the rate of reaction 3, or even the enthalpy change in reaction 3, are not easily approximated. The stabilities of the organometallic reagents $(RLi)_n$ are involved as well as the stabilities of the radicals $R\cdot$ and $R\cdot'$. Apparently (3) occurs readily for $R\cdot' =$ *t*-butyl in the presence of excess *n*-butyllithium.

As a further test of the above rationalization, the results with methyl iodide and allyl bromide are of particular interest. The reactivity of methyl iodide in reaction 2 would be expected to be orders of magnitude less than for the other acyclic alkyl iodides. Experimentally in this case we observed (with *n*-butyllithium) a mixture of methyl and *n*-butyl radicals. One interpretation is that the rates of reactions 2 and 3 are now approximately equal. Allyl bromide would be expected to be much more reactive in bromine atom transfer than the simple alkyl bromides. Experimentally, we observed (with *n*-butyllithium) that only the allyl radical is detected by esr.

Reactions 2 and 3 provide a reasonable mechanism for metal–halogen interchange.[6] However, extensive metal–halogen interchange under our reaction conditions would be expected to give rise to mixtures of radicals, particularly in cases such as $R' =$ *n*-propyl, $R =$ *n*-butyl. With the exception of methyl iodide–*n*-butyllithium, we have never observed mixtures of radicals in reactions of alkyl iodides even when the reaction had proceeded to much higher conversions than required for the optimum esr signals.

A possible explanation to this dilemma is that the concentration of RI never reaches an appreciable fraction of the R′I concentration under conditions where the esr signal can be detected, *i.e.*, the consumption of R′I must be much faster than the rate of formation of RI. Thus, by the time that an appreciable fraction of the unreacted alkyl iodide has been converted into RI, the rate of process 1 has decreased to such a value that radicals can no longer be easily detected. Since steps 2 and 3 must be fast compared to steps 1 and 4 to yield the observed ratios of $[R\cdot']/[R\cdot]$, it follows that only a small fraction of the R′I (or RLi) consumed is being converted to free radicals observable by esr spectroscopy.[12] Presumably the same conclusion applies to alkyl bromides and chlorides.

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[12] Some retention of configuration in the reaction of 2-iodooctane with butyllithium [R. L. Letsinger, *J. Amer. Chem. Soc.*, **72**, 4842 (1950)] is probably the result of an ionic or cage process; see also H. J. S. Winkler and H. Winkler, *ibid.*, **88**, 964, 969 (1966).

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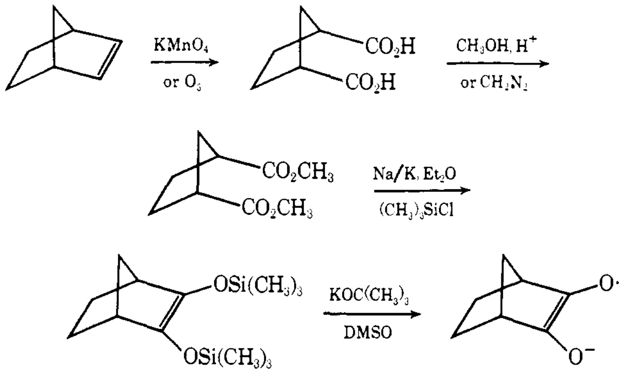
Stereochemistry of the Reaction of the 7-Norbornenyl Radical with Tri-*n*-butyltin Deuteride[1]

Sir:

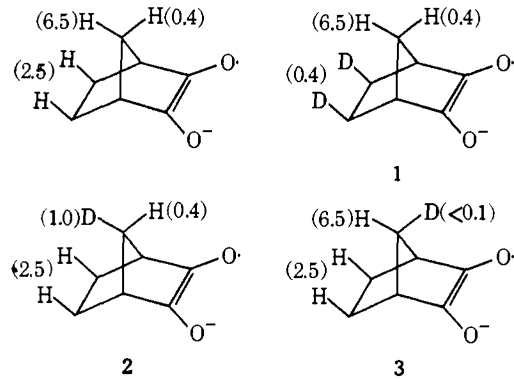
It was recently reported that the reaction of tri-*n*-butyltin deuteride with *syn*- or *anti*-7-bromonorbornene yielded exclusively *anti*-7-deuterionorbornene.[2] The analysis was performed by pmr spectroscopy. Since we had already demonstrated that *exo,exo*-5,6-dideuterionorbornene[3] could be converted into the semidione **1** without rearrangement, we have applied the sequence of reactions in Scheme I[4] to the product of the reaction of tri-*n*-butyltin deuteride with 7-*syn*- and 7-*anti*-bromonorbornene.

Scheme I



The semidiones produced were analyzed by esr spectroscopy. The spectrum (Figure 1) obviously was a mixture of two semidiones (**2** and **3**) with *syn* and *anti* deuterium atoms with the hyperfine splitting constants as assigned in Chart I at 25° in DMSO solution.[5] Analysis was performed by comparison of the height of the wing peaks of **3** ($^1/_{32}$ of total intensity) with the fourth peaks of **2** ($^1/_{96}$ of total intensity).[6] The intensity ratios indicate a ratio of **2**/**3** = 4.9 ± 0.1. The same ratio was obtained from both the *syn*- and *anti*-7-bromonorbornene.[7,8] Although there is some stereospecificity in the reaction of tri-*n*-butyltin deuteride with the 7-norbornenyl radical, it does not appear necessary to invoke a

Chart I



[a] Bridgehead hfsc = 2.5 G in all cases.

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[1] Application of Electron Spin Resonance Spectroscopy to Problems of Structure and Conformation. XVI. This work was supported by a grant from the National Science Foundation.

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

[3] D. R. Arnold, D. J. Trecker, and E. B. Whipple, *ibid.*, **87**, 2596 (1965).

[4] G. A. Russell and P. R. Whittle, *ibid.*, **89**, 6781 (1967).

[5] See also G. A. Russell and K.-Y. Chang, *ibid.*, **87**, 4381 (1965).

[6] It is assumed that the line widths of **2** and **3** are the same, *i.e.*, that any unresolved hfs is the same in **2** and **3**. Since **3** contains an unresolved *syn*-7-deuterio hyperfine splitting, we expect that the line width of **3** may be slightly greater than **2** and the ratio of **2**/**3** of 4.9 is a maximum limit; *e.g.*, the yield of **3** may be greater than 16%.

[7] H. Kwart and L. Kapan, *J. Amer. Chem. Soc.*, **76**, 4072 (1954).

[8] The *anti*-7-bromonorbornene was prepared by the action of hydrobromic acid on 7-*anti*-norborneol: P. Story, *J. Org. Chem.*, **26**, 287 (1961). Solvolysis of this *anti*-7-bromonorbornene in the presence of sodium borodeuteride yielded *anti*-7-deuterionorbornene: H. C. Brown and H. M. Bell, *J. Org. Chem.*, **27**, 1928 (1962); A. P. Marchand and J. E. Rose, *J. Amer. Chem. Soc.*, **90**, 3724 (1968). Conversion to the semidione yielded only **2**; the wing peaks from **3** (Figure 1) were completely missing from the esr spectrum.

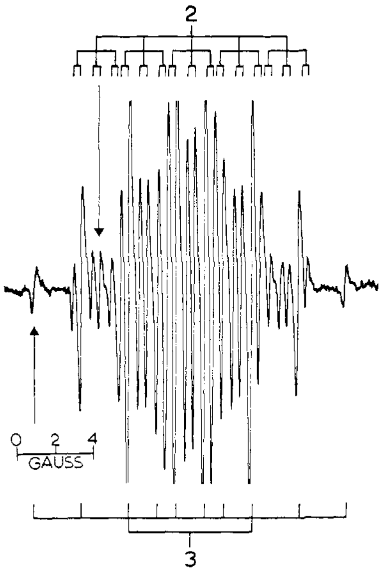

Figure 1. First-derivative esr spectrum of 7-deuteriobicyclo[2.2.1]-heptane-2,3-semidiones obtained from the 7-deuterionorbornene produced by the reaction of tri-*n*-butyltin deuteride with *syn*- or *anti*-7-bromonorbornene.

"nonclassical" structure to explain the result. For example, a nonplanar radical at C-7[9] would be expected to have the C-7 hydrogen *syn* to the double bond (on the basis of nonbonded interactions). Reaction with the available orbital at C-7 would thus lead to the *anti*-7-deuterionorbornene. Further evidence not supporting a "nonclassical" structure is the observation that a nearly 1:1 mixture of 7-*syn*- and 7-*anti*-methylnorbornenes has been reported in the tributyltin hydride reduction of *syn*-7-bromo-*anti*-7-methylnorbornene,[10] and we have verified this report. It appears that the 7-methylnorbornenyl radical may be more nearly planar at C-7 than the unsubstituted norbornenyl radical.

The process outlined in Scheme I provides a convenient technique for the conversion of a cyclic or bicyclic olefin to the semidione on the scale of ~100 mg. Since the esr spectra of the semidiones are easily interpreted in terms of first-order splittings,[11] and since considerable stereospecific long-range splitting is seen,[5] this technique offers the possibility of advantages over structural assignments based solely on pmr spectroscopy.

The values of $a^{\mathrm{H}}/a^{\mathrm{D}}$ for the *anti*-7 position of the bicyclo[2.2.1]heptanesemidione is 6.5, in agreement with the ratio of nuclear moments of hydrogen and deuterium atoms (6.514). The value of $a^{\mathrm{H}}/a^{\mathrm{D}}$ for the *exo*-5,6 positions is only 6.2, possibly indicating a difference in the time-averaged positions of *exo*-5,6 deuterium and hydrogen atoms.[12]

(9) See J. E. Williams, Jr., R. Sustmanu, L. C. Allen, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 1037 (1969).

(10) J. B. Dence, Ph.D. Thesis, California Institute of Technology, 1968.

(11) G. A. Russell, "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Interscience Publishers, New York, N. Y., 1968, p 87.

(12) For examples of anomalously low (~6.2) values of the ratio $a^{\mathrm{H}}/a^{\mathrm{D}}$ in molecules in which there is a strong coupling of vibrational and electronic wave functions, see M. T. Jones, A. Cairn, and D. W. Wiley, *J. Chem. Phys.*, **43**, 3403 (1965).

(13) National Science Foundation Predoctoral Fellow, 1965–1969.

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Bridged Polycyclic Compounds. LVI. On the Question of Nonclassical *anti*-7-Norbornenyl Free Radicals[1]

Sir:

Although carbon-bridged, homallylic and cyclopropylcarbinyl nonclassical free radicals have been postulated many times, extensive studies have shown that all of the available experimental results can be accommodated by considering only discrete classical intermediates. Indeed most of the results are entirely inconsistent with the assumption that only delocalized radicals are involved (except as transition states between classical radicals).[2] The recent claim[3] that reduction of both *syn*- (**1**-Br) and *anti*-7-bromonorbornene (**2**-Br) with

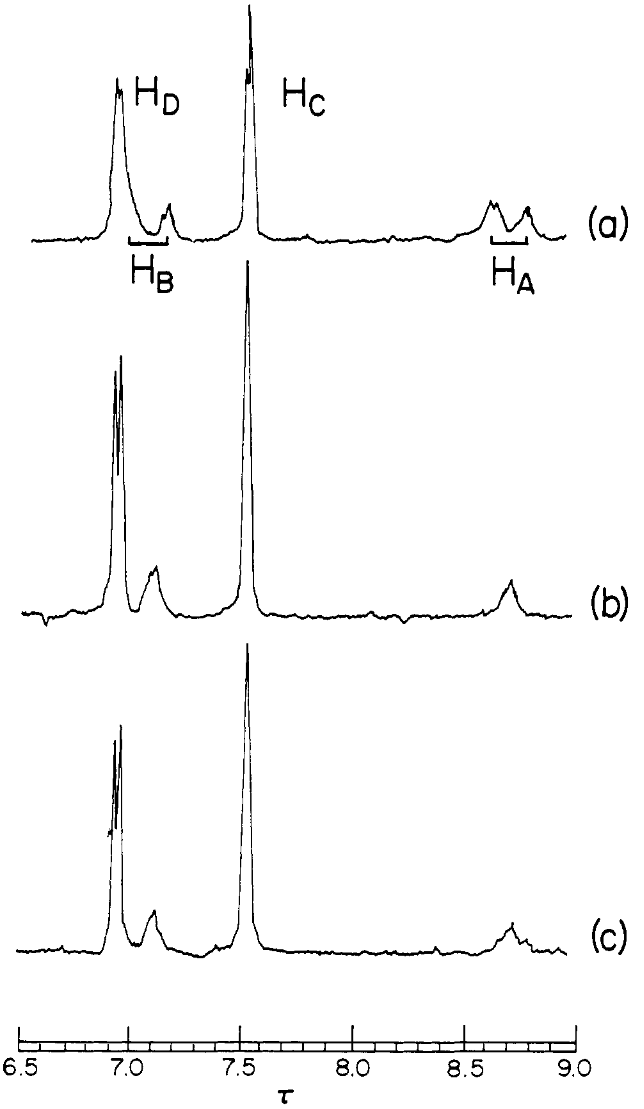

Figure 1. Pmr spectra of (a) **7**; (b) monodeuterio-**7** mixture resulting from reduction of **6**-Br; (c) monodeuterio-**7** mixture resulting from reduction of **5**-Br.

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(1) Paper LV: S. J. Cristol, G. O. Mayo, and G. A. Lee, *J. Amer. Chem. Soc.*, **91**, 214 (1969).

(2) One of us has reviewed the appropriate literature on this topic several times. Recent discussions may be found in (a) D. I. Davies and S. J. Cristol in "Advances in Free-Radical Chemistry," Vol. 1, G. H. Williams, Ed., Elek-Academic Press, London, 1965, Chapter 5; and (b) S. J. Cristol and R. V. Barbour, *J. Amer. Chem. Soc.*, **90**, 2832 (1968).

(3) J. Warkentin and E. Sanford, *ibid.*, **90**, 1667 (1968).