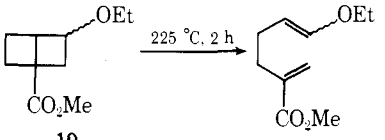
$Eu(C_{11}H_{19}O_2)_3$-shifted NMR spectrum. The *cis-anti-cis*, head-to-head structure for ketoester **6** is based on its conversion ($NaBH_4$, ethanol; 1 N HCl, 45 min) to crystalline lactone **7** [65% yield; IR (CCl_4) 1760 cm^{-1}; NMR ($CDCl_3$) δ 4.82 (C-6 hydrogen, dt, J = 5 and 9.5 Hz), 1.15—2.95 (multiplet with C-5 hydrogen as doublet (J = 9.5 Hz) at δ 2.62, 10), 1.30 (s, 3), 1.01 (s, 3), and 0.92 (s, 3))[11] and recovery after prolonged exposure (5 h) to alumina.[12]

Pyrolysis of lactone **7** (0.3 M benzene, 185 °C, 1 h) afforded cyclodecadiene lactone **8** and methylene lactone **9** in a ratio of 2:1. This ratio of lactones **8** and **9** reflects the products of kinetic cleavage of lactone **7** since subjection of either **8** or **9** to the above pyrolysis conditions showed no sign of equilibration and heating either **8** or **9** (0.3 M benzene, sealed Pyrex tube) at 240 °C for 12 h provided the equilibrium mixture, **8**/**9** = 1/2. The structure of cyclodecadiene lactone **8** is assigned from its spectroscopic properties (IR (CCl_4) 1750 cm^{-1}; NMR ($CDCl_3$) δ 6.62 (bs, 1), 5.18 (m, 1), 5.03 (m, 1), 1.38–2.92 (m, 8), 1.84 (s, 3), 1.13 (s, 3), and 1.10 (s, 3)) including an observed NOE effect (11%) between the C-1 hydrogen and C-10 methyl signals.[13] The structure of methylene lactone **9** follows from its spectroscopic data (IR (CCl_4) 1770 cm^{-1}; NMR (CCl_4) δ 6.20 (C-3 hydrogen, bs), 5.57 (C-3 hydrogen, bs), 4.40–6.10 (vinyl ABX overlapping with C-6 hydrogen multiplet, 4), 2.80 (m, 1), 1.18–2.50 (m, 4), 1.14 (s, 3), 1.06 (s, 3), and 1.02 (s, 3)) and interconversion with **8**.[8] The formation of lactones **8** and **9** from the rearrangement of lactone **7** is consistent with orbital symmetry predictions[14] and parallels the related transformations of bicyclo[2.2.0]hexanes[15] and dihydrophotoisabelin.[16]

The above metathetical strategy can also be extended to the preparation of acyclic 1,5-dienes as indicated by the exclusive formation of ester **11** upon rearrangement (225 °C, 2 h) of photoadduct **10**.[17]



10 11

The method reported above provides a convenient route to cyclic and acyclic 1,5-dienes which is readily performed on a preparative scale. Furthermore, the metathetical strategy offers several important features, which bear on its application to germacradiene synthesis, including a convergent, highly regioselective route to the ten-membered ring and the capability of transferring stereochemistry and functionality from a readily elaborated small ring precursor to the target carbocycle. Further studies are in progress.

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(10) This procedure and that used in the preparation of photoadduct **3** represent in regard to excited and ground state reactants complementary photochemical routes to the uncommon tricyclic skeletons. As such, considerable flexibility can be exercised in the selection of reactants.

(11) Examination of molecular models indicates that of the possible photoadducts only ketoester **6** would be expected to provide a stable lactone derivative.

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(18) National Science Foundation fellow, 1975–1976.

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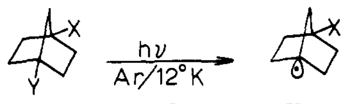
Anomalously Large Long-Range Halogen Hyperfine Coupling in 4-Halo-1-norbornyl Radicals

Sir:

A good deal of experimental and theoretical work has been devoted to studies of long-range proton hyperfine splitting constants (hfsc) over three or more σ-bonds.[1] In contrast, very few investigations of long-range hfsc involving halogen atoms have been reported. It seemed worthwhile to investigate the magnitude of long-range halogen coupling by electron paramagnetic resonance spectroscopy (EPR) since it has been suggested that halogen substituents located three or more bonds removed from the radical center may influence both the stereochemistry and kinetics of various homolytic processes.[2-4] The rigid structure of the 1-norbornyl radical[5] makes this system an ideal substrate for studies of long-range interactions of this type. In this communication we wish to report the results of our preliminary EPR investigation of long-range coupling in 4-halo-1-norbornyl radicals.

As suggested by the reported photobehavior of 1-iodonorbornane,[6] it proved possible to prepare the necessary 1-norbornyl radicals (**4, 5, 6**) from suitably substituted 1-iodonorbornanes[7] (**1, 2, 3**) by irradiation of a dilute mixture of the appropriate iodide in argon at 12 K with a filtered (Cs-7-54) mercury resonance lamp.[8]

Photolysis of a dilute mixture of **1** in argon at 12 K gave the EPR spectrum shown in Figure 1A. This 1:2:1 pattern results from the two exo β-protons of the 1-norbornyl radical (**4**) as has been shown by Kawamura et al.[5] for this radical in solution. Although these β-proton hfsc are small (9.81 G in solution) due to their orientation with respect to the unpaired electron orbital and to the strained geometry at the radical site,[5] they



1, X = H; Y = I
2, X = Br; Y = I
3, X = Y = I

4, X = H
5, X = Br
6, X = I

Table I. EPR Parameters of 4-Substituted-1-norbornyl Radicals[a]

	Hyperfine splittings, G		
Radical	4-Substituent	exo H_β	*g*-value
4	2.45[b]	$a_{\|} = 13.2$ $a_{\perp} = 8.1$	2.0026
5	13	$a_{\|} = 8$	2.0062
6	16	$a_{\|} = 10$	2.0116

[a] Values from a preliminary analysis, complete results will be reported at a later date. [b] From the solution data of ref 5.

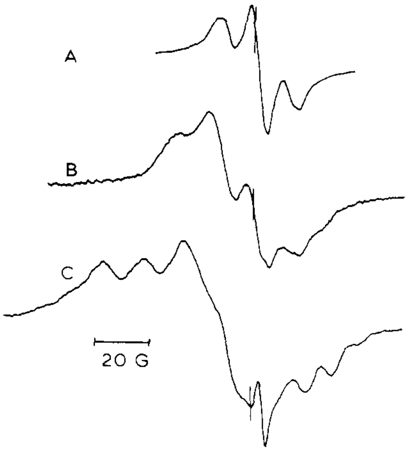
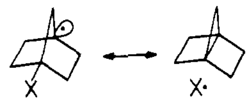


Figure 1. (A) EPR spectrum of **4** in argon at 12 K; (B) EPR spectrum of **5** in argon at 12 K; (C) EPR spectrum of **6** in argon at 12 K. Vertical bars indicate position of DPPH resonance; *g* = 2.0037.

retain a sizable anisotropy since a reasonable fit to the spectrum can be made with $a_{\|} = 13.2$ G and $a_{\perp} = 8.1$ G (Table I). The next largest hfsc in this radical is a long-range coupling of 2.45 G to the proton at the 4-position[5] which is not resolved in our spectrum.

Replacement of the 4-proton in the parent 1-norbornyl radical with either bromine or iodine results in sizable long-range halogen hyperfine coupling as evidenced by the EPR spectra of **5** and **6** shown in Figures 1B and 1C, respectively. Analysis of these spectra (Table I) reveals a bromine hfsc of 13 G (*g* value of 2.0062) for **5** and an iodine hfsc of 16 G (*g* value of 2.0116) for **6**. These hfsc and *g* values are much larger than one might expect from consideration of EPR data available for acyclic analogues of the 4-halo-1-norbornyl radicals. For example, the bromine hfsc of **5** is at least an order of magnitude larger than that of the γ-bromopropyl radical.[3] In fact, the hfsc and *g* values of **5** and **6** are among the largest reported for long-range halogen interaction and are comparable to those observed in radicals derived from 1-bromo- and 1-iodofluorenone oximes which have bromine hfsc of 10.4 G and iodine hfsc of 13.5 G with *g* values of 2.0068 and 2.0090, respectively[9] (cf. Table I).

The magnitudes of the hfsc and *g* values observed in the 4-halo-1-norbornyl radicals suggest the operation of a facile spin-delocalization mechanism in this system. The etiology of the 1,4-interaction in the norbornyl system has been investigated in theoretical studies by Hoffman and co-workers.[10] Their prediction of a predominantly "through-space" interaction in this system is supported by the results of Kawamura et al.[5] which suggests that the magnitude of the bridgehead proton hfsc in **4** may be adequately explained in terms of a direct "through-space" interaction. Such a mechanism, in valence-bond terminology, would take the form of a hyperconjugative interaction between the radical center and the C(4) to substituent bond. This interaction is represented pictorially below.



On this basis, it is perhaps not unreasonable to expect enhanced interaction (hence, larger hfsc and *g* values) as the 4-substituent is varied from hydrogen through bromine to iodine.

We are currently investigating possible chemical consequences of interactions of the type suggested by our data.

Acknowledgments. This work was supported in part by grants from the Research Foundation of the University of Connecticut and in part by Grant No. MPS 74-19380 from the National Science Foundation.

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Nonrigidity in Eight-Coordinate Tetrakis Chelates: the Stereochemical Integrity and Geometrical Isomerism of Tungsten (5-Methylpicolinato) (5,7-Dichloro-8-quinolinolato) Complexes

Sir:

All previous reports of eight-coordinate transition metal tetrakis chelates indicate nonrigidity on a nuclear magnetic resonance time scale at temperatures appreciably below room temperature.[1-8] In fact, Fay and his co-workers[1] have designated the tetrakis(*N*,*N*-dimethyldithiocarbamato)tantalum(V) cation as stereochemically rigid based on its nonequivalent proton magnetic resonance (^{1}H NMR) methyl resonances below −62 °C. We report here slow exchange limit ^{1}H NMR methyl signals at and above room temperature for the tetrakis eight-coordinate heterochelate tris(5-methylpicolinato)(5,7-dichloro-8-quinolinolato)tungsten(IV), abbreviated WP_3Q.

Furthermore, to our knowledge, geometrical isomers of an eight-coordinate transition metal complex in solution have not been obtained previously.[11,15] We wish to report the solution