Selected answers to Homework #4: NMR theory, equivalent nuclei, and ^{13}C NMR

1. proton and carbon

2. Nuclear—it is the nucleus which absorbs light in this technique; magnetic—the nucleus exists in two populations of different energy when under a magnetic field; resonance—when the RF radiation is at the same frequency (in resonance) with the energy difference between the spin states, then the RF energy is absorbed by the nucleus, causing a spin flip.

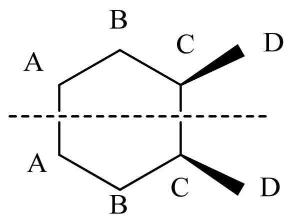
3. Many nuclei have “spin” characteristic. Proton and C-13 nuclei both have two spin states. “Spin” can be pictured as the nucleus twirling in one direction or the other. When charge particles spin, they generate a magnetic field. Since protons and C-13 have two spins, half of the nuclei spin one direction to generate an “up” magnetic field; the other half spin the opposite direction and generate the magnetic field in the opposite direction. When placed in an external magnetic field, the state that generates a field in line with the external filed is lower in energy, and the spin state that generates a field opposed to the external field is higher in energy. This creates an energy gap with a particular energy. If that exact energy is absorbed by a nucleus, it will spin flip, and we can measure the frequency and amount of this energy.

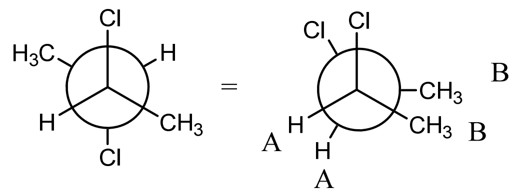
4. Shielding is caused by the magnetic field generated by moving negative particles (electrons) that opposes (partially cancels out) the externally applied magnetic field. If a nucleus has LESS electrons shielding it from the external field, it is said to be deshielded. If a nucleus is deshielded, it experiences a higher energy magnetic field, which causes the two spin states of the nucleus to be energetically farther apart. This means that only light of a higher energy (greater frequency) can be absorbed by these deshielded nuclei.

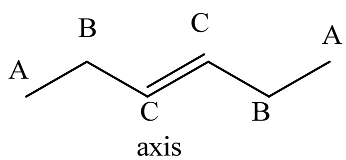
5. The number of Hertz (frequency) absorbed by the nucleus depends on the frequency (power) of the magnet. Therefore, a nucleus will absorb a larger frequency of light in a stronger instrument. Since no two instruments are exactly alike, the same compound will have different chemical shifts in every unique instrument. Since the number of Hz absorbed is proportional to the frequency of the magnet in MHz, the ratio of Hz/MHz is the same for a compound on every instrument. Hz/MHz is a unit of 1/Mega or ppm.

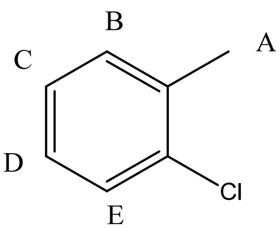
6. TMS is tetramethylsilane. Because silicon is electropositive, the protons are extremely shielded compared to most organic compounds, which is a convenient “zero” point. All larger numbers belong to more deshielded nuclei.

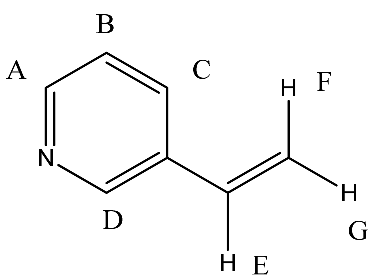
7. Label all sets of equivalent protons in these molecules.

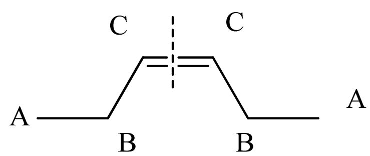


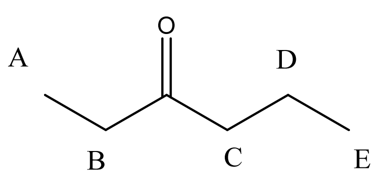


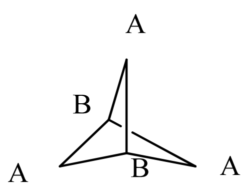






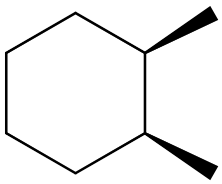




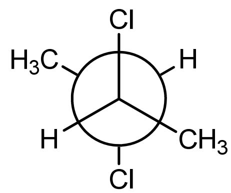


8. Label all sets of equivalent carbons in these molecules. How many ^{13}C NMR signals would you expect to see for each compound?

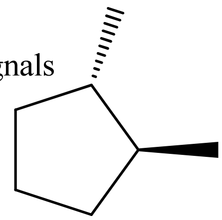
4 signals

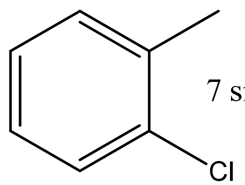


2 signals



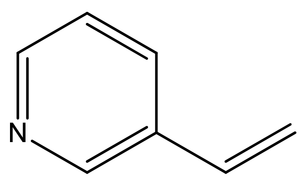
4 signals

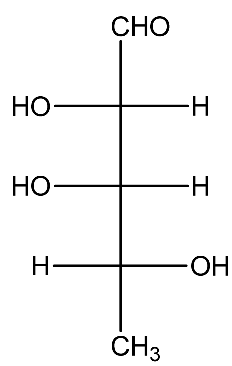




7 signals

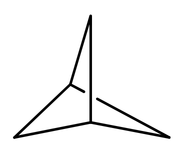
7 signals



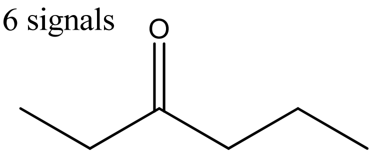


5 signals

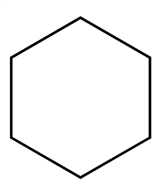
2 signals



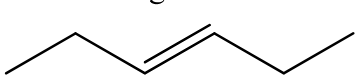
6 signals



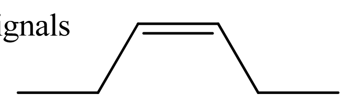
1 signal



3 signals

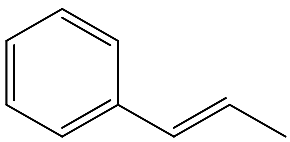


3 signals

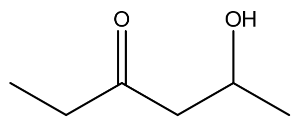


9. Give estimated ^{13}C NMR chemical shift ranges for the carbons in these molecules. Draw a predicted ^{13}C NMR spectrum for each compound.

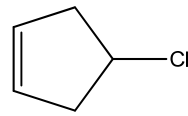
A

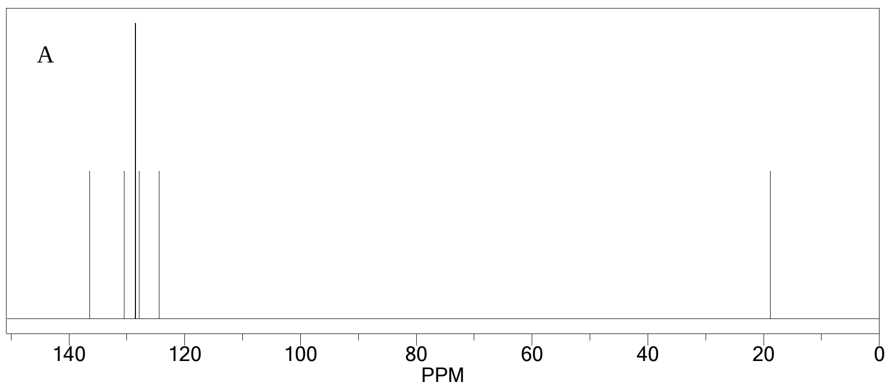


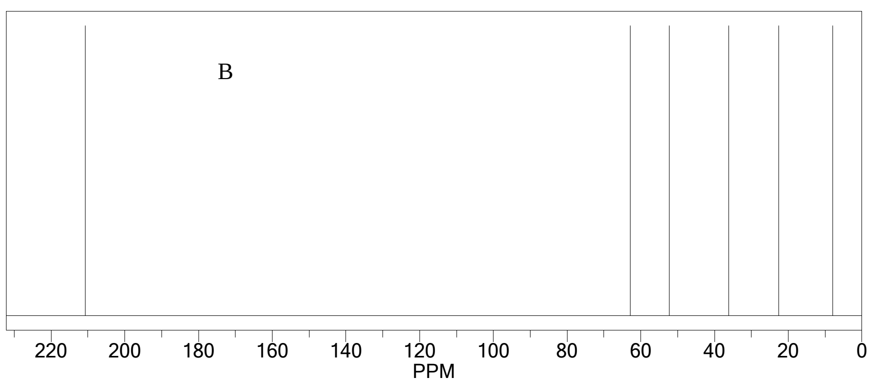
B

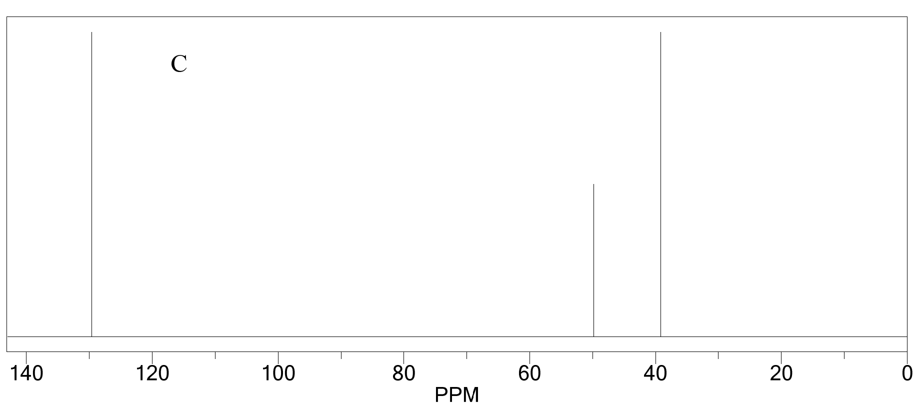


C

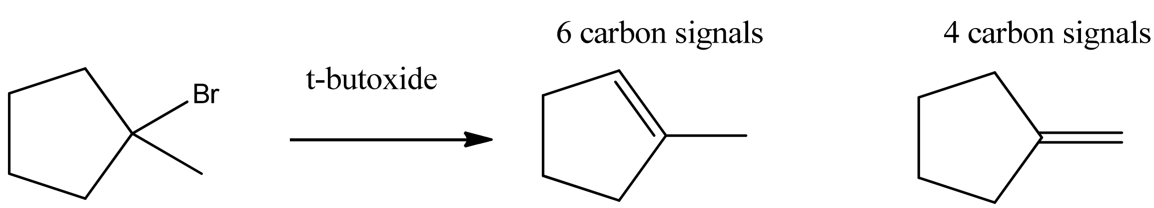


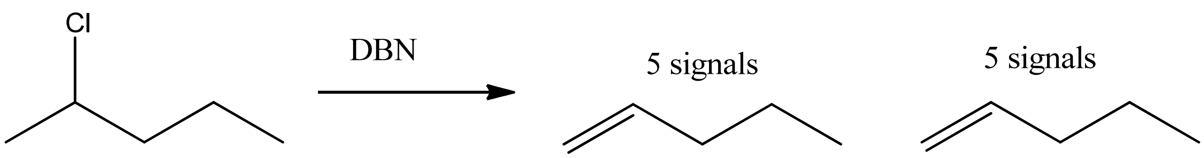




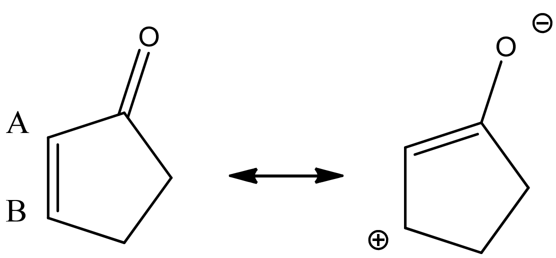


10. The following elimination reactions were carried out, and the major and minor products were isolated. Would ^{13}C NMR data alone be able to differentiate the identity of the major and minor products?





11. The following compound has ^{13}C NMR signals at 29, 34, 134, 164, and 210 ppm. Which signals correspond to carbons A and B? Give a physical explanation for your prediction.

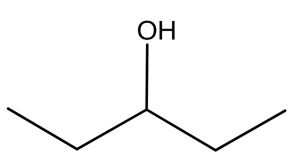


B is more deshielded, therefore 164 ppm

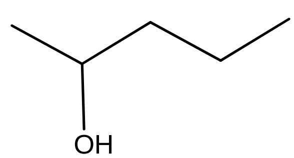
12. Consult your lab notebook.

13.

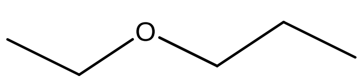
A.



B



C.



D.