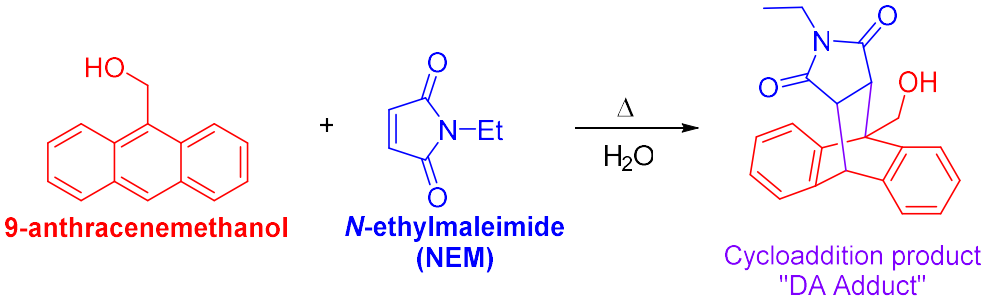
Experiment 6 - Diels-Alder [4+2] Cycloaddition Reaction in Water: Addition of 9-Anthracenemethanol with *N*-Ethylmaleimide (NEM)

Students perform a Diels-Alder [4+2] cycloaddition reaction in water as a solvent under refluxing conditions. Analysis and interpretation of UV-vis, IR, and NMR spectra is performed.



How to Prepare for Lab + Assignments: Follow Canvas Exp 6 Module…

Before Lab

- Read this PDF – procedure, safety, pre-lab questions, & lab report criteria
- Attend and/or watch **lab lecture**
- Preview the lab online *via* **Slugs@home platform** - sites.google.com/ucsc.edu/slugshome/home
- Complete the **pre-lab questions** at the end of this doc - incorporated into Canvas quiz
- **Pre-lab quiz** on Canvas due midnight Monday before your enrolled section
- Use **Exp 6 worksheet** as a template for preparing lab notebook pages – see below

During Lab (Tu-Th)

- Arrive early, dressed for lab; Show your TA: completed notebook pages
- Perform the lab as you fill out data in notebook

After Lab

- Upload **Exp 6 Notebook Pages** to Canvas by midnight on lab day
- Complete & upload the **Exp 6 Lab Report** on GradeScope (GS) one week after lab

Notebook Preparation – refer to the worksheet on Canvas for suggested templates for the lab notebook

- *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.
- *Procedure* – hand-drawn comic strip, flow chart, bullet-points, or whatever format works for you. Avoid copying the procedure word-for-word. Break it up and make it easy for anyone to follow your procedure without referring to this document.
  - **Purpose, reagent table, & procedure diagrams** –complete before you can start lab
  - All **labeled equipment, chemical names** with **amounts**, **transfers**, **cleanup & safety** notes
    - Help w diagrams: Slugs@home Exp 6 website & class notes
- *Safety & Clean*-up*:* copy table that follows the procedure

EXPERIMENTAL PROCEDURE

One student please 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 25-mL round-bottom flask. Add 6 mL of water and a stir bar. Attach a water-jacketed condenser and heat to reflux directly on the hot plate with stirring for one hour. It will 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 **at least 15 minutes** with the vacuum on to pull air through the sample. Weigh the product and determine its melting temperature range after drying a small sample on a porous plate.

Recrystallize the product from hot toluene and diethyl ether (Et_2O) 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!

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.

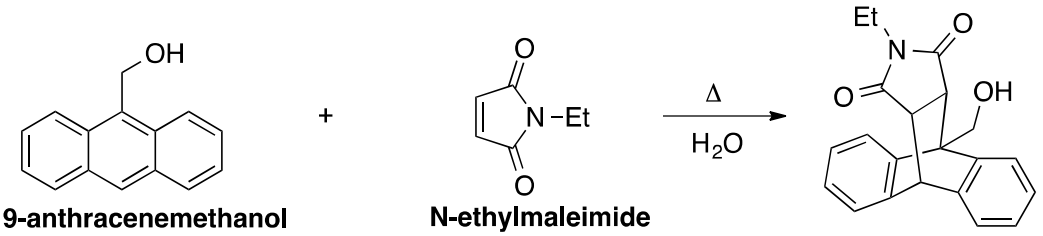
Prepare the solution of **product** for UV-vis analysis by dissolving about 4 mg in methanol in a 25-mL volumetric flask. Obtain the UV-vis spectrum with TA support in the 200-400 nm range.

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.

Additional background 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

Pre-lab Questions - incorporated into the auto-graded Canvas quiz



9-anthracenemethanol **N-ethylmaleimide**

1. Calculate the **mmoles** of each reactant from the amounts given in the procedure, then determine the **theoretical yield** of product.

2. Upon initial inspection of the structures of the starting materials and predicted product, describe any drastic changes that will be observed in the **^{1}H NMR spectra**. In other words, which peaks will shift significantly, appear, or disappear?

3. 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.

LAB REPORT

Abstract

Please refer to the writing guidelines on Canvas for general format and structure.

- **Purpose** – why are we doing this experiment? What is the main goal / result?
- **Methods** – Not the procedure! What chemicals and techniques are used in this reaction? Omit reaction workup details but do include the purification technique with solvents involved.
- **Results** – main results only, no raw data – yield (mg and %); product formation confirmed by (insert analytical tools); list 2-3 key values with units from analysis – ex. one IR stretch, UV-vis absorbance, and/or NMR signal.
- **Conclusion** – tie the purpose back to the main result. Was the goal achieved? Were results as expected? Give a brief explanation to support your conclusion.

Post-Lab Questions

1. **Predict and sketch the expected ^{1}H NMR of 9-anthracenemethanol and *N*-ethylmaleimide** as follows: Draw the structures with H's shown and clearly indicate the chemical shift, integration, and splitting pattern for each type of proton. Label and sketch each unique splitting pattern – there should be 5 types, not counting singlets.

2. Calculate **mmoles** of **9-anthracenemethanol and *N*-ethylmaleimide** and report the **yield** (mg and %) of the synthesis. **Show your work.**

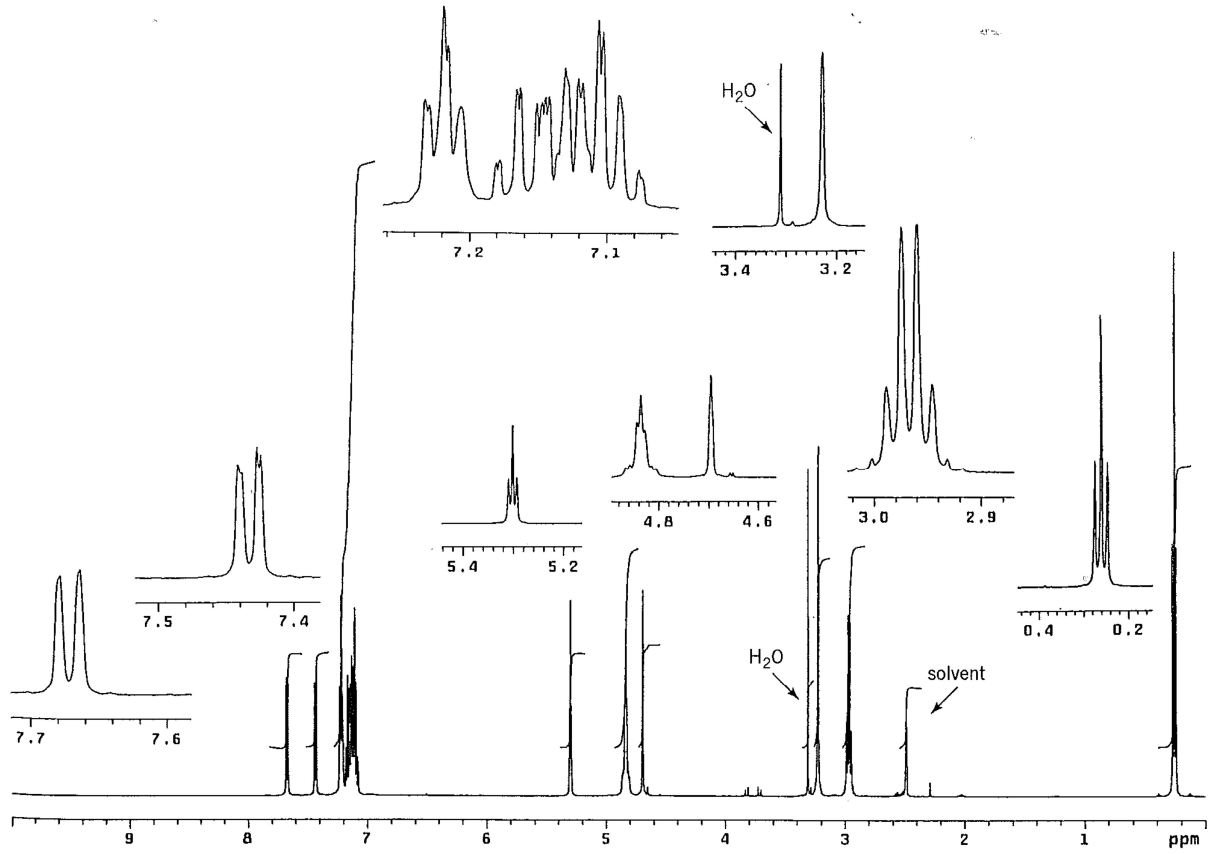
3. Report the **melting temperature range** of the crude and recrystallized product. Comment on the success of the recrystallization and purity of that final product.

4. Report and briefly explain the **UV-vis spectra** of starting material and product (relative λ_{max}).

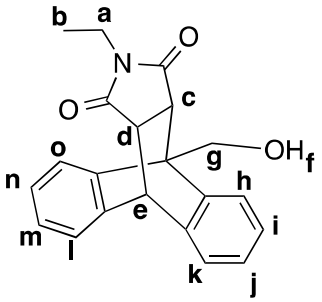
5. Interpret the **^{1}H NMR of the product**, including chemical shifts, integration, and splitting patterns. There is a fair amount of signal overlap so it is not necessary/possible to assign each signal in the aromatic region to a specific hydrogen on the structure. Otherwise, provide a labeled structure and assign the signals to the best of your ability using the spectra & tables on the following pages.

6. 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.

7. Interpret the **IR of the starting material and the product** (table with functional group, bond, expected & observed stretches). What are the **main points of interest** and what **changes** were observed in the spectrum after the reaction?



ure 19.13 500-MHz ^{1}H-NMR spectrum of 9-anthracenemethanol-NEM adduct in DMSO-d_6.



Signal (a-o)	Integration	Splitting	Expected Chemical Shift	Observed Chemical Shift
				0.4
				3.0
				3.2
				4.7
				4.8
				5.3
	5H (overlap)			7.1
				7.2
				7.4
				7.7

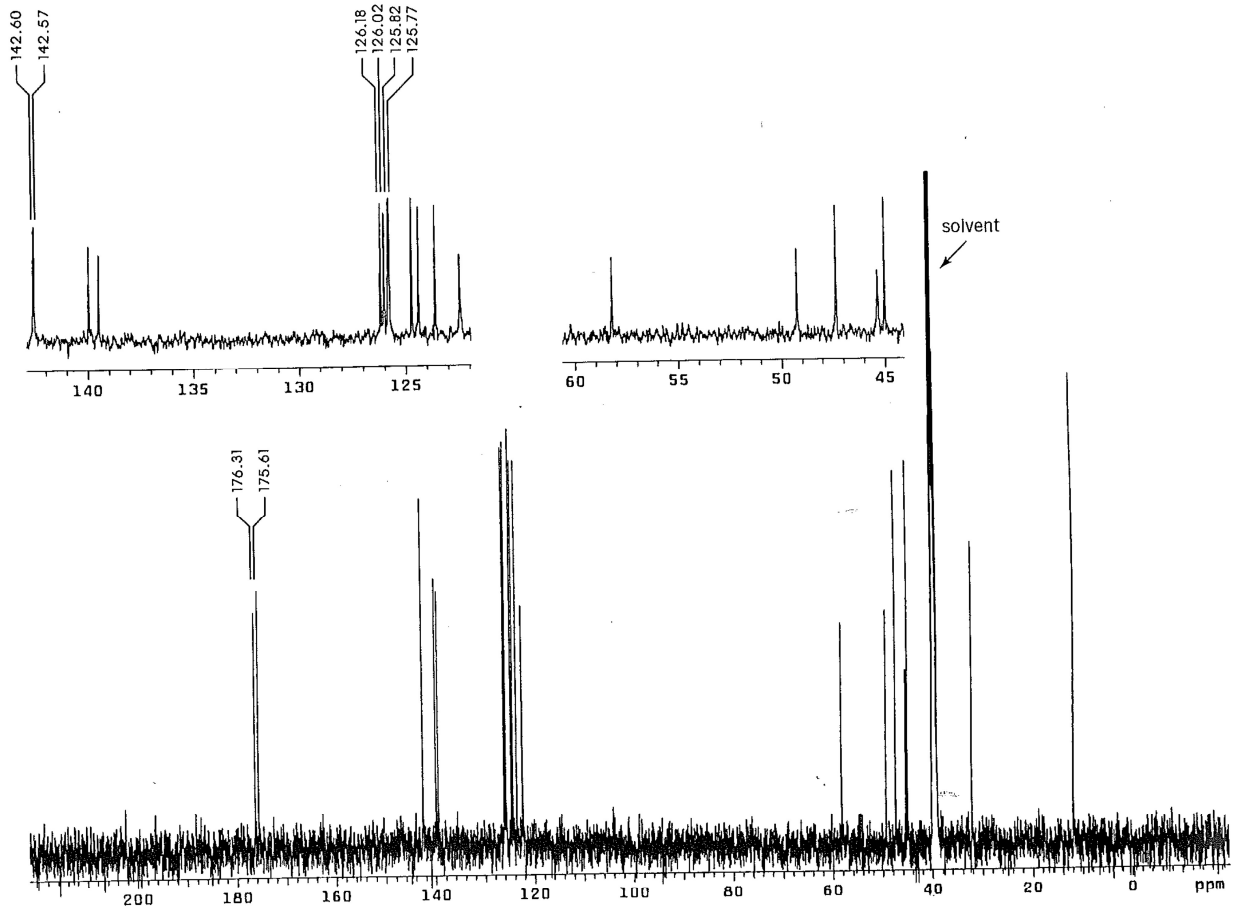
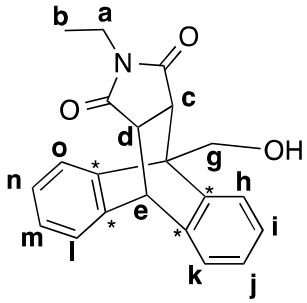


Figure 19.14 125.7-MHz ^{13}C-NMR spectrum of 9-anthracenemethanol-NEM adduct in DMSO-d_6.



Use these designations for unlabeled carbons...
* = aromatic C's without H's
Amide C=O
4º (between c-g)

Signal	Observed Shift (ppm)	Expected Shift
	10	
	32	
	46	
	45 & 47	
	50	
	57	
	123-125 (4 signals)	
	125-126 (4 signals)	
	139-142 (4 signals)	
	175 & 176	