Table II. Nmr Spectrum of Bis(6-*tert*-butyl-1,3,5-trimethylcyclohexadienyl)iron(II) in Carbon Disulfide at $-38°$

Position (τ)	Rel area	Assignment
6.35	1	2-H
6.95	1	4-H
7.86	3	5-Methyl
7.98	1	Endo 6-H
8.02	3	3-Methyl
8.95	3	1-Methyl
9.56	9	*exo*-6-*tert*-Butyl

The representations given in eq 1 differ from resonance structures in that they are intended to imply a rocking of the rings with respect to the iron atom so that changes in the relative positions of nuclei occur. At high temperatures delocalized structures would better represent the molecules. The failure of the peaks assigned to the 3-methyl protons to shift as the temperature is changed suggests that an alternative limiting structure with σ bonding from position 3 to iron is insignificant.

The spectra allow either free rotation with respect to the ring–Fe–ring axis at the temperature of measurement or lack of rotation, but they do not permit interpretation on the basis of partially restricted rotation. If that were the case, the peaks assigned to the 3-methyl protons and the 6 proton would also be expected to separate to two peaks each. Furthermore, the rotamers would be unequal in energy, the populations would be unequal, and the areas of the divided peaks should be unequal.

The elemental analyses and molecular weights (mass spectra) are consistent with the assigned structures. *Anal.* Calcd for the di-*tert*-butyl adduct, $C_{26}H_{42}Fe$: C, 76.08; H, 10.31; Fe, 13.61; mol wt, 410. Found: C, 75.52; H, 10.10; Fe, 13.6; mol wt, 410. *Anal.* Calcd for the diphenyl adduct, $C_{30}H_{34}Fe$: C, 79.99; H, 7.61; Fe, 12.40; mol wt, 450. Found: C, 79.86; H, 7.75, Fe, 11.29; mol wt, 450. Both complexes are soluble in hydrocarbons and may be chromatographed on alumina. The di-*tert*-butyl adduct, mp 203–204°, may be sublimed *in vacuo* and is thermally stable to about 250°. The diphenyl adduct undergoes thermal decomposition just above its melting range, 102–105°. Both are stable to air and water although the diphenyl compound deteriorates during long storage. The absence of infrared absorption in the region 2700–2800 cm^{-1} of the kind which has been attributed to exo C–H stretching in certain related complexes[4] supports the assignment of exo positions to the *tert*-butyl and phenyl groups.

In view of the marked spectral changes which have been observed for these compounds it is somewhat surprising that neither of the corresponding monoadduct hexafluorophosphates described in the preceding paper exhibits any temperature dependence of the nmr spectrum in deuterioacetone. To the best of our knowledge such temperature dependence has not been described for other cyclohexadienyl complexes of transition metals either.

At and above the temperature at which the limiting high-temperature spectrum is found, one may speculate as to the possibility of cyclic delocalization of π-electron density, a situation which would allow the interpretation that these are complexes of homocyclopentadienide anions, that they might be described as pseudoferrocene systems, and that they may exhibit some chemical properties like those of ferrocene.

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[4] P. H. Bird and M. R. Churchill, *Chem. Commun.*, 777 (1967).

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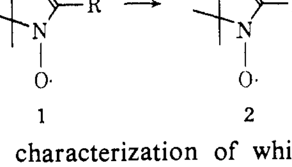
Stable Free Radicals. IX.[1] Use of Halogen Nuclear Quadrupole Coupling in Electron Spin Resonance Spectra of Imino Nitroxides for Determination of Solvent Effects on Rotational Correlation Times

Sir:

Hyperfine coupling to bromine and iodine in the esr spectra of organic radicals is rarely observed. The only previous examples include some iminoxyl σ radicals[2] and the bromo nitronyl nitroxide **1** (R = Br).[3] The difficulty in observing coupling is due to the large nuclear quadrupole moments of these elements. Fluctuations in the electric-field gradients at the halogen nuclei due to molecular tumbling produce nuclear spin relaxation that is fast relative to the hyperfine splitting and leads to averaging of the magnetic field contributions of the nuclear spin states. Where coupling is observed the line widths are predicted to be proportional to the rotational correlation time τ_c.[4] We describe here an empirical correlation of the effect of solvent on rotational correlation times employing esr spectra of new halo radicals.

The bromo and iodo nitronyl nitroxides **1**, R = Br and I, react with sodium nitrite in dimethylformamide to give the imino nitroxides, 2-bromo- and 2-iodo-4,4,5,5-tetramethylimidazoline-1-oxyl (**2**, R = Br and I). These products are stable orange radicals, the



1 2

chemistry and characterization of which will be described elsewhere.[1] They display coupling to both nitrogens which has a small solvent dependence:[1] **2**, R = Br (C_6H_{14}), $a_{N(1)}$ 8.65 G, $a_{N(2)}$ 4.25 G; **2**, R = I (C_6H_{14}), $a_{N(1)}$ 8.60 G, $a_{N(2)}$ 4.20 G. In addition, coupling to bromine in **2**, R = Br, gives rise to four lines, a_{Br} 1.9 G (solvent independent), expected of nuclei with $I = {}^3/_2$. Resolution of separate lines due to ^{79}Br and ^{81}Br which have similar gyromagnetic moments was

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[1] For paper VIII see E. F. Ullman, L. Call, and J. Osiecki, *J. Org. Chem.*, **35**, 3623 (1970).

[2] (a) W. M. Fox and W. A. Waters, *J. Chem. Soc.*, 4628 (1965); (b) R. O. C. Norman and B. C. Gilbert, *J. Phys. Chem.*, **71**, 14 (1967); (c) B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc. B*, 981 (1967); *ibid.*, 123 (1968).

[3] D. G. B. Boocock and E. F. Ullman, *J. Amer. Chem. Soc.*, **90**, 6873 (1968).

[4] J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 326 (1963).

Table I. Coalescence Temperatures of the Electron Spin Resonance Spectra of **2**, R = I, in Solvents of Different Polarity

No.	Solvent	E_T[a]	T_c, °K	η, cP	$(T/\eta)_c \times 10^{-2}$
1	Water	63.1	359	0.331[b]	10.85
2	Formamide	56.6	390	0.467[c]	8.37
3	Methanol	55.5	333	0.368[d]	9.05
4	Isopropyl alcohol	48.6	360	0.469[d]	7.68
5	Nitromethane	46.3	300	0.605[b]	4.96
6	Acetonitrile	46.0	285	0.388[b]	7.35
7	Acetone	45.0	296	0.320[d]	9.25
8	Dimethyl sulfoxide	45.0	400	0.570[e]	7.02
9	Nitrobenzene	42.0	363	0.779[f]	4.66
10	Benzonitrile	42.0	360	0.594[g]	6.06
11	1,2-Dichloroethane	41.9	333	0.522[d]	6.40
12	Methylene chloride	41.1	289	0.450[d]	6.42
13	Pyridine	40.2	338	0.545[f]	6.20
14	Chloroform	39.1	320	0.525[d]	6.10
15	Ethyl acetate	38.1	300	0.422[d]	7.13
16	Chlorobenzene	37.5	320	0.590[b]	5.42
17	Tetrahydrofuran	37.4	318	0.382[h]	8.32
18	Anisole	37.2	320	0.650[i]	4.92
19	*p*-Dioxane	36.0	350	0.550[j]	6.36
20	Diethyl ether	34.6	271	0.288[d]	9.41
21	Toluene	33.9	291	0.604[k]	4.83
22	Carbon disulfide	32.6	236	0.525[d]	4.50
23	Carbon tetrachloride	32.5	318	0.683[d]	4.66
24	*n*-Hexane	30.9	246	0.550[d]	4.47

[a] Solvent polarity parameter, see ref 8. [b] "Handbook of Chemistry and Physics," 50th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1969. [c] K. Chuyo, *Bull. Chem. Soc. Jap.*, **30**, 782 (1967). [d] Calculated from temperature dependence data in "Technique in Organic Chemistry," A. Weissberger, Ed., Vol. 7, 2nd ed, Interscience, New York, N. Y., 1955. [e] H. L. Schläfer and W. Schaffernicht, *Angew. Chem.*, **72**, 618 (1960). [f] International Critical Tables, Vol. 7, 1931. [g] F. J. Wright, *J. Chem. Eng. Data*, **6**, 454 (1961). [h] C. Carvajal, K. J. Tölle, J. Schmid, and M. Szwarc, *J. Amer. Chem. Soc.*, **87**, 5548 (1965). [i] J. A. Geddes and E. Bingham, *ibid.*, **56**, 2625 (1934). [j] W. Herz and E. E. Lorenz, *Z. Phys. Chem.*, **140**, 407 (1929). [k] E. B. Evans, *J. Inst. Petr. Technol.*, **24**, 537 (1938).

not achieved. In the esr spectra of **2**, R = I, taken even under the most favorable conditions, the six theoretical iodine lines ($I = {}^5/_2$) were partially collapsed due to rapid nuclear relaxation, and only two lines were observable; line separation 3.9 G (solvent independent).

Good resolution of bromine coupling in **2**, R = Br, was observed at room temperature except in the polar viscous solvents, water and dimethyl sulfoxide, where resolution was improved on warming. At low temperatures in all solvents, **2**, R = I, displayed seven-line patterns due to coupling only to the nitrogens. At higher temperatures iodine coupling produced eight-line patterns.[5] The temperatures of coalescence of the eight-line patterns in various solvents are given in Table I.

The molecular tumbling correlation time τ_c for nuclear quadrupole relaxation is usually taken as $4\pi a^3\eta/3kT$ for a spherical molecule of radius a in a solvent of viscosity η.[6] Since the coalescence temperatures define conditions where the line widths are identical, the temperature–viscosity ratios at coalescence $(T/\eta)_c$ should be invariant. However, the experimental values do not support this prediction (Table I).

Numerous attempts to relate rotational correlation times, as well as the closely related dielectric relaxation times, in different solvents have met with limited success.[6,7] The above expression for τ_c is derived from Debye's model of a molecule which behaves like a large sphere in a viscous medium obeying Stokes' law. Although the model has been successfully employed to correlate nuclear spin relaxation rates in a single solvent,[6,7b] it fails to account satisfactorily for variations in solvent parameters other than viscosity that affect intermolecular interactions. Important additional restrictions to molecular rotations arise from induced solvent polarization and hydrogen bonding to polar molecules. These factors increase the effective molecular volume. The Debye expression may thus be modified by including an empirical solvent–solute interaction parameter. In eq 1, E_T is a solvent polarity parameter derived from the effect of solvent on electronic transitions in dyes,[8] E_{T_0} is the E_T value for a hypothetical completely nonpolar solvent, E_s is a solute polarity parameter, and V is the molecular volume.

$$\tau_c = \frac{\eta V}{kT}[1 + (E_T - E_{T_0})E_s] \qquad (1)$$

A plot of $(T/\eta)_c$ against E_T (Figure 1) confirms the utility of this expression. Despite some scatter, 16 of the 24 solvents studied fall gratifyingly close to a straight line. Moreover, those points that fall off the line are not random but fall into three solvent types with some internal consistencies. Thus all the ethers **17–20** and carbonyl derivatives **2**, **7**, and **15** show deviations which are mostly positive and vary monotonically with the boiling points. On the other hand the nitro compounds (**5** and **9**) display large negative deviations.

Considering that the empirical parameter E_T was derived from a very different type of measurement, deviations of specific solvent types are not unexpected. Hopefully, examination of other solutes will permit

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(5) See ref 1 for actual spectra.

(6) N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.*, **73** 679 (1948).

(7) (a) V. V. Daniel, "Dielectric Relaxation," Academic Press, New York, N. Y., 1967; (b) P. W. Atkins and D. Kivelson, *J. Chem. Phys.*, **44**, 169 (1966); (c) H. S. Gutowsky and D. E. Woessner, *Phys. Rev.*, **104**, 843 (1956); (d) J. Crossley and C. P. Smyth, *J. Amer. Chem. Soc.*, **91**, 2482 (1969); (e) O. F. Kalman and C. P. Smyth, *ibid.*, **82**, 783 (1960).

(8) C. Reichardt, *Angew. Chem., Int. Ed. Engl.*, **4**, 29 (1965).

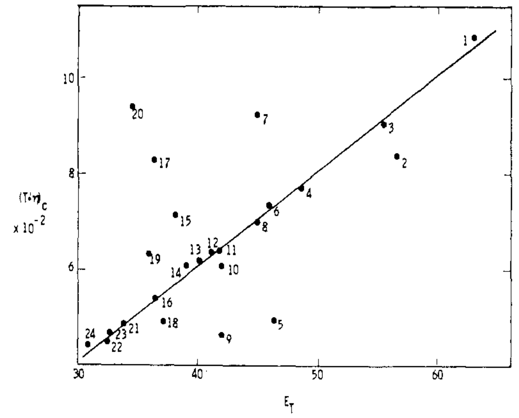

Figure 1. Temperature–viscosity ratios at coalescence of the low-field pair of lines of the eight-line esr pattern of **2**, R = I.

construction of a specific empirical solvent scale of general utility for rotational correlation times.

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The Formation of Alkyl Bromides in the Dark Reaction of Bromine with Organoboranes. Evidence for an Unusual Pathway Involving the Prior Bromination of the Organoborane

Sir:

Tri-*n*-butylborane reacts readily with dry bromine in the absence of a solvent to yield *n*-butyl bromide, di-*n*-butylboron bromide, *n*-butane, and hydrogen bromide.[1,2] The reaction is greatly facilitated by the use of methylene chloride as a solvent and provides a convenient procedure for the anti-Markovnikov hydrobromination of olefins (eq 1).[3]

$$\begin{array}{l} 3(CH_3)_2C{=}CH_2 + BH_3 \longrightarrow [(CH_3)_2CHCH_2]_3B \\ \qquad\qquad\qquad\qquad\qquad \big\downarrow{\scriptstyle Br_2} \\ \qquad\qquad (CH_3)_2CHCH_2Br + [(CH_3)_2CHCH_2]_2BBr \quad (1) \end{array}$$

Investigation revealed an unexpected feature—the reaction does not involve simple rupture of the carbon–boron bond by bromine. Instead, the reaction proceeds through the fast α bromination of the organoborane[4] followed by a subsequent reaction of the intermediate with the hydrogen bromide (eq 2).

$$\begin{array}{l} R_2BCH_2CH(CH_3)_2 + Br_2 \xrightarrow{\text{fast}} R_2BCHBrCH(CH_3)_2 + HBr \\ \qquad\qquad\qquad\qquad\qquad\qquad \big\downarrow{\scriptstyle \text{slow}} \\ \qquad\qquad\qquad\qquad R_2BBR + (CH_3)_2CHCH_2Br \quad (2) \end{array}$$

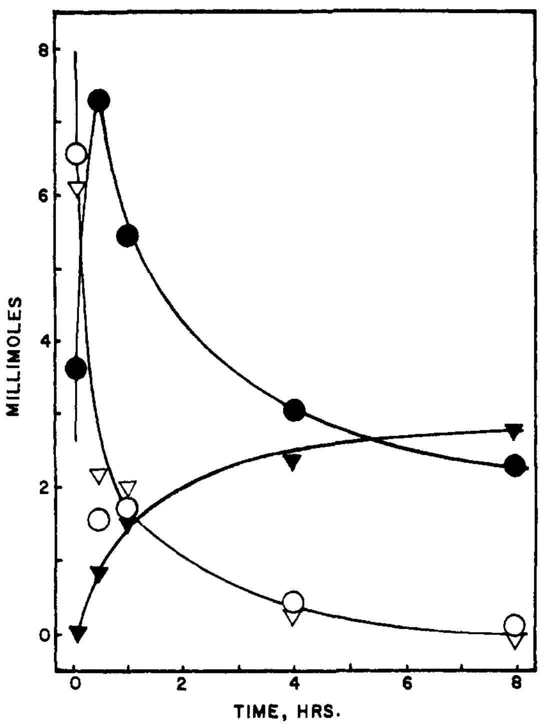

Figure 1. The dark reaction of tri-*sec*-butylborane (10 mmol) with bromine (10 mmol) in 20 ml of carbon tetrachloride solvent: ○, Br_2; ▽, R_3B; ●, total HBr; ▼, 2-bromobutane.

For the initial exploration of the reaction of bromine with organoboranes, simple conditions were selected. Three isomeric tributylboranes (10 mmol) (*n*-butyl, *sec*-butyl, and isobutyl) were treated in the dark at 25° with 10 mmol of bromine in 20 ml of several representative solvents (cyclohexane, carbon tetrachloride, chloroform, and methylene chloride). At the end of appropriate intervals of time, 20 mmol of cyclohexene was added to convert the residual bromine to 1,2-dibromocyclohexane and residual hydrogen bromide to bromocyclohexane. An internal standard was added and the reaction mixture was analyzed directly by glpc. Hydrogen bromide which escaped from the reaction mixture was trapped in sodium hydroxide and determined by titration.

The rate of reaction was fastest with tri-*sec*-butylborane, slower with tri-*n*-butylborane, and slowest with triisobutylborane. The yields appeared to be most favorable in methylene chloride, so this solvent was selected for the preparative studies. The results of these studies are summarized in Table I.[5]

In methylene chloride the organoborane and bromine disappeared at approximately the rate at which the alkyl bromide appeared. This corresponds to the expected mechanism involving formation of the product by direct reaction of bromine with the alkyl–boron bond (eq 3). However, in cyclohexane, carbon tetrachloride, and chloroform, it was observed that bromine and the tributylborane disappear at essentially the same rate, *but the corresponding butyl bromide makes its*

$$R_3B + Br_2 \xrightarrow[25^\circ]{CH_2Cl_2,\ \text{dark}} RBr + R_2BBr \qquad (3)$$

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[1] J. R. Johnson, H. R. Snyder, and M. G. Van Campen, Jr., *J. Amer. Chem. Soc.*, **60**, 115 (1938).

[2] Similarly, tri-*n*-hexylborane reacts with excess bromine in the absence of a solvent to give equimolar amounts of 1-bromohexane and *n*-hexane, the total amount being equivalent to one *n*-hexyl group.

[3] For an alternative procedure involving hydroboration–mercuration–bromodemercuration, see J. J. Tufariello and M. M. Hovey, *Chem. Commun.*, 372 (1970).

[4] It has recently been reported that triethylborane and bromine react rapidly in the gas phase, with no detectable amount of ethyl bromide observed: J. Grotwald, E. A. Lissi, and J. C. Scaiano, *J. Organometal. Chem.*, **19**, 431 (1969).

[5] The reaction of bromine with organoboranes in the presence of base provides for a higher utilization of alkyl groups: H. C. Brown and C. F. Lane, *J. Amer. Chem. Soc.*, **92**, 6660 (1970).