Course Chem 345 Lecturer Grellman

Day ~~Thursday~~ Friday Date 1/30/15

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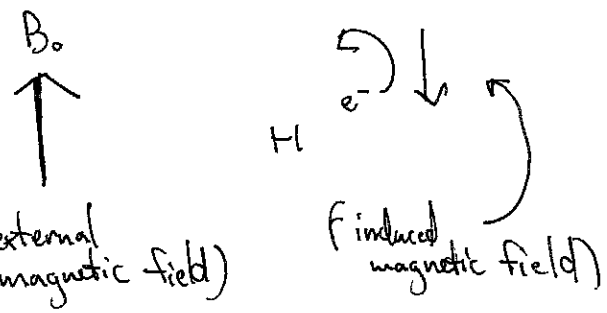
Recall: NMR - interpretation of chemical shift (δ)

→ nearby electronegative atoms → larger δ ("downfield signal")

Ex: H_3C-F, $\delta = 4.26$ vs. H_3C-Cl, $\delta = 3.05$

Explanation: 2ndary magnetic field arising from induced motion in nearby e⁻'s.



Thus,

- More e⁻-density near H ⇒ more shielding
- More shielding ⇒ lower δ ("right", "upfield")
- ∈ N atom nearby ⇒ lower e⁻ density nearby ⇒ less shielding ⇒ larger δ (left)

Multiplicity of NMR signals ("splitting")

- Recall: $CH_3-O-CH_2-O-CH_3$

  [CH_3: δ 3.35] ⇒ single resonances ("singlet")

  [CH_2: δ 4.56]

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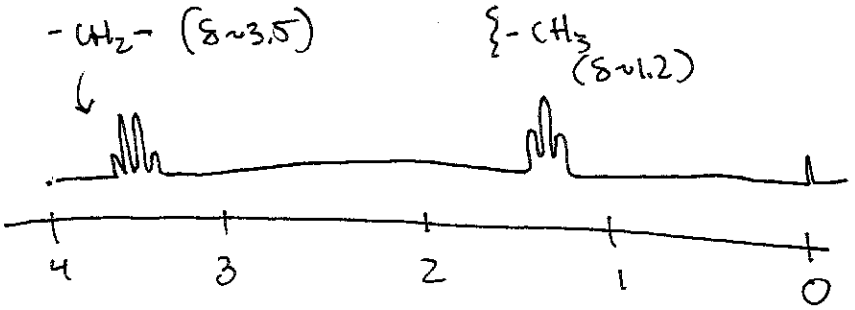
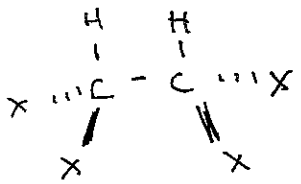
Contrast: $CH_3CH_2OCH_2CH_3$

Part of ^1H-NMR spectrum



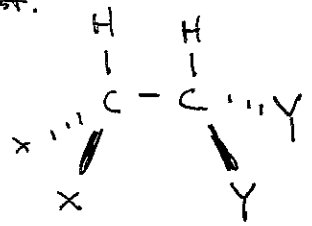
Splitting within an NMR signal
- arises from influence of H's that are "nearby" and non-equivalent (influence = local magnetic field)

Consider:



⇒ H's are equivalent.
∴ One NMR signal

Contrast:



⇒ H's are non-equivalent
∴ 2 signals and each signal is split into 2 parts ("doublets")

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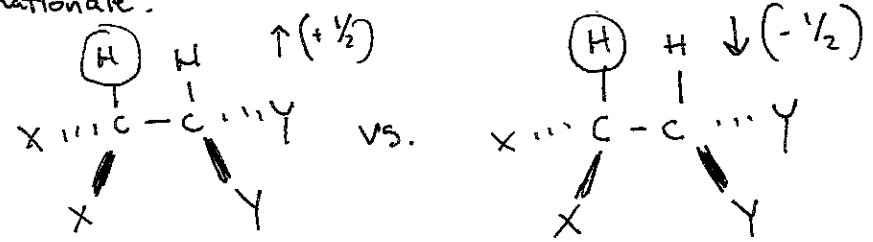
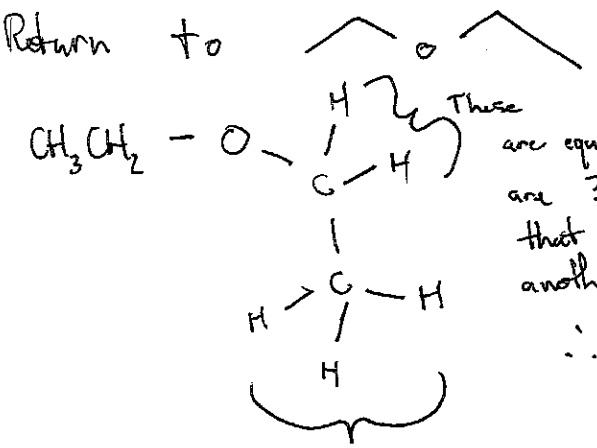
Rationale:



3 bonds between H's

n+1 rule: For a given H, if there are n H's on neighboring C, and these n H's are equivalent to one another, but not to the H in question, then the given H has a resonance split into n+1 lines.

Return to



These are equivalent, and there are 3 equivalent H's that are equiv. to one another, but not to these 2.

∴ n + 1 = 4 ⇒ quartet splitting

These 3 equivalents ... n=2 ∴ n+1=3 ⇒ triplet splitting

Perspective: Types of info in NMR spectra:
1) Chemical shift - local environment w/in a molecule.
2) Integration - info on # H's (ratios)
3) splitting - info on # of neighboring H's

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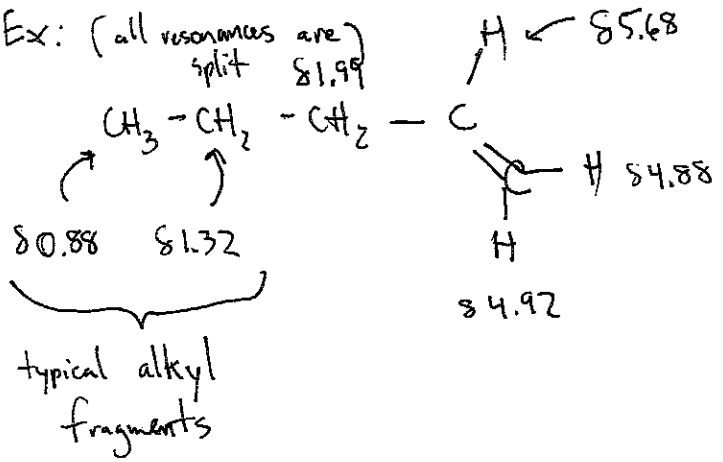
Functional group - [redacted] based view:

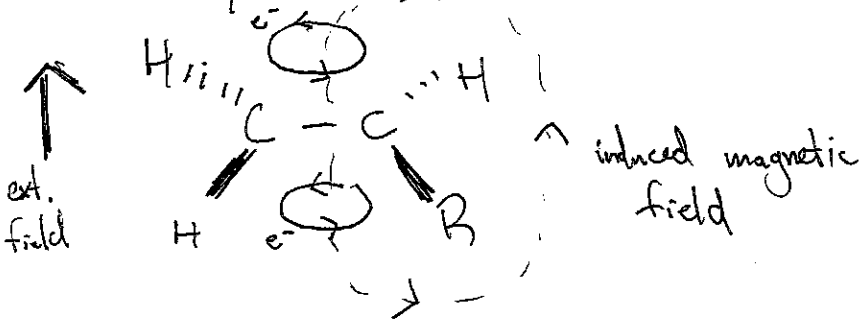
pick up examples from last semester.

1) Alkenes - H's on sp^2 carbon are downfield (larger δ), relative to H's on sp^3 C.

Ex: (all resonances are split)



Origin of large δ: stems from secondary magnetic field caused by motions* induced in π e's.



This, for H's bonded to alkene sp^2 carbons, induced mag. field augments external field ⇒ larger δ

See text for splitting patterns associated w/ alkenes. [Table 13.3]

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