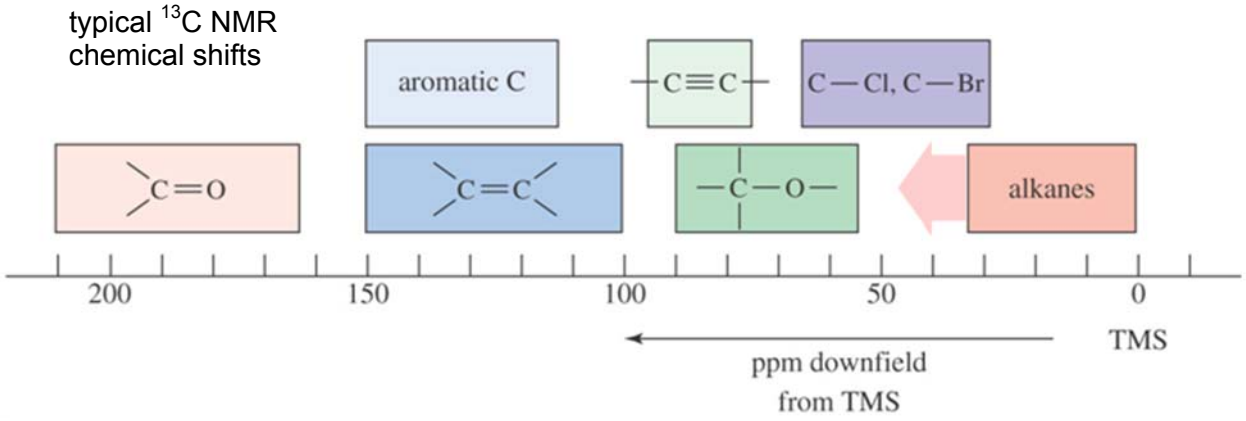
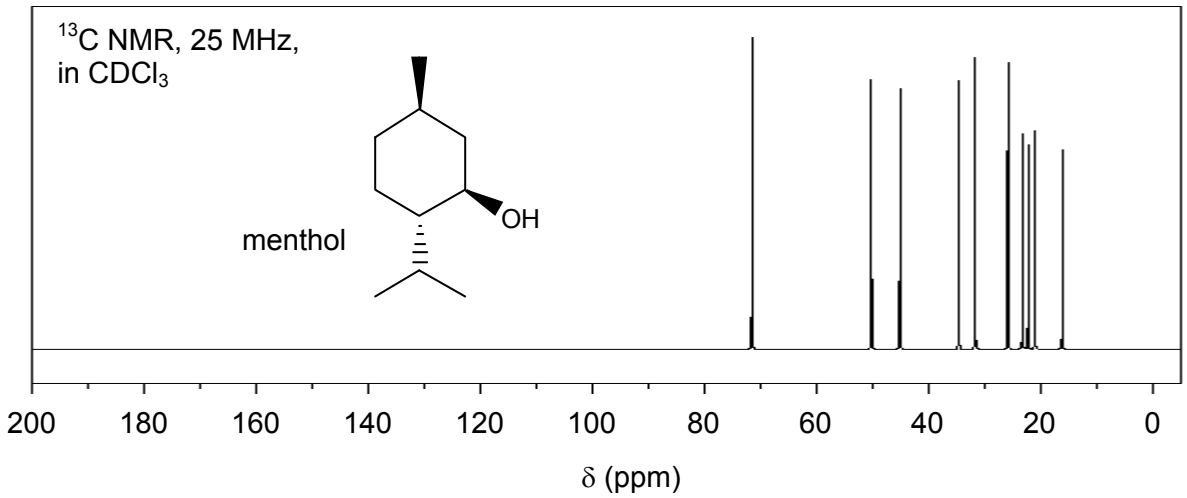
Chemistry 2301 Thursday, July 31

In-Class Exercise Solutions: ^{13}C NMR Analysis

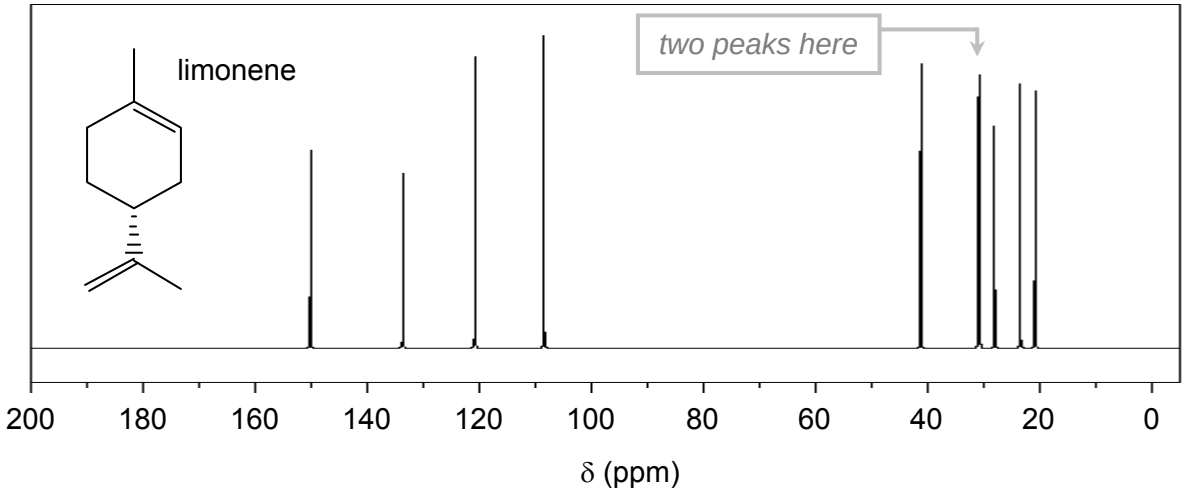
All of our terpenoids have 10 carbons, which could give rise to ten peaks in each ^{13}C NMR spectrum. Sure enough, both of our spectra have 10 peaks. That means we need to look more closely at the chemical shifts of those peaks to determine which spectrum belongs to which molecule. In class, we used the chart below to assign ^{13}C chemical shifts to peaks in a ^{13}C NMR spectrum:



Our first ^{13}C NMR has 9 peaks in the 0-50 ppm, alkane region of the spectrum, and one peak at ~70 ppm which could be from a carbon with single-bonded oxygen attached. Of the five terpenoids, only menthol has just one carbon with a single bonded oxygen. (Eucalyptol has two such carbons.)

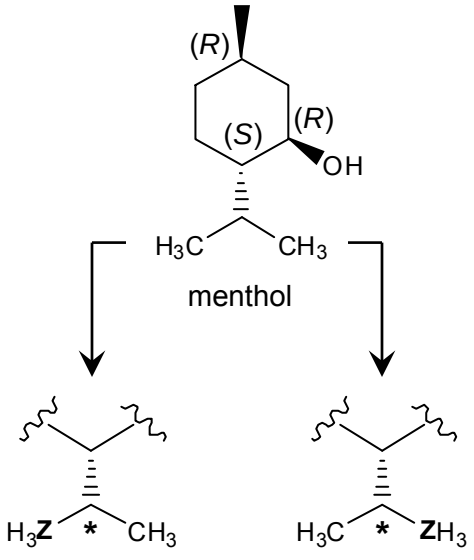


Our second spectrum has four peaks in the 100-150 ppm, alkene region of the NMR spectrum, corresponding to a molecule with four sp^2-hybridized carbons. Only limonene has that.

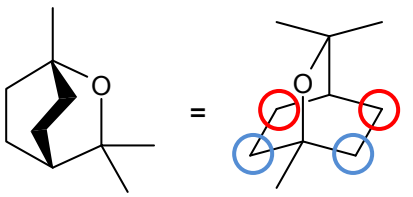


On the previous page, I wrote that each molecule had ten carbons, which **could** give rise to ten peaks in each ^{13}C NMR spectrum. This would occur only if all ten carbons were inequivalent. Out of the five candidate structures, four have ten inequivalent carbons, but one has many less than ten. Which one?

Is it menthol? Looking at the structure of menthol, it looks as though maybe the two methyls in the isopropyl group (on the bottom) might be equivalent. But they're not; according to our criterion for equivalence, replacing each one with a different atom in sequence would create a new stereocenter and yield different diastereomers. So the two carbons are diastereotopic, and inequivalent. Menthol has ten inequivalent carbons, just like we thought.



Eucalyptol, on the other hand, has far fewer inequivalent carbons. Redrawing the molecule makes it clearer that there is a plane of symmetry, such that two pairs of carbons in this molecule are equivalent (and the molecule is achiral).



eucalyptol

circled carbons are equivalent