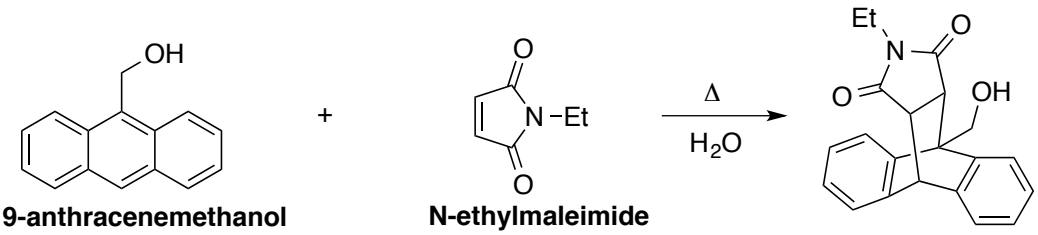
E19B.1 Diels-Alder Reaction in Water:
Reaction of 9-Anthracenemethanol with N-Ethylmaleimide (NEM)

Reading: Diels-Alder Reaction - McMurry 8th edition, Chapter 14.4-14.5
UV-vis Spectroscopy – McMurry Chapter 14.7-14.9 or Mohrig 4th edition Chapter 25

Students work in pairs to perform a Diels-Alder cycloaddition reaction in water solvent under refluxing conditions. Analysis and interpretation of UV-vis, IR, and NMR spectra is performed individually.



9-anthracenemethanol **N-ethylmaleimide**

Notebook Preparation

- *Purpose:* Reaction scheme (starting materials, solvent, product)
- *Reagent table*: List the amounts (mg or mL and mmol), molar equivalents ("equiv.")*, and physical properties (MW, bp or mp, density, one-word hazard) of each chemical in the reaction scheme.
- *Hand-written procedure*: in your own words
- *Safety & Clean*-up*:* copy the following table into your notebook. If anyone in the lab doesn't follow these guidelines, everyone stands the chance of losing points. Hold each other accountable for providing a clean and safe workspace. ***It is not your TA's fault if you lose points – it's yours or your classmate's!***

Safety	*Clean-up*
Toluene, methanol, and petroleum ether are flammable	Shared glassware should be returned cleaned to the reagent counter.
Students should wear gloves, goggles, and lab coat. Gloves should be removed before leaving the room, or if they become contaminated. Same for lab coats.	Quartz cuvettes for UV-Vis must remain in matched pairs – DO NOT MIX Quartz cuvettes are very expensive. There are no extras. Be careful.
9-anthracenemethanol is an irritant	*Liquid waste:* filtrates, UV-vis solutions
NEM is corrosive	*Solid waste:* used pipets, capillaries, and filter papers. Dispose of your product after analysis.

EXPERIMENTAL PROCEDURE

One student should volunteer to make a UV-vis solution of starting material before starting to set up their reaction (see below*). Transfer 200 mg of 9-anthracenemethanol and 150 mg of N-ethylmaleimide (NEM) into a 15-mL round-bottom flask. Add 6 mL of water and a stir bar. Attach a microscale water condenser and heat to reflux directly on the hot plate with stirring for one hour. It may be necessary to occasionally loosen the clamp and swirl the whole assembly to dislodge solid stuck to the walls of the flask above the liquid. Use hot mitts when handling the hot apparatus. During this time, students will take turns preparing solutions for analysis of the 9-anthracenemethanol using UV-vis spectroscopy (see below).

Allow the system to cool to room temperature and collect the solid by vacuum filtration. Wash the product with 2 mL of cold water and let it dry for about 10 minutes with the vacuum on. Weigh the product and determine its boiling point after drying a small sample on a porous plate.

Recrystallize the product from hot toluene and ether in the fume hood: In a medium-sized test tube, dissolve the product in a minimum amount of hot toluene while stirring in a sand bath. Remember that solids may take time to dissolve between additions. After the solid has completely dissolved, add ether in small portions with heating and stirring until turbidity (cloudiness) persists. Then, add a few more drops of hot toluene to bring the solid back into solution. Let the system crystallize at room temperature first, then in an ice-water bath. Isolate via vacuum filtration. Weigh the product and determine its melting point.

Obtain the IR spectrum of the product in a nujol mull. The IR spectrum of the starting materials will be posted in the instrument room for everyone to share (don't take it with you!).

Students will obtain the UV-vis spectra of 9-anthracenemethanol (340-400 nm) and product (200-400 nm). Solutions are made differently for reactant & product…

*Transfer 40 mg of 9-anthracenemethanol into a 25-mL volumetric flask and dilute with methanol. It may take approximately 20 minutes for the solid to dissolve. Mix periodically while setting up the reaction. Once this solution is ready, each pair will prepare their own UV-vis solution by further diluting 0.1 mL of the 9-anthracenemethanol solution to 10 mL in a volumetric flask. Whoever made the 25 mL solution gets to go first! Obtain the UV-vis spectrum under TA supervision in the 340-400 nm range.

Prepare the solution of product for UV-vis analysis by dissolving about 4 mg in methanol in a 25-mL volumetric flask. Obtain the UV-vis spectrum under TA supervision in the 200-400 nm range.

Introduction: Pre-Lab Questions

1. Calculate the theoretical yield of product.

2. Draw the structures of the starting materials and sketch the expected ^{1}H NMR of each. Loosely estimate chemical shifts using the simplified tables provided on eCommons and predict splitting patterns. Instead of integration lines, simply write "1H", "2H", etc. above each signal. Provide labels on the structure to correspond with each proton.

3. Upon initial inspection of the structures of the starting materials and predicted product, describe any drastic changes that will be observed in the spectra (it's not just the spectra of starting materials on top of each other!). In other words, which peaks will shift significantly, appear, or disappear?

4. Although you are not expected to calculate the expected λ_{max} for the starting material and products, how do you expect the λ_{max} to shift in the UV-visible spectrum of the starting material (9-anthracenemethanol) vs. the product? Will the product have a higher or lower λ_{max}? Briefly explain.

Post-Lab Questions

Turn in neatly hand-written responses on a separate sheet of paper before leaving lab. NMR assignments can be made directly on the spectra from lecture (also posted separately on eCommons).

1. Calculate and report the yield (mg and %) of the synthesis.

2. Report the melting point of the crude and recrystallized product.

3. Report and briefly explain the UV-vis spectra of starting material and product.

4. Interpret the ^{1}H NMR of the product, including chemical shifts, integration, and splitting patterns. *Explain the reason behind the observed splitting pattern for the signal at 5.3 ppm.* There is a fair amount of signal overlap so it is not necessary/possible to assign each signal in the aromatic region to a specific hydrogen on the structure. Otherwise, provide a labeled structure and assign the signals to the best of your ability.

5. Interpret the ^{13}C NMR of the product to the best of your ability. You may assign groups of signals to groups of potential carbons on the structure.

6. Interpret the IR of the starting material and the product. What are the main points of interest and what changes were observed in the spectrum after the reaction?

Exp 6 - Diels-Alder Reaction in Water Name _____

Section Day _____ Time _____ TA Name _____

CHEM 110L GRADING RUBRIC - Use as cover page for report

SECTION	INSTRUCTOR COMMENTS	POINTS ASSIGNED
IN-LAB QUIZ		**/ 5**
LAB REPORT		
ABSTRACT One paragraph, four sentences: Purpose, procedure, main result(s), and conclusion(s).	NONE	/ 0
INTRODUCTION Original responses to pre-lab questions with TA initials		/ **20**
RESULTS The main results are stated, as outlined in the in-lab questions, using complete sentences.		/ **30**
EXPERIMENTAL SECTION The experimental details (including final amount used and obtained) are *briefly* described in a few sentences.	NONE	/ 0
NOTEBOOK PAGES Proper format: reaction scheme, chemical info table, procedure, waste and clean-up procedure.		/ **20**
NEATNESS, ORGANIZATION, and LAB TECHNIQUE Proper order and format (see syllabus for full descriptions of each section). Safety rules followed, equipment used properly		**/ 15**
DRAWER CHECK OUT Drawer contents are complete, clean, and organized		**/ 10**
	LAB REPORT TOTAL	**/ 100**