

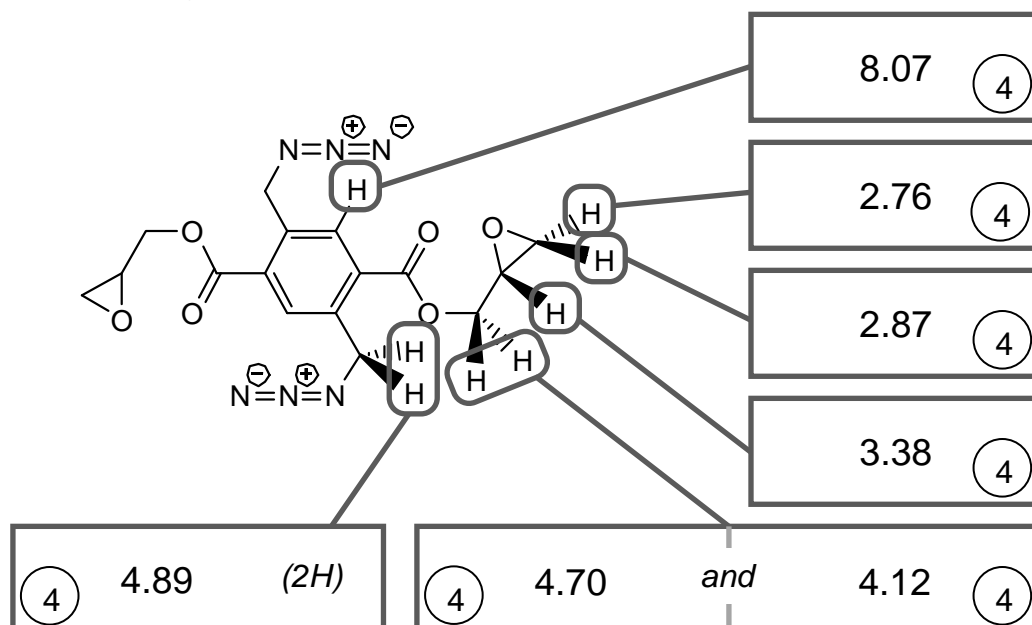
Exam 3 Answer Key

Exam 3 Mean: 82
Exam 3 Median: 83
Exam 3 St. Dev.: 10

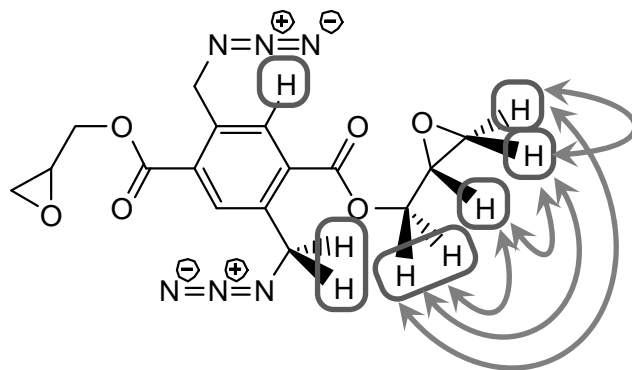
1. The ^1H NMR spectrum of Walt's mixture of bis(epoxide) diastereomers [(*R,R*)/(*S,S*) and (*R,S*)-*meso*] is very straightforward—it has just as many multiplets as there are inequivalent protons in one diastereomer—and that leads me to believe that the two sides of the molecule don't really “talk” to one another, that each epoxide side gives the same NMR spectrum no matter what its relative stereochemistry.

Some of the NMR spectrum was pretty easy to assign. There is just one aromatic proton at $\delta = 8.07$ ppm, and the 2H signal at $\delta = 4.89$ ppm must be the benzylic CH_2 group. Of the five remaining (glycidyl) protons, the two α to the ester oxygen should be the farthest downfield ($\delta = 4.70$ and 4.12 ppm), but I don't think we can assign these two stereochemically. The broad multiplet at $\delta = 3.38$ ppm has to be the epoxide proton in the middle that couples to everything.

That leaves the two other epoxide protons. These are coupled to each other, and then coupled to the central epoxide proton. Pretsch says that the coupling constant J for the *cis*-pair of protons will be larger than that of the *trans*-pair, which means the downfield protons belong to the *cis*-H.



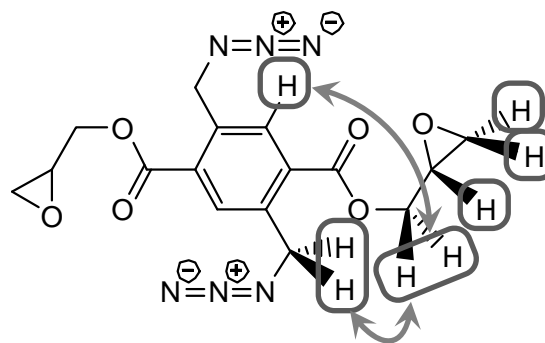
2. Draw two ^1H - ^1H correlations that you would expect to observe in both the ^1H - ^1H NOESY spectrum and the ^1H - ^1H TOCSY spectrum of Walt's bis(epoxide). Draw each correlation as a double-headed arrow on the structure at right.



③ for each correct arrow (x2).

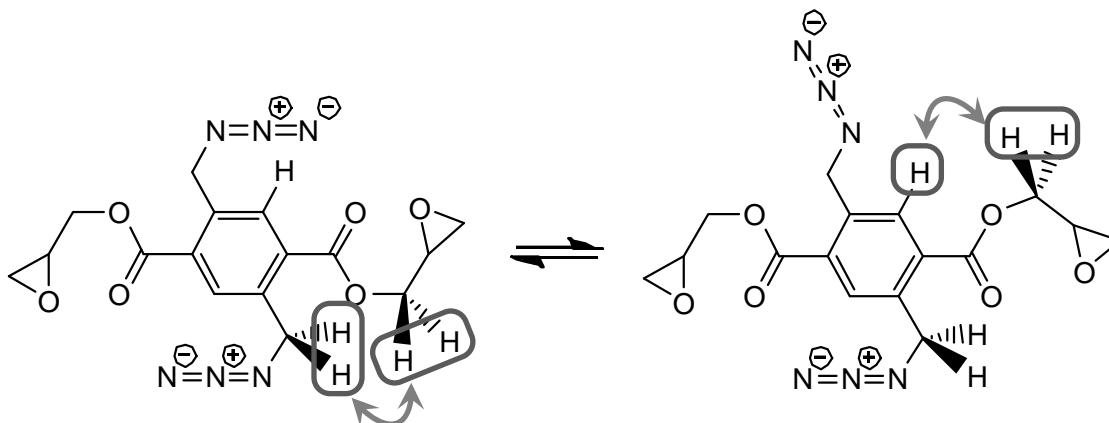
The TOCSY spectrum shows crosspeaks for any protons that are part of a coupled set. In Walt's molecule, these include only the glycidyl (epoxymethyl) group. You could draw an arrow between any two non-equivalent protons in this set.

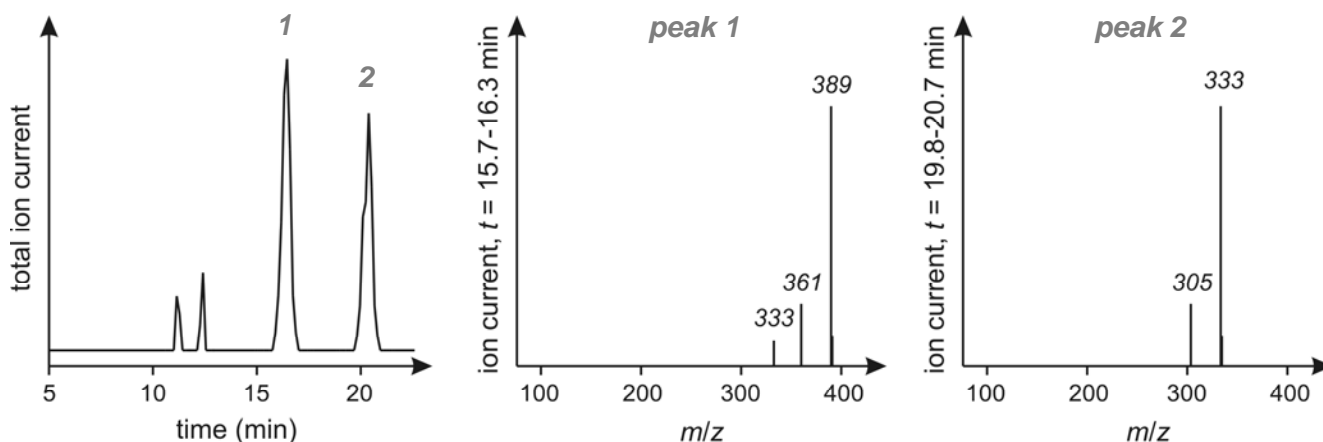
3. Then, draw two ^1H - ^1H correlations that you would expect to observe in the ^1H - ^1H NOESY spectrum, but not in the ^1H - ^1H TOCSY spectrum of Walt's bis(epoxide). Once again, draw each correlation as a double-headed arrow on the structure at right.



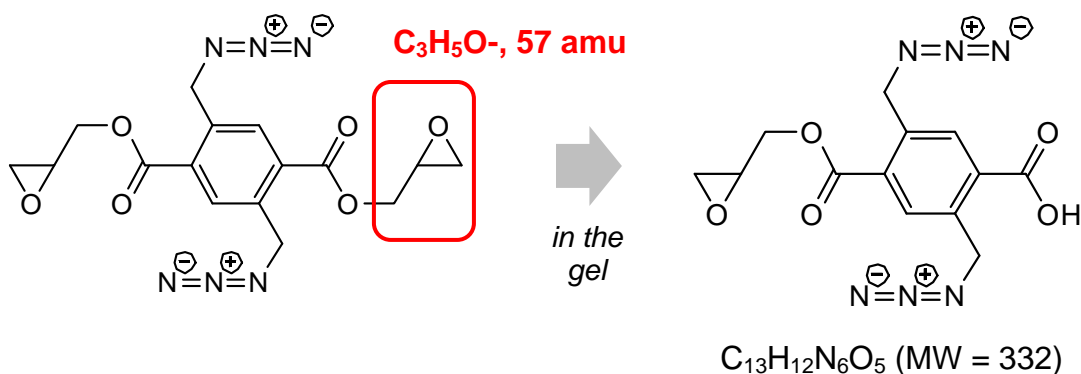
③ for each correct arrow (x2).

The carbon-carbon bond between the aromatic ring and the carbonyl is free to rotate; there is a barrier to rotation due to conjugation, but it's rather low (~5 kcal/mol maybe?). But, regardless of how that bond is rotated, the CH_2 group attached to the ester will always be close to the center of the molecule, and the epoxide will always stretch away. I think the NOE's illustrated below are the only two that Walt would see.



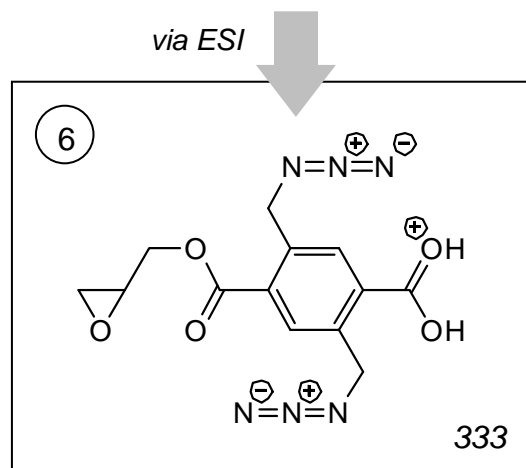


4. Peak 1 may correspond to Walt's bis(epoxide), but it's important to note that the m/z value observed for the parent mass in this peak is 1 amu higher than that of the molecule itself. This is totally normal for positive-ion-mode ESI-MS, where ions are ordinarily formed by protonation of neutrals. We can expect the same thing for the molecule in peak 2. It looks like peak 2 could be the bis(epoxide), minus 56 amu. Looking at our molecule, there aren't a lot of ways it could shed 56 amu; no combination of nitrogen atoms add up to that, but we could lose one of the glycidyl groups:



Losing the glycidyl group, and gaining an H, would yield the right mass.

Rubric: (6 points total this problem.)
 4 points for correct cleavage product.
 2 points for protonating it somewhere.



5. The relative, integrated intensity of peaks 1 and 2 in the TIC trace is about 50/50, but this is not necessarily equal to the ratio of bis(epoxide) to the second molecule. What would Walt need to do to calculate this ratio?

The intensities of the TIC peaks depend not only on the amount of material being delivered to the MS, but also the molecules' relative ionization efficiencies. To account for this, the instrument needs to be calibrated to the molecules being analyzed. Walt needed to prepare the two molecules in peaks 1 and 2 as pure materials—well, the molecule in peak 2 anyway, because he already had the bis(epoxide)—and inject mixtures of the two molecules at known ratios into the ESI-MS. The resulting TIC peak intensities can then be correlated to those observed in the unknown sample.

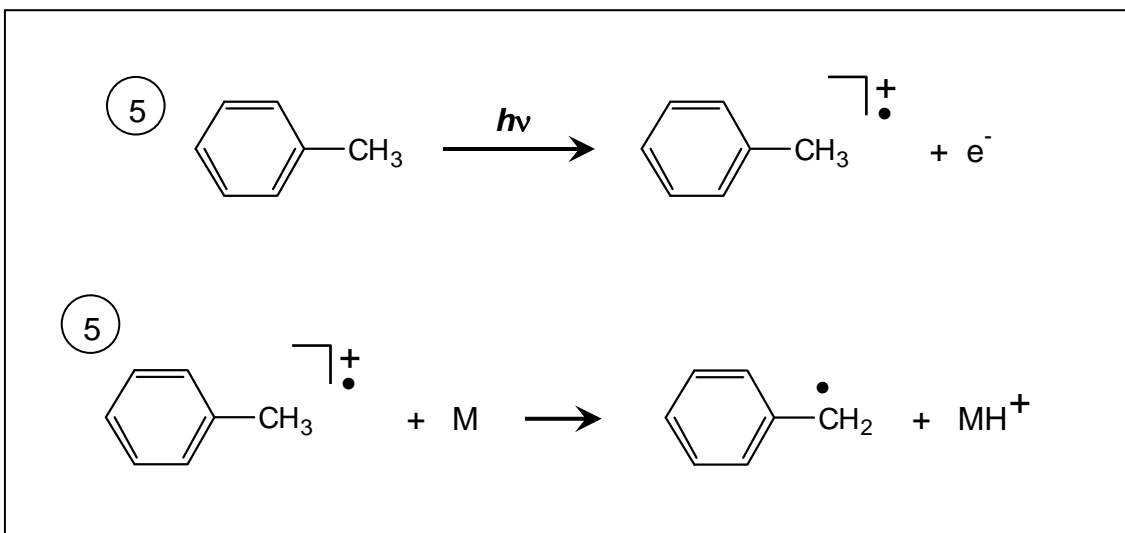
Rubric: (10 points this problem)

4 points partial for using the word “calibrate”. *Don't have to have this word for full credit, but without any explanation, this word alone gets you 4.*

Grader discretion on your essay answer.

6. Walt observed the same parent masses when he measured the mass spectrum using atmospheric pressure photoionization (APPI) MS, but only when he used toluene as a dopant. Draw a pair of reaction steps—including one photoionization step—that explains how an $m/z = 389$ parent would be observed in this experiment.

If APPI is to yield the same parent masses as ESI-MS, then it needs to protonate the molecules somehow. This would be uncharacteristic for direct APPI, which ionizes molecules by removing an electron. Here, indirect APPI can ionize a toluene molecule, which then needs to transfer a proton to our neutral molecule. That can happen.



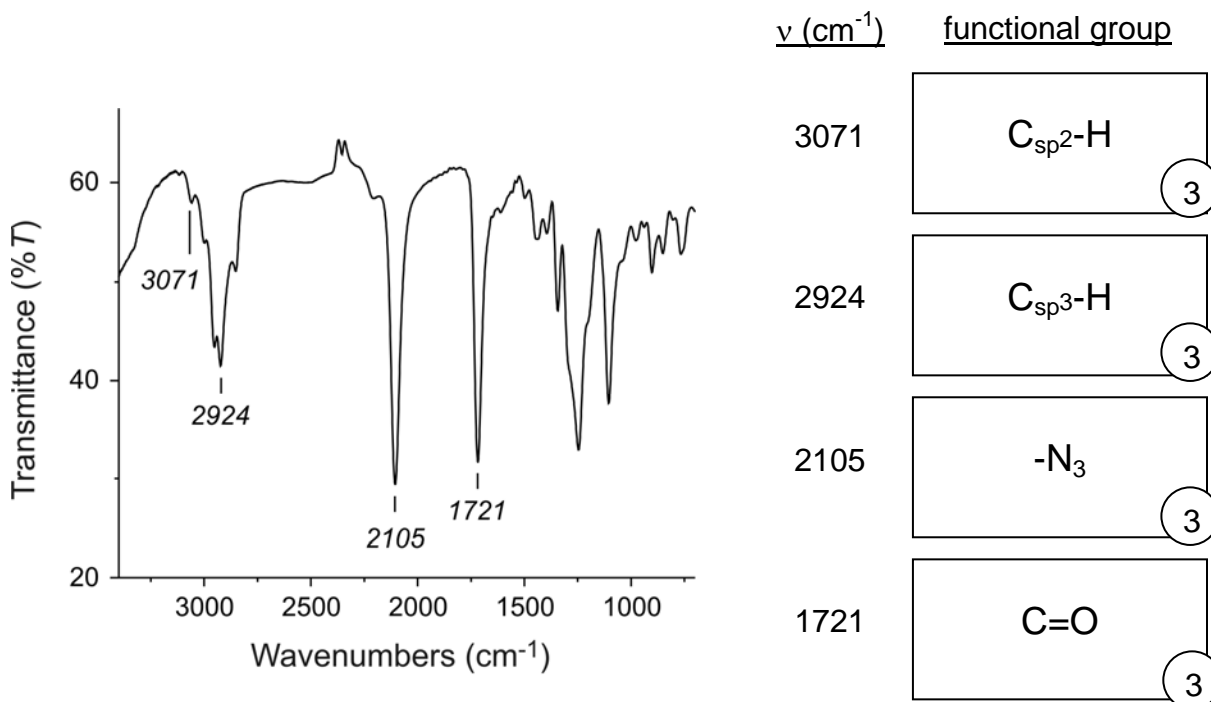
Rubric: (10 points this problem)

5 points each reaction step.

Can draw out bis(epoxide), or abbreviate (as "M", or whatever). Need to spell out what's happening to toluene though.

Grader discretion on the details.

7. Walt deposited a solution of his bis(epoxide) on an NaCl plate, and collected an IR spectrum of the molecule, shown below. What functional groups are responsible for the four labeled peaks?



8. Walt wanted to measure a transmission IR spectrum (like the one shown on the previous page) of the functional groups in his crosslinked hydrogel, but found that his materials were too opaque to allow the IR light to pass through. What alternative sampling technique might he use to get around this problem? Your answer should (i) name the technique, and (ii) describe how the configuration of the experiment addresses Walt's issue.

Attenuated total reflectance (ATR)-IR. In this method, the IR beam doesn't actually pass through the sample; instead, it reflects many times off of the surface of a prism that is placed in contact with the sample, and can be absorbed by functional group vibrations at each reflection.

Rubric: (12 points this problem)

5 points for "ATR".

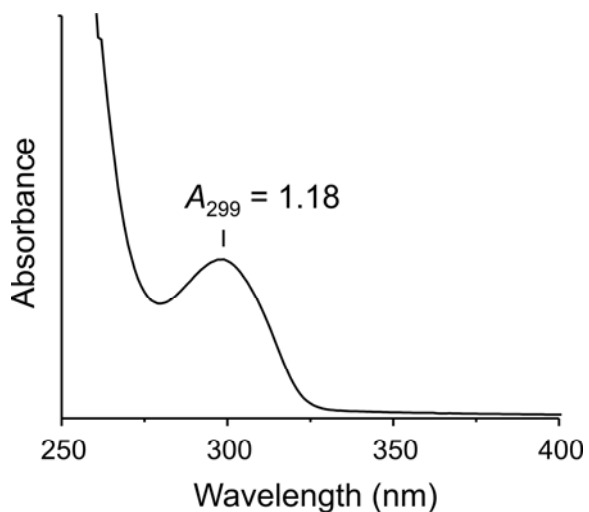
5 points for describing ATR prism and internal reflection.

2 points for explaining that sample sits on prism.

Grader discretion on the details.

9. Walt collected a UV-vis spectrum of his bis(epoxide), shown at right, as a 0.0086 M solution in chloroform in a cuvette with a 1-cm path length. What is ϵ_{299} for this molecule?

4 $137 \text{ M}^{-1} \text{ cm}^{-1}$



10. What type of electronic transition is responsible for the absorbance peak at $\lambda = 299 \text{ nm}$? Electrons are excited from what ground-state orbital, to what excited-state orbital?

