Chem 216 S11 Notes - Dr. Masato Koreeda Date: June 2, 2011
Topic: NMR-III (C-13 NMR) page 1 of 2.

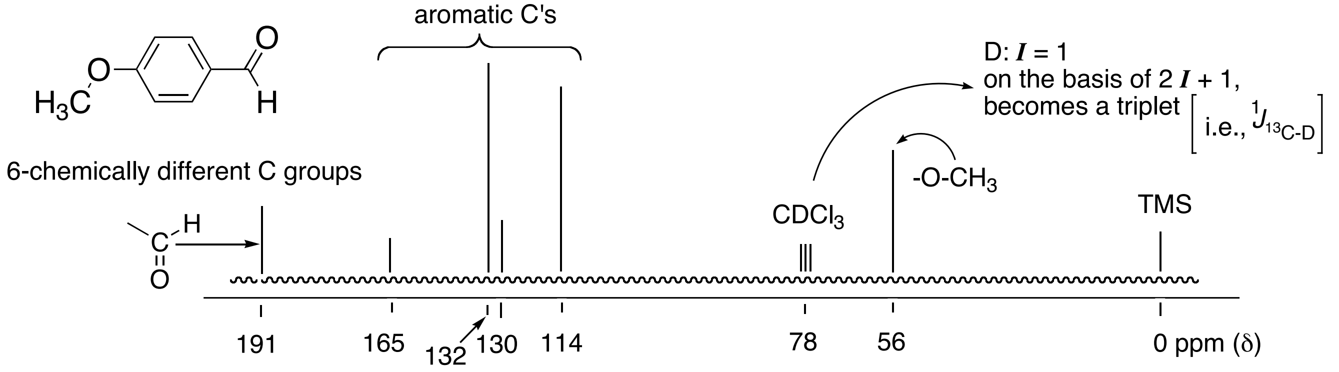
^{13}C NMR Spectroscopy

(1) ^{13}C Isotope (I = 1/2; the same as ^{1}H)

Natural abundance of ^{13}C is only 1% [99% of carbon is ^{12}C (I = 0)].
For example, for CH_3CH_2OH: A probability of finding ^{13}C in the CH_3 is 0.01 (1%) and
a probability of finding ^{13}C in the CH_2 is 0.01 (1%).
Thus, a probability of finding ^{13}C in both the CH_3 and CH_2 at the same time is 0.001 (1% of 1%). Therefore, the contribution of ^{13}C-^{13}C coupling in natural abundance ^{13}C NMR may be ignored. However, ^{13}C found at any ^{1}H-attached carbon exhibits spin-spin coupling with the ^{1}H(s) (one-bond coupling; $^{1}J_{13C,1H}$). In order to avoid complications due to these ^{13}C-^{1}H couplings, ^{13}C NMR spectra are usually obtained by eliminating these couplings by irradiating the entire ^{1}H NMR absorption range (called decoupling). Consequently, all ^{13}C NMR peaks are observed as *singlets*. This mode of obtaining ^{13}C NMR spectra is called a **proton-decoupled** (or broad-band decoupled) method.

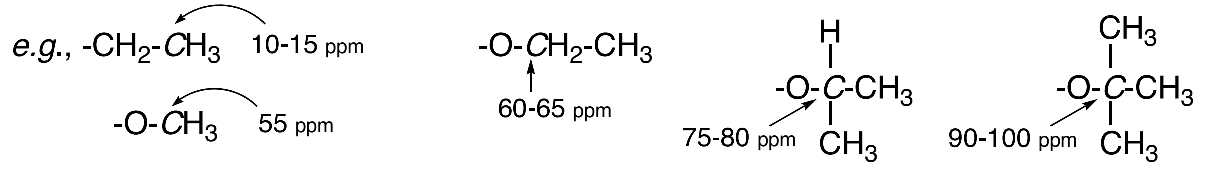
(2) Proton-decoupled ^{13}C NMR Spectra

As in the case of ^{1}H NMR, ^{13}C NMR spectra are obtained typically in $CDCl_3$ with tetramethylsilane (TMS) as internal reference, i.e., $\delta = 0$ ppm for TMS methyl carbons. Most of the ^{13}C NMR chemical shift values fall in the range between 0 and 220 ppm. For representative ^{13}C NMR chemical shifts, see Table 11.2, p. 403 of Ege's book.

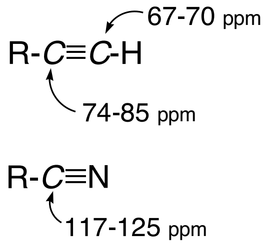


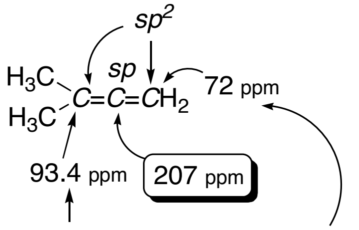
(a) Unlike ^{1}H NMR, the intensity of each of the ^{13}C peaks is *not* proportional to the number of ^{13}C nuclei belonging to each peak.

(b) ^{13}C NMR chemical shifts are predictable primarily based upon the electron density on each C.



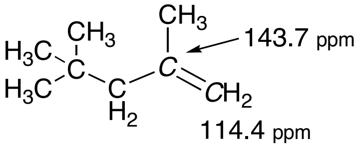
(c) The chemical shifts of alkynic sp carbons are unusual as in the case of alkynic Hs in ^{1}H NMR. However, allenic sp carbons have expected chemical shifts (~ 200 ppm).





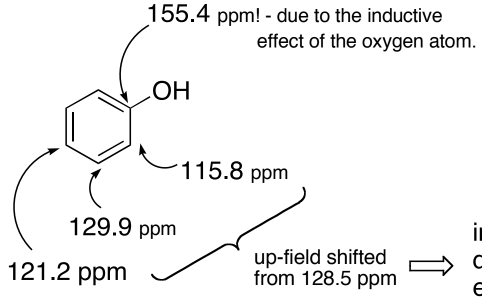
These are quite high-field shifted for sp^2 carbons!

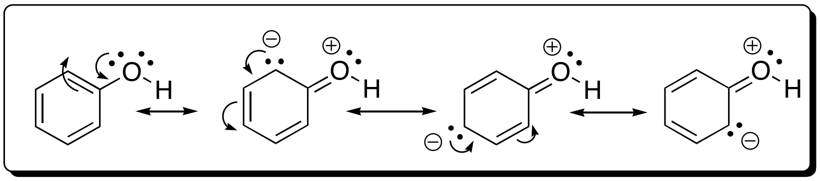
cf.



(d) Unlike ^{1}H NMR, alkenic and aromatic carbons have similar chemical shifts (δ 110 – 140 ppm) (i.e., no significant ring current effect observed in C-13 NMR).

(e) Chemical shifts of aromatic carbons: predictable on the basis of the resonance and inductive effects of the substituents on the ring.





⟹ increased p-electron density due to the resonance effects caused by the OH.

(3) Proton-coupled ^{13}C NMR Spectra

By irradiating slightly off the ^{1}H NMR region, each of the ^{13}C NMR peaks can be designed to exhibit couplings with the ^{1}H nuclei attached to the C, i.e., one-bond ^{13}C-^{1}H coupling(s).

Under such conditions: a CH_3 (methyl) carbon appears as a quartet.
a CH_2 (methylene) carbon appears as a triplet.
a CH (methine) carbon appears as a doublet.
a quaternary carbon appears as a singlet.