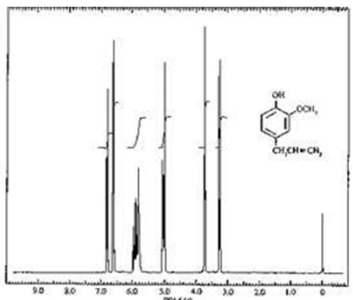
# NMR Theory and C-13 NMR

## Nuclear Magnetic Resonance

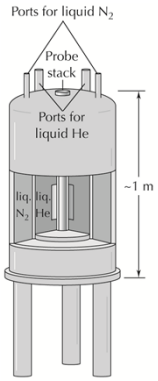
- Powerful analysis
  - Identity
  - Purity
- No authentic needed
- Analyze nuclei
  - $^{1}H$, $^{13}C$, $^{31}P$, etc
  - Get information of how they are attached

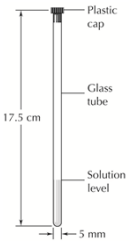



250 MHz $^{1}H$ NMR spectrum of eugenol

# Nuclear Magnetic Resonance

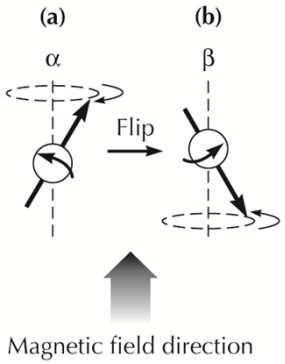
- Nuclear
  - Based on nuclear spin
- Magnetic
  - Large electromagnets create energy differences in nuclei
- Resonance
  - Signal based on absorbed light in resonance with energy difference

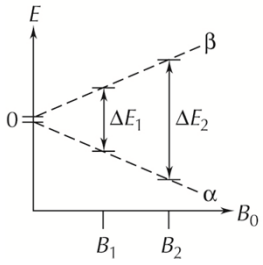

# Nuclear Spin

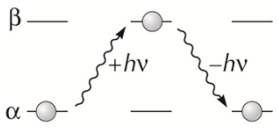
- Some nuclei have spin
  - $^{1}H$, $^{13}C$
- No spin if nuclei have even number of protons and neutrons ($^{12}C$)
- Nuclei align spin with and against magnetic field




# External Magnetic Field

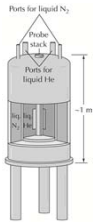
- Bigger energy difference between spin states
- For absorption, $E_{photon} = E_{spin\ gap}$
- Spin flip occurs
- Consider the proton NMR spectrum of $CH_4$

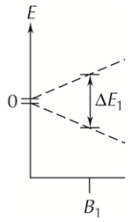


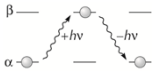



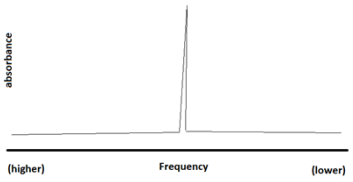
# NMR Spectrum

- $CH_4$ in magnet
- Protons line up with/against
- RF energy
- Only RF energy = gap energy absorbed
- Spectrum shows an absorption



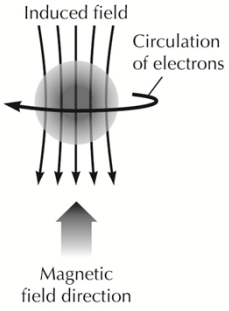



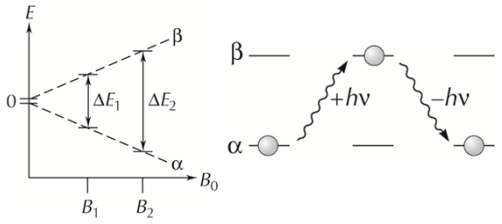

# Magnetic Field Experienced

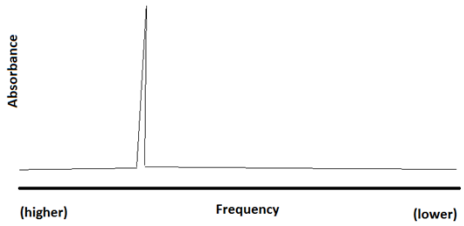
- Not all nuclei in a molecule experience the same magnetic field, even if they are in the same magnet
- Why? Shielding!
- Consider $CH_3Cl$



# NMR Spectrum

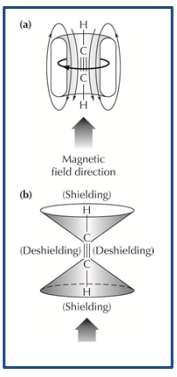
- $CH_3Cl$ in magnet
- Electronegative Cl deshield protons
- Protons experience bigger external field
- Only RF energy = gap energy absorbed
- Spectrum shows a higher frequency absorption

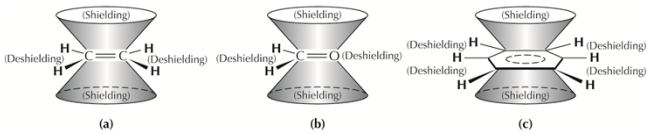



# Other Sources of Shielding

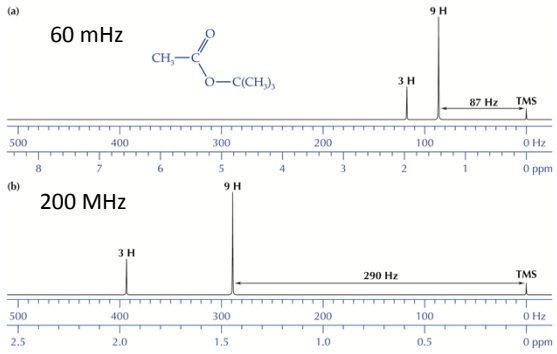
- Anisotropy
- Different effect along different axis
- Can have dramatic shielding/ deshielding effects

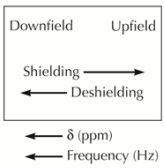


# NMR Spectrum

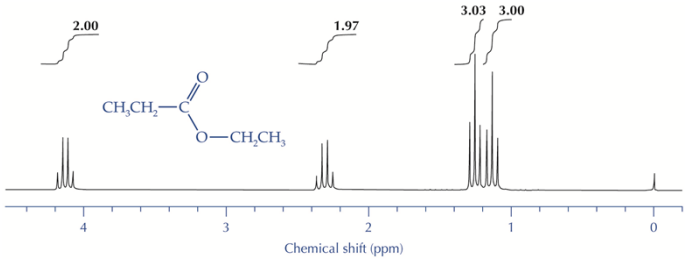
- Need standard: TMS (shielded)
- Need relative frequency: ppm
- ppm = Hz shift/ MHz magnet



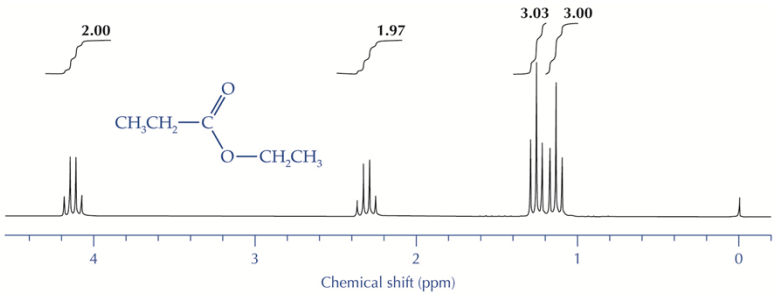

# Four Questions

- How many signals? Equivalence
- Where on spectrum? Chemical Shift
- How big? Integration
- Shape? Splitting (coupling)



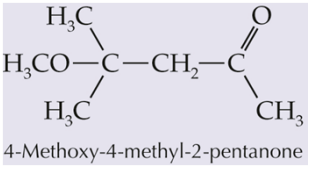
# Number of Signals

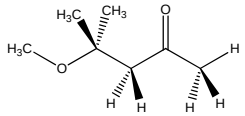
- Four sets of protons in different chemical environments
- Four sets of equivalent protons
- Leads to four distinct signals

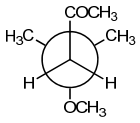



# Equivalence

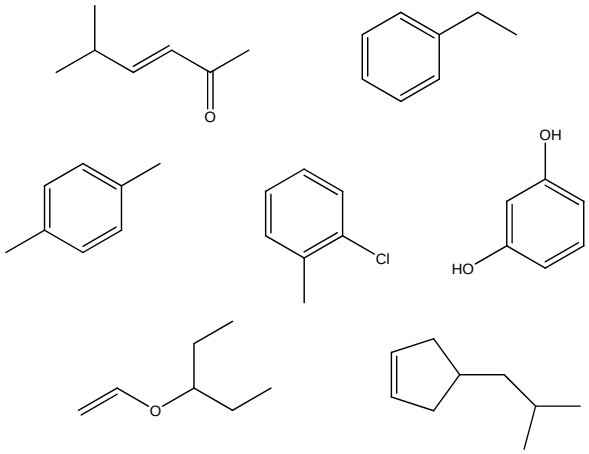
- Experience same average magnetic field due to
  - Free rotation
  - Plane of symmetry
  - Axis of symmetry



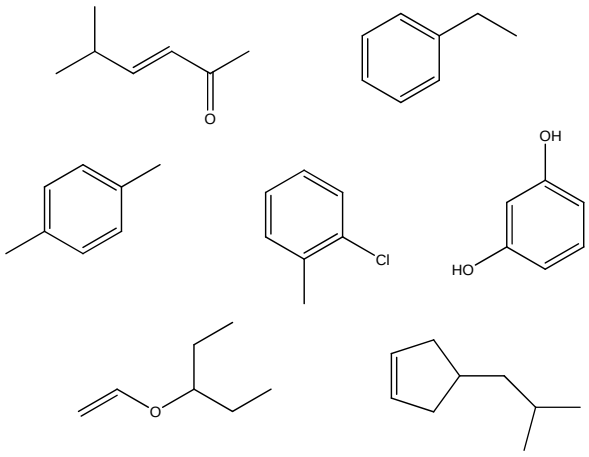





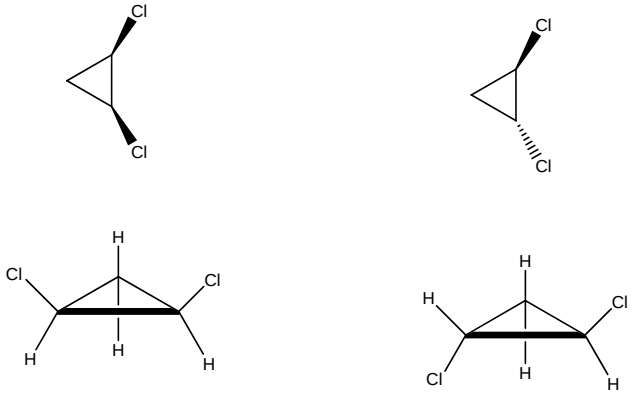
# How many $^{13}C$ signals?




# How many $^{1}H$ signals?

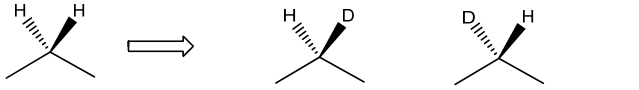


# A more complicated problem



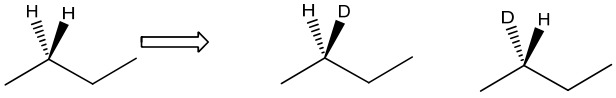

# Equivalence and Chiral Molecules

- Homotopic



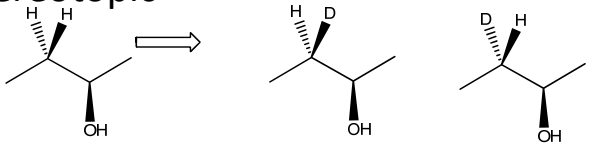

same compound--chemically equivalent protons

- Enantiotopic



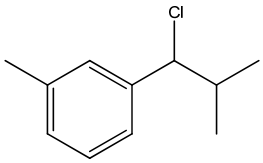

enantiomers--equivalent under achiral conditions

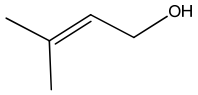
- Diastereotopic

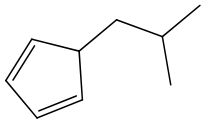


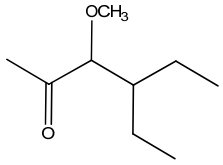

diastereomers--not equivalent under any conditions

# How Many C-13 Signals?



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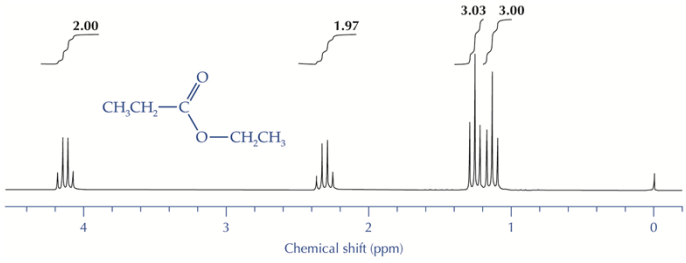
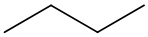
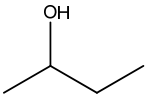
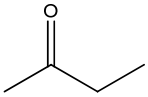


# Carbon-13 Spectra

- How many C-13 signals?
- Which signals are further upfield?
- Can the compounds be differentiated?

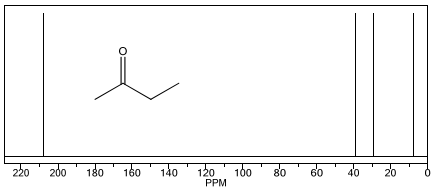


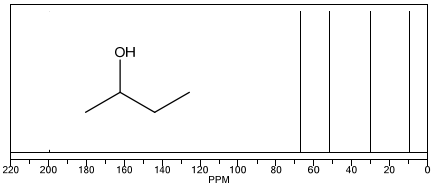



# Correlation Chart

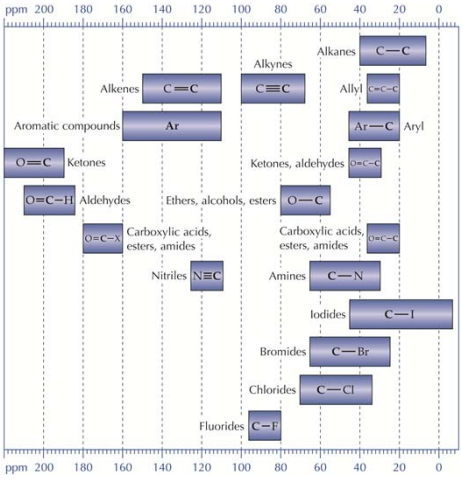
- Same number of signals
- Occur in different areas of spectrum
- Predictable shifts



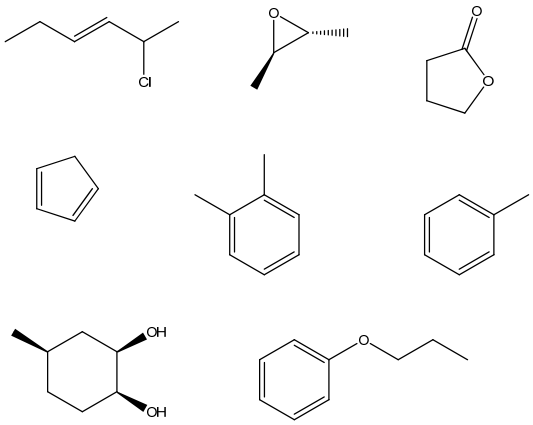



# Chemical Shift Tables

- Complex vs simple
- Basics:
  - Alkane: 5-45ppm
  - C-Q: 40-70ppm
  - sp: 70-100ppm
  - $sp^2$: 100-160 ppm
  - Carbonyl: 160-220 ppm



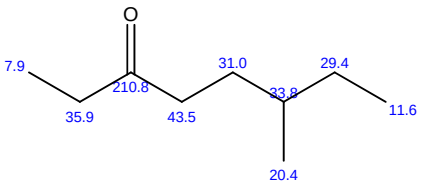

# Predict C-13 Chemical Shifts

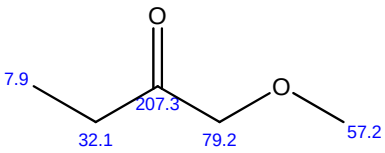



- If carbon fits two categories, choose higher shift

# More subtle points

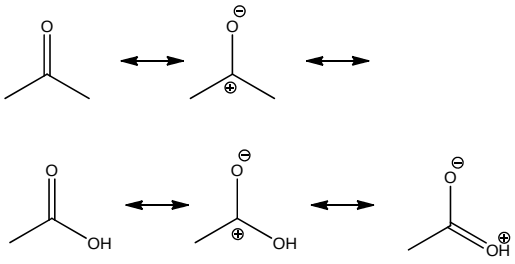
- Inductive effects
- Additive effects
- More substituted $sp^3$ carbon is further downfield

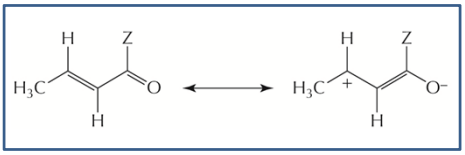



# More subtle points

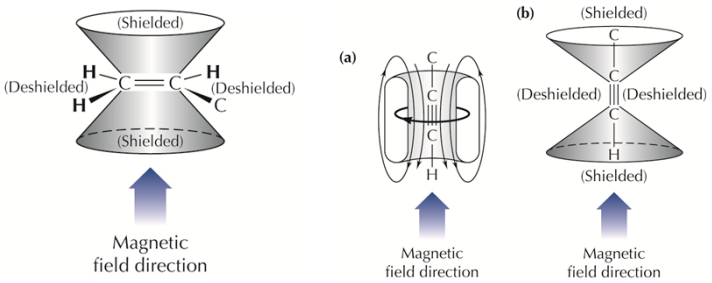
- Carbonyls
  - Above 200ppm, ketone and aldehyde
  - Below 200ppm, O=C-Q
  - Explain by shielding and resonance



# More subtle points

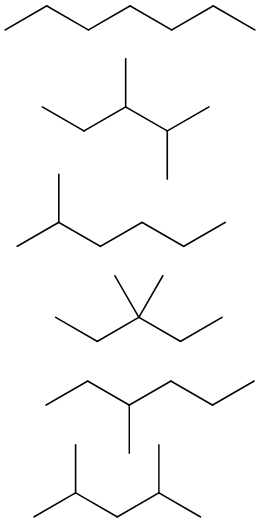
- Alkene vs Alkyne

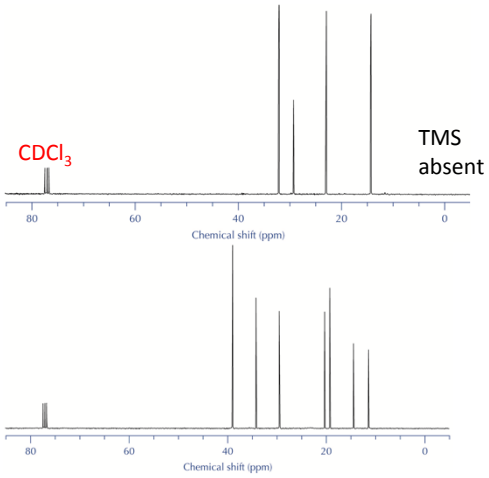



# Two Types of Problems

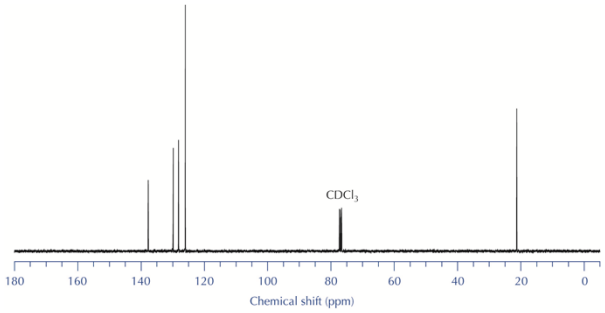
- Predicting spectra: given a structure, what will the C-13 NMR look like?
  - Useful in synthesis of known target
  - A little more straightforward
- Interpreting spectra: given a spectrum, what is the structure of compound?
  - Identify an unknown; side products in synthesis
  - More experience needed

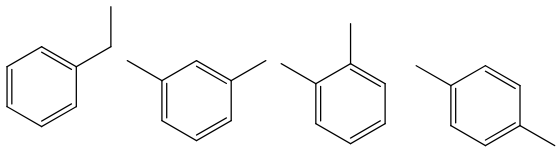
# Which Structure(s) Fit?






# Which Structure Fits?



$C_3H_8O$