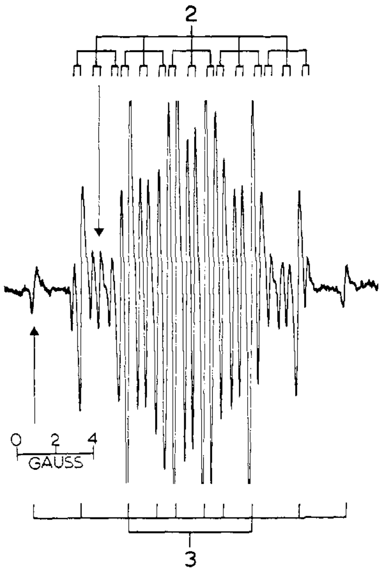

Figure 1. First-derivative esr spectrum of 7-deuteriobicyclo[2.2.1]-heptane-2,3-semidiones obtained from the 7-deuterionorbornene produced by the reaction of tri-*n*-butyltin deuteride with *syn*- or *anti*-7-bromonorbornene.

"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^{H}/a^{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^{H}/a^{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^{H}/a^{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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Received March 17, 1969

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

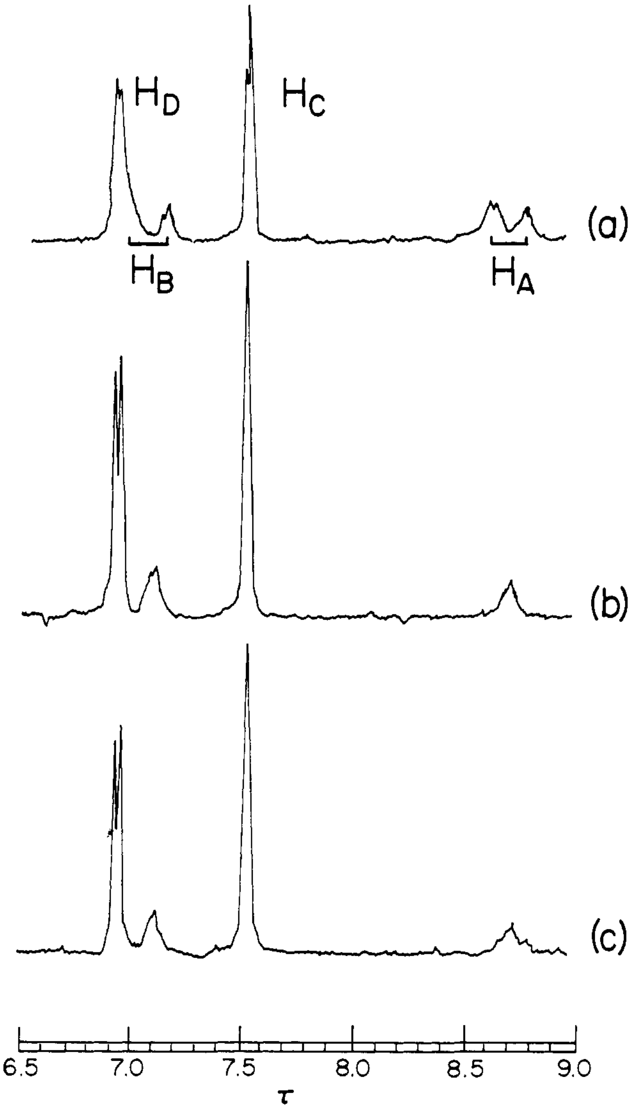

Figure 1. Pmr spectra of (a) **7**; (b) monodeuterio-**7** mixture resulting from reduction of **6**-Br; (c) monodeuterio-**7** mixture resulting from reduction of **5**-Br.

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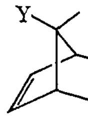
(1) Paper LV: S. J. Cristol, G. O. Mayo, and G. A. Lee, *J. Amer. Chem. Soc.*, **91**, 214 (1969).

(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).

tri-*n*-butyltin deuteride in hexane leads solely to *anti*-7-deuterionorbornene (**2**-D), and the rationalization that the intermediate 7-norbornenyl radical (**3**) is nonclassical (**4**) seemed to us very interesting and possibly incorrect.



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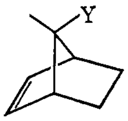

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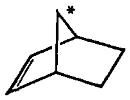

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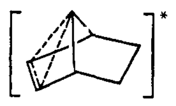
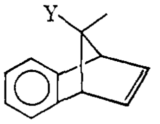


4

The analogous *syn*- (**5**-Cl) and *anti*-7-chlorobenzonorbornadienes (**6**-Cl) were available from previous work in our laboratory.[4,5] As both isomers have been shown[5] to solvolyze with retention of configuration, it was felt that a study of the reduction of these epimeric halides might offer pertinent information regarding the possibility of delocalized (or at least geometry-retaining) radical intermediates.



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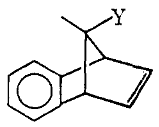

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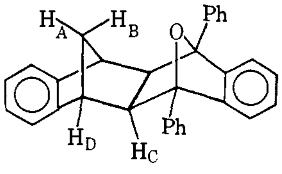

7

Unfortunately reduction of the chlorides did not occur (<10%) under mild conditions (30–60°, azobisisobutyronitrile (AIBN) initiation), and more strenuous conditions (85°, neat, sealed tube, AIBN) resulted in complications due to addition of tri-*n*-butyltin deuteride to the double bond. Since the reduction of bromides generally proceeds under milder conditions,[6] it was reasonable to use the corresponding bromides. *anti*-7-Bromobenzonorbornadiene (**6**-Br) had previously been prepared and characterized.[4,7] The *syn* epimer (**5**-Br), mp 63.0–64.0°, was prepared by the reaction of *syn*-7-benzonorbornadienyl acetate (**5**-OAc)[5] with *ca.* 1 *M* hydrogen bromide in glacial acetic acid for 10 min at 28°. The pmr spectrum of **5**-Br was very similar to the analogous **5**-Cl and distinct from those of the *anti* epimers **6**-Cl and **6**-Br.[4]

Reduction of both bromides at 60° in benzene (with AIBN) resulted in identical mixtures of *syn*- (**5**-D) and *anti*-7-deuteriobenzonorbornadiene (**6**-D). Direct pmr analysis of the epimeric 7-deuteriobenzonorbornadienes was not completely satisfactory owing to overlap of some proton absorptions.[4] Therefore a supplementary method of determining the product ratios was used. The Diels–Alder adduct (**7**)[8] of benzonorbornadiene and 1,3-diphenylisobenzofuran shows a clean separation of the two C-7 protons (see Figure 1). In the undeuterated adduct the C-7 proton (H_B) adjacent to the oxygen (τ 7.08) absorbs 1.65 ppm downfield from the proton (H_A) *syn* to the benzene ring (τ 8.73, $J_{gem} = 9$ Hz).[8] After treatment of the bromide with tri-*n*-butyltin deuteride, the entire reaction mixture was treated with 1 equiv of 1,3-diphenylisobenzofuran (sealed tube, 120°, 20 hr). The deuterated adducts were purified by repeated crystallization from ethanol–chloroform. Mass spectral analysis showed 99% deuterium incorporation. The pmr spectra ($CDCl_3$) (Figure 1) showed that the geminal coupling of the C-7 protons had disappeared, further evidence of complete deuteration at C-7. The ratio of proton peak areas showed that *anti* to *syn* deuteration in each case was 43:57 ± 3.[9]

These results would appear to be inconsistent with the reported[3] stereospecificity of reduction of the 7-bromonorbornenes. We have therefore compared the published spectra[3] for the reduction products with that[10] of authentic **2**-D (prepared[10] by the solvolysis of *anti*-7-norbornadienyl *p*-toluenesulfonate in the presence of sodium borodeuteride). Our comparison suggests that the apparent singlet at τ 8.93 in each of Warkentin's spectra[3] is due to the presence of *syn*-7-deuterionorbornene (**1**-D).[11] A rough analysis of the areas in the published spectra suggests that tin hydride reduction of both **1**-Br and **2**-Br leads to an approximately 70:30 mixture of *anti*- (**2**-D) and *syn*- (**1**-D) deuterionorbornenes.[12] These results seem then to be in agreement with those of benzo analogs and rule out any need to consider the existence of nonclassical radical intermediates.

Acknowledgments. The authors are indebted to the Institute of General Medical Services (Public Health Service Grant GM-12139) and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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(4) S. J. Cristol and G. W. Nachtigall, *J. Org. Chem.*, **32**, 3727, 3728 (1967).

(5) S. J. Cristol and G. W. Nachtigall, *J. Amer. Chem. Soc.*, **90**, 7132, 7133 (1968).

(6) H. G. Kuivila in "Progress in Organometallic Chemistry," G. A. Stone and R. West, Ed., Academic Press, New York, N. Y., 1964, p 71.

(7) J. W. Wilt, G. Gutman, W. J. Ranus, Jr., and A. R. Zigman, *J. Org. Chem.*, **32**, 893 (1967).

(8) G. W. Nachtigall, Ph.D. Thesis, University of Colorado, Boulder, Colo., 1968.

(9) Pmr analyses were conducted on Varian Associates HA-100 and A-60A instruments. All new compounds had satisfactory carbon–hydrogen analyses.

(10) A. P. Marchand and J. E. Rose, *J. Amer. Chem. Soc.*,, **90**, 3724 (1968).

(11) This proton is labeled H_c in Warkentin's spectra and the apparent doublet in the **1**-H (≡**2**-H) spectrum becomes an apparent singlet when the geminal hydrogen is replaced by a deuteron (**1**-D).

(12) Note Added in Proof. Dr. Warkentin has informed us that he has essentially confirmed our analysis of their mixture and that these results will be published later.

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Received November 30, 1968

Competitive 1,2 and 1,6 Cycloadditions to Bullvalene[1,2]

Sir:

Although recognition of the highly fluxional character of bullvalene (**1**) has engendered considerable interest in molecules which exhibit rapid and degenerate valence isomerization,[3] only two examples of electrophilic addition to **1** have been reported, these being bromination[4a] and chlorination.[4b] We have examined the

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(1) Unsaturated Heterocyclic Systems. LIX. For paper LVIII, note L. A. Paquette, T. Kakihana, J. F. Kelly, and J. R. Malpass, *Tetrahedron Letters*, 1455 (1969).

(2) Support of this research by the National Science Foundation is gratefully acknowledged.

(3) (a) G. Schröder, J. F. M. Oth, and R. Merenyi, *Angew. Chem. Intern. Ed. Engl.*, **4**, 752 (1965); (b) G. Schröder and J. F. M. Oth, *ibid.*, **6**, 414 (1967); (c) L. A. Paquette, J. R. Malpass, G. R. Krow, and T. J. Barton, *J. Am. Chem. Soc.*, in press.

(4) These halogenation reactions have been formulated as 1,4 additions: (a) J. F. M. Oth, R. Merenyi, J. Nielsen, and G. Schröder, *Chem. Ber.*, **98**, 3385 (1965); (b) J. F. M. Oth, R. Merenyi, H. Röttele, and G. Schröder, *Tetrahedron Lett.*, 3941 (1968).