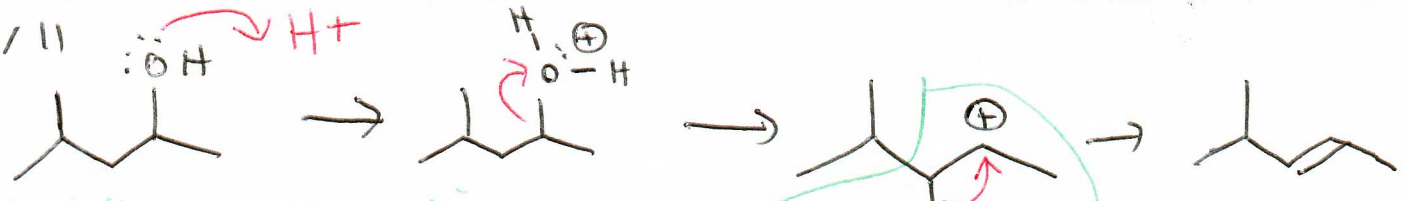
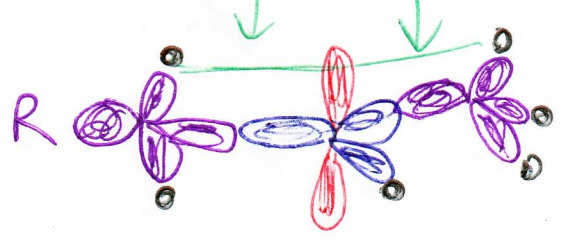


11/2/11

#1

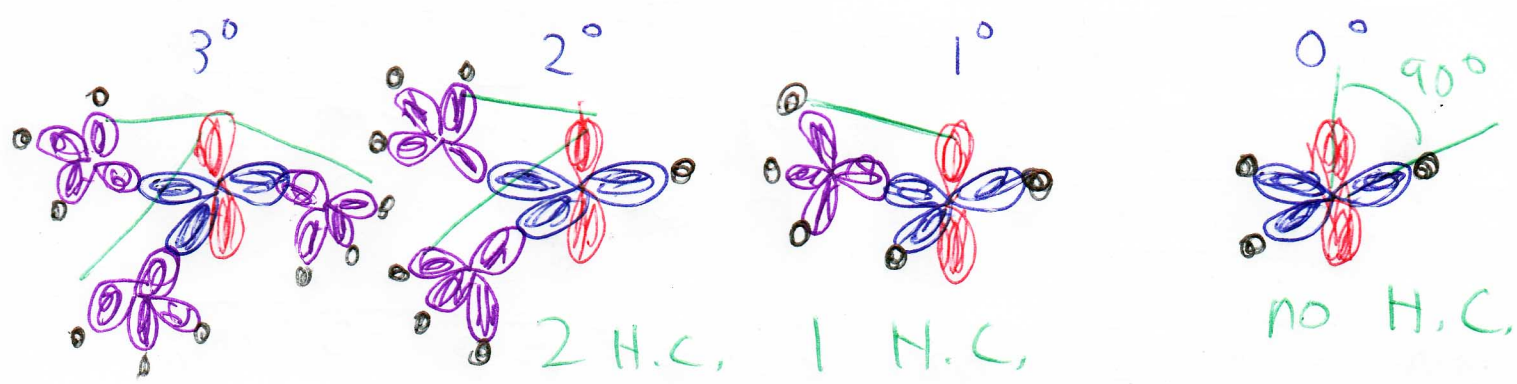
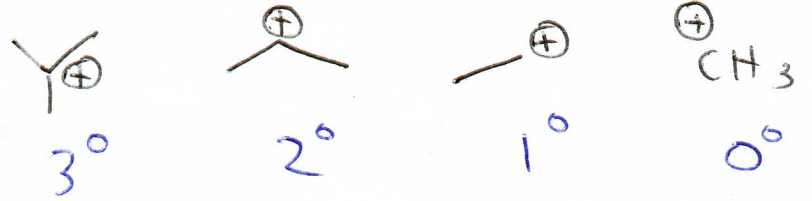


Hyperconjugation



- sp^3
- sp^2
- s
- p

on the exam!!!



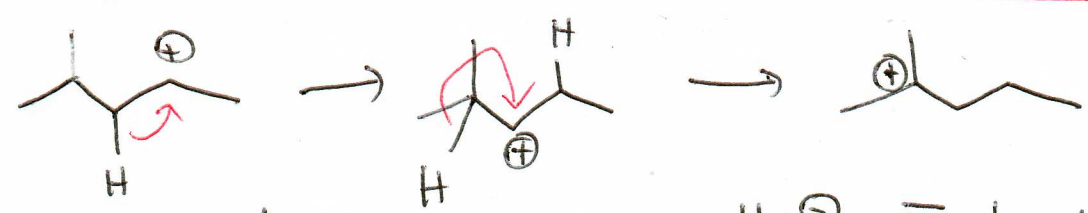
3 H.C.

2 H.C. 1 H.C.

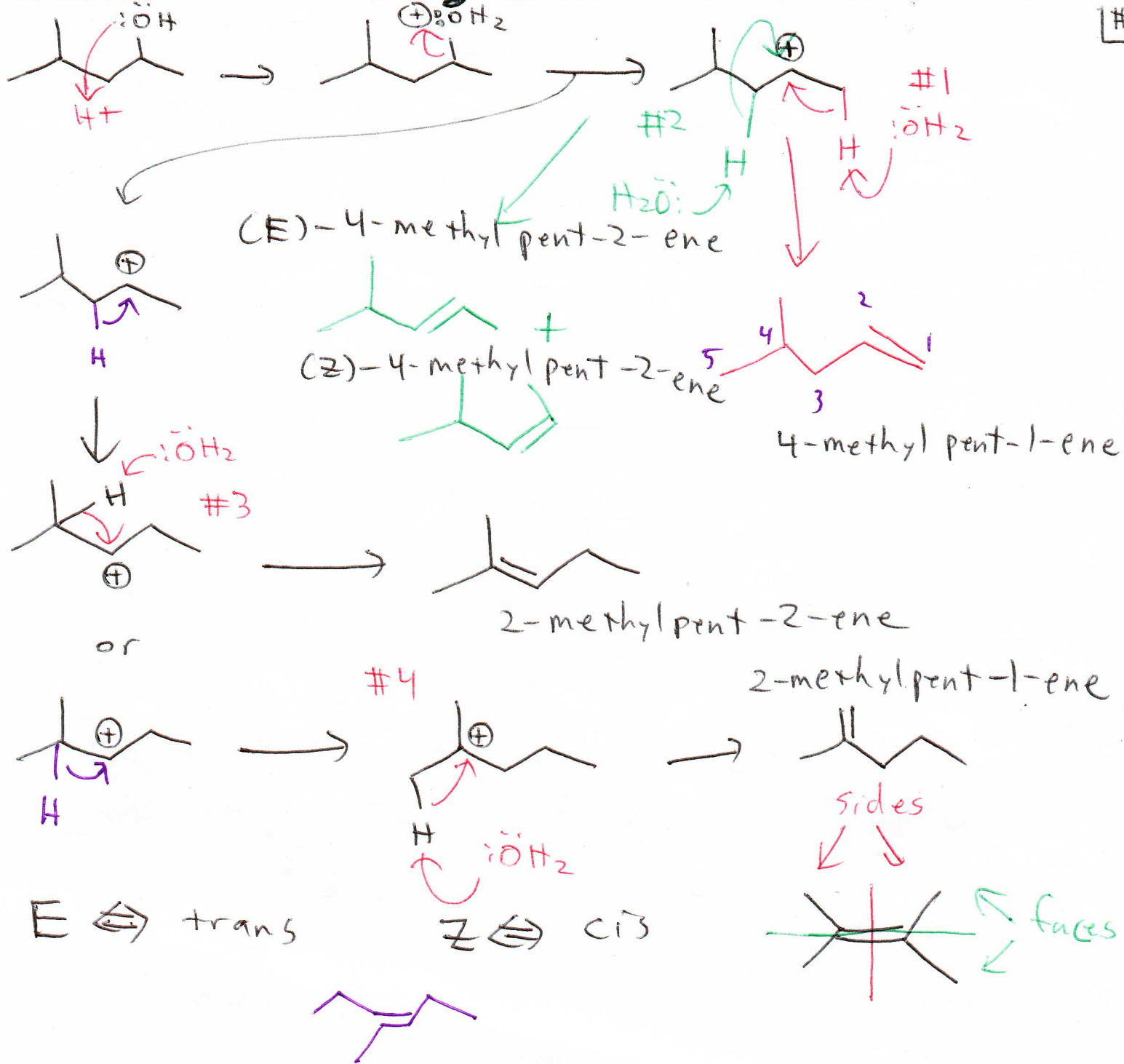
no H.C.

The greater the extent of hyperconjugation, the easier it is to form a \oplus charge, since that charge is spread out over the molecule.

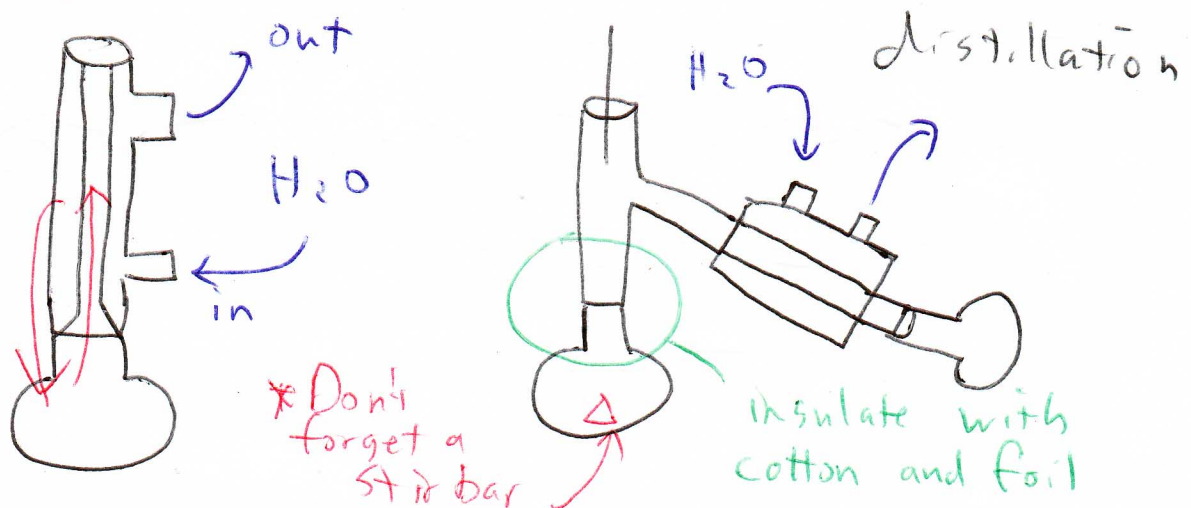
on the exam



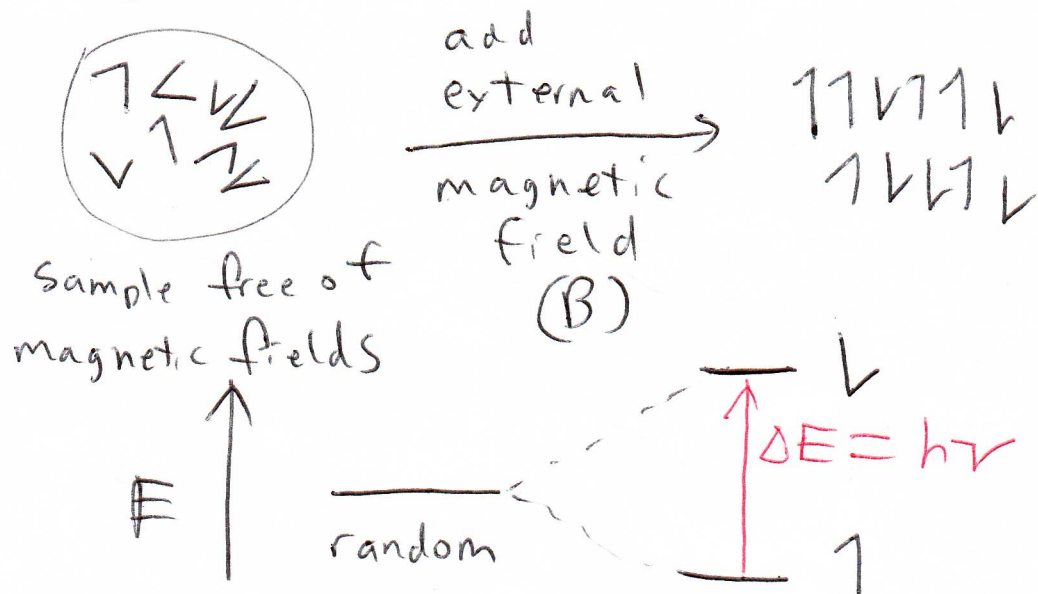
hydride shift $H:^- \equiv$ hydride
 carbocation rearrangement



heating at reflux

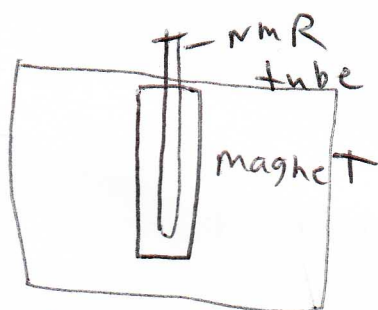


^1H and ^{13}C are atoms with nuclei of spin $1/2$



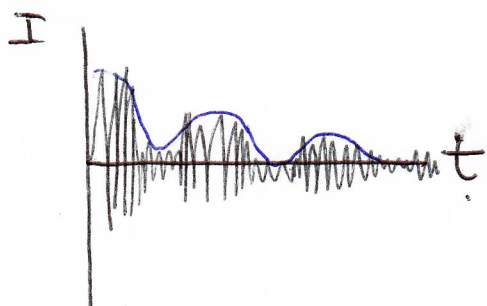
Factors that affect this energy gap:

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

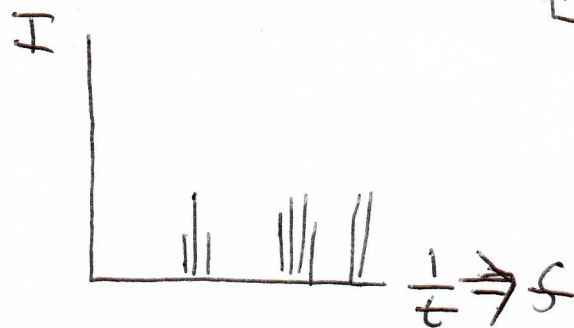


In most modern NMR spectrometers, a sample suspended in a magnetic field is irradiated with a range of EM frequencies. Only those frequencies

that correspond to the energy gaps generated by the sample being in the magnetic field will be absorbed. After irradiation, the various frequencies of light emitted (and originally absorbed by the sample) are observed.



Fourier Transform

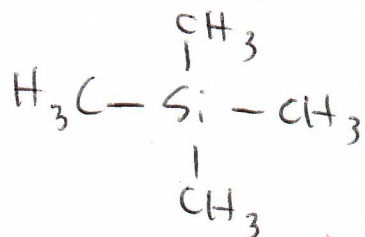


Free Induction Decay

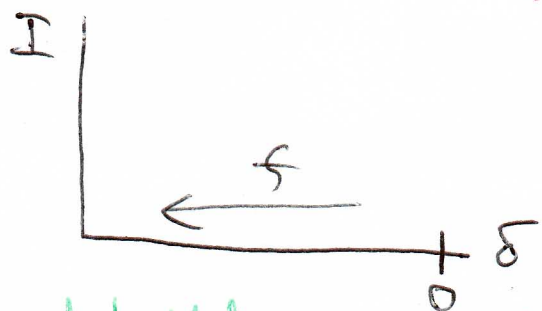
Chemical shift (ppm)

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

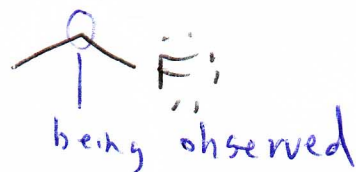
Machine frequency - the frequency measured on a particular spectrometer for a particular reference compound. For organic compounds, the reference is almost always tetramethylsilane (TMS),



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



Deshielded:

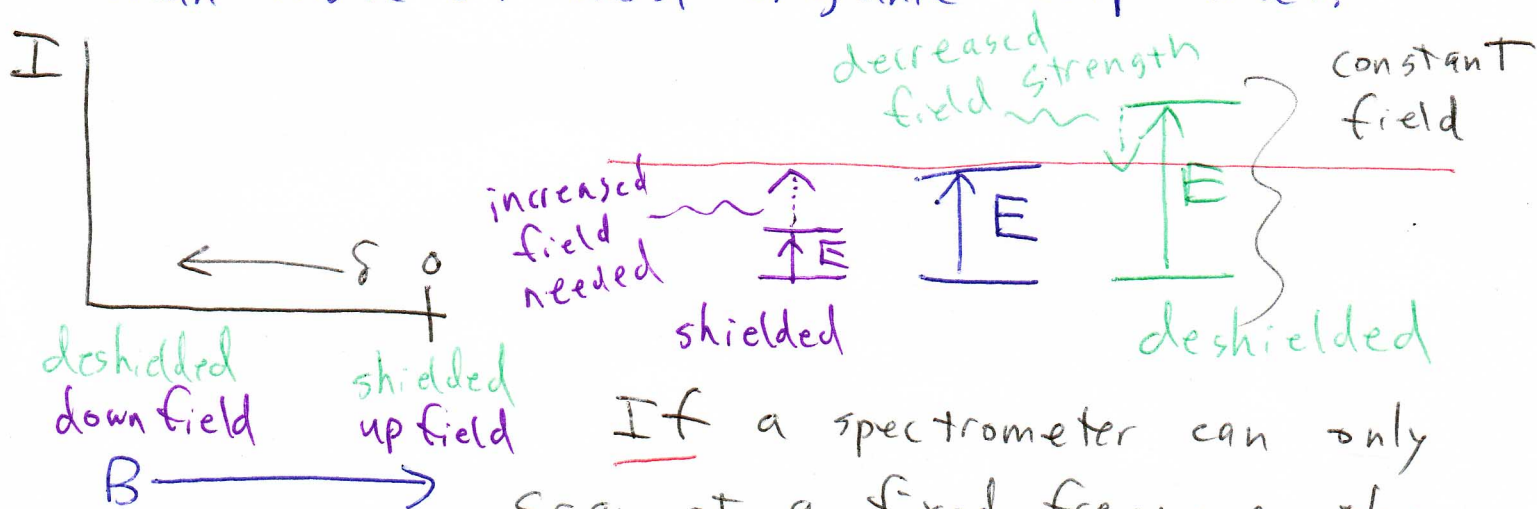


When a nucleus being observed is close to an atom that is electron-withdrawing, electron density will be pulled away

from the nucleus being observed. This means the nucleus will be more exposed to the magnetic field, so it will experience a large energy gap, which results in a larger observed frequency, which results in a larger chemical shift,

Silicon is less electronegative than most elements typically found in organic molecules. Atoms attached to silicon are therefore shielded by comparison, which means their nuclei are not as exposed to the external 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 it will be lower than those of most organic compounds.



If a spectrometer can only scan at a fixed frequency, then the magnetic field used must be varied in order to make the energy gap 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