step 1)

1. Balance the redox reaction of  $\text{KMnO}_4$  with p-nitrotoluene to form  $\text{MnO}_2$  and p-nitrobenzoic acid using the half cell method under basic conditions. Show all work.
2. Calculate the theoretical yield of p-nitrobenzoic acid based on your starting amount of p-nitrotoluene.
3.  $\text{NaHSO}_3$  reacts with  $\text{MnO}_2$  to form  $\text{NaHSO}_4$  and  $\text{Mn}^{+2}$ , which provides an easy cleanup method for the insoluble  $\text{MnO}_2$  produced in the oxidation of p-nitrotoluene. Balance this reaction via the half cell method. Show all work.