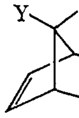
tri-*n*-butyltin deuteride in hexane leads solely to *anti*-7-deuterionorbornene (**2**-D), and the rationalization that the intermediate 7-norbornenyl radical (**3**) is nonclassical (**4**) seemed to us very interesting and possibly incorrect.



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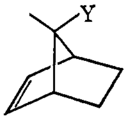

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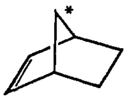

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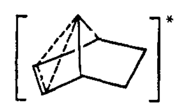

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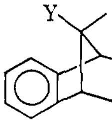
The analogous *syn*- (**5**-Cl) and *anti*-7-chlorobenzonorbornadienes (**6**-Cl) were available from previous work in our laboratory.[4,5] As both isomers have been shown[5] to solvolyze with retention of configuration, it was felt that a study of the reduction of these epimeric halides might offer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



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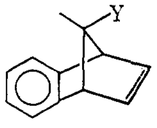

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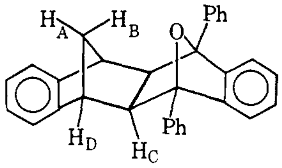

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Unfortunately reduction of the chlorides did not occur (<10%) under mild conditions (30–60°, azobisisobutyronitrile (AIBN) initiation), and more strenuous conditions (85°, neat, sealed tube, AIBN) resulted in complications due to addition of tri-*n*-butyltin 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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Received November 30, 1968

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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.

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).

intriguing possibility of achieving controlled 1,2 and 1,6 electrophilic cycloadditions to **1**, and wish to report our initial realizations of this goal.

Admixture of equimolar amounts of **1** and chlorosulfonyl isocyanate (CSI) in CH_2Cl_2 solution at 0°, followed by standing at ambient temperature for 15 min, hydrolysis with thiophenol–pyridine in acetone at 0°, and chromatography on Florisil gave lactone **5b** (mp 71–73°, 31%),[5] β-lactam **3b** $\rightleftarrows$ **4b** (mp 151–152°, 19%),[5] and lactam **6b** (mp 172–173°, 15%),[5] respectively, in order of elution. Significantly, if the solution was warmed to 40° for 2 hr prior to work-up, the yield of β-lactam dropped to only 2%; **5b** (15%) and **6b** (17%) were the remaining characterizable products. The progress of the cycloaddition reaction could be conveniently followed by both infrared and nmr spectroscopy. In the first instance, there appeared two bands at 1820 and 1770 cm^{-1} immediately upon preparation of a *ca.* 10% solution of **1** and CSI in $CHCl_3$ at room temperature. Repeated scanning of the 1600–2000-cm^{-1} region revealed a gradual diminution in the intensity of the 1820-cm^{-1} absorption due to **3a** → **4a** and a corresponding intensification of the 1770-cm^{-1} band. Nmr spectroscopy likewise demonstrated that although **3a** $\leftrightarrows$ **4a** was produced somewhat faster than either **5a** or **6a** at lower temperature (10°), the N-(chlorosulfonyl) β-lactams were thermodynamically unstable relative to **5a** and **6a** into which they were transformed quite rapidly at 38°. Of added relevance is the observation that execution of the cycloaddition under either of the two previous sets of conditions but with hydrolysis in a more polar medium (NaOH, aqueous acetone) gave good yields of **5b** and **6b**, and variable but low yields of β-lactam.

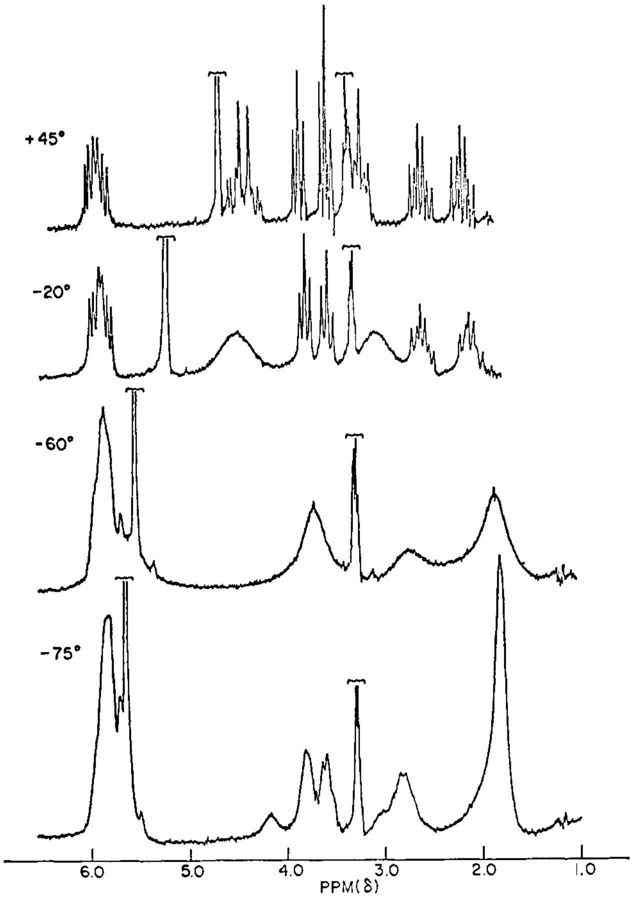
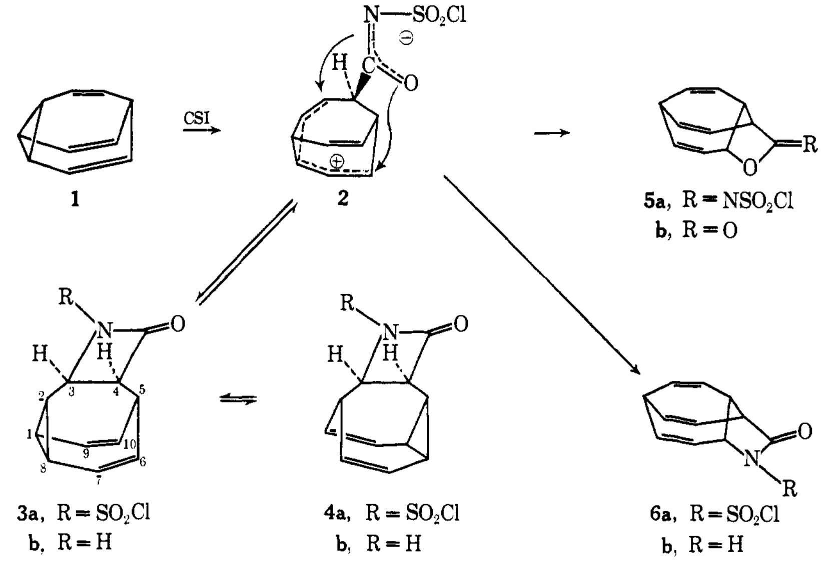


Figure 1. 100-MHz nmr spectra of **3b** $\leftrightarrows$ **4b** in CD_3OD at −75, −60, −20, and +45°. Peaks under the brackets are due to solvent.



The temperature dependence of the 100-MHz nmr spectra of β-lactam **3b** $\leftrightarrows$ **4b** ($\nu_{max}^{CHCl_3}$ 1752 cm^{-1}) is shown in Figure 1. Such behavior is now recognized to be typical of *cis*-fused bicyclo[5.1.0]octa-2,5-diene systems.[3] However, because valence isomers **3b** and **4b** are not structurally identical, a difference in ground-state populations is to be expected. Double-resonance experiments at 38° permitted detailed analysis of the spectrum and established, *inter alia*, that H-2 is spin-coupled to H-1, H-3, and H-8, whereas H-5 is spin-coupled to H-4, H-6, and H-10. The nmr spectra of numerous β-lactams attest to the fact that the proton adjacent to amide nitrogen invariably resonates at lower field than the α-carbonyl proton;[6] accordingly, H-3 and H-4 can be assigned with certainty to the triplet patterns at δ 3.79 and 3.51, respectively. Because of the low-field position (δ 4.38) of H-1 and H-8 in this temperature range, it follows that these two protons experience

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(5) Satisfactory elemental analyses (±0.3%) were obtained for all new compounds described herein.

(6) Unpublished results from this laboratory.

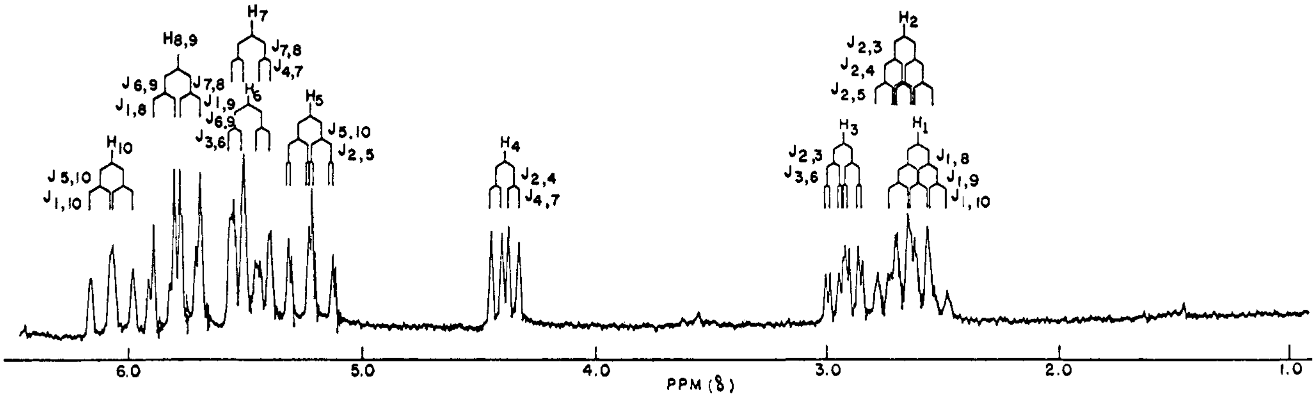


Figure 2. 100-MHz nmr spectrum of **5b** in C_6D_6 at ~38°

an average lifetime which has appreciable vinylic character; conversely, the chemical shift of H-6 and H-10 (δ 3.13) requires that these protons reside chiefly in a cyclopropyl environment. These observations are uniquely congruent with the conclusion that **4b** is more stable than **3b**.

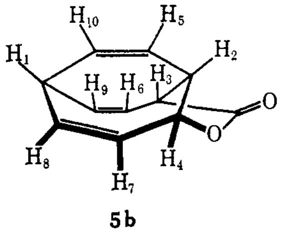
The equilibrium constant for this β-lactam mixture at any given temperature can, in principle, be calculated from the equations

$$\delta_m = p\delta_v + (1 - p)\delta_c$$

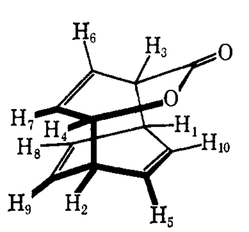
$$p = (\delta_m - \delta_c)/(\delta_v - \delta_c)$$

$$K_m = p/(1 - p)$$

where δ_m is the observed chemical shift at a temperature m of a proton undergoing rapid exchange, δ_v and δ_c are the chemical shifts, respectively, of the vinyl and cyclopropyl protons in the absence of rapid exchange, and p is the mole fraction of one of the isomers.[7] In the present instance, $\delta_v = 5.82$ and $\delta_c = 1.80$;[8] at 45°, δ_m for the signal due to H-1 and H-8 is seen to be 4.36 (Figure 1). Thus, the concentration of **4b** at this temperature is 64%. K_m is then calculated to be 1.78 which represents a standard free-energy difference ($\Delta G°_{45°}$) of 365 cal/mole. The cause of the intrinsically higher energy of **3b** is not known at this time.



5b



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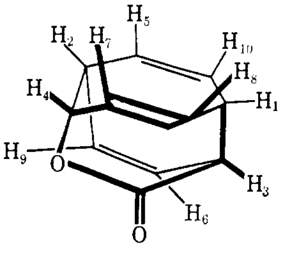

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The structure assigned to lactone **5b** rests firmly on spectral and chemical evidence. Thus, the substance was shown to be nonconjugated by the ultraviolet spectrum (C_2H_5OH, end absorption only), and the presence of the lactone function was apparent from the intense infrared (CCl_4) carbonyl stretching frequency at 1765 cm^{-1} with a shoulder at 1735 cm^{-1}. The 100-MHz nmr spectrum of **5b** in C_6D_6 was characterized by well-separated multiplets, spin decoupling of which permitted analysis of all the major coupling constants (Figure 2).[9] Catalytic hydrogenation of **5b** over 5% Pd–C in methanol solution resulted in the rapid uptake of 3 equiv of hydrogen to yield a hexahydro lactone, mp 170–172° (ν_{max} 1758 cm^{-1}).[5] The degree of unsaturation in this lactone, when coupled with the requirement that no conjugation be present, suggested the possibility of three structures: **5b**, **7**, and **8**. In view of the observed spin coupling between proton pairs H-2:H-3 (8.2 Hz) and H-2:H-4 (7.5 Hz), these three protons must exist in vicinal relationships. Furthermore, H-1 and not H-2 was affected on simultaneous irradiation of H-8, -9, and -10. On this basis, structures **7** and **8** can be removed from further consideration. In contrast, all of the observed chemical shifts and coupling constants are completely compatible with **5b**. Final confirmation for this assignment was obtained by ozonization of **5b**, decomposition of the ozonide with 30% hydrogen peroxide in aqueous formic acid,[10] and esterification with diazomethane; the principal (>90%) volatile product was identified as dimethyl malonate.

The structure of lactam **6b** [$\nu_{max}^{CHCl_3}$ 1696 cm^{-1}; uv (C_2H_5OH): shoulder at 247 nm (ϵ 650)] was assigned on the basis of a similar nmr analysis[11] and like degradation to dimethyl malonate. When **6b** was treated with trimethyloxonium fluoroborate in methylene chloride solution at room temperature for 6 hr, imino ether **9** [mp

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(7) For application of the same principle to conformational analysis, see (a) E. L. Eliel, *Chem. Ind.* (London), 78 (1959); (b) N. S. Bhacca and D. H. Williams, "Applications of Nmr Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, pp 153–154; see also (c) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 10.

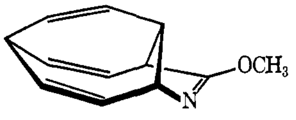
(8) These values are derived from spectra taken at −75° or below.

(9) The small allylic coupling constants have not been completely analyzed. Although it has proved possible to measure $J_{3,9}$ (1.7 Hz), $J_{1,5}$ (1.3 Hz), and $J_{4,8}$ (0 Hz), spin–spin interactions between $J_{1,6}$, $J_{1,7}$, and $J_{2,10}$, although present, were not measurable.

(10) The expected methanetricarboxylic acid is known to undergo decarboxylation to malonic acid under these conditions: J. N. Labows, Jr., J. Meinwald, H. Röttele, and G. Schröder, *J. Am. Chem. Soc.*, **89**, 612 (1967).

(11) To be described in detail at a future date in our full paper on this subject.

49-50°;[5] $\nu_{max}^{CHCl_3}$ 1634 cm^{-1}; uv (C_2H_5OH): shoulder at 245 nm (ε 165)] was obtained in 78% yield.



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Although these 1,2 and 1,6 additions to bullvalene can be satisfactorily represented by collapse of **2** *via* four- and five-centered transition states, a modification which includes concerted or nearly concerted addition of CSI to **1** and irreversible passage of **3a** to **2** cannot yet be excluded. Also, questions concerning the precise electronic character of the cationic moiety in **2** remain open and await answers which we hope to provide in due course.

Acknowledgment. We wish to thank Badische Anilin und Soda Fabrik for a generous gift of cyclooctatetraene which made this study possible.

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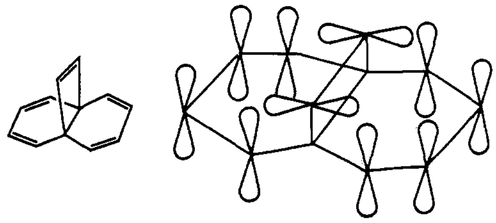
Received April 18, 1969

[4.4.2]Propella-2,4,7,9,11-pentaene[1]

Sir:

An awareness that the interrelationship between electronic interaction and the presence or absence of thermodynamic stabilization is a function of the geometry of orbital overlap (neutral molecules) and the sum and distribution of π electrons (charged species) has developed appreciably in recent years. For example, it is now clear that, whereas alignment of the terminal p orbitals of hexatriene within orbital overlap as in benzene produces aromatic stabilization, similar arrangement of the p orbitals of butadiene as in cyclobutadiene results in loss of delocalization energy.[2] Placement of three ethylenic moieties in a cylindrical array as in barrelene results in no obvious delocalization;[3] in contrast, the bicycloheptadien-7-yl cation is decidedly stabilized and bicycloaromatic.[4] To the present time, barrelene represents the only polyene with ($4n + 2$) p electrons arranged for orthogonal (or nearly orthogonal) interaction. We wish now to describe the synthesis and properties of [4.4.2]propella-2,4,7,9,11-pentaene (**1**), a system in which orthogonal overlap of two cyclobutene p orbitals with terminal p lobes of two cyclohexadiene units makes possible a unique form of interaction of ten π electrons along the top surface of the hydrocarbon.



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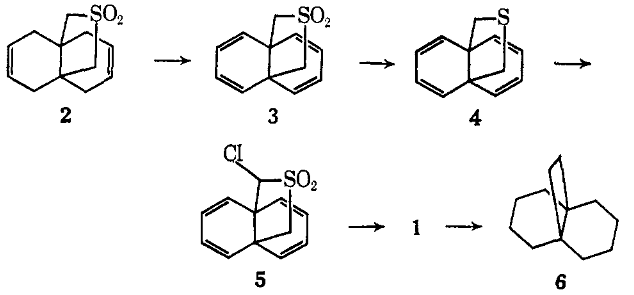
Dibromination of 12-thia[4.4.3]propella-3,8-diene 12,12-dioxide (**2**),[5] followed by direct dehydrobromination of the unpurified tetrabromide with sodium methoxide in refluxing anhydrous tetrahydrofuran, gave sulfone **3**, mp 160-162°,[6] in 45% yield; $\delta_{TMS}^{CDCl_3}$ 3.36 (singlet, 4 H, $-CH_2SO_2-$) and 5.82 (center of A_2B_2 pattern, 8 H, vinyl protons). Reduction of **3** with ethereal lithium aluminum hydride proceeded readily to give **4** in quantitative yield. This sulfide was chlorinated directly with N-chlorosuccinimide and oxidized with monoperphthalic acid, thus affording the critical α-chloro sulfone intermediate **5**, mp 151-153°,[6] in 42% over-all yield from **3**; $\delta_{TMS}^{CDCl_3}$ 5.14-6.47 (complex multiplet including sharp singlet at 5.29, 9 H, vinyl protons, and $-CHClSO_2-$), 3.56 and 3.30 (AB pair, $J = 13$ Hz, 2 H, $-CH_2SO_2-$). Exposure of **5** to a slurry of powdered potassium *t*-butoxide in anhydrous ether at ambient temperature for 4 hr resulted in smooth conversion to **1** which was purified by preparative vapor-phase chromatography at 110° (10% SE-30 on Chromosorb G, 14% isolated yield).[6,7] Hydrogenation of the colorless oil in methanol over 10% palladium on carbon proceeded with the constant uptake of 5 equiv of hydrogen and formation of previously characterized [4.4.2]propellane (**6**).[5,8]



The nmr spectrum of **1** demonstrated the presence of two cyclobutene (singlet, δ 5.90) and eight other vinyl protons (A_2B_2 pattern, δ 5.68). Its ultraviolet spectrum in isooctane displayed two maxima at 247 nm (ε 2500) and 290 nm (ε 2100). These spectral properties compare favorably with those of related cyclohexadienes (Table I) and support the conclusion that **1** is polyolefinic in nature.[9]

The cleavage of **1** into naphthalene and acetylene involves a ($_{\sigma}2_s + {}_{\sigma}2_s$) bond cleavage which on the basis of orbital symmetry considerations[10] is not likely to proceed thermally in concerted fashion. In actual fact, [4.4.2]propella-2,4,7,9,11-pentaene exhibited pronounced thermal stability as evidenced by essentially quantitative recovery from a gas chromatographic column maintained at 120° (residence time, 20 min).

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[1] α-Halo Sulfones. XIV. Part XIII is L. A. Paquette and J. C. Philips, *Chem. Commun.*, in press.

[2] M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 3255 (1965), and pertinent references cited therein.

[3] H. E. Zimmerman and R. M. Paufler, *ibid.*, **82**, 1514 (1960); H. E. Zimmerman and G. L. Grunewald, *ibid.*, **86**, 1434 (1964); C. F. Wilcox, Jr., S. Winstein, and W. G. McMillan, *ibid.*, **82**, 5450 (1960).

[4] M. J. Goldstein, *ibid.*, **89**, 6357 (1967).

[5] L. A. Paquette and J. C. Philips, *Tetrahedron Letters*, 4645 (1967).

[6] All new compounds cited herein gave acceptable (±0.3%) combustion analysis values.

[7] Calcd: *m/e* 154.0782. Found: *m/e* 154.0776.

[8] (a) E. Vogel, W. Maier, and J. Eimer, *Tetrahedron Letters*, 655 (1966); (b) J. J. Bloomfield and J. R. S. Irelan, *ibid.*, 2971 (1966); (c) J. Altman, E. Babad, J. Itzchaki, and D. Ginsburg, *Tetrahedron Suppl.*, **8**, 279 (1967).

[9] It is interesting to note, however, that the 290-nm band of **1** represents the longest wavelength absorption band yet reported for a cyclohexadienyl system.

[10] R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965).