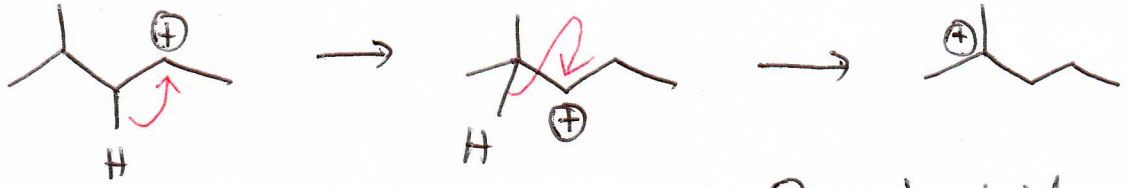
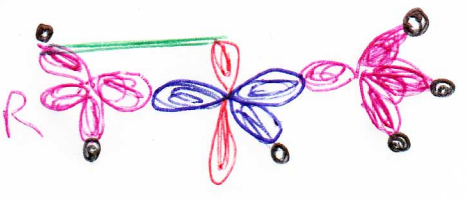
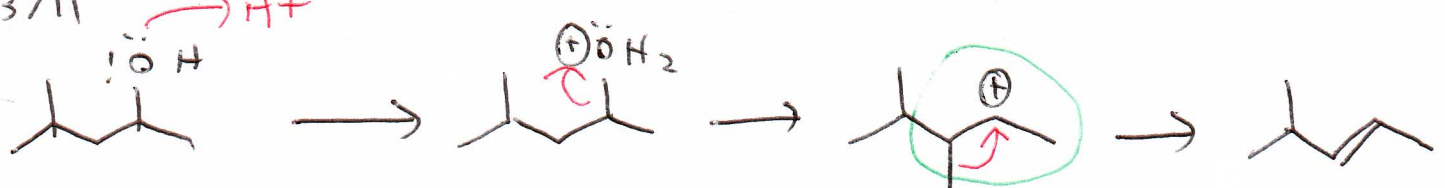
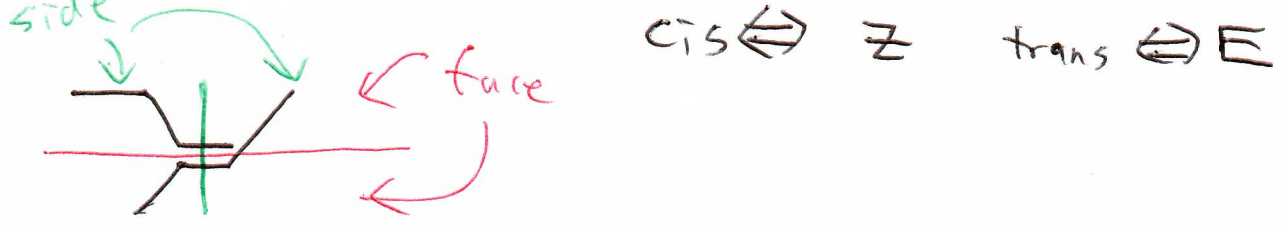
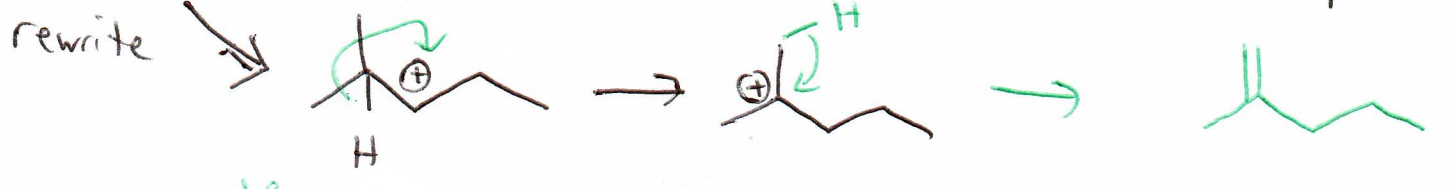
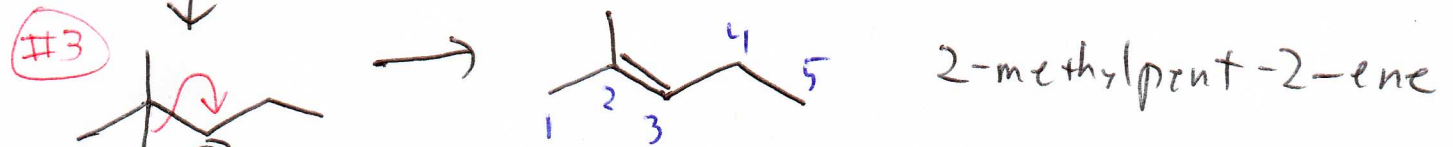
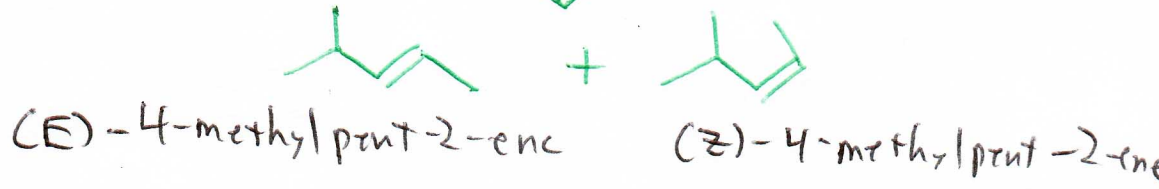
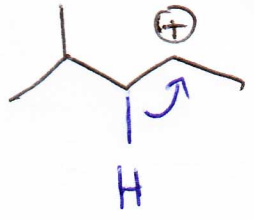
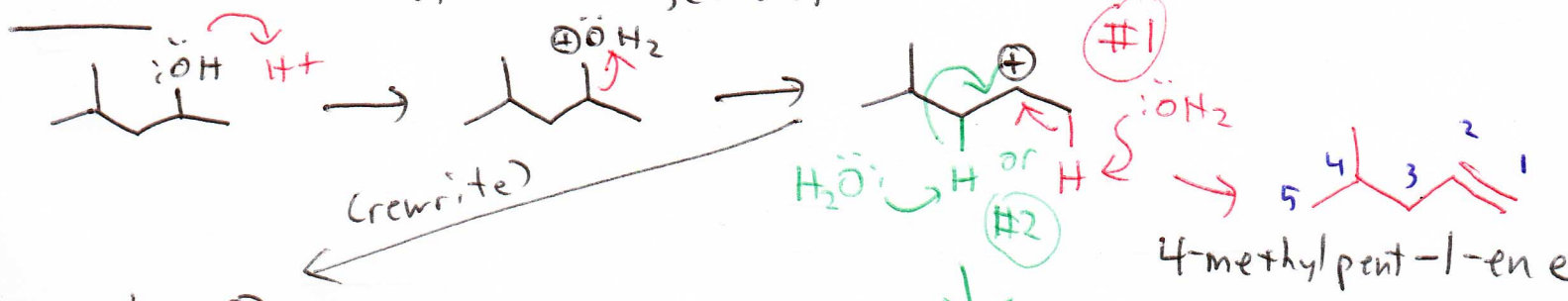


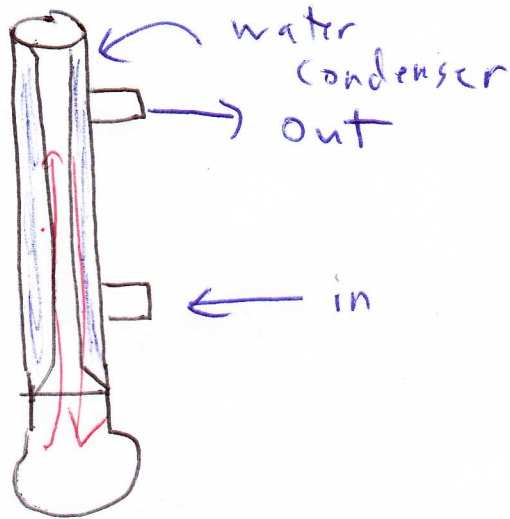
11/3/11

#



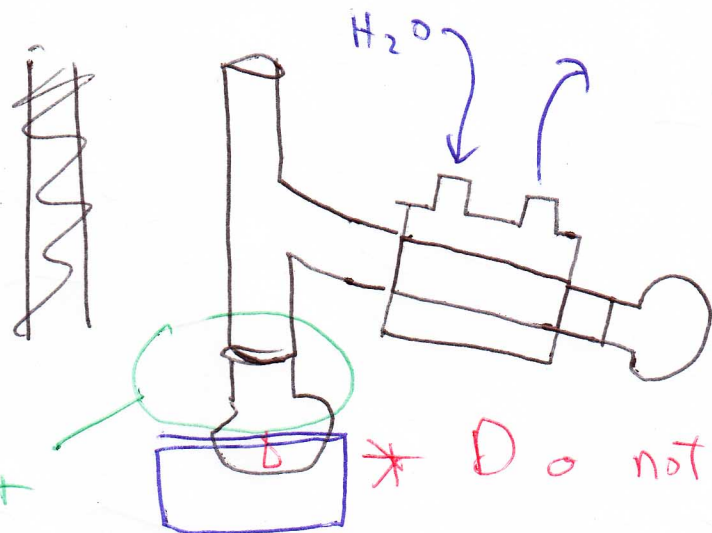
hydride shift \longrightarrow H- <=> H- \equiv hydride
 carbocation rearrangement





Heating at reflux - Heating a sol'n to its boiling point then recollecting the solution by using a condenser.

In this experiment, distillation is being used to separate the lower boiling point alkenes from the higher boiling point starting material (alcohol).



Cotton foil

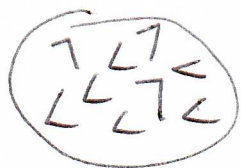
Sand bath

* Do not forget your stirbar!!

NMR

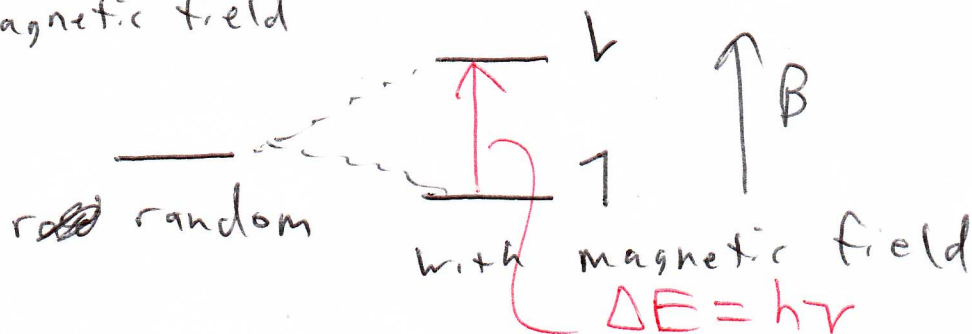
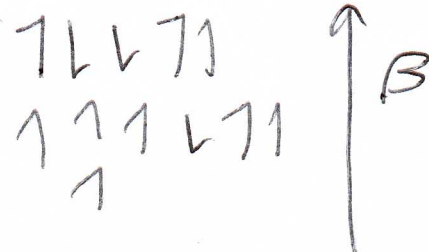
#3

^1H and ^{13}C are atoms with nuclei of spin $1/2$



Spins randomly arranged in the absence of a magnetic field

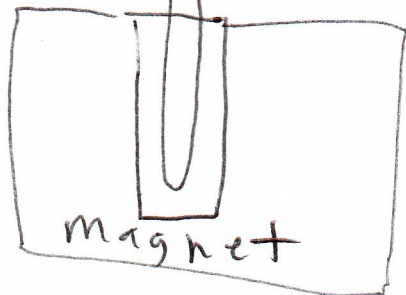
add external magnetic field (B)



Factors that affect the energy gap:

- Strength of the magnetic field (B)
- magnetogyric constant (γ)
(how sensitive is a nucleus to the mag. field)
- chemical environment

- NMR tube

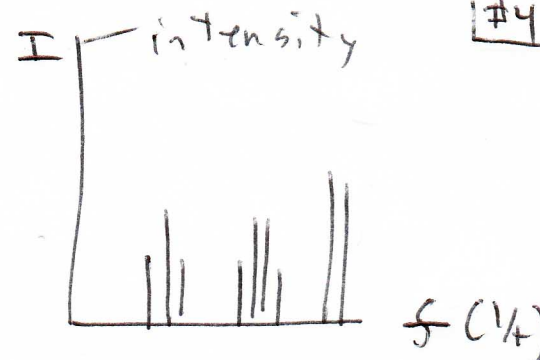


In most modern NMR spectrometers, a sample suspended in a magnetic field is irradiated with a range of EM frequencies.

Only those frequencies that correspond to the energy gaps generated by the sample being in the magnetic field will be absorbed. After being irradiated, the various frequencies re-emitted by the sample are observed.



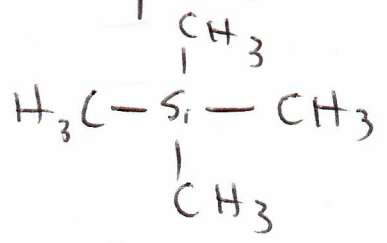
Fourier Transform →



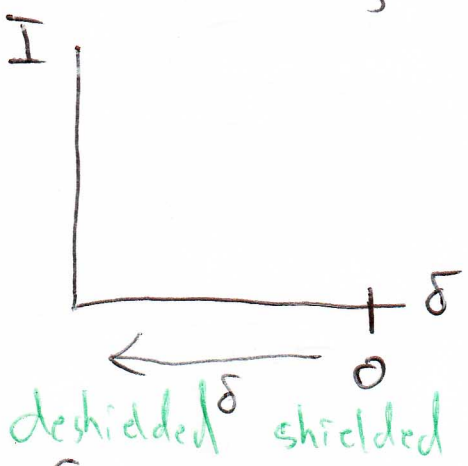
Chemical shift (ppm)

$$\delta = \frac{\text{observed frequency} - \text{machine frequency}}{\text{machine frequency}} \times 1,000,000$$

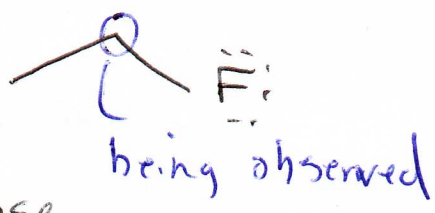
Machine frequency - the frequency measured on a particular spectrometer for a particular reference compound. For organic molecules, the reference compound is almost always tetramethyl silane (TMS).



Chemical shift is a machine-independent quantity, meaning the same value will be obtained regardless of the spectrometer used.



Deshielding

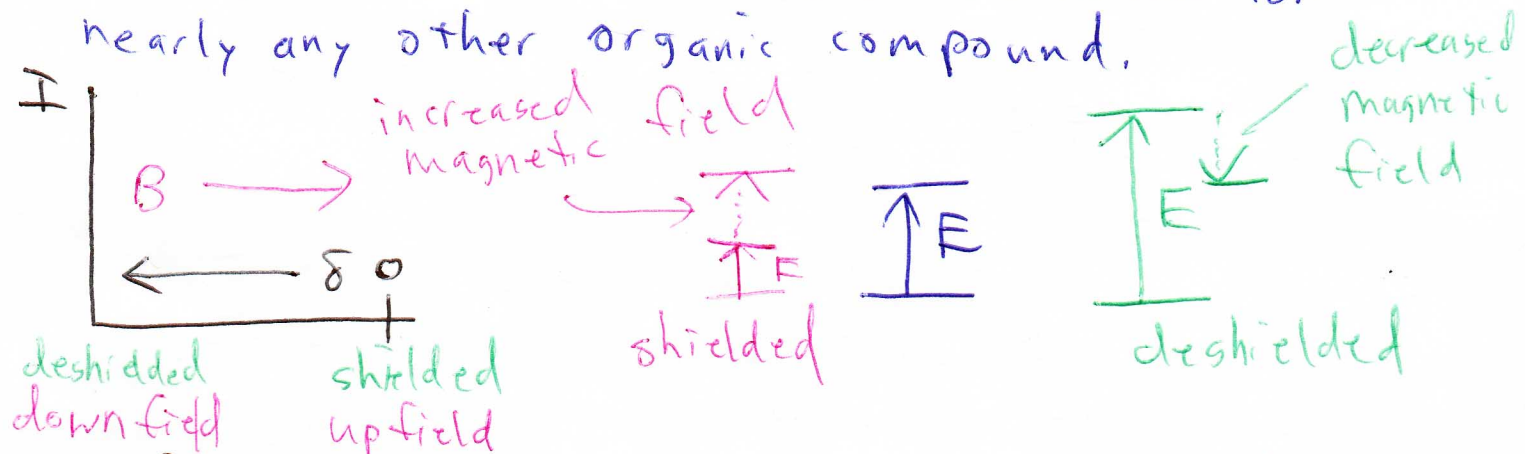


When a nucleus being observed is close to an atom that is electron-withdrawing, electron density will be pulled away

from that nucleus. The nucleus is therefore more exposed (deshielded) to the spectrometer's magnetic field. Since it interacts more greatly with the magnetic field, the energy gap increases, which corresponds to a greater observation frequency, which corresponds to a larger chemical shift.

Silicon is less electronegative than most elements typically found in organic compounds. Atoms attached to silicon would therefore be shielded by comparison, which means the nuclei are not as exposed to the magnetic field, which means the energy gap is not as large, which results in a lower observed frequency and chemical shift.

∴ TMS is used as a reference compound since the frequencies generated by the carbons + hydrogens on TMS would be lower than those observed for nearly any other organic compound.



If a spectrometer can only scan at a fixed frequency, then the magnetic field used must be varied in order to make the energy gaps for different nuclei match the observation frequency.

If an atom is shielded, a larger magnetic field will be required to generate the appropriate energy gap → upfield.

If an atom is deshielded, a weaker magnetic field must be used to generate the appropriate energy gap → downfield.

NMR solvents

For liquid NMR experiments, deuterated solvents (solvents in which hydrogen is replaced by deuterium) must be used, otherwise the signals from the solvent could mask the signals of the compound being observed.

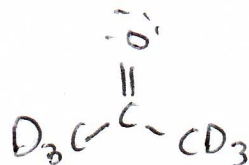
Common solvents



chloroform-d



benzene-d₆



acetone-d₆

Sometimes, 100% deuterated solvents are used, but frequently solvents that are only 99+% deuterated are used. In these cases, the residual signal caused by the non-deuterated solvent is used to calibrate a spectrum.

Sometimes, TMS is included in NMR solvents so that it can be used to calibrate a spectrum.