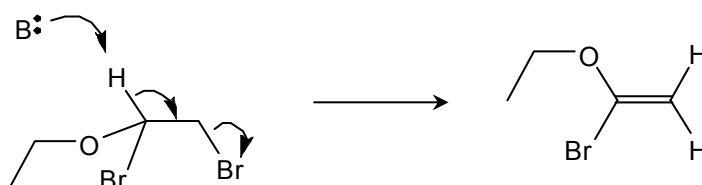
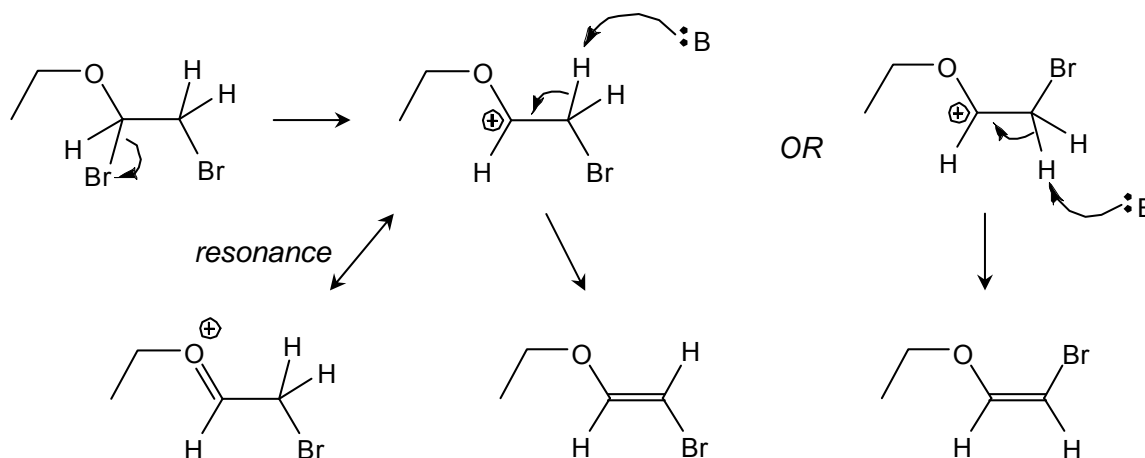


Workshop 28 Solutions Structure Determination with NMR

The problem tells us that the decomposition reaction is an elimination reaction, in which one of the two Br atoms acts as a leaving group. It's not clear from the problem whether the elimination is E1 or E2. If the primary Br was the leaving group, it would probably have to be E2:



But if the secondary Br left, the oxygen might ensure that it occurred by E1:

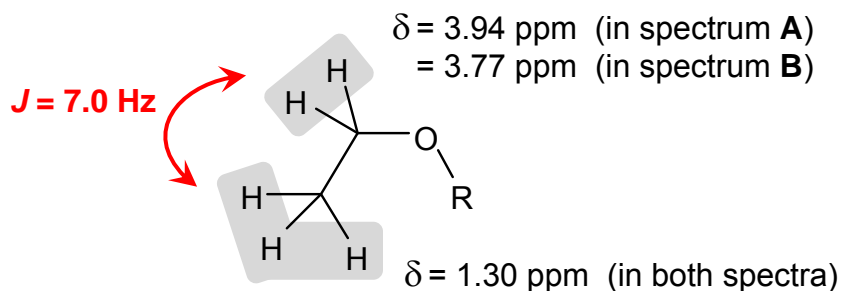


All three products shown above have chemical formula C_4H_7BrO , so they are all candidates. In principle, the NMR spectra can be used to determine which two of these three potential products are Morgan's degradation products.

Some notes on the NMRs:

- Both NMR spectra show a total of 7 H's worth of integrated intensity, which makes sense for any of the three products.
- The two multiplets on the right, in both spectra, have the same coupling constants ($J = 7.0$ Hz) and therefore represent protons that are coupled to one another. All three

proposed products have a set of five protons that match this pattern: the ethoxy group.

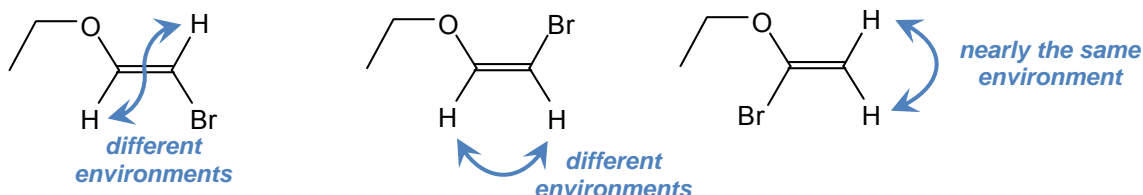


The protons on top are shifted downfield (to higher frequency) by the electron-withdrawing oxygen atom. You can confirm this by looking at the table in the NMR chemical shift table (Appendix F) of Smith and see that protons with the generic “ether” structure (which the top protons have) appear in the $\delta = 3\text{-}4$ ppm range. These show up as a quartet, indicated three simply split neighbors. The bottom –CH₃ protons appear in the alkyl region of the spectrum (again see the table in the Appendix) and are a triplet, indicating two simply split neighbors. Integrals are also correct for the two multiplets.

All of this makes sense for the ethoxy group. But this doesn’t help us identify the degradation products—all of our candidates have this group.

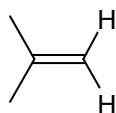
- In all three of our candidates, the other two protons are on alkenes. In both spectra, the two remaining resonances are doublets, coupled to each other with the same coupling constant ($J = 5.6 \text{ Hz}$ in one case, $J = 12.0 \text{ Hz}$ in the other)—this could be true for any of our candidates. The chemical shifts of the peaks in both spectra match the range in Smith’s chemical shift table for alkene protons.

One interesting feature of the resonances is that they have very different chemical shifts. In both spectra, one peak is in the low 5’s in ppm, and the other is mid-to-high 6’s. That suggests that the two protons have very different electron environments—that one is much more shielded than the other, for some reason. It’s not clear to me why this would be true for any of our molecules, but I think this is more consistent with the protons not being attached to the same carbon:

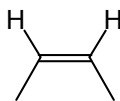


Of course, those “different environments” both have the proton attached to a carbon with an electronegative atom (Br or O), so it’s not clear why the shift would be so different.

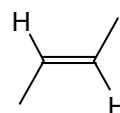
- For me, the biggest piece of evidence is the magnitude of the coupling constant J for the alkene protons. The table I showed in class says that the three configurations of H’s in our three candidates would give very different coupling constants:



$J \approx 2$ Hz



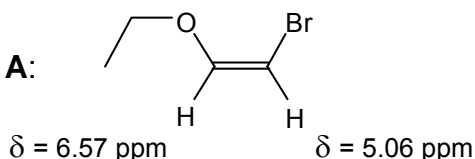
$J \approx 10$ Hz



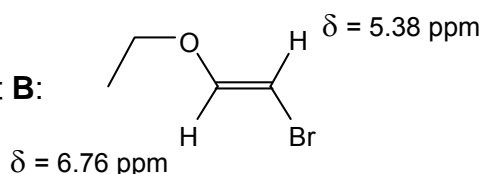
$J \approx 15$ Hz

Our coupling constants are 5.6 and 12.0 Hz—annoyingly, right in between these values. Actually, if you go to a more exhaustive source (say, Hans Reich’s NMR page at Wisconsin, <http://www.chem.wisc.edu/areas/reich/Handouts/nmr-h/hdata.htm>), you’ll find our J values match those of *cis*- and *trans*-alkenes pretty well, respectively. So, our J values tell us that:

Decomposition Product **A**:



Decomposition Product **B**:



That website also tells us which chemical shifts go with which H (see “Alkene, Substituent Effects”); I’ve labeled these on the structures above.