

bridgehead proton at δ 4.01, four methylenes α to the positive charge at 3.63, and two sets of four methylene protons centered at 2.96 ppm.

We are at present investigating the synthetic utility of ionizing and quenching readily available bicyclo-[2.2.2]- and [-3.2.1]octyl precursors to prepare bridgehead [3.3.0] derivatives which are difficult to prepare by conventional routes.

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(24) Postdoctoral Research Associate, 1969

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Electron Spin Resonance Spectrum of the 7-Norbornenyl Radical

Sir:

There has been considerable controversy recently concerning the nonclassical nature of the 7-norbornenyl radical.¹⁻³ Chemical studies have largely formed the basis for these speculations. According to a recent SCF-MO-CNDO calculation,⁴ almost all the spin density in the 7-norbornenyl radical has been transferred from carbon atom 7 to the two equivalent carbon atoms 2 and 3. Furthermore, the calculated structure has been found to be highly distorted with the carbon atom 7

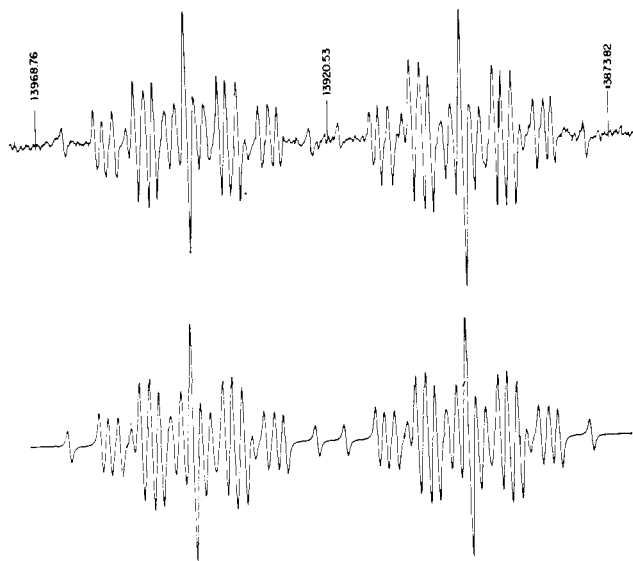


Figure 1. Experimental and calculated esr spectra of the 7-norbornenyl radical in ethane-cyclopropane solution at -134° . The proton nmr field markers are in kilohertz.

(1) J. Warkentin and E. Sanford, *J. Amer. Chem. Soc.*, **90**, 1667 (1968).

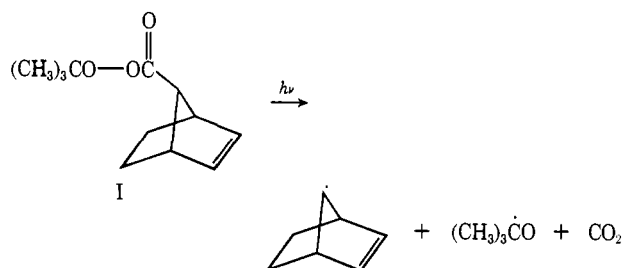
(2) G. A. Russell and G. W. Holland, *ibid.*, **91**, 3969 (1969).

(3) S. J. Cristol and A. L. Noreen, *ibid.*, **91**, 3870 (1969).

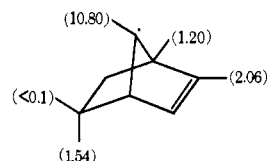
(4) (a) H. O. Ohorodnyk and D. P. Santry, *ibid.*, **91**, 4711 (1969); *Chem. Commun.*, 510 (1969). (b) It should be pointed out that CNDO theory neglects the one-center atomic exchange integrals and, therefore, the spin-polarization mechanism for isotropic hyperfine interaction in radicals. Spin densities calculated by this theory are therefore questionable.

strongly displaced toward the double bond and with a pronounced pyramidal structure for the trigonal carbon. This radical is thus purported to be at least as nonclassical as the corresponding cation.⁵

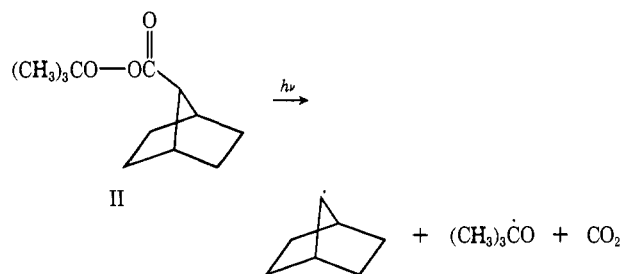
We feel that the most definitive evidence for the structure of the 7-norbornenyl radical would be obtained by examination of its electron spin resonance spectrum which we present in Figure 1. This spectrum was obtained by photolysis (2500-3000 Å) of a solution of *t*-butyl *anti*-peroxy-2-norbornene-7-carboxylate (I) in cyclopropane or mixtures of ethane and cyclopropane.⁶ The spectrum was essentially unchanged when observed between -98 and -134° .⁷



The most prominent feature of this spectrum is a doublet splitting (10.80 G) which is, no doubt, due to the single H-7. Further splitting into three triplets (2.06, 1.54, and 1.20 G) is substantiated by computer simulation (Figure 1). The tentative assignments for the hyperfine coupling constants of the 7-norbornenyl radical given below are partly based on analogy with the 7-norbornyl radical (*vide infra*).⁸



The esr spectrum of the saturated analog (Figure 2), 7-norbornyl radical, was obtained similarly from *t*-butyl 7-peroxynorbornanecarboxylate (II). This spec-



trum consists of a doublet (16.78 G) of triplets (1.05 G) split further into a pair of quintets (3.53 and 0.72 G).

(5) S. Winstein, *Quart. Rev. (London)*, **23**, 141 (1969).

(6) (a) The general technique for production of a specific alkyl radical for esr study has been described: J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **91**, 3940 (1969); (b) the photolysis of pure *t*-butyl *syn*-peroxy-2-norbornene-7-carboxylate was not examined but a mixture containing 70% *syn* and 30% *anti* isomer gave the same esr spectrum.

(7) There is a slight increase in two of the four coupling constants with increasing temperature. $T(^{\circ}\text{C})$, $a_{\text{H}7}$, $a_{\text{H}2}$, a_{endo} , a_{bridge} (G): -98 , 10.98, 2.17, 1.57, 1.17; -102 , 10.80, 2.06, 1.54, 1.20; -134 , 10.72, 1.98, 1.58, 1.24.

(8) The preparation of deuterated derivatives now in progress will allow us to make unambiguous assignments for the three pairs of protons involved in the fine structure of the spectrum.

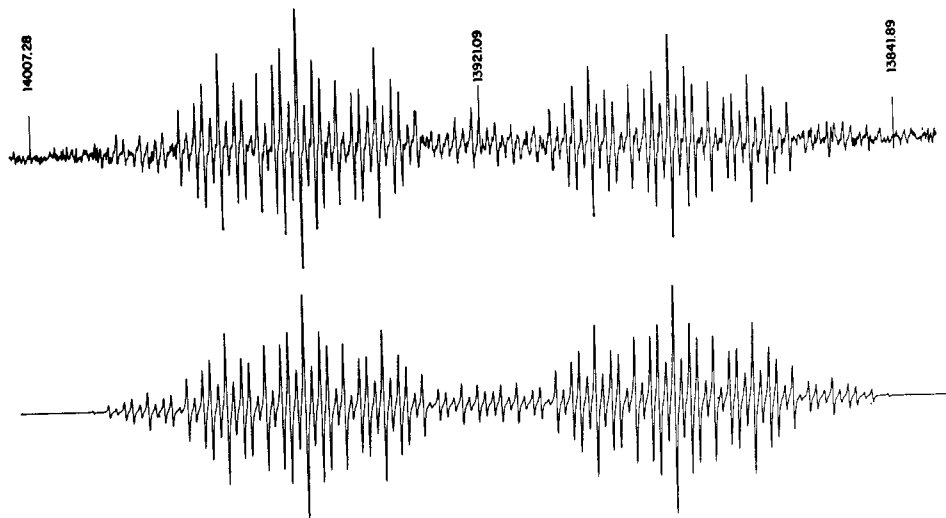
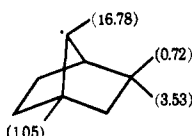
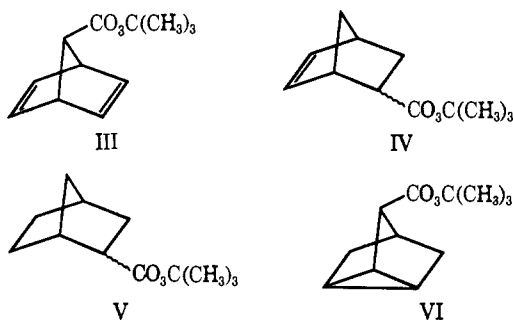


Figure 2. Experimental and calculated esr spectra of the 7-norbornyl radical in ethane-cyclopropane solution at -130° .

The assignments of these hyperfine coupling constants are as follows⁹



The esr spectra of analogous radicals derived from *t*-butyl peroxy-2,5-norbornadiene-7-carboxylate¹⁰ (III), *t*-butyl *endo*- and *exo*-peroxy-2-norbornenecarboxylates (IV), *endo*- and *exo*-peroxy-2-norbornanecarboxylates (V), and *t*-butyl peroxy-2-nortricyclene-7-carboxylate¹¹



(VI) were also examined. In all cases, however, we were unable to obtain spectra of sufficiently high quality to be analyzed completely.¹²

It is difficult to interpret the esr spectrum of the 7-norbornenyl radical in terms of a nonclassical structure. The extent to which the spin density at C-7 is

(9) The assignment of the *endo* and *exo* hydrogens is based on the W-plan formulation: G. A. Russell, "Radical-Ions," L. Kevan and E. T. Kaiser, Ed., Interscience Publishers, New York, N.Y., 1968, p 87 ff.

(10) The esr spectrum obtained from the photolysis of *t*-butyl peroxy-2,5-norbornadiene-7-carboxylate consisted of at least three radical species. Temperature dependence studies showed slight variations in the relative intensities but we are, as yet, unable to analyze the spectrum completely. One of these species appears to show a small doublet splitting of 4.60 G which is further split into triplets (1.86 G).

(11) The doublet splitting due to H-7 in 7-nortricyclenyl radical is 18.71 G.

(12) We also attempted to generate these radicals from the corresponding hydrocarbons by selective hydrogen abstraction with *t*-butoxy radical.¹³ A mixture of radical species was obtained and the analysis of the spectra is incomplete.

(13) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **90**, 7155 (1968).

delocalized should be reflected in the hyperfine coupling constants of the protons attached to C-2 and C-3. Despite some ambiguity in the assignments for each of the three pairs of triplets,⁸ it is clear that the splitting by hydrogens at the 2 and 3 positions cannot be larger than 2.06 G. The magnitude of this splitting is the same as the average value for the *endo*- and *exo*-hydrogens in 7-norbornyl radical which certainly cannot be classified in any other way than classical.

Both the 7-norbornenyl and 7-norbornyl radicals show significantly diminished α coupling constants for the 7 proton. Such anomalously small α interactions have been associated with bent radical sites¹⁴ (e.g., 6.5 G for cyclopropyl¹⁵ and 12.64 G for 2-bicyclobutyl¹⁶) and have been successfully predicted by INDO molecular orbital calculations.¹⁶⁻¹⁸ We have carried out such calculations for the 7-norbornenyl radical as a function of the two most important structural parameters, θ_2 and θ_3 (Figure 3).¹⁹⁻²¹ The calculated values of the hyperfine coupling constants for the protons attached to carbon atoms 7 and 2 are given in Figures 4 and 5. The areas between the dotted curves represent

(14) Chemical evidence exists for pyramidal structures at the trigonal carbon atom of cyclopropyl radicals: M. J. S. Dewar and J. M. Harris, *ibid.*, **91**, 3652 (1969); L. J. Altman and B. W. Nelson, *ibid.*, **91**, 5163 (1969); J. Jacobs and D. Pensak, *Chem. Commun.*, 400 (1969).

(15) (a) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2180 (1963); (b) unpublished results.

(16) P. J. Krusic, J. P. Jesson, and J. K. Kochi, *J. Amer. Chem. Soc.*, **91**, 4566 (1969).

(17) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *ibid.*, **90**, 4201 (1968); D. L. Beveridge, P. A. Dobosh, and J. A. Pople, *J. Chem. Phys.*, **48**, 4802 (1968).

(18) We obtained a copy of this program from The Quantum Chemistry Program Exchange, Indiana University.

(19) The remaining parameters used for the calculations are:²⁰ $d(\text{CC single}) = 1.54 \text{ \AA}$, $d(\text{CC double}) = 1.33 \text{ \AA}$, $d(\text{CH}) = 1.09 \text{ \AA}$, $\theta_1 = 95^{\circ}$, $\theta_4 = 120^{\circ}$, $\theta_5 = 0^{\circ}$. The following assumptions were also made: (a) the two HCH angles are tetrahedral; (b) the HCH planes bisect the opposing CCC angle; (c) the *exo* and *endo* hydrogens are symmetrically disposed with respect to the $\text{C}_1\text{C}_4\text{C}_5$ plane, (d) H-2 and H-3 lie in the $\text{C}_1\text{C}_2\text{C}_3$ plane and in the planes bisecting the opposing CCC angles.

(20) These values were derived from the structural parameters for the related hydrocarbons, norbornane and norbornadiene.²¹ We have assumed that a slight increase in θ_1 and θ_4 accompanies the transformation from the hydrocarbon to the radical.

(21) (a) Y. Morino, K. Kuchitsu, and A. Yokozeki, *Bull. Chem. Soc. Jap.*, **40**, 1552 (1967); (b) J. F. Chiang, C. F. Wilcox, Jr., and S. H. Bauer, *J. Amer. Chem. Soc.*, **90**, 3149 (1968); (c) R. Destro, G. Filipini, C. M. Gramaccioli, and M. Simonetta, *Tetrahedron Lett.*, 3223 (1969).

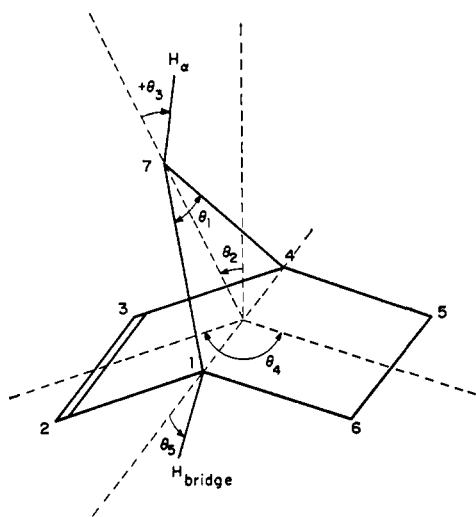


Figure 3. Structural parameters for the 7-norbornenyl radical.

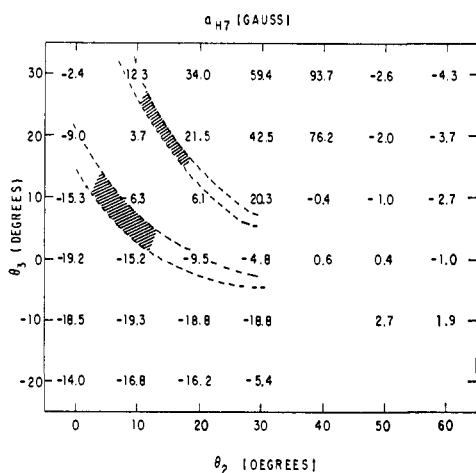


Figure 4. INDO isotropic hyperfine coupling constants for H-7 of the 7-norbornenyl radical. Shaded areas represent structures consistent with the absolute values of a_{H-7} and a_{H-2} obtained experimentally. Note that the calculated values of a_{H-7} are positive in the upper area and negative in the lower.

structures compatible with the observed couplings allowing the uncertainties of ± 2 G and ± 1 G in the calculated values for a_{H-7} and a_{H-2} , respectively.¹⁷ The shaded areas result by superposition of the two maps and further restrict the allowed structures. We assume that the α coupling constant is negative in accord with other alkyl radicals. This limits the structure of the 7-norbornenyl radical to one in which θ_2 is no more than 13° and θ_3 is less than 14° in the *anti* direction.

The calculated values for the couplings to H_{endo} , H_{exo} , and H_{bridge} (Figure 3) for structures within the shaded areas are also consistent with the experimental values. They show much less variation with structure. Bonding situations that can be termed nonclassical indeed arise in very distorted models and are characterized (Figures 3, 4, and 5) by very small α couplings and by relatively large and negative couplings to the protons attached to C-2 and C-3.²²⁻²⁴ Such coupling

(22) The C-7 hyperfine coupling constant is also strongly dependent on θ_2 and θ_3 . For very distorted structures ($\theta_2 > 35^\circ$), a_{C-7} becomes negative, indicating that the unpaired electron is no longer localized on C-7.

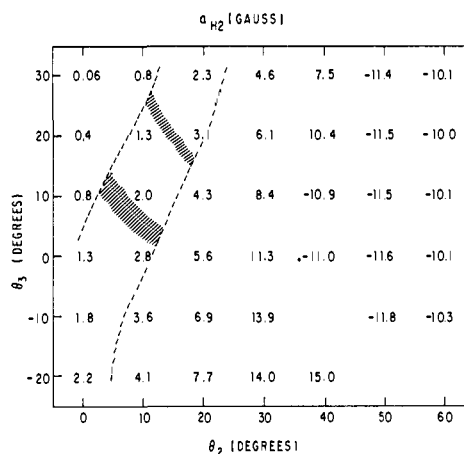


Figure 5. INDO isotropic hyperfine coupling constants for H-2 of the 7-norbornenyl radical. Shaded areas represent structures consistent with the absolute values of a_{H-2} and a_{H-7} obtained experimentally.

constants, however, are clearly at variance with experiment.

The reduced value of the α coupling constant indicates that the 7-norbornenyl radical is also bent at C-7 though less so than the 7-norbornenyl radical. However, all four *exo* and all four *endo* hydrogens in the 7-norbornenyl radical show magnetic equivalence and, therefore, the rate of inversion of C-7 must be rapid between equivalent potential minima. The rate of inversion of the 7-norbornenyl radical should be relatively slower. The bent sites at C-7, however, are inequivalent and could account for the slight selectivity observed in hydrogen transfer from trialkylstannanes.¹⁻³ The latter is also supported by the quantitative analysis of the products derived from the photolysis of either pure *syn*- or *anti*-perester.

Acknowledgments. We thank Dr. Claibourne Smith and Dr. James Wilt for helpful suggestions on synthesis. P. B. also wishes to thank the National Science Foundation for generous financial support.

(23) We have also calculated the partial derivatives of the proton hyperfine coupling constants with respect to all structural parameters of our model for a representative structure within the shaded areas ($\theta_2 = 7.5^\circ$ and $\theta_3 = 7.5^\circ$). The largest values were obtained for $\partial/\partial\theta_2$ and $\partial/\partial\theta_3$ justifying our parametrization.

(24) Small values for a_{H-2} do not, by themselves, invalidate a nonclassical structure for this radical. Such values would be expected if H-2 and H-3 were below the $C_1C_2C_3$ plane rather than in the plane as in the assumed structure (*cf.* ref 19). We are indebted to a referee for bringing to our attention this possibility.

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Nuclear Magnetic Resonance Spectra of Quinodimethanes

Sir:

The chemistry of *p*-xylylene or quinodimethane, **1**, has been extensively studied¹⁻⁴ since the species was