6. Introduction to Original Research

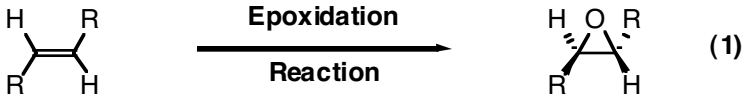
6.1. Olefin Epoxidation with Mn(salen) Complexes

Introduction:

Your "advisor" has carefully monitored your progress in 5.301 and believes that you are ready to move from the technique modules to an actual project. This project will require you to use many of the skills that you have learned over the past three weeks to address a specific question. In addition, you and your labmates will learn to work as a research group in order to reach an ambitious goal in a short period of time.

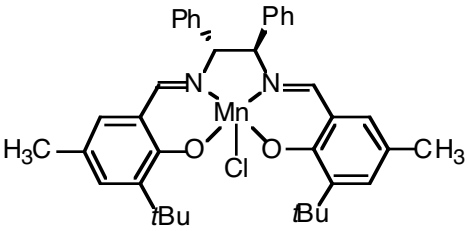
Overview: (written by your advisor)

Our group has had a longstanding interest in the epoxidation of olefins (eq 1), and would like to take another look at an important report from a decade ago. Eric Jacobsen (former MIT Post-doc and current Harvard Professor) showed that Mn(salen) complexes such as **1** are effective epoxidation catalysts (eq 1). Because Mn(salen) complexes are easy to make, I am interested in probing the relative reactivity of a series of different Mn(salen) derivatives. A graduate student in the lab has investigated several Mn(salen) complexes, but I want you and your labmates to complete a more comprehensive study. So, look over the attached Jacobsen paper, talk to the graduate student on the project about the reactions you will be running, and be sure to organize your efforts with your fellow labmates. Let me know what trends you discover.

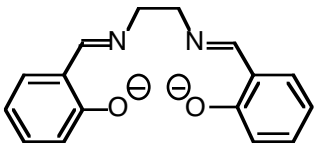


(1)

Olefin Epoxide



1
(one of Jacobsen's Mn(salen) catalysts)



salen =
bis(salicylaldehyde)ethylenediamine

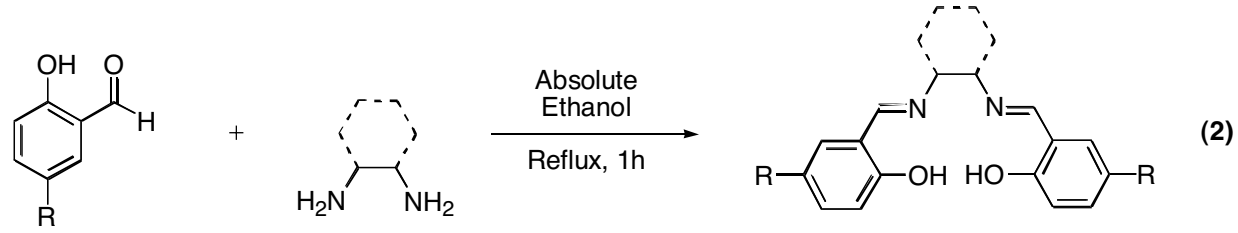
Goals:

- Synthesize a new salen complex (eq 2), and obtain a ^{1}H NMR spectra.
- Synthesize the corresponding Mn(salen) complex (eq 3).
- Compare isolated yields of the catalyst with your labmates.
- Epoxidize stilbene using the published Jacobsen procedure and your catalyst (eq 4).
- Determine the conversion of your reaction using ^{1}H NMR analysis.
- Purify your crude reaction mixture by flash column chromatography, and obtain a yield.
- Obtain a ^{1}H NMR spectrum of the pure epoxidation product.
- Compare conversions and isolated yields with your labmates.
- Use your results to make predictions about the correlation between catalyst structure and catalyst efficiency. This will help us to plan better catalysts in the future.

Hints from Your Graduate Student Mentor:

1. Making the Salen Ligand (eq 2)

- Reactions that you shouldn't try: (I had problems making the Mn(salen) complex with these ligands.)
    1) ethylenediamine + salicylaldehyde
    2) *trans*-diaminocyclohexane + 3,5-di-*tert*-butyl, 2-hydroxybenzaldehyde
    3) ethylenediamine + nitrosalicylaldehyde
    4) ethylenediamine + chlorosalicylaldehyde
- You should aim to make 1.00 g of the Mn(salen) complex. Do your calculations based on the two reactions proceeding in 70% overall yield.
- There will be a large amount of solid produced, so use a large stir bar and fast stirring rate.
- Don't forget that after the reaction finishes you'll need to add water to precipitate the product, so don't start with too small a reaction flask.
- When you first isolate the ligands (and later the metal complexes), they will be very wet, so dry them overnight in your desiccator before you determine their weight.
- Note the difference between ethanol and *absolute* ethanol.

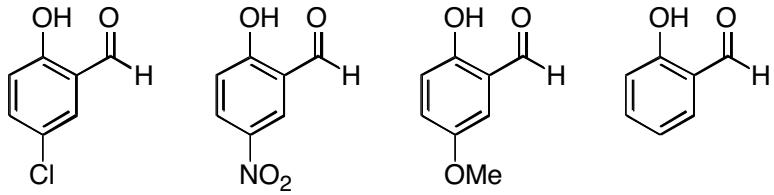


(2)

R = H, OMe, NO_2, or Cl

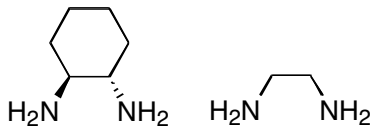
Starting Materials:

Salicylaldehyde Derivatives:



FW = 156.57 | FW = 167.12 | FW = 152.15, d = 1.219 | FW = 122.12, d = 1.146

Diamines:

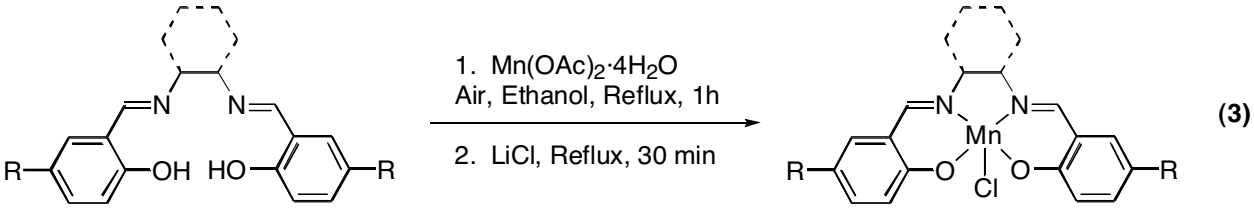


FW = 114.19, d = 0.951 | FW = 60.10, d = 0.899

2. Making the Mn(salen) Complex (eq 3)

• Some of our salen ligands behave a little differently than the ones Jacobsen describes. For some cases toluene needs to be added to the hot ethanol solution to dissolve the ligand.

• After the reaction is complete, it is crucial to cool the solution down to promote the precipitation of the Mn(salen) complex. It's easiest to put the flask in an ice-bath for about an hour, then filter the mixture. If no solids form after the ice-bath cooling, it may be necessary to leave the solution in the fridge overnight.

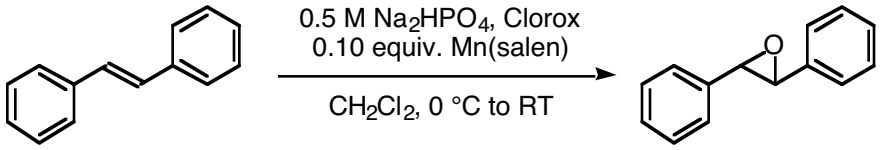


(3)

3. Epoxidizing Stilbene (eq 4)

• The best way to get the proper pH for this reaction is to use a pH meter. When it comes time to do this step, the TAs can show you how to use our meter.

• Monitoring this reaction by TLC can be tricky since the organic layer is on the bottom. The best way to do it is to dip a pipet as deep as possible into the mixture. The liquid drawn into the pipet by capillary action can then be rinsed into a vial using pentane. The less dense organic phase will now be present on top of the aqueous phase and will be easy to obtain using your TLC spotter. Note: we are only using this extravagant dilution procedure because this is a biphasic solution in dichloromethane. Most homogeneous reaction solutions (or biphasic mixtures with less dense organic solvents) can be directly spotted onto TLC plates for analysis.



(4)