Course Chem 345 Lecturer Gellman

Day Monday Date 2/2/15

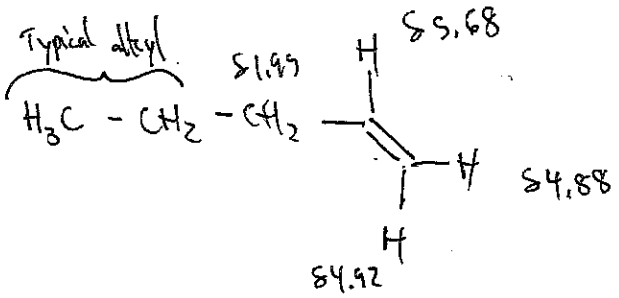
Notes Taken By C. Weatherly Total # of Pages

Submit a *Single-sided Copy* to the Undergraduate Office

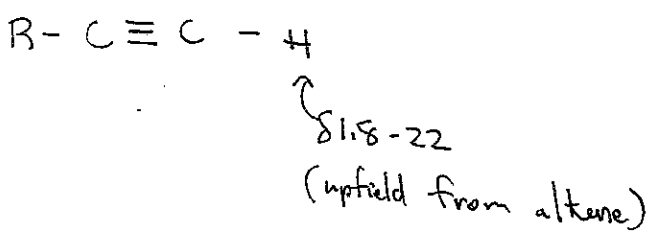
NO NOT STAPLE - ONLY WRITE NOTES INSIDE THE SQUARE BELOW

Recall: ^{1}H-NMR characteristics of specific functional groups

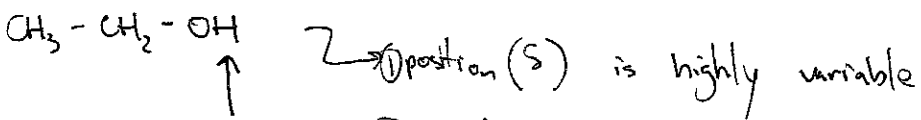
① Alkenes



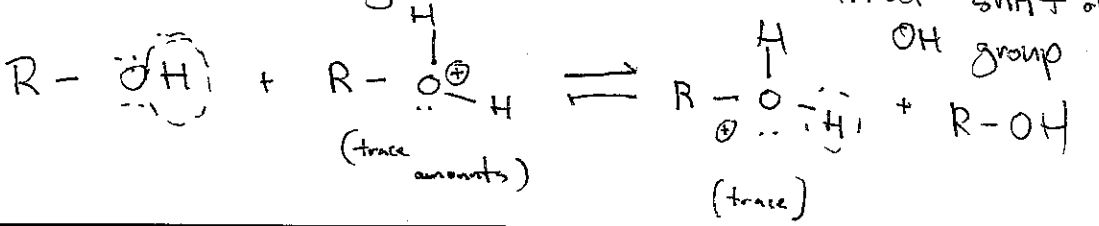
② Alkynes (see ch. 15, pp. 650 - 651)



③ Alcohols (hydroxyl)



OH ^{1}H-NMR signals are variable due to hydrogen-bonding & because of chemical exchange: → Trace acids affect shift of OH group



Course Chem 345 Lecturer Gellman

Day Mon Date 2/2/15

Notes Taken By C. Weatherly Total # of Pages _____

Submit a *Single-sided Copy* to the Undergraduate Office

NO NOT STAPLE - ONLY WRITE NOTES INSIDE THE SQUARE BELOW

Chemical exchange allows a diagnostic expt. based on rapid H vs D exchange

(deuterium)

(^2H)

D is "silent" in ^1H-NMR

Expt.

$R-OH$ in $CDCl_3$ → 1) Contains -OH? 2) Add a drop of D_2O → $RO-D$ (+ HOD)

∴ Hypothetical -OH resonance "disappears". Protons bonded to carbon remain.

- Carbon NMR

→ very useful because organic chemists focus on carbon-rich compounds

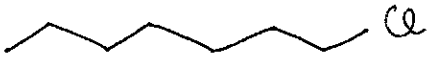
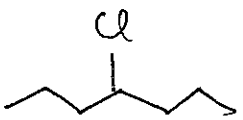
Major technical challenges:

- most abundant carbon isotope (carbon-12) is NMR-silent
- ^{13}C-NMR active - only ~ 1%

Key features of ^{13}C-NMR data.

1) Broad range (~200 ppm) vs. ~10 ppm for ^1H)

2) Direct insight into molecular symmetry

Ex.  7 ^{13}C resonances vs.  4 ^{13}C resonances

Course Chem 345 Lecturer Gellman

Day Monday Date 2/2/15

Notes Taken By C. Weatherly Total # of Pages _____

Submit a *Single-sided Copy* to the Undergraduate Office

NO NOT STAPLE - ONLY WRITE NOTES INSIDE THE SQUARE BELOW

3) Because ^{13}C is rare, don't observe $^{13}C - ^{13}C$ coupling

4) Can observe $^{1}H - ^{13}C$ coupling, however conventional ^{13}C-NMR is "proton-decoupled."

∴ No $^{1}H - ^{13}C$ coupling is observed. Each ^{13}C resonance is a single line.

5) Because of point #4, we cannot use integration in ^{13}C-NMR spectra.

→ See appendix IV for shifts in ^{13}C-NMR data.

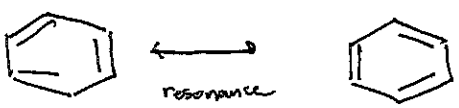
→ Doing problems is crucial for learning ^{13}C-NMR interpretation.

Chap. 16 - Benzene & derivatives

→ reactivity w/ electrophiles.

Rec. problems - 2, 4-9, 12-34, 36-47, 49-56, 58-64.

Recall: C_6H_6



π electrons are fully delocalized

Course Chem 345 Lecturer Grellman

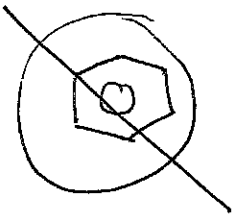
Day Monday Date 2/2/15

Notes Taken By C. Weatherly Total # of Pages _____

Submit a *Single-sided Copy* to the Undergraduate Office

NO NOT STAPLE - ONLY WRITE NOTES INSIDE THE SQUARE BELOW

Another cartoon:

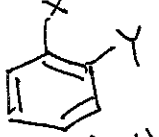


- Important to understand, but not to draw

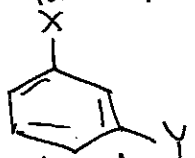
→ full cyclic delocalization of 6 π electrons gives rise to the special property of "aromaticity"

Terminology -  (phenol), etc. (not important to memorize)

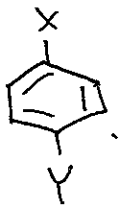
- 3 crucial terms for relative position of ring substituents



"ortho"



"meta"

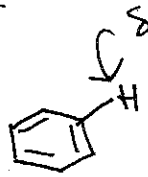


"para"

Spectroscopy -

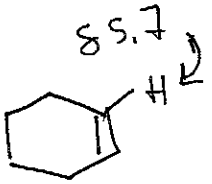
1) IR - see text

2) ^{1}H-NMR:



"large δ values"

vs.



Course Chem 345 Lecturer Gellman

Day Monday Date 2.2.15

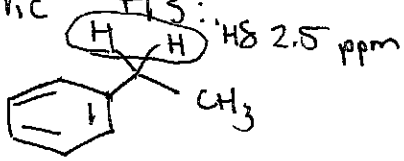
Notes Taken By C. Weatherly Total # of Pages _____

Submit a *Single-sided Copy* to the Undergraduate Office

NO NOT STAPLE - ONLY WRITE NOTES INSIDE THE SQUARE BELOW

^{13}C - ring carbons in range: 110 - 160 ppm

- substituents show characteristic δ values:

Benzylic H's: 

~2.5 ppm

Skip. § 16.3 D

Major reactivity pattern:

Electrophilic aromatic substitution (EAS)