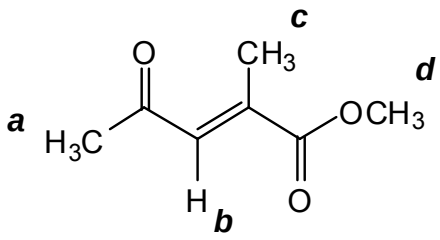
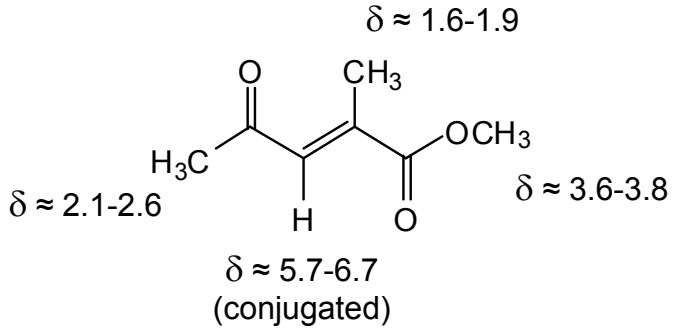
Chemistry 2331H Monday, November 25

In-Class Exercise Solutions:
Using NMR to Analyze a Typical Chemical Reaction

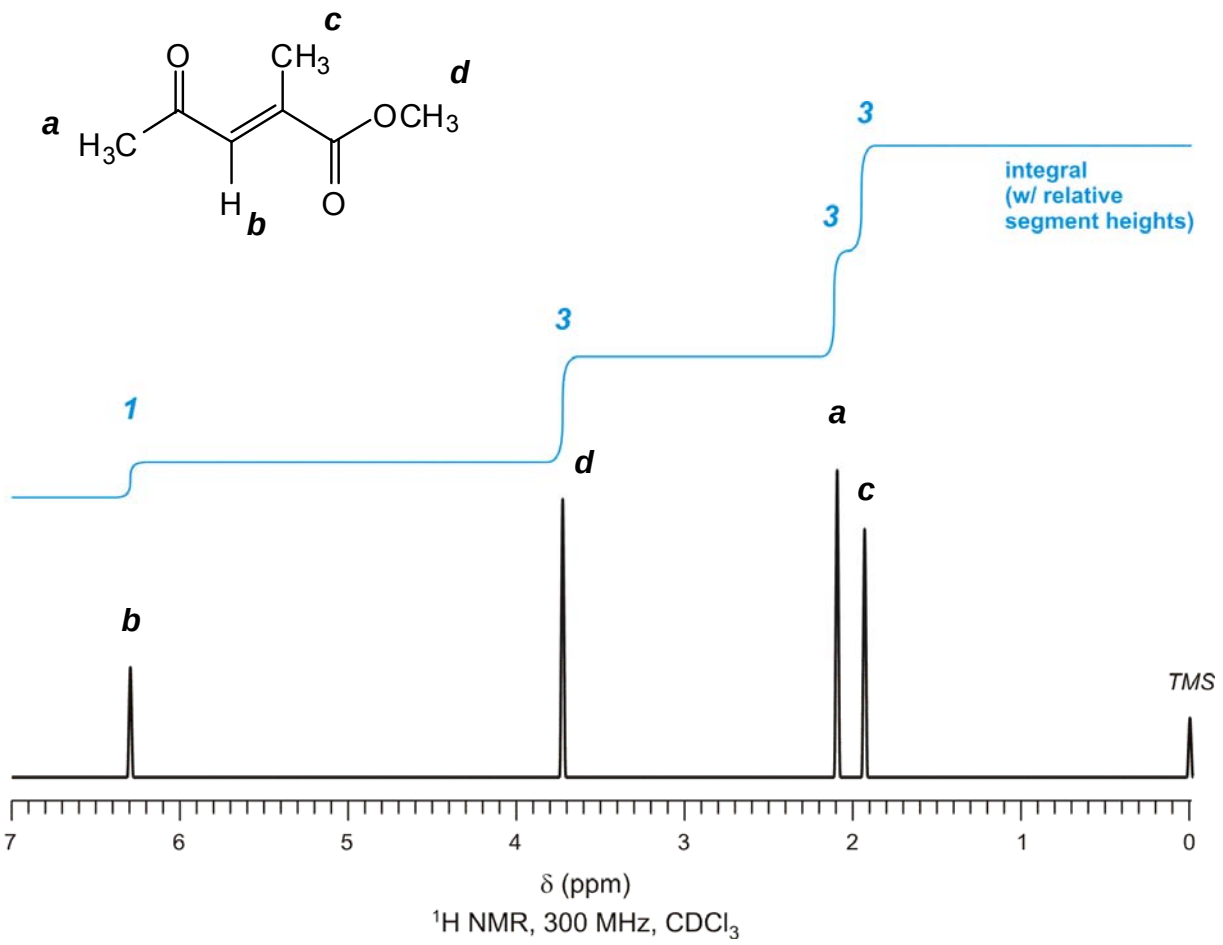
1. The starting material has four different types of inequivalent protons (that is, protons with distinct environments):



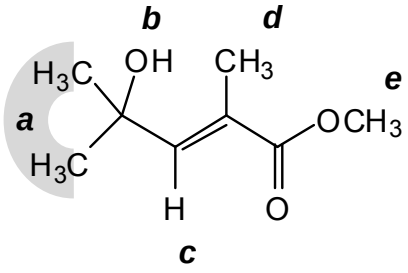
The molecule has three sets of 3 equivalent protons, and one single proton. That's exactly what the NMR spectrum shows—three peaks of intensity 3, and one peak of intensity 1. We looked at a chemical shift table in class, but a more complete one is in Appendix 1A of your textbook. That table suggests the following chemical shift ranges for this molecule:



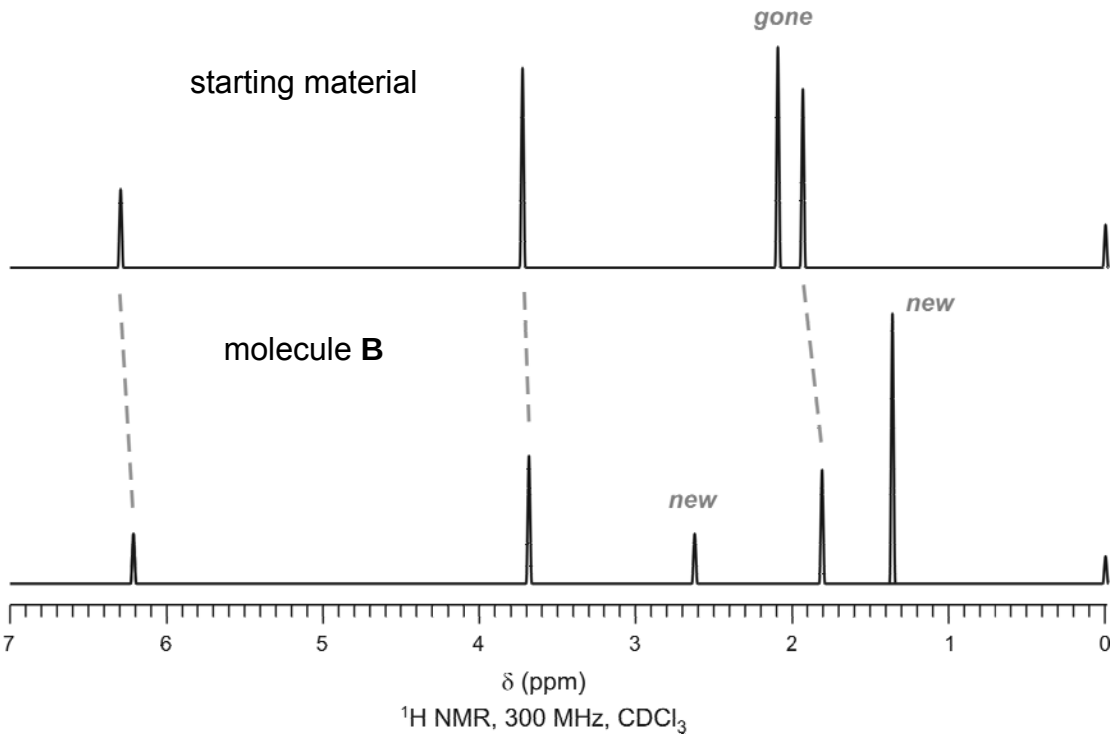
All of those chemical shifts are represented in the NMR spectrum of the starting material (next page). So it looks like Sydney's starting material is the right stuff, and ready to be used in the reaction.



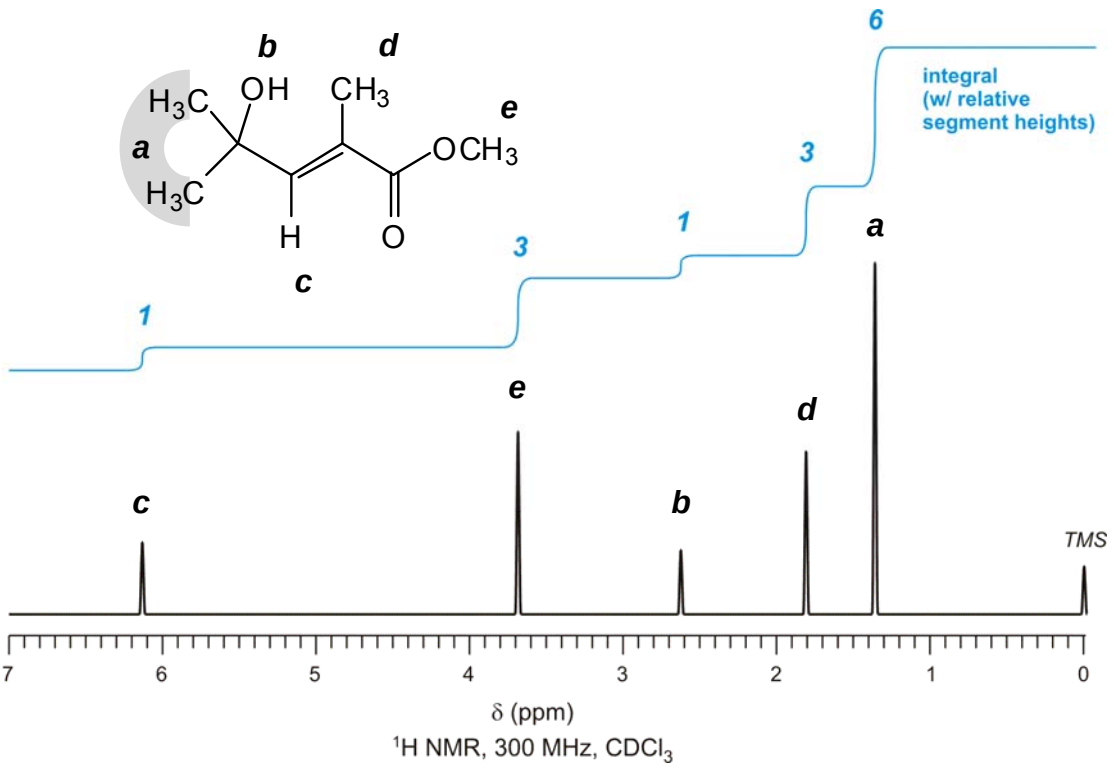
2. We can label the protons in Sydney's expected product:



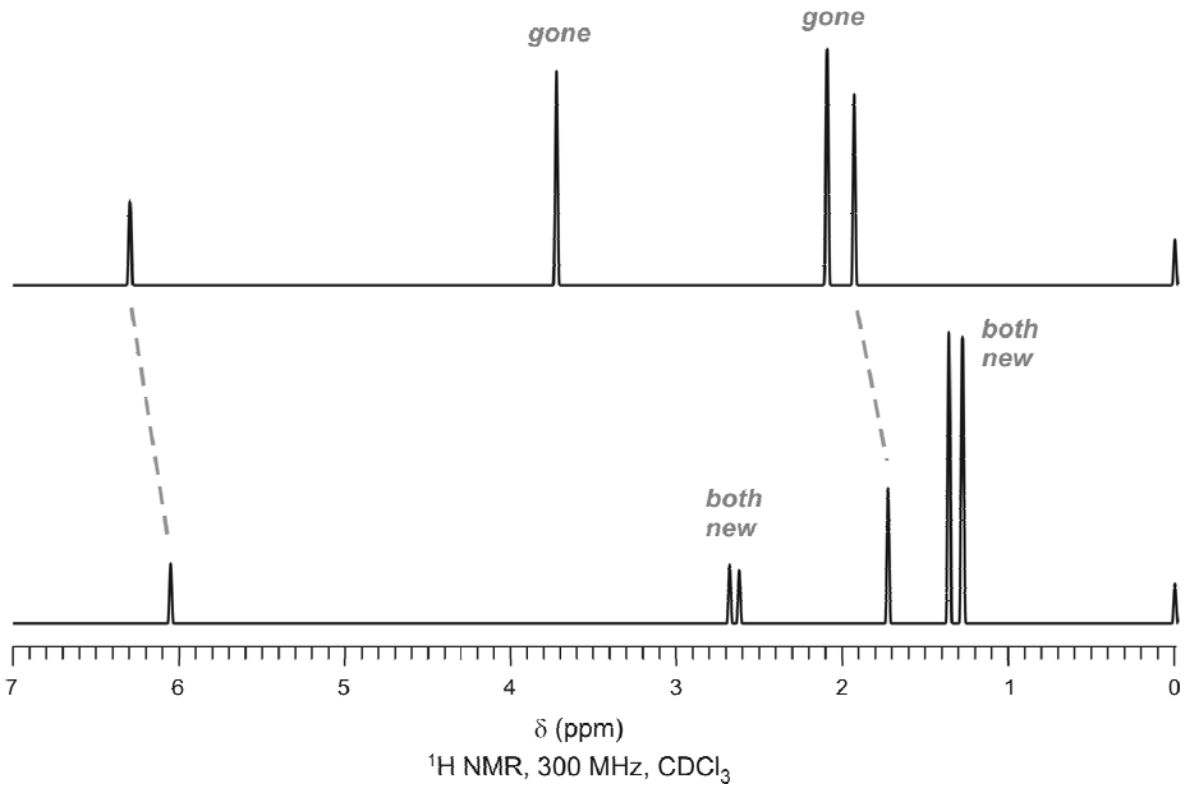
So we're looking for a spectrum with five peaks—one with intensity 6, two with intensity 3, and two with intensity 1. The NMR spectrum for molecule **A** has too many peaks, but the NMR for molecule **B** looks good. More importantly, we can judge whether the reaction has worked by looking at what peaks in the starting material have changed, and what peaks haven't changed.



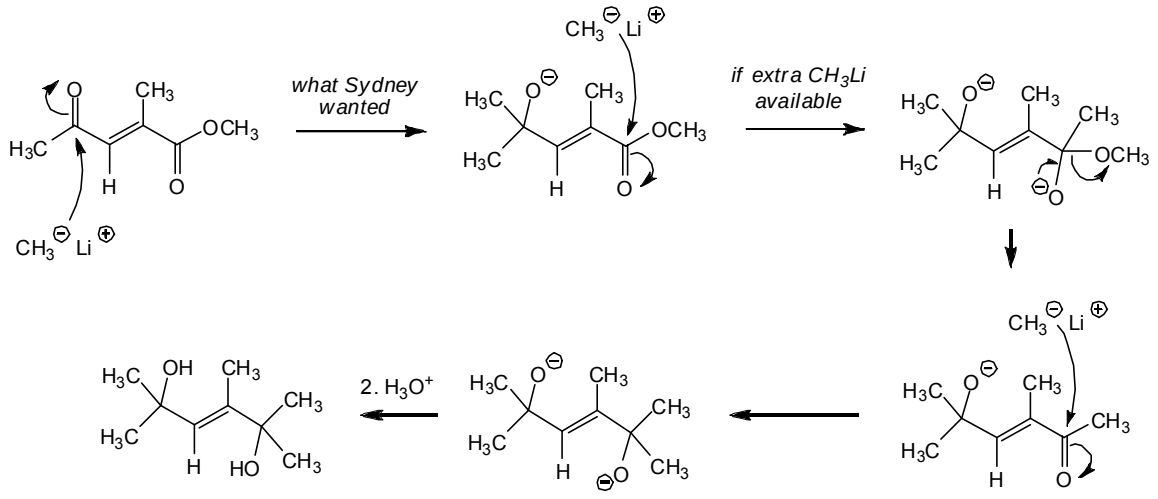
A couple of peaks shift a little—presumably because of the way that changes in distant groups can still affect the electronic environment of a proton—but the major changes are that the ketone –CH_3 of the starting material is gone, and new peaks corresponding to an alcohol –OH and 6 equivalent protons at low frequency have appeared. That's exactly what we would expect for our reaction. So, just to clarify,



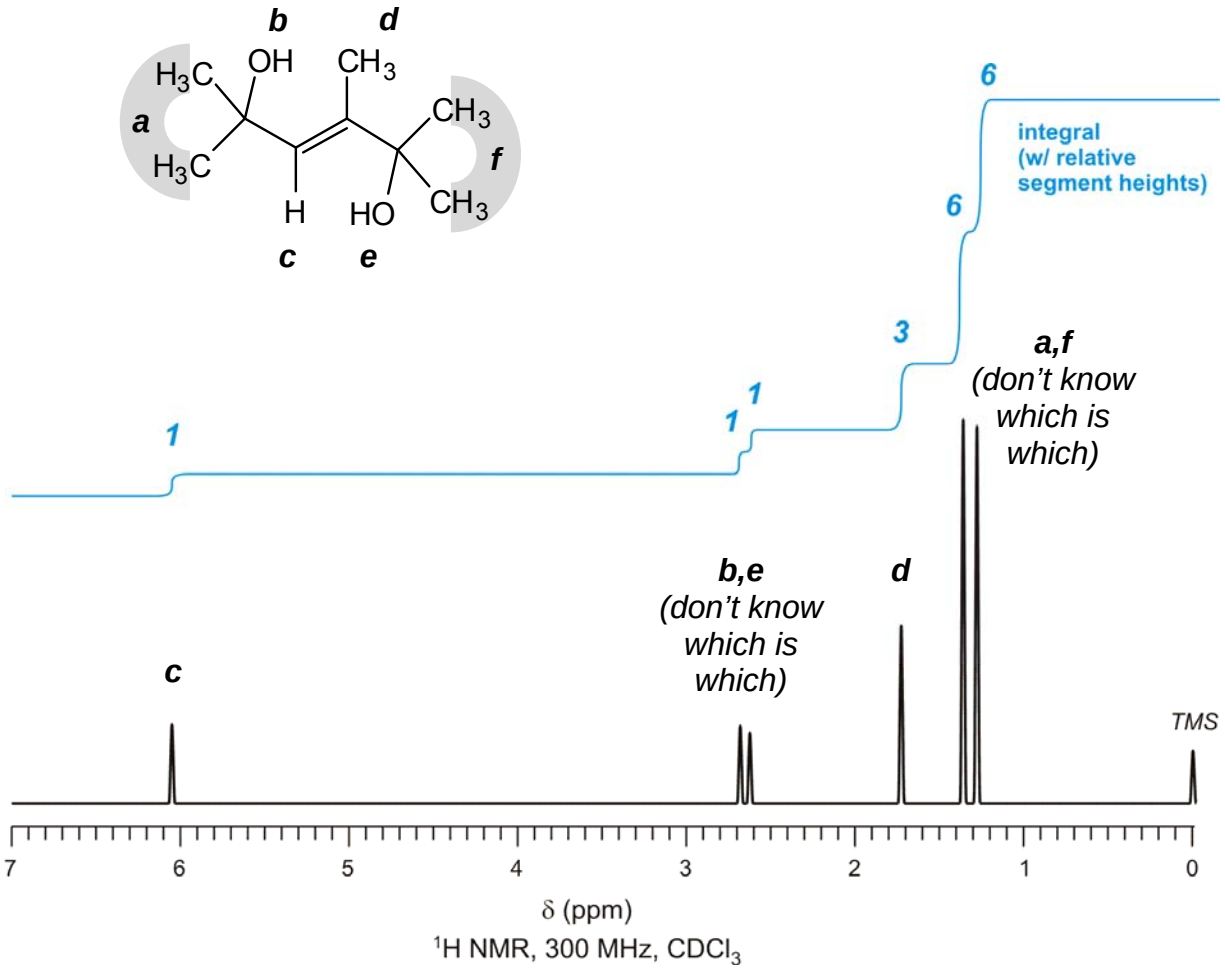
So then what is molecule **A**? Assuming that it is somehow related to the starting material, we can once again compare the product spectrum to the starting material spectrum:



In this case it looks like not only the ketone has reacted, but also the ester, because the ester $–OCH_3$ isn't there any more. CH_3Li will certainly react with esters—not as fast as with ketones, which is surely what Sydney was relying on for selectivity, but they will react. In fact, as we talked about in class, once an ester has reacted once with an alkyllithium it is difficult to prevent it from reacting again:



Presumably, this could happen if Sydney had accidentally added too much CH_3Li. So is the NMR spectrum consistent with this other product?



You bet.