The 7-Norbornenyl Radical. Chemical and Electron Spin Resonance Studies

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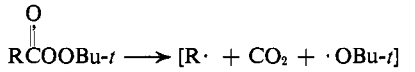
Abstract: The 7-norbornenyl radical is generated in solution by photolysis of *syn-* and *anti-tert*-butylperoxy 7-norbornenecarboxylates. Geminate combination of the 7-norbornenyl and *tert*-butoxy radicals favors *anti-* relative to *syn*-7-*tert*-butoxynorbornene from both isomeric peresters. Deuterium labeling at the 7 position indicates that hydrogen abstraction from the solvent also occurs preferentially from the anti side of the norbornenyl radical. The 7-norbornenyl radicals generated from the photolysis of syn or anti perester are, thus, chemically indistinguishable. The esr spectra of the 7-norbornenyl radical and of some deuterium substituted 7-norbornenyl radicals are also reported. The hyperfine isotropic coupling constant for the proton in the 7 position is unusually small (10.8 G) and has a temperature coefficient of opposite sign to those hitherto reported for α protons in alkyl radicals (*e.g.*, methyl). The unusual temperature dependence together with an anomalous isotope shift in the magnitude of the corresponding coupling constant for the deuterium labeled species in the 7 position is consistent with a *positive* sign for the α-proton coupling constant. INDO–MO calculations support this interpretation and are used in conjunction with the esr data to probe the vibrational behavior and the equilibrium structure in this radical.

The 7-norbornenyl system offers a structural framework from which long-range nonbonded interactions may be examined. Thus, the cation shows such bonding to an unusual degree.[2] Similarly, the nonclassical nature of the 7-norbornenyl radical has been proposed,[3] but there are differences as to the magnitude of the effect.[4] According to a recent SCF–MO–CNDO calculation, almost all of the spin density in the 7-norbornenyl radical has been transferred from carbon atom 7 to the two equivalent ethylenic carbon atoms 2 and 3.[5] Furthermore, the optimum structure based on the minimization of the energy was a highly distorted one in which carbon atom 7 was strongly displaced toward the double bond and with a pronounced pyramidal structure for the trigonal carbon. This radical was thus purported to be at least as nonclassical as the corresponding cation. However, it should be pointed out that CNDO theory neglects one-center exchange integrals and therefore the spin polarization mechanism for isotropic hyperfine interactions in radicals. The values of spin densities calculated using this theory are thus questionable.

More definitive evidence for the structure of the 7-norbornenyl radical has been obtained by the examination of its electron spin resonance (esr) spectrum which we presented earlier in a preliminary form.[6] In this report, we wish to provide supporting chemical studies of the 7-norbornenyl radical together with additional esr data yielding a more complete assignment of the coupling constants based on deuterium labeling as well as further information concerning the sign of the α coupling constant, the equilibrium molecular geometry, and the vibrational effects in this interesting radical.

Results

Photolysis of Peresters. The esr spectra of a variety of transient alkyl radicals (R·) were readily observed when solutions of peresters, particularly *tert*-butyl derivatives, were photolyzed directly in the cavity of the spectrometer.[7] Quantum yield studies carried out with 2537-Å radiation showed that the homolysis of peresters occurred with unit efficiency, largely independent of the structure of R according to eq 1.[8]



$$\mathrm{R\overset{O}{\overset{\|}{C}}OBu\text{-}\mathit{t}} \longrightarrow [\mathrm{R\cdot} + \mathrm{CO_2} + \cdot\mathrm{OBu\text{-}\mathit{t}}] \qquad (1)$$

Ethers and alkenes resulted from cage combination and cage disproportionation, respectively, of the geminate

$$[\mathrm{R\cdot} + \cdot\mathrm{OBu\text{-}\mathit{t}}] \left\langle \begin{array}{ll} \longrightarrow \mathrm{ROBu\text{-}\mathit{t}} & (2) \\ \longrightarrow \mathrm{R(-H)} + \mathit{t}\text{-}\mathrm{BuOH} & (3) \end{array} \right.$$

radicals. Alkanes and *tert*-butyl alcohol arose from reaction with solvent (SH) after diffusion of the radicals from the cage.

$$\mathrm{R\cdot} + \mathrm{SH} \longrightarrow \mathrm{RH} + \mathrm{S\cdot} \qquad (4)$$

$$\mathit{t}\text{-}\mathrm{BuO\cdot} + \mathrm{SH} \longrightarrow \mathit{t}\text{-}\mathrm{BuOH} + \mathrm{S\cdot} \qquad (5)$$

Peresters of *syn-* and *anti*-7-Norbornenecarboxylic Acids. *syn*-7-Bromonorbornene was isolated from the dibromo adducts of norbornene after treatment with potassium *tert*-butoxide.[9] Conversion to the Grignard reagent followed by carbonation led to a 3:2 mixture of *syn-* and *anti*-7-norbornenecarboxylic acids,[10] which

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[1] (a) Contribution No. 2152 from Chemistry Department, Indiana University; (b) Contribution No. 1805 from Central Research Department, E. I. du Pont de Nemours and Co.

[2] S. Winstein, *Quart. Rev., Chem. Soc.*, 23, 141 (1969).

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

[4] (a) G. A. Russell and G. W. Holland, *ibid.*, **91**, 3969 (1969); (b) S. J. Cristol and A. L. Noreen, *ibid.*, 91, 3870 (1969); (c) P K. Freeman, R. S. Raghavan, and G. L. Fenwick, *ibid.*, **94**, 5101 (1972).

[5] H. O. Ohorodnyk and D. P. Santry, *ibid.*, **91**, 4711 (1969); *Chem. Commun.*, 510 (1969).

[6] P. Bakuzis, J. K. Kochi, and P. J. Krusic, *ibid.*, **91**, 1434 (1970).

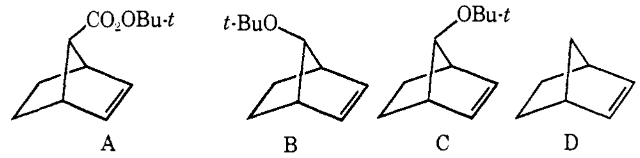
[7] (a) J. K. Kochi and P. J. Krusic, *ibid.*, **91**, 3940 (1969); (b) P. J. Krusic and J. K. Kochi, *ibid.*, **93**, 846 (1971); (c) J. K. Kochi and P. J. Krusic, *Chem. Soc., Spec. Publ.*, No. 24, 147 (1971).

[8] R. A. Sheldon and J. K. Kochi, *J. Amer. Chem. Soc.*, **92**, 5175, 4395 (1970).

[9] H. Kwart and L. Kaplan, *ibid.*, 76, 4076 (1954).

[10] R. C. Sauers and M. Hawthorne, *J. Org. Chem.*, **29**, 1685 (1964).

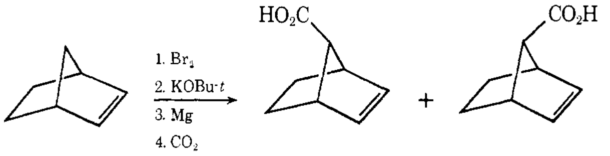
Table I. Products from the Photolysis of *syn*- and *anti*-*tert*-Butylperoxy 7-Norbornenecarboxylate[a]



A	Solvent	% CO_2	% B	% C	% D	% *t*-BuOH	*B*/*C*
Syn	Cyclohexane	81	12	3.8	31	31	3.1
Anti	Cyclohexane	84	13	3.5	30	37	3.6
Syn	*n*-Pentane	94	~21[b]	~10[b]	53	52	~2.0
Anti	*n*-Pentane	87					~1.6[b]
Syn	Nujol	91					~2.1[b]
Syn	Cyclopentene	73					2.7
Anti	Cyclopentene	84					2.9
7-Deuterio							
Syn	Cyclohexane	70	10	3.6	24[c]	33	2.9
Anti	Cyclohexane	95	12	4.6	36[d]	41	2.5

[a] Photolysis carried out in quartz tubes at 30°. Yields based on mol of product per mol of perester charged. [b] Approximate values. [c] *syn*- and *anti*- 7-Deuterionorbornene in ratio 65:35. [d] *syn*- and *anti*-7-deuterionorbornene in ratio 72:28.

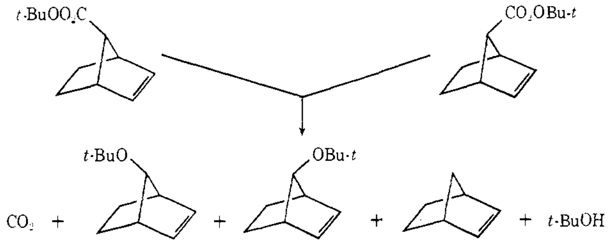
were separated by column chromatography. The *tert*-butyl perester of each isomer was prepared by



(6)

treating the acid chloride with *tert*-butyl hydroperoxide. Attempts to prepare the pure per esters directly from the acid with carbonyldiimidazole[11] were unsuccessful.

The photolysis of each isomeric perester was carried out in hydrocarbon solutions with radiation (2537 Å) from a low-pressure mercury lamp. More or less the same mixtures of carbon dioxide, 7-*tert*-butoxynorbornene, norbornene, and *tert*-butyl alcohol were produced as the principal products (Table I). Less than 2% methane was detected. The relative amounts of *syn*- and *anti*-7-*tert*-butoxynorbornene formed from each perester was significantly the same, but varied somewhat with the solvent.



(7)

Examination of Table I reveals that the material balance found for the photolysis did not coincide with that predicted from eq 2–5. Furthermore, the high yields of carbon dioxide indicated that induced decomposition of the perester was not an important complication. The survival of norbornene was tested by photolyzing a solution of it and *tert*-butylperoxy oxalate under similar reaction conditions. If it was assumed that the rates of photochemical production of *tert*-butoxy radicals (taking into account cage combinations) was the same under these conditions, then 89% of the norbornene was recovered. Under the same conditions 75% of *anti*-7-*tert*-butoxynorbornene was recovered. When an equimolar mixture of *syn*- and *anti*-7-*tert*-butoxynorbornene was so treated, the syn isomer was more rapidly consumed, since only 80% of the original amount and 95% of the anti isomer could be recovered.

Since these experiments indicated that the norbornenyl products were susceptible to further attack, a variety of hydrogen donor solvents including diisopropyl, acetonitrile, diisopropyl ether, and cyclopentene were examined for their ability to minimize these side reactions. Cyclopentene was chosen despite inordinate difficulties encountered in its purification to specifications required for ultraviolet spectroscopy. Photolysis of *syn*- and *anti*-7-norbornenyl perester in cyclopentene each produced the same mixture of *syn*- and *anti*-7-*tert*-butoxynorbornene in which the anti predominated over the syn isomer by a factor of 2.7 to 1. The mass spectrum obtained from a GC–MS combination was compared with authentic samples. In addition to the usual products, others derived from attack on solvent such as *dl*- and *meso*-dicyclopentenyl and a small amount of *tert*-butylcyclopentyl ether were also found.

A deuterium label was placed in the 7 position of *syn*- and *anti*-7-norbornenyl peresters in order to examine the stereochemistry of the norbornene product. Photolysis of each isomer again afforded the same mixture of *syn*- and *anti*-7-*tert*-butoxynorbornene as shown in Table I. The norbornene fraction was separated by preparative gas chromatography and nuclear magnetic resonance (220 MHz) analysis indicated that from each perester the same mixture of *syn*- and *anti*-7-deuterionorbornene was formed in which the ratio of the syn to anti isomer was approximately 2 (Table I). Attempts were also made to examine the reaction between norbornenyl radical with 2,3-dideuterio-2,3-dimethylbutane prepared by the catalytic addition of deuterium to 2,3-dimethyl-2-butene. However, deuterium scrambling during reduction complicated the analysis.

Finally, we could find no evidence for rearrangement of the 7-norbornenyl radical to the tricyclic isomer (eq 9). The parent hydrocarbon and the *tert*-butyl

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(11) R. Hecht and C. Ruchardt, *Chem. Ber.*, 1281 (1963).

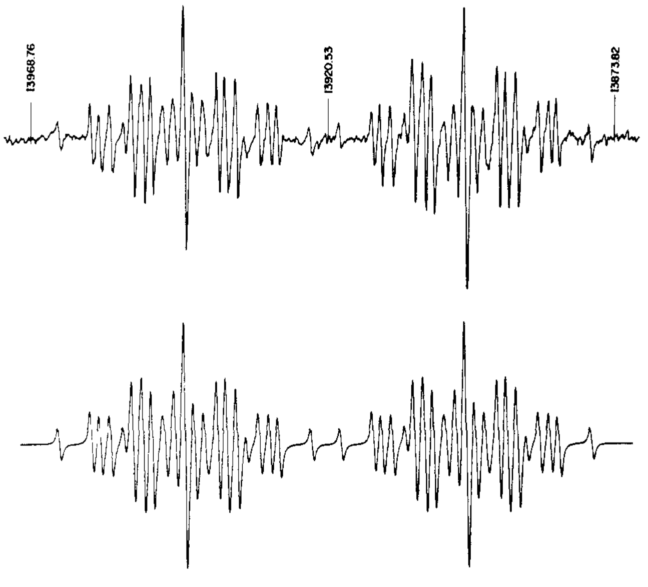


Figure 1. Experimental and calculated esr spectra of the 7-norbornenyl radical in ethane–cyclopropane solution at −134°. The proton nmr field markers are in kilohertz.

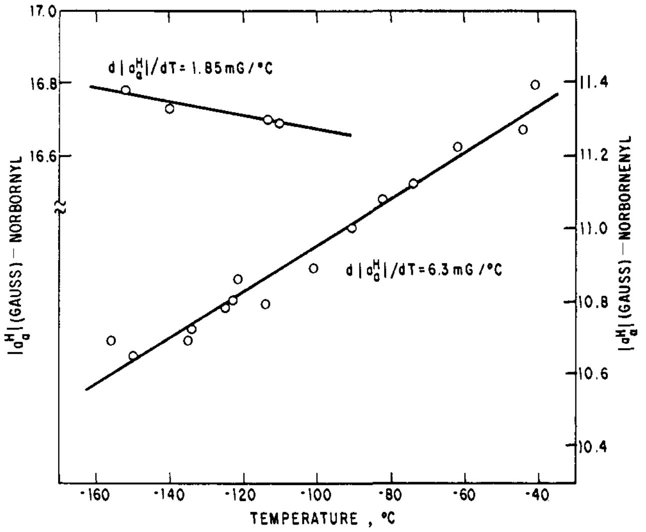
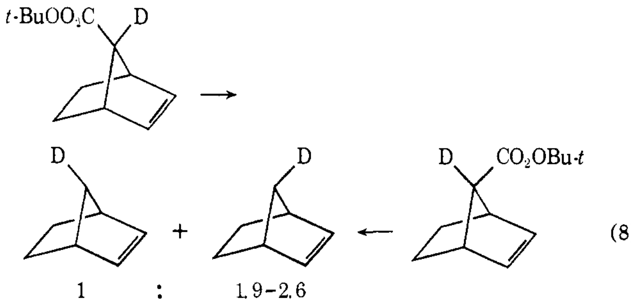


Figure 2. Temperature dependences and coefficients of the α-proton hyperfine coupling constants in 7-norbornenyl and 7-norbornyl radicals.



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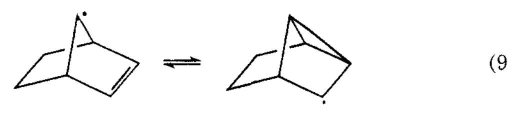

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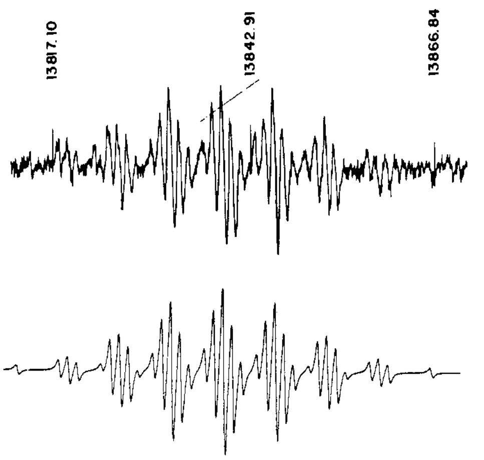

Figure 3. Experimental and calculated esr spectra of 7-deuterio-7-norbornenyl radical at −137° in cyclopropane solution.

ether were unsuccessfully sought, by taking into account the solvolytic instability of the latter and the hydrogenation of the tricyclic compounds to norbornyl derivatives.[12]

Esr Spectra of 7-Norbornenyl Radicals. The esr spectrum of the 7-norbornenyl radical shown in Figure 1[13] was obtained during photolysis (2500–3000 Å) of a solution of *tert*-butylperoxy *anti*-7-norbornenecarboxylate in a mixture of ethane and cyclopropane at −134°. The same spectrum was obtained from a sample of the pure syn isomer and in other solvents up to −90°. The signal-to-noise ratio decreased rapidly at higher temperatures. The most prominent feature of this spectrum is a doublet splitting of 10.80 G, which is further split into three triplets of 2.06, 1.54, and 1.20 G. The temperature dependence of these hyperfine splittings is indicated in Table II and Figure 2.

Table II. Hyperfine Coupling Constants for 7-Norbornenyl Radicals

Radical	Temp, °C	—Coupling constants, G^a— a_2 (t)	a_4 (t)	a_5 (endo) (t)	a_7 (d)
Norbornenyl	−134	1.54	1.20	2.06	10.80
	−98	1.57	1.17	2.17	10.98
7-Deuterio-7-norbornenyl	−137	1.59	1.31	1.87	1.60^b
endo-5,6-Dideuterio-7-norbornenyl	−140	1.59	1.28	0.30^b	10.74

^{a} Proton coupling constants. For location of the protons see Figure 7. t = triplet, d = doublet. ^{b} 1:1:1 triplet.

Replacement of the α proton in the 7-norbornenyl radical by deuterium led to the esr spectrum shown in Figure 3. The computer simulated spectrum shown in

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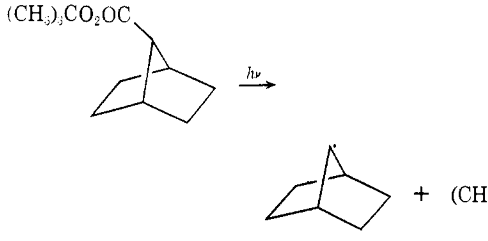
(12) (a) S. Winstein, A. H. Lewin, and K. C. Pande, *J. Amer. Chem. Soc.*, **85**, 2324 (1963); (b) H. C. Brown and H. M. Bell, *ibid.*, **85**, 2324 (1963).

(13) The computer simulated spectrum of Figure 1 is based on Lorentzian line shapes and includes a triplet splitting of 0.075 G. The addition of this small splitting, suggested by the lack of resolved structure attributable to the fourth pair of distinct protons of the norbornenyl framework, makes the effective line shapes approach the Gaussian form. It also improves appreciably the match between the experimental and calculated spectra with regard to the relative intensities of the resultant absorption curve. The presence of this unresolved splitting is also indicated by the noticeably broader lines observed for this radical compared with the saturated analog, 7-norbornyl (*vide infra*), where the hyperfine splitting pattern accounts for all the protons of the molecular structure.

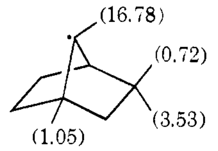
the lower half of the figure was based on the hyperfine splitting constants listed in Table II and was obtained by a systematic variation of the coupling constants consistent with the total spread of the spectrum.[14] The principal difference between the spectrum of the 7-norbornenyl and its 7-deuterio analog is thus the replacement of the large doublet splitting (10.80 G at $-134°$) by a 1 :1 :1 triplet splitting, which is diminished by a factor of 6.75 rather than 6.514 expected theoretically in the absence of vibronic effects. This large isotope effect has important implications which will be discussed later.

A similar analysis of the esr spectrum of *endo*-5,6-dideuterio-7-norbornenyl radical, illustrated in Figure 4, led to assignment of the 2.06 G triplet splitting in the parent radical to the 5 and 6 endo protons. Unfortunately, we were unable to assign the pair of triplet splittings of 1.54 and 1.20 G and the unresolved splitting (<0.1 G) to the bridgehead ($H_{1,4}$), vinylidene ($H_{2,3}$), or exo ($H_{5,6}$) protons. The 2,3,7-trideuterio-7-norbornenyl radical was generated from the corresponding perester, but the quality of the spectrum was insufficient to resolve the complex splitting pattern. However, comparison with the spectral parameters for the 7-norbornyl radical suggests the assignment of the 1.20 G splitting to the bridgehead protons. For the remaining protons we favor the assignment of the 1.54 G splitting to the vinylidene protons. The esr spectrum of *exo*-5,6-dideuterio-7-norbornenyl radical was essentially identical with that of the perhydro analog, and indicated that the splittings due to the exo-5,6 protons were too small to be resolved.

The esr spectrum (Figure 5) of the saturated analog, 7-norbornyl radical, was obtained similarly from *tert*-butylperoxy 7-norbornanecarboxylate, and consisted



of a doublet (16.78 G) of triplets (1.05 G), due to the α and bridgehead protons, respectively, split further into a pair of quintets (3.53 and 0.72 G). The assignment of the larger of these splittings to the endo protons is based on a comparison with the 7-norbornenyl radical, in which the relationship $|a^{\mathrm{H}}_{\mathrm{endo}}| > |a^{\mathrm{H}}_{\mathrm{exo}}|$ obtains as



$T = -152°$

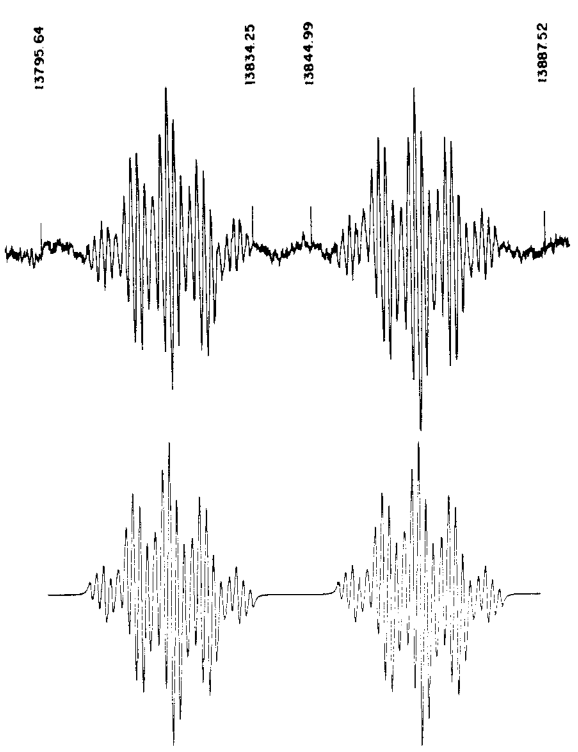
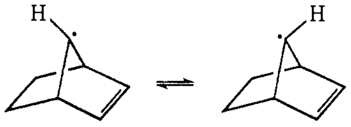


Figure 4. Experimental and calculated esr spectra of *endo,endo*-5,6-dideuterio-7-norbornenyl radical at $-140°$ in cyclopropane solution.

previously shown by isotopic substitution. The coupling constant of the α proton in the 7-norbornyl radical showed a temperature coefficient of *opposite sign* to that of the α-proton coupling in the 7-norbornenyl radical (Figure 2).

Discussion

Stereochemistry of the 7-Norbornenyl Radical. The chemical results indicated that either only one norbornenyl radical, a rapidly equilibrating, or an equilibrated pair of isomeric radicals



(10)

was produced from the photolysis of either *syn*- or *anti-tert*-butylperoxy 7-norbornenecarboxylate.

Two reactions of the 7-norbornenyl radical representing quite different energy requirements occur during photolysis of these peresters,[8] namely, combination (eq 11) and hydrogen transfer (eq 12).

Combination of the 7-norbornenyl radical with *tert*-butoxy radicals undoubtedly occurs readily with little or no activation energy in analogy with other systems.[15] On the other hand, hydrogen transfer from alkenes and especially alkanes used as solvents requires more than 8 kcal/mol[16] of activation. Despite this difference, the stereochemistries of the products derived from the norbornenyl radicals are similar. Minor complications arising from the partial destruction of the products under reaction conditions precluded an accurate quan-

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(14) The assignment of the 1.60-G splitting to the deuterium was not without problems especially since deuteration of the 7 position also affected the coupling constants of the remaining protons. The spectrum consisted of four overlapping triplets of comparable splittings (two triplets are essentially degenerate) of which three are due to pairs of equivalent protons and have 1 :2 :1 relative intensities while the remaining triplet is due to the deuteron and has 1 :1 :1 relative intensities. Thus, any one of the three distinct coupling constants can be assigned to the deuterium without altering the positions of the hyperfine lines. A good match of the relative intensities of the resultant absorption curve could be obtained, however, only with the chosen assignment.

(15) S. A. Weiner and G. S. Hammond, *J. Amer. Chem. Soc.*, **91**, 986 (1969); D. J. Carlsson and K. U. Ingold, *ibid.*, **90**, 7047 (1968).

(16) J. A. Kerr and A. F. Trotman-Dickenson, *Progr. React. Kinet.*, 1, 107 (1961).

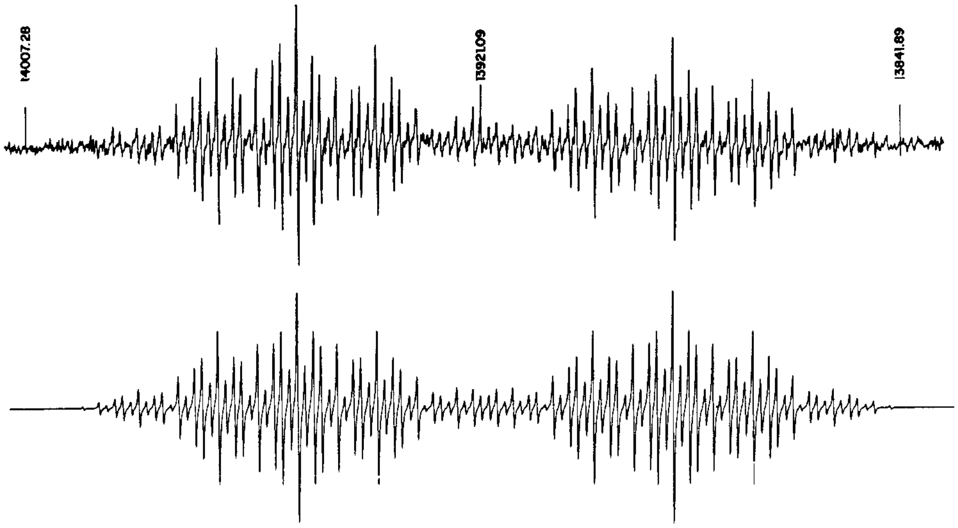
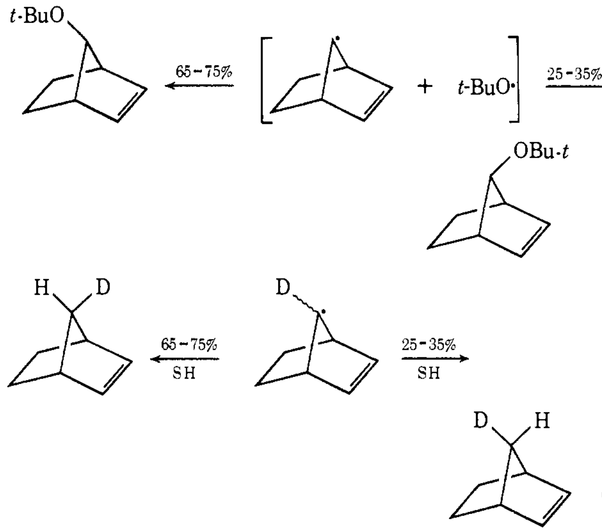


Figure 5. Experimental and calculated esr spectra of the 7-norbornyl radical in ethane–cyclopropane solution at −130°.



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titative assessment of the stereochemistries of the coupling and hydrogen transfer processes. It is clear, however, that the attachment of a new bond to the radical site at carbon 7 was favored from the anti relative to the syn side by a factor conservatively estimated to be between 2 and 3 in both reactions 11 and 12. Similar results were obtained with other chain transfer agents.[3,4]

The possibility that dynamic equilibrium (eq 10) of the norbornenyl radical is attained is not without some difficulties. In order to invoke the Curtin–Hammett principle, the differences in the free energies of the isomeric transition states would have to be fortuitously the same for reactions 11 and 12. Alternatively, the barrier to inversion (eq 10) is higher than the activation energy for reaction 11 or 12, and the composition of isomeric products is determined largely by the distribution of radicals. In such an event, equilibration must have accompanied the photoproduction of the radicals (eq 1, R = 7-norbornenyl), an undesirable alternative. A better understanding of the stereoselectivity effects in the 7-norbornenyl radical, however, is afforded by the analysis of the esr information.

Vibronic Effects in the 7-Norbornenyl Radical. Considerable information concerning the equilibrium structure at a carbon radical center can be obtained from the α-proton isotropic hyperfine splittings in radicals of the type $X_2\dot{C}H$ and $X\dot{C}H_2$ (X = halogen,[17] oxygen,[18] sulfur,[19] and nitrogen[20]) and in radicals derived from strained cyclic hydrocarbons.[21] Radicals of this type exhibit anomalous α-proton hyperfine splittings which differ substantially in magnitude from the 21 to 23 G range expected for planar acyclic alkyl radicals and which are now recognized as being diagnostic of a pyramidal structure at the trivalent carbon. In most studies, heretofore, only the magnitudes of the α couplings at a particular temperature or, less frequently, the ^{13}C splittings (which are regarded as the preferred indicators of the local radical geometry) have been measured. Only for the methyl radical (as well as for some orbitally degenerate radicals and aromatic radical ions[22]) have there been extensive experimental[23] and theoretical[24] studies of the temperature dependence of the hyperfine splittings and of their shifts upon isotopic

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(17) (a) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **43**, 2704 (1965); (b) M. T. Rogers and L. D. Kispert, *ibid.*, **55**, 2360 (1971); (c) A. Hudson and H. A. Hussain, *Mol. Phys.*, **16**, 199 (1969), (d) J. Cooper, A. Hudson, and R. A. Jackson, *iibd.*, **23**, 209 (1972); (e) C. Hesse, N. Leray, and J. Roncin, *ibid.*, **22**, 137 (1971).

(18) (a) A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *Chem. Commun.*, 1353 (1969); (b) *J. Chem. Soc. A*, 124 (1971).

(19) P. Neta and R. W. Fessenden, *J. Phys. Chem.*, **75**, 2277 (1971).

(20) (a) D. E. Wood and R. V. Lloyd, *J. Chem. Phys.*, **53**, 3932 (1970); (b) H. Paul and H. Fischer, *Ber. Bunsenges. Phys. Chem.*, **73**, 972 (1969).

(21) (a) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963); (b) P. J. Krusic, J. P. Jesson, and J. K. Kochi, *J. Amer. Chem. Soc.*, **91**, 4566 (1969); (c) J. Gloux, M. Guglielmi, and H. Lemaire, *Mol. Phys.*, 17, 425 (1969); (d) T. Kawamura, T. Koyama, and T. Yonezawa, *J. Amer. Chem. Soc.*, **92**, 7222 (1970); (e) P. J. Krusic, T. A. Rettig, and P. v. R. Schleyer, *ibid.*, **94**, 995 (1972).

(22) Representative references include: (a) G. Vincow, M. L. Morrell, F. R. Hunter, and H. J. Dauben, *J. Chem. Phys.*, **48**, 2876 (1968); (b) M. Karplus, R. G. Lawler, and G. K. Fraenkel, *J. Amer. Chem. Soc.*, **87**, 5260 (1965); (c) R. Lawler and G. K. Fraenkel, *J. Chem. Phys.*, **49**, 1126 (1968); (d) A. H. Reddoch, C. L. Dodson, and D. H. Paskovich, *ibid.*, **52**, 2318 (1970); and references cited therein.

(23) (a) I. A. Zlochower, W. R. Miller, Jr., and G. K. Fraenkel, *ibid.*, 42, 3339 (1965); (b) H. Fischer and H. Hefter, *Z. Naturforsch. A*, **23**, 1763 (1968); (c) G. B. Garbutt and H. D. Gesser, *J. Chem. Phys.*, **48**, 4605 (1968); (d) J. M. Riveros and S. Shih, *ibid.*, **50**, 3132 (1969); (e) R. W. Fessenden, *J. Phys. Chem.*, 71, 74 (1967).

(24) (a) R. E. Moss, *Mol. Phys.*, 10, 339 (1966); (b) I. A. Zlochower, Ph.D. Thesis, Columbia University, New York, N. Y., 1966; (c) D. M. Schrader and M. Karplus, *J. Chem. Phys.*, 40, 1593 (1964); (d) D. M. Schrader, *ibid.*, **46**, 3895 (1967); (e) D. L. Beveridge and K. Miller, *Mol. Phys.*, **14**, 401 (1968); (f) D. M. Schrader and K. Morokuma, *ibid.*, 21, 1033 (1971); (g) S. Y. Chang, E. R. Davidson, and G. Vincow, *J. Chem. Phys.*, **52**, 5596 (1970).

substitution. These effects are intimately associated with the vibrational out-of-plane bending motion of the radical. In this section, we wish to show that useful information not otherwise available can be obtained by also considering the temperature dependence of the α-proton hyperfine splittings as well as the deuterium isotope effect. Detailed treatments such as those carried out for the methyl radical are not yet possible for a radical of such structural and vibrational complexity as the 7-norbornenyl species. Such treatments would be feasible for a polyatomic radical when only one low frequency normal mode can be singled out as being responsible for the vibronic effects on the esr parameters.[25]

The starting point in discussing the temperature dependence of α-proton coupling constants and the isotope effect attending the substitution of one or more α protons with deuterons is the knowledge of the dependence of a^{H} on the normal coordinate η for the isolable mode of lowest frequency written as a power series

$$a(\eta) = a_0 + a_1\eta + a_2\eta^2 + \ldots \qquad (13)$$

The expectation values $\langle a(\eta)\rangle_n$ for each vibrational level n are then obtained using the wave functions appropriate for the particular potential. Since vibrational relaxation times are short compared with the time scale of the esr experiment, the observed coupling at a given temperature $a(T)$ is given by the average of the expectation values weighted by the Boltzmann populations of the vibrational energy levels.

$$a(T) = \frac{\sum\limits_n \langle a(\eta)\rangle_n \exp(-E_n/kT)}{\sum\limits_n \exp(-E_n/kT)} \qquad (14)$$

If the oscillation is assumed to be harmonic, the problem can be solved in a closed form up to the quartic term in the power expansion (*cf.* ref 22d and 24g). The result of the vibrational and statistical averaging including the cubic term is given by

$$a^{\mathrm{H}}(T) = a_0 + \frac{a_2}{2\beta_{\mathrm{H}}} + \frac{a_2}{\beta_{\mathrm{H}}}[\exp(hc\omega_{\mathrm{H}}/kT) - 1]^{-1} \qquad (15)$$

with $\beta_{\mathrm{H}} = 4\pi^2h^{-1}\mu c\omega_{\mathrm{H}}$ in which μ is the reduced mass of the oscillator and ω_{H} is the frequency in cm^{-1} of the isolable normal mode. The odd powers of η give, of course, vanishing contributions. The derivative with respect to temperature yields the temperature coefficient

$$\frac{\mathrm{d}a^{\mathrm{H}}(T)}{\mathrm{d}T} = \frac{a_2}{\beta_{\mathrm{H}}}\frac{hc\omega_{\mathrm{H}}}{kT^2}\exp(hc\omega_{\mathrm{H}}/kT)[\exp(hc\omega_{\mathrm{H}}/kT) - 1]^{-2} \qquad (16)$$

Thus, in the first approximation, the temperature coefficient is proportional to a_2 which determines the *curvature* of the dependence of a on the atomic displacements characteristic of the isolable normal mode and also has the same *sign* as a_2. Moreover, the temperature coefficient vanishes for a linear $a(\eta)$ dependence.

An expression analogous to eq 15 can also be written for the deuteron coupling constant. If it is assumed that the ratio of the proton-to-deuteron coupling constants in the absence of zero-point and excited vibrations can be approximated by the proton–deuteron nuclear moment ratio 6.5144

$$6.5144\,a^{\mathrm{D}}(T) = a_0 + \frac{a_2}{2\beta_{\mathrm{D}}} + \frac{a_2}{\beta_{\mathrm{D}}}[\exp(hc\omega_{\mathrm{D}}/kT) - 1]^{-1} \qquad (17)$$

where β_{D} incorporates now the reduced mass μ_{D} for the deuterated species and its vibrational frequency ω_{D} for the mode under consideration. The deuterium isotope shifts at the temperature T is then given by the difference $a^{\mathrm{H}}(T) - 6.5144\,a^{\mathrm{D}}(T)$. With the assumption that at low temperatures $hc\omega$ is sufficiently greater than kT [an assumption which is amply justified for the methyl radical (*vide infra*)], the last term in both equations 15 and 17 can be neglected, and the deuterium isotope effect Δ_{D} is simply given by

$$\Delta_{\mathrm{D}} = a^{\mathrm{H}}(T) - 6.5144a^{\mathrm{D}}(T) = \frac{a_2}{2}\left(\frac{1}{\beta_{\mathrm{H}}} - \frac{1}{\beta_{\mathrm{D}}}\right) \qquad (18)$$

which can also be written in the equivalent form

$$\Delta_{\mathrm{D}} = a^{\mathrm{H}}(T) - 6.5144a^{\mathrm{D}}(T) = \frac{a_2}{2\beta_{\mathrm{H}}}[1 - (\mu_{\mathrm{H}}/\mu_{\mathrm{D}})^{1/2}] \qquad (19)$$

This approximation amounts to treating the problem in terms of the zero-point vibrations alone. Thus, in the first approximation, the deuterium isotope shift is also proportional to the coefficient determining the *curvature* of the $a(\eta)$ dependence. Furthermore, since $\mu_{\mathrm{H}} < \mu_{\mathrm{D}}$, the direction of the shift will be determined by the sign of a_2. It should also be noted that Δ_{D} is inversely proportional to ω_{H} while the temperature coefficient (eq 16) has an approximately $\exp(-K\omega_{\mathrm{H}})$ dependence on ω_{H}. Therefore, both these effects, particularly the temperature coefficient, will soon become negligible as the frequency of the normal mode increases, *i.e.*, as the potential function becomes narrower and steeper about the equilibrium geometry.

It is instructive to consider the methyl radical on the basis of this simplified vibronic treatment. The methyl radical is a planar molecule with six normal vibrational modes. It is assumed that only the nondegenerate A′′ mode corresponding to the out-of-plane bending vibration contributes to the esr vibronic effects.[24e] The frequencies for these bending vibrations for $\dot{\mathrm{C}}\mathrm{H}_3$ and $\dot{\mathrm{C}}\mathrm{D}_3$ are known to be 580 and 447 cm^{-1}, respectively.[26] The normal coordinate for this vibration[27] can be written in terms of the angle θ between the CH bond direction and the plane containing the three hydrogen atoms. In the approximation of small displacements

$$\eta = \left[\frac{3m_{\mathrm{H}}m_{\mathrm{C}}}{3m_{\mathrm{H}} + m_{\mathrm{C}}}l_{\mathrm{CH}}{}^2\right]^{1/2}\theta = (\mu l_{\mathrm{CH}}{}^2)^{1/2}\theta \qquad (20)$$

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(25) (a) Even under these favorable circumstances, the dependence of the hyperfine splitting on the atomic displacements characteristic for the isolable normal mode as well as the precise shape of the potential function for the vibration must be known. In pyramidal radicals this function will be of the double minimum type. Moreover, the shape of the potential function is extremely important since it is closely associated with the stereoselectivity observed in the reactions of asymmetric radicals such as the 7-norbornenyl. Unfortunately, at present the only source of information on the barriers to inversion in bent radicals comes from molecular orbital calculations.[25b] The results of these calculations confirm the notion that the introduction of angular strain between two bonds at the trigonal carbon center produces a structure of minimum energy, the geometry of which is indeed bent. (b) M. J. S. Dewar and M. Shanshal, *J. Amer. Chem. Soc.*, **91**, 3654 (1969); M. J. S. Dewar and W. W. Schoeller, *Tetrahedron*, 27, 4401 (1971); (c) M. Shanshal, *Z. Naturforsch. A*, **26**, 1336 (1971); (d) V. Buss, P. von R. Schleyer, and L. C. Allen, to be submitted for publication.

(26) G. Herzberg, *Proc. Roy. Soc., Ser. A*, 262, 291 (1961).

(27) S. Silver and W. H. Shaffer, *J. Chem. Phys.*, **9**, 599 (1941).

Table III. α-Proton Coupling Constants and Vibronic Effects in Methyl, 7-Norbornenyl, and 7-Norbornyl Radicals

Radical	$\lvert a^H \rvert$, G	Temp, °K	$\lvert a^H \rvert - 6.5144\lvert a^D \rvert$, G	Temp, °K	$d\lvert a^H \rvert/dT$, mG/°K	Temp, °K
Methyl	23.038[a]	96	−0.257[a]	96	−1.3[b]	245
7-Norbornenyl	10.80	139	+0.38	139	+6.3	173
7-Norbornyl	16.78	121			−1.9	130

[a] Reference 23e. [b] Reference 23b.

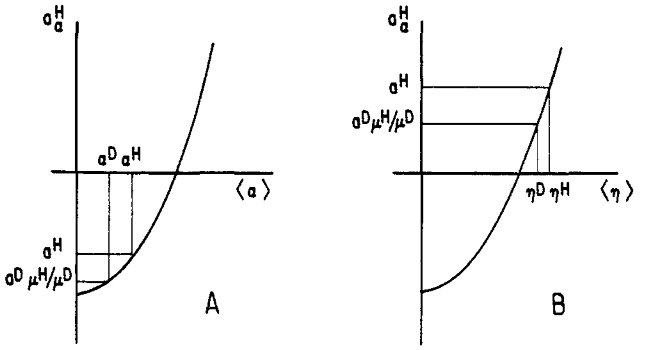

Figure 6. Diagrammatic representation of the deuterium isotope effect in methyl (A) and 7-norbornenyl (B) radicals.

The foregoing equations apply to the new variable with $\beta = 4\pi^2 h^{-1}\mu c\omega l_{CH}{}^2$ [$\beta_H = 48.35$ for $\dot{C}H_3$ and $\beta_D = 62.01$ for $\dot{C}D_3$ with $l_{CH} = 1.079$ Å[26]]. We can now use Fessenden's data for $\dot{C}H_3$ and $\dot{C}D_3$ at 96°K[23e] ($\lvert a^H \rvert = 23.038$ G and $\lvert a^D \rvert = 3.576$ G, and, therefore, $\lvert a^H \rvert - 6.5144\lvert a^D \rvert = -0.257$ G) in conjunction with eq 18 (or preferably its equivalent containing the exponential terms), to calculate a_2 of the angular dependence $a(\theta)$ which for methyl by symmetry must contain only even powers. We obtain $a_2 = \pm 113.6$ G/radian^2 with the exponential terms and ± 112.8 G/radian^2 from eq 18, justifying our assumption. Although the sign of a_2 cannot be determined directly, a positive value is consistent with elementary theory. Indeed, increasing the displacement of the protons from the nodal plane of the π orbital increases the direct delocalization of positive unpaired spin density into the valence s orbitals of the hydrogens. This choice of sign for a_2 demands negative values for a^H and a^D in accord with the theory of spin polarization. If we now calculate the temperature coefficient of a^H from eq 16 using $a_2 = +113.6$ G/radian^2, we obtain $(da^H/dT)_{245°K} = +1.16$ mG/°K which must be compared with the experimental result, $(d\lvert a^H \rvert dT)_{245°K} = -(1.3 \pm 0.2)$ mG/°K.[23b] A negative a^H is again required to have agreement with respect to the sign of these quantities. Finally, we can calculate a_0 from eq 15 and obtain the expression $a^H(\theta) = -24.2 + 114\theta^2$ for the angular dependence of a^H in the methyl radical.

These results for $\dot{C}H_3$ are illustrated qualitatively in Figure 6A. An increase in the reduced mass by deuterium substitution leads to a decreased average out-of-plane bending angle and a more negative (but larger absolute) value of the coupling constant (after correction for the reduced nuclear moment). The sign of the temperature coefficient for the absolute value of a^H is equally accounted for in terms of an increase in the average out-of-plane bending angle with an increase in temperature.

The 7-norbornenyl radical can now be compared with the methyl radical as a prototype of a planar alkyl radical. The pertinent data are presented in Table III. The 7-norbornenyl radical has an α-proton coupling constant of greatly reduced magnitude compared with that of methyl and opposite signs for the *isotope shift* as well as for the temperature coefficient. Moreover, the magnitudes of both the isotope shift and the temperature coefficient are much larger than in methyl. From the foregoing discussion, the latter is clearly indicative of a vibrational motion of very low frequency (and, therefore, of large amplitude). If it is assumed that this vibrational motion is governed by a harmonic potential and that the $a(\eta)$ dependence can be approximated by a quadratic function with positive a_2, it follows that the positive signs of the isotope effects and of the temperature coefficient require the *α-proton coupling constant to be positive*. This situation is illustrated qualitatively in Figure 6B. If $a_7{}^H$ in the norbornenyl radical is positive, increasing the reduced mass on deuteration, which is equivalent to reducing the average amplitude for the vibrational motion, will cause a less positive coupling constant as observed experimentally. An increase in temperature, on the other hand, will increase the coupling constant since it increases the average amplitude of the motion.

This behavior is quite unusual for alkyl radicals. α-Proton coupling constants which increase in magnitude with temperature have been found, however, in some aromatic π-radical ions at carbon positions having *negative* π-spin densities.[22d] Such proton coupling constants must be positive (since they arise through spin polarization) as has been experimentally verified for the proton in the 2-position in an allylic system by a complete determination of the A tensor in a single crystal study.[28] Positive α-proton coupling constants have also been inferred for two strongly pyramidal alkyl radicals, namely $\dot{C}F_2H$[17a, 29] and $\underline{O{-}CH_2{-}\dot{C}H}$,[18b] on the basis of molecular orbital calculations and by comparing all available data within a series of related radicals. Interestingly, these two radicals exhibit no appreciable temperature dependence for the α-proton coupling constant.[30] Initially, we expected a temperature coefficient of the same sign as that observed for the 7-norbornenyl radical (Table III), if the α-proton coupling constants in these radicals were indeed positive. A more careful examination of the problem, however, yields additional insight into the vibrational behavior of these radicals. It was pointed out above that the temperature coefficient of $a_\alpha{}^H$ should diminish rapidly with increasing vibrational frequency in view of its approximate $\exp(-K\omega)$ dependence. Clearly, the barriers to inversion in $\dot{C}F_2H$ and $\underline{O{-}CH_2{-}\dot{C}H}$ must be sufficiently high so that these radicals mostly exist

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(28) C. Heller and T. Cole, *J. Chem. Phys.*, 37, 243 (1962).

(29) D. L. Beveridge, P. A. Dobosh, and J. A. Pople, *ibid.*, 48, 4802 (1968).

(30) P. J. Krusic, unpublished results.

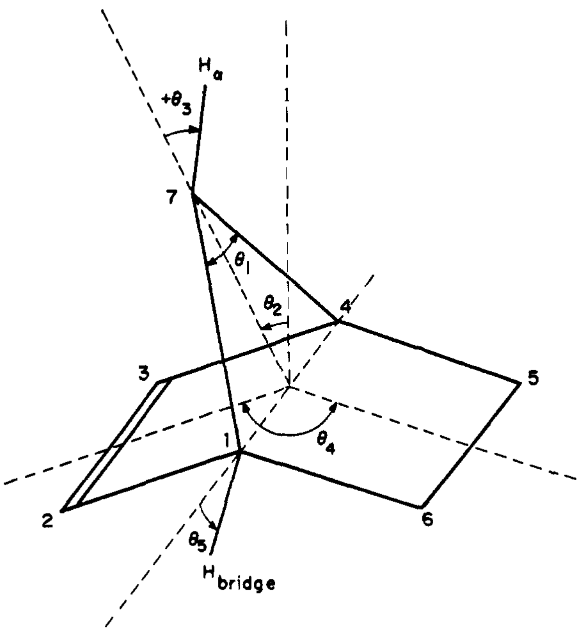

Figure 7. Structural parameters for the 7-norbornenyl radical.

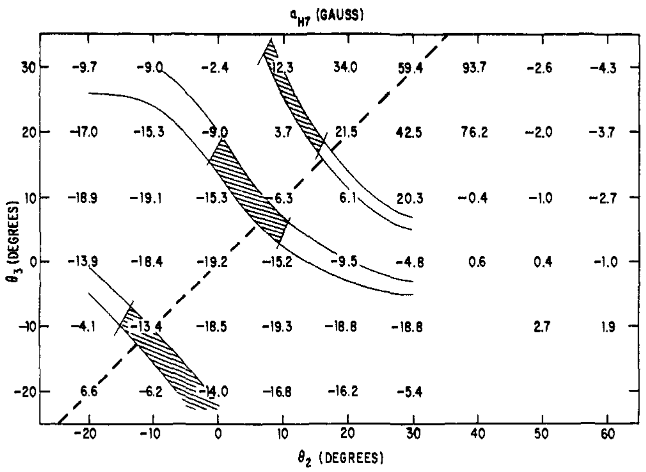

Figure 8. INDO isotropic hyperfine coupling constants for H-7 in the 7-norbornenyl radical. The shaded areas represent structures consistent with the experimental absolute values of a_7^H and a_2^H. The coupling constant along the straight dotted line represents the predicted dependence of a_7^H on a coupled motion in which θ_2 and θ_3 vary simultaneously (see text).

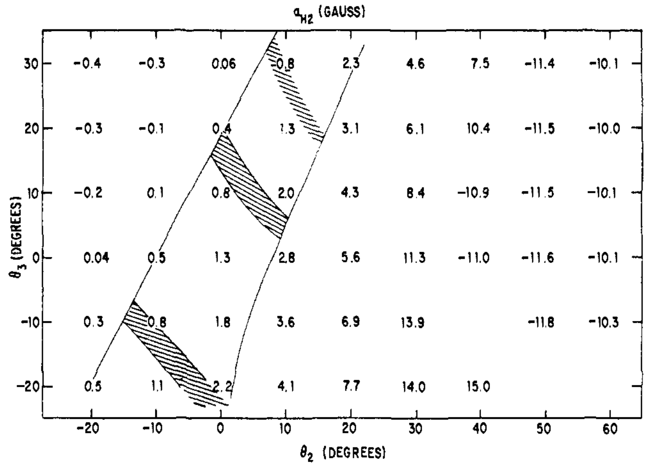

Figure 9. INDO isotropic hyperfine coupling constants for H-2 in the 7-norbornenyl radical. The shaded areas represent structures consistent with the experimentally observed absolute values of a_2^H and a_7^H.

in vibrational states contained in either well of the double-minimum potential. Transitions between these states are of sufficiently high frequency to yield a negligible temperature coefficient. Moreover, making again the reasonable assumption of a parabolic dependence of a^H on the angle for out-of-plane bending, the angular dependence of a^H within each well of the double-minimum potential will be of low curvature, further precluding an appreciable temperature coefficient for a^H. It must be concluded, therefore, that the existence of an unusually strong temperature dependence of a^H and of an appreciable deuterium effect in the 7-norbornenyl radical is a convincing argument for a very low barrier to inversion in this radical (eq 10).

INDO Molecular Orbital Calculations for 7-Norbornenyl. The INDO molecular orbital method[31] has been applied successfully to the study of the vibrational effects in the methyl radical[24e] and of the α-proton coupling constants of some bent radicals.[18b,21b,e,29] It was of interest to see if any additional insight might be forthcoming from such calculations on the 7-norbornenyl radical as a function of the atomic displacements most likely involved in the vibrational mode of lowest frequency.

Calculations were carried out for the 7-norbornenyl radical as a function of the two most important structural parameters, θ_2 and θ_3, shown in Figure 7. The structural parameters which were used in the calculations were derived from the related hydrocarbons, norbornane and norbornadiene.[32] We also assumed that a slight increase in θ_1 accompanied the transformation from the hydrocarbon to the radical. The remaining parameters used for the calculations were: d(CC single) = 1.54 Å, d(CC double) = 1.33 Å, d(CH) = 1.09 Å, $\theta_1 = 95°$, $\theta_4 = 120°$, and $\theta_5 = 0°$. 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 $C_1C_6C_5$ plane, and (d) the 2 and 3 hydrogens lie in the $C_1C_2C_3$ plane and in the planes bisecting the opposing CCC angles.

The calculated values of the hyperfine coupling constants for the protons attached to carbon atoms 7 and 2 are given in Figures 8 and 9 in the form of nomographs. In Figure 8, there are three narrow areas representing those structures which give calculated values of a_{H_7} within ±2 G of the observed absolute values for this coupling (10.8 G at −134°). In Figure 9 the structures compatible to within ±1 G of the observed coupling for the vinylidene protons (H_2) are located in a broad band running diagonally across the nomograph. The shaded areas result by superposition of the two maps and further restrict the allowed structures. A fourth area of agreement can be extrapolated

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(31) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, 90, 4201 (1968). The program was obtained from the Quantum Chemistry Program Exchange, Indiana University.

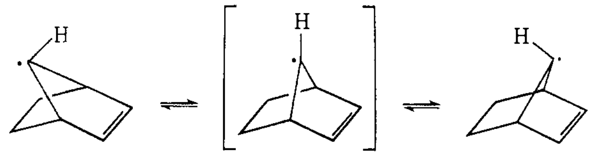
(32) (a) Y. Morino, K. Kuchitsu, and A. Yokozeki, *Bull. Chem. Soc. Jap.*, 40, 1552 (1967); (b) J. F. Chiang, C. F. Wilcox, Jr., and S. H. Bauer, *J. Amer. Chem. Soc.*, 90, 3149 (1968); (c) R. Destro, G. Filippini, C. M. Gramaccioli, and M. Simonetta, *Tetrahedron Lett.*, 3223 (1969).

for the bottom left-hand-side corner of Figure 8.[33,34] The calculated values of the coupling constants for H_{endo}, H_{exo}, and H_{bridge} (*cf.* Figure 7) for structures located in the shaded areas are also consistent with the experimental values within the same reliability margins used above. They show much less variation with structure than a_{H_7} and a_{H_2}.

From the discussion of the preceding section, it is clear that a single equilibrium structure, such as might be represented by the structural parameters θ_2 and θ_3 corresponding to a shaded area of Figure 8, is not compatible with the esr information. A dynamic structure must be considered capable of giving rise to a strong temperature dependence of a_{H_7}, a pronounced isotope effect and a positive α-proton coupling constant.

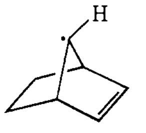
Several simplified vibrational representations can be considered in connection with the coupling constants of Figure 8. For example, θ_2 can be fixed at the value of 0° with the α-proton executing out-of-plane θ_3 vibrations. The dependence of the coupling constant on the vibrational coordinate (θ_3) is given by the numbers in the column corresponding to $\theta_2 = 0$. These numbers could be fitted approximately by a quadratic expression with a minimum near -19.2 G, but the curvature is low and inordinate displacements of H_7 would be required to produce a positive coupling constant. Similarly, one may consider the remaining columns of Figure 8 (H wagging for a fixed θ_2) as well as the rows (θ_2 skeletal motions with fixed θ_3). These dependences are even more wanting in terms of curvature than the curve corresponding to the wagging of the 7-hydrogen in an undistorted $\theta_2 = 0$ carbon skeleton. It is also difficult to see how these curves could lead to a positive a_{H_2}.

One may also consider a coupled motion involving simultaneous changes in both angles θ_2 and θ_3. A possible motion of this sort is represented by the dashed straight line in Figure 8, and is shown diagrammatically below. The numbers along the dashed line in Figure 8 define a dependence of the α coupling constant on the atomic displacements for the motion, and can be fitted very closely to a *parabola*. The curvature of this dependence is greater than along any curve in the θ_2 or θ_3 directions alone. Furthermore, reasonable displacements (*e.g.*, $\theta_2 = \pm 20°$, $\theta_3 = \pm 20°$) on either side of the minimum are sufficient to produce a *positive* coupling constant. A large amplitude of vibration in such a mode is clearly the most likely source of a large da/dT and a large isotope effect for the 7-norbornenyl radical. Thus, all experimental observations are accounted for with a *single minimum* vibration in this mode. If a *double*-minimum potential exists, the height of the barrier must be quite low.

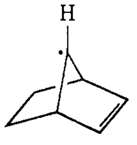


I II III

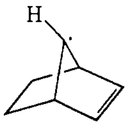
More information concerning the potential function governing the motion of the 7-methine group is not provided by the extant esr data. An attractive rationalization for the stereoselectivity observed in the radical coupling and hydrogen abstraction reactions of the 7-norbornenyl radical would be afforded by a double-minimum potential, with the deeper well corresponding to structure I. In this configuration the sp-hybrid orbital is primarily directed toward the anti side and the radical is thus predisposed for the formation of a new bond from this direction. The greater stability of I would imply, however, that the interaction between the π orbitals of carbons 2,3 and the half-occupied orbital on carbon 7 has a destabilizing effect. Thus, in the formation of the radical, the stabilization (energy) of the norbornenyl cation is apparently offset by addition of an electron to the antibonding LUMO orbital. Supporting evidence for the greater stability of I and hence destabilization of the homoconjugative interaction is provided by our recent esr work on the 7-norbornadienyl radical which is highly metastable and rapidly undergoes rearrangement. A recent MINDO-1 molecular orbital calculation[25c] carried out on the three configurations (no displacement of C-7 was included in the model) also indicated that I′ was more stable than III′, and II the least stable. A double-minimum potential with a deeper well corresponding to configuration I is, thus, quite plausible and consistent with the esr vibronic effects, provided the barrier to inversion is sufficiently low.[34a]



I′



II



III′

7-Norbornyl Radical. The temperature coefficient, $d|a_\alpha|dT$, for the 7-norbornyl radical has a "normal" sign (Table III) from which a negative value of the α splitting is inferred. The reduced magnitude of a_α (16.8 G at $-152°$) also implies a bent structure at the radical site. This conclusion is supported by INDO calculations (Table IV) which, in the interest of economy, have been carried out only as a function of the out-

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(33) Unfortunately, the structures within the shaded areas do not correspond to local energy minima. With other large radical structures, such as the adamantyl radical,[21e] a similar problem was encountered in which the structure giving the best fit to the observed couplings did not correspond to an energy minimum. The energy criterion alone would favor in this case extremely distorted structures. Such structures might be termed nonclassical and are characterized by rather large and negative couplings for the vinylidene protons (about -10 G, Figure 9) and by very small α couplings, both of which are clearly at variance with the experiment.

(34) The C-13 coupling constant at the 7 position is also strongly dependent on θ_2 and θ_3. For very distorted structures ($\theta_2 > 35°$), this coupling becomes negative, indicating that the unpaired electron is no longer localized on carbon atom 7. Despite the discordance caused by the odd behavior of the energy, we consider the fitting based on the coupling constants to be reliable in view of the invariably good correlation between INDO proton splittings with the experimentally observed esr parameters.[31] The structural parametrization limited to only two angles also mitigates this problem.

(34a) NOTE ADDED IN PROOF. After the completion of this work, a much more pronounced stereoselectivity has been reported for reactions proceeding through the intermediacy of the 7-norbornenyl anion (J. K. Stille and K. N. Sannes, *J. Amer. Chem. Soc.*, 94, 8489 (1972)). The latter was shown to capture a deuteron from deuterium oxide or *tert*-butyl alcohol-*O-d* to form a mixture of *anti*- and *syn*-7-deuterionorbornene in approximately a 94:6 ratio. This preference for anti capture was explained in terms of an equilibrated pair of isomeric anions with structures corresponding to I′ and III′, with I′ predominating. The interaction between the π orbitals on carbons 2,3 and the doubly occupied orbital on carbon 7 (bishomocyclopropenyl interaction) is much more antibonding in the anion than in the corresponding radical, since in the former one more electron must occupy an antibonding orbital.

Table IV. INDO Hyperfine Coupling Constants and Energies for the 7-Norbornyl Radical[a,b]

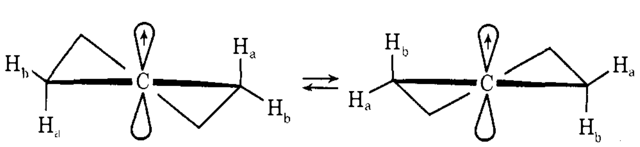
θ_3, deg	$a(H_\alpha)$	$a(C_\alpha)$	$a(H_{endo}^{anti})$	$a(H_{exo}^{anti})$	$a(H_{exo}^{syn})$	$a(H_{endo}^{syn})$	Energy[c]
0	−20.53	41.16	0.73	−1.10	−1.10	0.73	−56.5787
5	−20.00	42.42	0.21	−1.07	−1.11	1.17	−56.5787
10	−18.44	46.08	−0.07	−1.04	−1.12	1.62	−56.5789
15	−16.07	51.83	−0.39	−1.00	−1.11	2.06	−56.5792
20	−13.17	59.25	−0.66	−0.95	−1.10	2.47	−56.5793
25	−10.02	67.86	−0.86	−0.89	−1.08	2.85	−56.5793
30	−6.86	77.24	−1.01	−0.84	−1.05	3.19	−56.5788

[a] The structural assumptions and parameters are discussed in the text. [b] Coupling constants in gauss. [c] Total electronic energy in hartrees (1 hartree = 626.81 kcal mol^{-1}).

of-plane angle θ_3 (*cf.* Figure 7) on a symmetric framework, although a coupled motion of the type discussed for the 7-norbornenyl might be a better approximation. The structural assumptions and parameters are the same as those for H_5 and H_6 of the 7-norbornenyl radical. In this case, the energy minimum is close to the configuration giving the best fit to the α coupling constant (θ_3 = 15°) and corresponds to a barrier to inversion of only 0.4 kcal mol^{-1}. Although one should not take these numbers too seriously, as must always be the case with semiempirical calculations particularly regarding configurational and conformational barriers, a low barrier is also indicated by the presence of a temperature dependent a_α and by the observation of four equivalent endo and four equivalent exo protons.

Other Alicyclic Radicals. Having presented the pyramidal nature of the 7-norbornyl radical, which can be thought of as consisting of two cyclopentyl rings in "envelope" conformations, it might be asked why the cyclopentyl radical is planar at the radical center as evidenced by its "normal" α-proton splitting (21.5 G).[21a] It is possible for the cyclopentyl radical to relieve some of the strain intrinsic in an "envelope" conformation by adopting a "twist" conformation. Molecular models also indicate less strain for such structures. The effect of the observed temperature dependence of the line shape in the spectrum of the cyclopentyl radical[21a] can then be accounted for, not by an exchange between two "envelope" conformations, but by the exchange between two twisted conformations.

A similar mechanism of exchange between twisted conformations could also be responsible for the line-shape effect in the cyclohexyl radical,[35] instead of the proposed chair–chair interconversion. With further increase in ring strain, as in the 3-cyclohexenyl radical, however, even a twisted conformation will not alleviate the angle strain at the trivalent carbon. In this radical, a distinctly pyramidal structure results, as judged by the "anomalous" α coupling constant observed ($|a_\alpha|$ = 13.1 G).[36]



Finally, it is noteworthy that INDO calculations predict the esr parameters remarkably well for the cyclopropyl radical, the simplest bent cyclic species. The results of the calculations are shown in Table V.

Table V. INDO Hyperfine Coupling Constants (G) and Energies for the Cyclopropyl Radical[a]

α,[b] deg	$a(H_{syn}^{\beta})$	$a(H_{anti}^{\beta})$	$a(C_\alpha)$	$a(H_\alpha)$	Energy[c]
0	30.3	30.3	40.3	−24.3	−24.1834
5	30.1	30.1	42.2	−23.6	−24.1836
10	29.4	29.5	47.9	−21.4	−24.1843
15	28.3	28.5	56.6	−18.1	−24.1853
20	26.9	27.3	67.8	−14.1	−24.1864
25	25.3	25.9	80.7	−9.9	−24.1875
30	23.6	24.5	94.5	−5.8	−24.1882
35	21.9	23.0	108.7	−1.9	−24.1885
40	20.2	21.6	123.0	1.4	−24.1881
45	18.4	20.2	137.1	4.3	−24.1868
50	16.8	18.9	150.9	6.6	−24.1845

[a] The structural parameters for the cyclopropyl ring are: *d*(CC) = 1.514 Å, *d*(CH ring) = 1.08 Å, HCH angle = 116.2°. The methylene protons are symmetrically disposed with respect to the cyclopropyl plane and lie in the plane bisecting the opposing CCC angle. The CH_α distance was assumed to be 1.09 Å. [b] Out-of-plane angle for the CH_α bond in a plane normal to the CCC plane and bisecting the opposing $CC_\alpha C$ angle. [c] Energies in hartrees (1 hartree = 626.81 kcal mol^{-1}).

The structure of minimum energy (−3.2 kcal mol^{-1} relative to the planar configuration) corresponds to an out-of-plane angle for the CH_α bond of 35°, while the structure giving best fit to the observed coupling constants ($|a_\alpha|$ = 6.5 G and $|a_\beta|$ = 23.4 G)[21a] has a CH_α out-of-plane angle of 30° (*cf.* Table V). The predicted negative sign for a_α has been recently confirmed indirectly by CIDNP experiments.[37] It is seen, moreover, that the coupling constants for the syn and anti β protons are nearly equal to each other for all values of α. This unexpected result is indeed consistent with the absence of line-shape effects in the spectrum of the cyclopropyl radical.

Experimental Section

***syn*- and *anti*-7-Norbornenecarboxylic Acids.** A mixture of *syn*- and *anti*-7-norbornenecarboxylic acids was prepared from *syn*-7-bromonorbornene *via* carbonation of the Grignard reagent.[38] The acids were separated by column chromatography using silicon gel and eluting with ether–pentane mixtures.

exo,exo-5,6-Dideuterionorbornene was obtained by addition of 1 mol of deuterium gas (0.5–1.0 atm) to 70 g of norbornadiene in 70 ml of methyl acetate and 2 g of 5% Pd/C in a Paar bomb.[39] The unreacted norbornadiene (14.3 g) was removed by distillation and the residue on further distillation (92–95°) afforded 97 g of a mixture containing 11% norbornadiene, 69% *exo,exo*-dideuterionorbornene, and 20% *exo,exo,exo′,exo′*-tetradeuterionorbornane.

To 92 g of the mixture containing dideuterionorbornene (0.67 mol) in 500 ml of carbon tetrachloride and 70 g of pyridine cooled

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[35] S. Ogawa and R. W. Fessenden, *J. Chem. Phys.*, 41, 994 (1964).

[36] P. J. Krusic and T. A. Rettig, unpublished results.

[37] R. Kaptein, Ph.D. Thesis, University of Leiden, Holland, 1971.

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[39] *Cf.* B. Franzus, *J. Org. Chem.*, 33, 1288 (1968).

in an ice–water bath was added 44 ml of bromine in 100 ml of carbon tetrachloride over 3 hr. After removal of the precipitate (py·HCl), the carbon tetrachloride solution was washed three times with 10% aqueous hydrochloric acid, water, aqueous hydrochloric acid, water, aqueous sodium bisulfite, and finally water, and then dried over sodium sulfate. Distillation afforded 13.2 g of tetradeuterionorbane, 11.8 of dideuterio-7-bromotricyclene (bp 36–37° (1.3 mm)), 25.2 g of dideuterio-2,3-dibromonorbornane (bp 64–67° (0.3 mm)), and 105.4 g of dideuterio-2,7-dibromonorbornane (bp 61–78° (0.1 mm)). Redistillation of the last fraction afforded 93.1 g (54%) of a material boiling at 77–78° (0.1 mm) whose nmr and ir spectra indicated that the two deuterium atoms were endo (5.6) to at least 95%.

The dibromide (66 g) dissolved in 50 ml of *tert*-butyl alcohol was added rapidly to a solution of 12 g of potassium in 200 ml of *tert*-butyl alcohol at 80° under nitrogen. The solution was stirred at 80° for 16 hr and cooled, and 50 ml of water was added. The pentane extract was washed three times with water and dried over sodium sulfate. Distillation afforded 28.3 g of 5,6-*endo*-dideuterio-7-*syn*-bromonorbornene boiling at 54–55° (9 mm) and 18.2 g of starting dibromide (bp 78–88° (0.1 mm)). Hydrogenation of this bromonorbornene in ethanol over a 5% Pd on charcoal catalyst afforded dideuterio-7-bromonorbornane. It was also converted to a mixture of 5,6-dideuterio-7-norbornenecarboxylic acid as described previously.

7-Norbornenecarboxylic acid (4.2 g) was refluxed for 1 hr with 4 ml of thionyl chloride. The excess thionyl chloride was removed by distillation and the residue, after dilution with pentane, was poured into a mixture of methanol and pentane. The mixture of methyl esters (4.01 g, bp 91° (28 mm)) was added to a mixture of 0.5 g of sodium in 50 ml of methanol-d_1[40] and refluxed for 6 days under nitrogen. Nmr analysis indicated that at least 92% deuterium exchange at the 7 position had occurred.[41] Further exchange was effected by treating this mixture with that prepared from 1.5 g of potassium in 30 ml of methanol-d_1, then adding 2 ml of deuterium oxide and refluxing for 12 hr. After cooling, 2 ml of deuterium oxide was added and the mixture worked up in the usual way to afford 3.44 g of acid. Column chromatography on 120 g of silica gel (packed with 4% diethyl ether and pentane) afforded 1.08 g of *syn*-7-deuterio-7-norbornenecarboxylic acid which was shown by nmr analysis to consist of greater than 96% 7-*syn*-deuterium. Continued elution with 4–10% diethyl ether–pentane mixtures afforded *anti*-7-deuterio-7-norbornenecarboxylic acid, the nmr spectrum of which also indicated greater than 96% 7-*anti*-deuterium.

The 7-norbornenecarboxylic acid was also treated with cyclohexylamine-d_2 and *n*-butyllithium in cyclohexane to effect deuterium exchange. Thus, the treatment with 0.73 g of the unsaturated acids with 20 g of cyclohexylamine-d_2 and 3 ml of 4.23 *M* butyllithium for 24 hr at 90° under nitrogen afforded 0.244 g of acid after work-up with deuterium oxide in which greater than 90% of the 7- as well as the 2,3-vinylic hydrogens was exchanged.

The *exo*-5,6-dideuterio-7-norbornenecarboxylic acid was prepared from 0.77 g of 7-norbornadienecarboxylic acid and 0.134 g of 5% palladium on charcoal in 5 ml of methanol with 138 ml of deuterium. The mixture was filtered, neutralized with potassium hydroxide, and extracted three times with ether. Acidification followed by extraction with methylene chloride–ether mixture afforded 0.64 g of a mixture of acids consisting of 77% *exo*-5,6-dideuterionorbornene-*syn*-7-carboxylic acid, 15% of tetradeuterio acid, and a small amount of dideuteriotricyclenic acid. Chromatography on 30 g of silica gel with 6% ether–pentane afforded a mixture of saturated acid together with *anti*-norbornene-7-carboxylic acid. Further elution with 10% ether–pentane afforded 358 mg of a mixture of *exo*-5,6-dideuterionorbornene-*syn*-7-carboxylic acid showing more than 90% substitution by exo deuteriums.

7-Norbornane-7-carboxylic acid was prepared from norbornadiene-7-carboxylic acid by hydrogenation with 5% palladium on charcoal in 95% ethanol.

Perester Synthesis. Each of the pure carboxylic acids was converted to the acid chloride with thionyl chloride. The distilled acid chloride was treated with *tert*-butyl hydroperoxide and pyridine in pentane at 0° for 1 hr. The peresters were purified by passing them through a column packed with Florisil with pentane.[7]

***tert*-Butoxynorbornenes.** 7-*tert*-Butoxynorbornadiene (10 g) was treated with 5 g of lithium aluminum hydride in 125 ml of tetrahydrofuran at a reflux for 24 hr under nitrogen. Work-up afforded 5.7 g (bp 43–44° (3.5 mm)) of a mixture of ethers containing mostly *anti*-7-*tert*-butoxynorbornene.[42] The pure ether was obtained by preparative gas chromatography on a FFAP column at 90°.

The syn isomer was prepared by controlled hydrogenation of 7-*tert*-butoxynorbornadiene. Thus, 4.03 g of ether in 10 ml of 95% ethanol was added to 0.2 g of prereduced Adam's catalyst in 5 ml of 95% ethanol and hydrogenated until 545 ml of hydrogen was taken up (1 hr).[43] After removal of the catalyst, 50 ml of water was added and the product extracted with pentane, which was washed repeatedly with water to remove ethanol and then shaken with 5 *M* silver nitrate (3 times with 20 ml). The hydrocarbon layer on work-up gave 1.28 g of a mixture of 7-*tert*-butoxynorbornane and tricyclenic ether together with unextracted unsaturated ethers. The combined aqueous layers were treated with 250 ml of cold 4 *N* potassium cyanide and extracted with pentane. It consisted of a 3:2 mixture of *syn*-7-*tert*-butoxynorbornene and unreacted starting material. When the hydrogenation was repeated with 7-*tert*-butoxynorbornadiene (10 g) and 0.40 g of prereduced 5% palladium on charcoal, it was carried out until 1.27 mol (9 l.) of hydrogen was taken up. Under these conditions, 1.70 g of *syn*-7-*tert*-butoxynorbornene (bp 37° (1.5 mm)) was obtained in quite pure form. Analysis of *syn*- and *anti*-7-*tert*-butoxynorbornene was readily effected by gas chromatography on a FFAP column at 80°.

The isomeric 7-*tert*-butoxytricyclene was prepared from the bromide *via* the Grignard reagent and *tert*-butyl perbenzoate.[44] Attempts were made to prepare the other isomeric *endo*-3-*tert*-butoxy-[2.2.1.0^{2,7}]tricycloheptane from the reaction between *anti*-7-tosyloxynorbornene with potassium *tert*-butoxide in *tert*-butyl alcohol.[45] However, the predominant product was *anti*-7-*tert*-butoxynorbornene. The tricyclic ether, however, is expected to undergo hydrogenolysis to *endo*-2-*tert*-butoxynorbornane. *exo*-2-Bromonorbornane was converted to the Grignard reagent and then treated with *tert*-butyl peracetate from which *exo*-2-*tert*-butoxynorbornane and the acetate were isolated. The presence of the endo isomer in this mixture was not established.

Esr Spectra. The esr spectra of norbornenyl radicals were obtained by photolysis of solutions of peresters dissolved in cyclopropane as described previously.[7] The irradiation was effected with a high-pressure mercury arc lamp (PEK No. A1B, 2 Kw) equipped with a filter consisting of an aqueous nickel chloride solution to remove light above 300 nm and much of the infrared radiation. Temperature in the tube was maintained by a cooled stream of nitrogen gas to ±5°.

Product studies were for the most part carried out at 32° in a merry-go-round reactor (Southern New England Ultraviolet Co.) equipped with low-pressure mercury lamps which produced most of their radiation at 254 nm. The reaction was monitored by the evolution of carbon dioxide which was analyzed by gas chromatography using a Porapak A column and ethane as an internal standard.[8] The hydrocarbons, mainly norbornene from tricyclene, norbornane, norbornadiene, and [2.2.1.0^{2,6}]tricycloheptane, were analyzed on a 5-ft SE-30 column at 42°. Similar results were obtained using a Carbowax 3M-KOH, Ucon polar or a FFAP column. The *tert*-butyl ethers were analyzed on a 20-ft X F-1150 column at 75°, which also separated *tert*-butyl alcohol. To establish identity, the products were compared mass spectroscopically using a GC mass spectrometer (Varian CH-7) combination with authentic samples. The deuterated compounds were first separated by preparative gas chromatography before they were analyzed by examination of their nmr (60- or 220-MHz) or mass spectrum.

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