cessible zirconocene derivatives represents a distinct breakthrough in transmetalation methodology. Further applications of this process are actively being investigated.

Supplementary Material Available: Experimental details and spectroscopic data for all new compounds (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Accurate Determination of Small Splitting Constants for Organic Radicals by NMR

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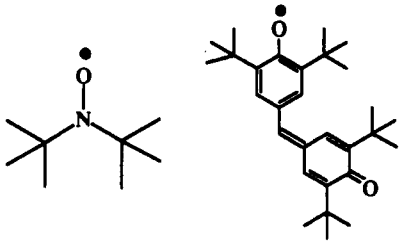
Summary: FT-NMR spectra of the radicals di-*tert*-butyl nitroxide (1) and glavinoxyl (2) are reported. Earlier CW NMR work using internal referencing gave inconsistent results for ESR splitting constants because the concentration dependence of the paramagnetic chemical shift $\Delta\delta$ was unaccounted for. This technique is a viable alternative to ENDOR and uses standard NMR equipment.

We report the use of ^1H and ^{13}C NMR to determine small ESR hyperfine coupling constants (hfcs) of 1 and 2.[1] These studies are the first using FT-NMR technology and represent, to our knowledge, the first reports of direct NMR determinations of ^1H and ^{13}C hfcs in nearly 10 years.[2] Early determinations hfcs via NMR were plagued by sensitivity, referencing, and reproducibility problems which ultimately led to the method's disrepute. For example, previous studies on 1 failed to arrive at a consistent hfc for the *tert*-butyl protons.[3] The inconsistencies plaguing the early investigations have now been resolved, allowing easy access to small hfcs for stable paramagnetic species.



1

2

NMR-observed $\Delta\delta$s are related to hfcs by eq 1, where X corresponds to the nucleus under observation.[4] The $\Delta\delta$s are given as the chemical shift difference of the paramagnetic resonance and an appropriate diamagnetic reference. The sign of the $\Delta\delta$ reveals the sign of the ESR hfc. When eq 1 is solved at a temperature of 300 K for ^1H and ^{13}C, respectively, the relationships in eqs 2 and 3 are obtained.[3a] These equations fail to explicitly account

$$\Delta\delta_X = \Delta H/H_0 = -a_X\gamma_E^2\hbar/4\gamma_X kT \quad \text{gauss/gauss} \quad (1)$$

$$\Delta\delta_H(300\text{ K})/-a_H = 73.76 \quad \text{ppm/gauss} \quad (2)$$

$$\Delta\delta_C(300\text{ K})/-a_C = 293.3 \quad \text{ppm/gauss} \quad (3)$$

for changes in bulk sample magnetic susceptibility as a function of the paramagnetic sample concentration. A clear concentration dependence of 1's ^1H contact chemical shift, $\Delta\delta_H$, is demonstrated in Figure 1.[5-7] Equations 1-3 only apply when the $\Delta\delta$s are extrapolated to infinite dilution, which for 1 yields an $a(18\text{ H}) = -0.077$ G (Figure 2).[8] *Failure to account for the concentration dependence has resulted in incorrect and variable determinations of hfcs.*[3] For instance, if the $\Delta\delta$ was obtained for 1 at a concentration of 1.26 M, the calculated ^1H hfc using eq 2 would be exactly zero. The negative sign of the hfc is clear from an extrapolated $\Delta\delta$ upfield of external tetramethylsilane. We have been unable to obtain data below a radical concentration of 5 mM due to broadening of the ^1H resonances. Figure 1 also demonstrates the futility of internal chemical shift referencing, since the resonance frequency of the internal standard (i.e. TMS) also changes as a

(1) For reviews of earlier paramagnetic NMR experiments, see: (a) Orrell, K. G. N.M.R. of Paramagnetic Species in *Nuclear Magnetic Resonance* (Specialists Periodical Reports); Webb, G. A., Ed.; The Royal Society of Chemistry: London; 1989; Vol 18, p 369. (b) *NMR of Paramagnetic Molecules: Principles and Applications*; La Mar, G. N., Horrocks, W., Jr., Holm, J. R., Eds. Academic Press: New York, 1973.

(2) (a) Pearson, G. A.; Walter, R. I. *J. Am. Chem. Soc.* **1977**, *99*, 5262. (b) Linkletter, S. J. G.; Pearson, G. A.; Walter, R. I. *J. Am. Chem. Soc.* **1977**, *99*, 5269. (c) Neugebauer, F. A.; Fischer, H.; Brunner, H. *Tetrahedron* **1981**, *37*, 1391. (d) Neugebauer, F. A.; Fischer, H. *J. Chem. Soc., Perkin Trans. II* **1981**, 896.

(3) Previous NMR studies on 1 have been performed. (a) $a(18\text{ H}) = -0.107$ G: Hausser, K. H.; Brunner, H.; Jochims, J. C. *Mol. Phys.* **1965**, *10*, 253. (b) $a(18\text{ H}) = +0.15$ G: Kreilick, R. W. *J. Chem. Phys.*, **1966**, *45*(6), 1922. (c) $a(18\text{ H}) = +0.30$ G: Stehlik, D.; Hausser, K. H. *Z. Naturforsch.* **1967**, *22a*, 914. (d) $a(18\text{ H}) = -0.092$ G: Faber, R. J.; Markley, F. W.; Weil, J. A. *J. Chem. Phys.* **1967**, *46*(5), 1652, via personal communication from R. W. Kreilick. ESR studies have also been reported. (e) $a(18\text{ H}) = 0.12$ G: Faber, R. J.; Markley, F. W.; Weil, J. A. *J. Chem. Phys.* **1967**, *46*(5), 1652. (f) $a(18\text{ H}) = 0.10$ G, $a(18\text{ H}) = 0.20$ G: Poggi, G.; Johnson, S. *J. Magn. Reson.* **1970**, *3*, 436. (g) a (18 H) = 0.10 G: Kotake, Y.; Kuwata, K. *Chem. Lett.* **1984**, 83.

(4) Brown, T. H.; Anderson, D. H.; Gutowsky, H. S. *J. Chem. Phys.* **1960**, *33*, 720.

(5) The contact chemical shift, $\Delta\delta_f$ is the difference between the chemical shift of the paramagnetic sample and that of an appropriate diamagnetic reference. Reduction products were used as diamagnetic references. For di-*tert*-butylhydroxylamine, $\delta(^1H, CDCl_3) = 1.10$ ppm, $\delta(^{13}C(q), CDCl_3) = 63.0$ ppm, $\delta(^{13}C(Me), CDCl_3) = 29.0$ ppm. For the phenol derived from 2, $\delta(^tBu, CDCl_3) = 1.47$ ppm.

(6) All ^1H experiments were performed on either a Bruker AM-500 or a Varian UNITY-300 spectrophotometer at a constant temperature of 300 ± 0.1 K in $CDCl_3$. ^{13}C experiments were performed on the Varian UNITY-300 instrument at the same temperature. Titration experiments were performed by titrating 1 and 2 into a solution of $CDCl_3$ (low concentration points) or $CDCl_3$ into neat 1 (high concentration). Spectra were obtained unlocked (with the field sweep disabled) and referenced externally. Roughly 60° pulse widths were used and long relaxation delays (relative to T_2) were employed (ca, 0.25-1.0 s).

(7) It is not clear that small changes in the ESR hfcs do not occur as a function of concentration.

(8) The NMR-derived splitting reported for 1 is smaller than the reported ESR splittings (ref 3), but the ^1H hyperfine was not directly observable by ESR; a(H) was estimated from the width of the envelope of the unresolved lines and from spectral simulation. In addition, ESR does not directly give the sign of an hfc. A TRIPLE experiment is often performed if the sign is desired. See ref 9 for more information on TRIPLE experiments.

(9) (a) Kurreck, H.; Kirste, B.; Lubitz, W. *Electron Nuclear Double Resonance Spectroscopy of Radicals in Solution: Application to Organic and Biological Chemistry*; Marchand, A. P., Ed.; VCH: New York, 1988. (b) Biehl, R.; Plato, M.; Möbius, K. *J. Chem. Phys.* **1975**, *63*(8), 3515-3522.

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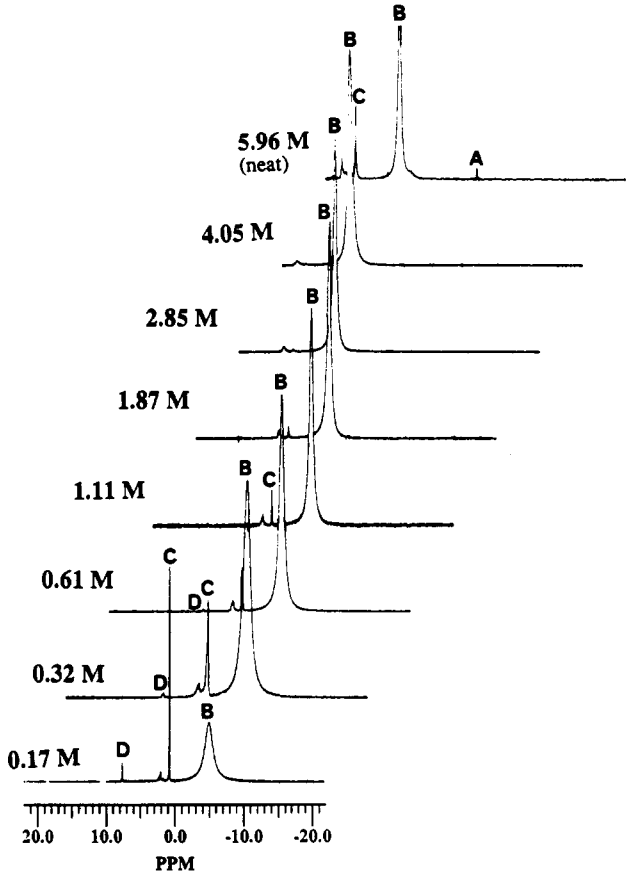

Figure 1. Stacked plots showing DBNO titrated into $CDCl_3$: (A) external TMS, (B) DBNO, (C) internal TMS, (D) residual $CHCl_3$. The top spectrum is neat DBNO (5.96 M) containing both internal and external TMS (C and A, respectively).

function of paramagnetic sample concentration. Therefore, *all chemical shifts of paramagnetic samples should be externally referenced.*

A hfc a(18 H) = +0.047 G is obtained for **2** when the same experimental approach is employed. This corresponds exactly with ESR studies and confirms our hypothesis with regards to the concentration dependence of the hfcs.[3a] The hfcs determined via ESR are not significantly concentration dependent,[7] whereas NMR $\Delta\delta$s are. Early NMR experiments were performed at very high concentrations (either neat or saturated solutions) as single point experiments and failed to properly account for the concentration dependence of the $\Delta\delta$s.[3,10] Extrapolation

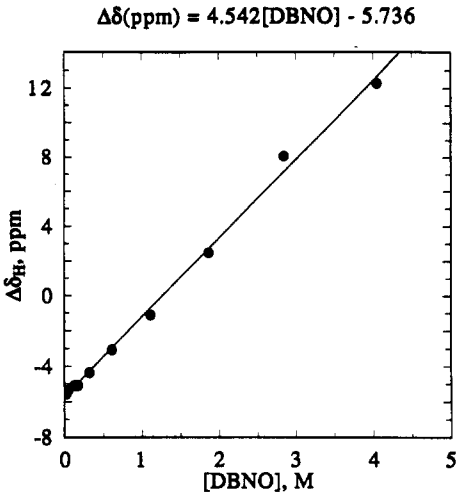

Figure 2. Plot of $\Delta\delta$ ^{1}H chemical shift vs [DBNO] in $CDCl_3$.

of $\Delta\delta$ values measured at several concentrations to zero concentration appears to be the best approach to obtain hfcs.

The above observations are also true for ^{13}C hfcs measured by NMR. A concentration study on the ^{13}C resonances of **1** (at natural abundance) yielded a(2 C) = −4.92 G and a(6 C) = +4.65 G at infinite dilution. These values compare well with hfcs of $|a(2C)|$ = 4.4–5.4 G and $|a(6\ C)|$ = 4.4–4.9 G determined by ESR and represent a significant improvement in accuracy over previous NMR on neat solutions.[11] The broadening observed in ^{1}H experiments occurs at a higher concentration for ^{13}C experiments (ca. 5 mM vs 2 M). Examination of **2** by ^{13}C proved futile since a saturated solution in $CDCl_3$ (ca. 1.5 M) showed no discernable resonances after 36 h.

NMR spectra of paramagnetic materials can be an important aid in interpreting complex ESR spectra where several small splittings are present. Given the ease with which these experiments can now be performed, and the widespread availability of NMR spectrometers, a renaissance of the use of NMR for determination of small hfcs is anticipated.

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(10) Kreilick reports that the concentration dependence does indeed exist, but he fails to comment upon its relevance with respect to the observed $\Delta\delta$s. See ref 4b.

(11) (a) Hatch, G. F.; Kreilick, R. *Chem. Phys. Lett.* **1971**, *10*, 490. (b) Hatch, G. F.; Kreilick, R. W. *J. Chem. Phys.* **1972**, *57*, 3696.

Mechanistic Study of a Synthetically Useful Monooxygenase Model Using the Hypersensitive Probe *trans*-2-Phenyl-1-vinylcyclopropane

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Summary: The use of *trans*-2-phenyl-1-vinylcyclopropane as a hypersensitive probe to study the epoxidation mechanisms of monooxygenases and their models is described; the high yield epoxide formation indicates that the Mn(III) salen mediated epoxidation of unfunctionalized alkyl-substituted olefins is a concerted process. A stepwise mechanism, however, is suggested for the epoxidation of aryl-substituted olefins.

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