

chloride (0.90 g, 3.85 mmol) was added over a 0.5-h period. The resulting suspension was stirred at -35°C for an additional half hour and then allowed to warm to room temperature and stirred for an additional 3 h. Hexane (50 mL) was added, the mixture cooled in ice and filtered. The solvents were evaporated under vacuum to leave 1.1 g of partially solid material, which was extracted with hexane, and the hexane was evaporated to leave 0.55 g of brown oil. Chromatography on neutral alumina (activity III) yielded hydrocarbon 1 (0.077 g, 0.38 mmol, 22%).

Reaction of 1 with Maleic Anhydride. A solution of hydrocarbon 1 (0.20 g, 0.97 mmol) and maleic anhydride (0.24 g, 2.4 mmol) in dry toluene was heated at reflux for 2.5 h. The solution was allowed to stand overnight at room temperature and the solvent evaporated under vacuum. The residue was heated at 105°C at a pressure of 0.3 Torr until sublimation of excess maleic anhydride was complete. The dark brown oil remaining crystallized on standing in the refrigerator. Recrystallization from ether yielded adduct 12 (0.081 g, 0.27 mmol, 29%) as white needles: mp $178-180^{\circ}\text{C}$; $^1\text{H NMR}$ δ 1.02 (s, 3 H), 3.23-3.50 (m, 2 H), 3.60-4.00 (m, 2 H), 5.30 (s, 1 H), 5.63 (s, 1 H), 6.32-6.50 (m, 3 H), 7.07-7.30 (m, 3 H), 7.40-7.65 (m, 1 H). Anal. Calcd for $\text{C}_{20}\text{H}_{16}\text{O}_3$: C, 78.93; H, 5.30. Found: C, 78.91; H, 5.29.

Photorearrangement of Hydrocarbon 1. A stream of argon was bubbled through a solution of 1 (0.224 g, 1.09 mmol) in 20 mL of benzene in a Pyrex flask for 10 min, and the solution was then irradiated by a GE 275-W sun lamp for 18 h. GLPC analysis by comparison with standard solutions on a 6-ft 3% SE-30 Chromosorb W column at 180°C showed the solution to contain 0.15 mmol (14%) of 1,10-dimethylantracene. Chromatography on alumina, eluting with petroleum ether, followed by recrystallization from benzene-hexane, yielded 7 mg (3.4 mmol, 3%) of pure 1,10-dimethylantracene.

1,10-Dimethylantracene. A solution of methylolithium in hexane (1.55 M, 5 mL, 7.75 mmol) was added to a stirred solution of 4-methylantrone¹² (0.62 g, 3.0 mmol) in 25 mL of anhydrous ether. Water was added and the ether layer was washed with water and with brine and dried over magnesium sulfate. Evaporation of the solvent left a yellow powder, which was chromatographed on Florisil, eluting with 10% dichloromethane in petroleum ether, to yield 1,10-dimethylantracene (0.405 g, 2.0 mmol, 67%) as yellow crystals: mp $127-128^{\circ}\text{C}$; $^1\text{H NMR}$ δ 2.82 (s, 3

H), 3.05 (s, 3 H), 7.28-7.60 (m, 4 H), 7.95-8.44 (m, 3 H), 8.48 (s, 1 H); IR (mineral oil) 868, 831, 789, 722 cm^{-1} ; UV (hexane) λ_{max} 342 (ϵ 4350), 358 (7550), 377 (12080), 398 (12090). Anal. Calcd for $\text{C}_{16}\text{H}_{14}$: C, 93.16; H, 6.84. Found: C, 92.95; H, 6.99.

Thermal Rearrangement of 1. a. In Diphenyl Ether Solution. Diphenyl ether (5 mL) was heated at $154-155^{\circ}\text{C}$ and degassed with a stream of argon. Hydrocarbon 1 (0.087 g, 0.42 mmol) was added and heating was continued under an argon atmosphere for 28 min. The solution was cooled in ice and analyzed by GLPC on a 6-ft, 3% OV 101 on Chromosorb W column at 170°C . In addition to a peak for residual 1 (t_{R} 10.4 min), new peaks were present at retention times of 8.7 and 9.2 min. These components were identified by GC/MS as 9-methylantracene and 9-ethylantracene, respectively. Calibration against standard solutions showed that 9-methylantracene and 9-ethylantracene were obtained in 4% and 27% yields, respectively, together with 9% of recovered 1.

Reactions at higher temperatures or in tetralin solutions were carried out by the same procedure.

b. In *N,N*-Dimethylaniline Solution. A solution of hydrocarbon 1 (0.157 g, 0.76 mmol) in 5 mL of *N,N*-dimethylaniline was heated at reflux in the dark under an atmosphere of argon for 2.5 h. The solution was allowed to cool, and water and 1 M hydrochloric acid were added. The resulting mixture was extracted with ether and the ether layer was washed with water and with brine and dried over magnesium sulfate. Evaporation of the solvent left 0.150 g of a viscous red oil. GLPC analysis showed the absence of 1 and the presence of 9-methylantracene (6%) and 9-ethylantracene (31%).

c. In the Absence of Solvents. A Pyrex tube (15.0 \times 0.8 cm) filled with Pyrex beads (ca. 0.4 cm in diameter) was heated to 375°C by electrical heating tape. A stream of argon was passed through the tube and hydrocarbon 1 (0.20 g, 1.0 mmol) was dropped into the tube, which was then immediately cooled in dry ice. The reaction product was dissolved in dichloromethane and the solvent evaporated to give 0.2 g of a red oil, which was analyzed by GLPC.

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Stereochemistry of Hydride Reductions of 4,8-Dihalo-2-thiaadamantanes and Related Thiabicyclo[3.3.1]nonanes

Raymond C. Fort, Jr.,*¹ Martha H. Stahl, and Anthony F. Sky

Departments of Chemistry, The University of Maine, Orono, Maine 04469, and Kent State University, Kent, Ohio 44242

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LiAlD_4 reductions of *anti*-4,8-dihalo-2-thiaadamantanes and *anti*-2,6-dihalo-9-thiabicyclo[3.3.1]nonanes in ether and THF solution occur with complete retention of configuration. Participation by sulfur to form intermediate thiiranium ions is the most likely explanation for this behavior. Reaction of the thiabicyclononanes with LiEt_3BD involves chiefly elimination; single-electron transfer is a significant (20-25%) pathway in the reaction of LiEt_3BD with the thiaadamantane.

Introduction

A neighboring heteroatom might affect the hydride reduction of an alkyl halide in several ways: (a) by nucleophilic participation to form an intermediate onium ion, leading to reduction with retention of configuration; (b) by formation of a monodentate complex with the reagent, delivering hydride intramolecularly (retention or inversion); (c) by formation of a bidentate complex of halide, neighboring group, and reagent, to be attacked by a second molecule of reductant (inversion); (d) by altering the reduction potential of the C-X bond so as to make single-

electron-transfer (SET) reduction more or less likely (no stereoselectivity); or (e) by a steric effect.

The possibility of effecting a choice among these mechanisms by appropriate selection of heteroatom and reagent, and thereby controlling the stereoselectivity of the reduction, seems to us a goal of some importance, given the widespread use of such reductions in synthesis. We therefore have begun to examine a number of systems suitable for the observation of each kind of behavior.

In this paper, we report our examinations of the stereochemical course of LiAlD_4 and LiEt_3BD reductions of

Table I. Yields and Deuterium Incorporation^a

substr	reducing agent	solvent	yield, %	% d ₁	% d ₂
1	LiAlD ₄	Et ₂ O	99	4.9	94.5
1	LiAlD ₄	THF	36	5.2	94.3
2	LiAlD ₄	THF	92	5.8	93.0
1	LiEt ₃ BD	THF	7	7.3	91.9
2	LiEt ₃ BD	THF	17	6.4	93.0
3	LiAlD ₄	Et ₂ O	78	3.6	96.2
3	LiAlD ₄	THF	53	7.8	92.0
3	LiEt ₃ BD	THF	27	55.8	43.0
3	LiAlH ₄	THF	75	10.4	5.1
3	(0.27 equiv of DCPD)				
3	LiEt ₃ BH	THF	26	9.6	4.4
	(0.30 equiv of DCPD)				

^a Deuterium incorporations are regarded as accurate to ±1%.

Table II. Deuterium Chemical Shifts of Reduction Products^a

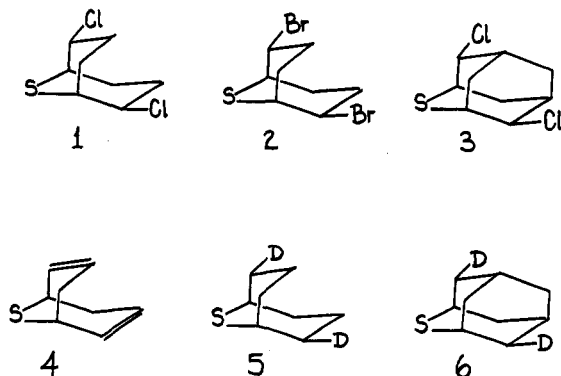
sulfide	chem shift	Pr(fod) ₃ shift
thiabicyclononane (5)	1.93	5.37
thiaadamantane (6)	2.09	5.63
authentic <i>syn</i> -bicyclononane (9)	2.14	13.78

^a Chemical shifts are referenced to CDCl₃ = 7.27 ppm; Pr(fod)₃ shift refers to the change in chemical shift calculated for a 1:1 mole ratio of shift reagent and sulfone.

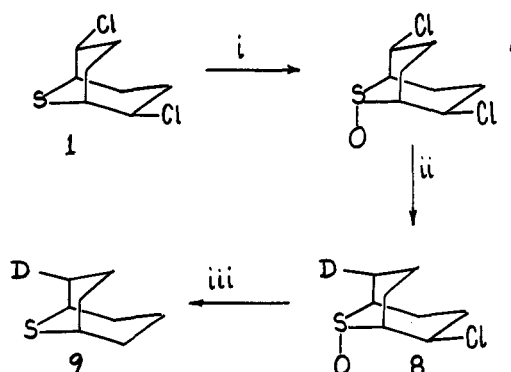
some thiaadamantanes and thiabicyclononanes. These substrates were chosen because earlier work in several laboratories had indicated them to form thiiranium ions with ease^{2,4b,7} and because the reduction of one of them with LiAlD₄ has previously been reported⁴ to occur with retention of configuration.

Results and Discussion

The necessary starting materials, compounds 1–3, were prepared by literature methods^{3,4} and subjected to reduction with LiAlD₄ or LiEt₃BD to yield sulfides 5 and 6. The results are shown in Table I.



The stereochemistry of the deuterium in the sulfides 5 and 6 was determined by ²H NMR spectroscopy, demon-

Scheme I. Synthesis of Authentic *Syn* Deuteriated 9^a

^a i = VaSO₄, H₂O₂; ii = LiEt₃BD, THF; iii = LiAlH₄, Et₂O.

strated by Nordlander⁶ to be a particularly effective method.⁶ As shown in Table II, each sulfide gave a single deuterium resonance, thus indicating that both deuterium atoms have the same stereochemistry. That the stereochemistry is anti,anti rather than syn,syn is demonstrable in two ways.

First, we prepared a compound having the deuterium authentically *syn* to the sulfur (Scheme I). Oxidation⁷ of 1 with hydrogen peroxide and vanadyl sulfate gives the sulfoxide 7 in which the oxygen both prevents nucleophilic participation by sulfur and blocks S_N2 displacement of the halogen on the same face of the sulfur. Reduction of 7 with LiEt₃BD proceeds with inversion of configuration at the unblocked site to form *syn*-deuteriated monohalosulfide 8 (59%). Reduction with LiAlH₄ now removes both the oxygen and the remaining halogen, producing 9 (59%), which has a distinctly different ²H chemical shift from the sulfide produced by direct reduction.

However, attempts to prepare a similarly authentic sample of a *syn*-deuteriothiaadamantane were thwarted when the thiaadamantane sulfoxide failed to react with LiEt₃BD, even under forcing conditions. Consequently, we turned to the use of a shift reagent, Pr(fod)₃, to demonstrate the spatial relationship of the S and D atoms.

Pr(fod)₃ does not complex strongly enough with sulfides to provide significant shifts of the deuterium resonances. However, conversion of the sulfides to the sulfones (H₂O₂ + VaSO₄), which do form strong complexes with Pr(fod)₃, allowed the observation of substantial shifts (Table II).

As the concentration of the shift reagent is increased, the deuterium resonances of the sulfones from 5 and 6 move steadily upfield. Extrapolation to a 1:1 mole ratio of shift reagent and sulfone yields a value for the chemical shift change in the complex of 5.63 ppm for 5 and 5.37 ppm for 6. These compounds clearly have the same stereochemistry for their deuteriums.

The sulfone from sulfide 9 likewise experiences an upfield shift of the deuterium resonance; however, in this case, the chemical shift change for the 1:1 complex is 13.78 ppm. The deuterium in this sulfone must lie distinctly closer to the Pr than the deuteriums in the other compounds. The deuterium in 9 is thus demonstrated to be *syn*, as expected from the mode of preparation of 9, and the distinctly different deuteriums in 5 and 6 are anti.

Thus, all of the deuterium introduced into 1–3, regardless of substrate or reducing agent, has entered with retention of configuration. The clear implication is that the thiiranium ions, 10 and 11, are easily accessible, even under the mild conditions of the reductions.

The LiAlD₄ reductions proceed cleanly, to give high yields of reduced material with high deuterium incorporation. The LiEt₃BD reductions, on the other hand, give

(1) To whom inquiries should be directed at the University of Maine.

(2) Flood, T. A. Ph.D. Dissertation, Kent State University, 1979.

(3) Labows, J. N., Jr.; Landmesser, N. *J. Org. Chem.* 1975, 40, 3798.

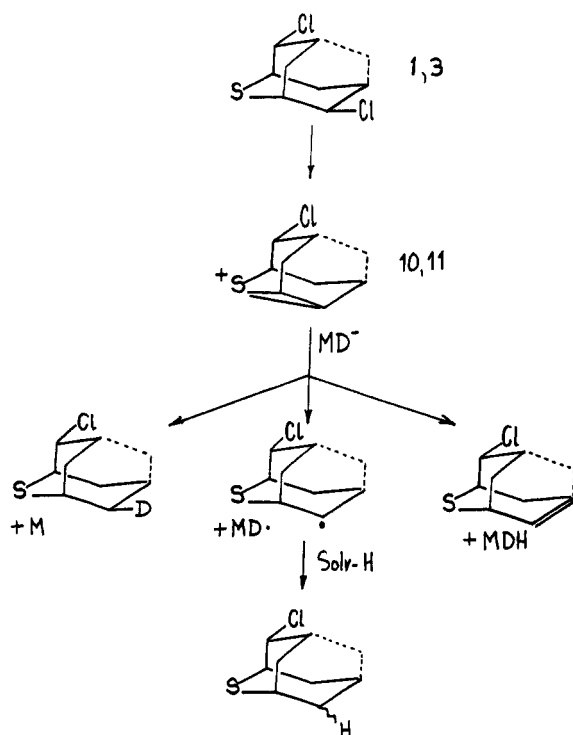
(4) (a) Stetter, H.; Schwartz, E. F. *Chem. Ber.* 1968, 101, 2464. (b) Corey, E. J.; Block, E. *J. Org. Chem.* 1966, 31, 1663.

(5) (a) Nordlander, J. E.; Haky, J. E. *J. Org. Chem.* 1980, 45, 4780. (b) Nordlander, J. E.; Haky, J. E. *J. Am. Chem. Soc.* 1981, 103, 1518.

(6) The usual method of determining deuterium stereochemistry is observation of the C–D stretch in the infrared, which allows assignment of axial or equatorial ligature; in the thiaadamantane, a D that is axial to one ring is equatorial to the other. We observed a peak at 2135 cm⁻¹ in the IR spectrum of 5 and one at 2130 cm⁻¹ in the IR spectrum of 6, both of which we assign to the C–D stretch.

(7) Weil, E. D.; Smith, K. J.; Gruber, R. J. *J. Org. Chem.* 1966, 31, 1669.

Scheme II. Mechanism of Reductions



low yields of reduction product and variable deuterium incorporation. The major product when compounds 1 and 2 are reduced with LiEt_3BD appears to be the diene 4, resulting from double dehydrohalogenation. Proton abstraction is not unknown behavior for LiEt_3BD ; Brown⁸ has reported formation of alkenes from halides such as 2-bromo-2-methylpentane and bromocyclohexane. Compound 3, which cannot undergo elimination, is nearly inert to LiEt_3BD , and evidence appears of a new mode of reduction.

The alternate mode of reaction is signaled by the observation that of the small amount of reduction product obtained from 3 and LiEt_3BD , about half contains only one deuterium. As Ashby has shown,⁹ the incorporation of protium during reductions with deuteride reagents is a signal of the reaction's taking an SET pathway, at least in part. We sought confirmation of this mechanism by conducting the reaction of 3 and LiEt_3BH in the presence of $(\text{C}_6\text{H}_{11})_2\text{PD}$ (DCPD), a well-known⁹ radical scavenger. In this case, the introduction of deuterium would confirm the intervention of SET.

In the event, a 27% yield of reduction product was obtained, 14% of which contained at least one deuterium. SET clearly is operating in this reduction. Repetition of this experiment with LiAlH_4 and DCPD also gave significant incorporation of deuterium, indicating that in these cases as well, some SET is occurring, accounting for the undeuterated reduction product. In order to reconcile these observations with the completely retained stereochemistry of the deuterated reduction product, we suggest that SET and deuteride (hydride) transfer both involve the thiiranium ion; that is, no $\text{S}_\text{N}2$ displacement at all occurs in these reductions. Although both SET and elimination could occur from neutral substrate, the thiiranium ions are expected to be more reactive in both processes, and so are written as the sole reacting species.

Scheme II summarizes these ideas. A thiiranium ion, once formed, has three possibilities for further reaction. It can accept a D from the reagent, forming deuterated reduction product with retention of configuration. It can donate a proton to the reagent, producing alkene. It can accept a single electron from the reagent, yielding a radical that then abstracts H from the solvent to give reduced material not containing deuterium. When protio reagents and DCPD are present, H transfer competes with D abstraction from the DCPD.

With the small reagent, LiAlD_4 , deuteride transfer predominates. When the reagent is bulkier (LiEt_3BD), transfer of D is hindered but still leads to some retained product. In the bicyclononanes, competition from elimination becomes effective. In the adamantane, which cannot eliminate, SET becomes the effective competitor.

Summary. Our results thus demonstrate that thiiranium ions can be derived from compounds 1–3 under mild conditions, and with an appropriate choice of reagent, can be used to favor retention of configuration in hydride reduction. Conversion of the sulfide to the sulfoxide prevents thiiranium ion formation and in unhindered systems leads to reduction with inversion. We are extending these investigations to other, synthetically more important systems.

Experimental Section

Materials. Reagent grade tetrahydrofuran (THF) was distilled from lithium aluminum hydride and used immediately. Reagent grade anhydrous diethyl ether was used as received from Fisher Scientific. Lithium aluminum deuteride (98 atom % D) and lithium triethylborodeuteride (98 atom % D; 1.0 M solution in THF) were obtained from Aldrich Chemical Company and used as received. Deuteriated dicyclohexylphosphine,⁹ *anti,anti*-2,6-dichlorothiabiacyclo[3.3.1]nonane,⁴ *anti,anti*-2,6-dibromothiabiacyclo[3.3.1]nonane,⁷ and *anti,anti*-4,8-dichloro-2-thiaadamantane⁴ were all prepared according to literature procedures. Shift reagents $\text{Eu}(\text{fod})$ and $\text{Pr}(\text{fod})$ were obtained 99% pure from Aldrich and used as received. Thin layer chromatography employed Kodak Chromatogram silica gel sheets, and flash chromatography was performed with Merck silica gel, grade 60, 230–400 mesh.

General Procedures. All reductions were performed under argon. Calibrated syringes equipped with stainless steel needles were used for transfer of reagents. Glassware and syringes were baked overnight at 110 °C, assembled while hot, and cooled while connected to a CaCl_2 drying tube. Melting and boiling points are uncorrected.

Reductions were conducted in round-bottom flasks equipped with condenser, argon inlet tube, and Teflon-coated magnetic stirring bar. Solvents and reagents were syringed into the flask as it was momentarily disconnected from the argon flow. After complete reaction, the argon was disconnected and the mixture was hydrolyzed with either water or saturated sodium sulfate solution. When DCPD was a reactant, it was mixed with the metal hydride, and the halide was added to the mixture.

NMR spectra were obtained at Kent State with a Varian FT-80 spectrometer, and at the University of Maine with a Varian XL-200 spectrometer. Deuteriochloroform was employed as solvent unless otherwise noted, with Me_4Si as the internal standard. Deuterium NMR spectra were obtained on CHCl_3 solutions with CDCl_3 at natural abundance as an internal reference. Proton-coupled ^2H spectra were obtained in the unlocked mode with the magnet shimmed on pure CDCl_3 prior to each spectrum. Assignments in ^{13}C spectra agree with the literature.¹⁰ Infrared (IR) spectra were obtained with a Perkin-Elmer 283 infrared spectrophotometer. Mass spectral analysis and deter-

(8) Krishnamurthy, S.; Brown, H. C. *J. Org. Chem.* 1983, 48, 3085.
 (9) (a) Ashby, E. C.; DePriest, R. N.; Goel, A. B.; Wenderoth, B.; Pham, T. N. *J. Org. Chem.* 1984, 49, 3545. (b) Ashby, E. C.; Wenderoth, B.; Pham, T. N.; Park, W.-S. *Ibid.* 1984, 49, 4505.

(10) (a) McCabe, P. H.; Nelsen, C. R. *J. Magn. Reson.* 1976, 22, 183.
 (b) Wiseman, J. R.; Krabbenhoft, H. O.; Anderson, B. R. *J. Org. Chem.* 1976, 41, 1518. (c) Morland, R. B. Ph.D. Dissertation, Kent State University, 1978. (d) Flood, T. A. Ph.D. Dissertation, Kent State University, 1980; among many.

mination of deuterium incorporation were performed with a Hewlett-Packard 5985 GC/MS system. Deuterium incorporations are not corrected for ^{13}C and ^{34}S contributions.

anti,anti-2,6-Dichloro-9-thiabicyclo[3.3.1]nonane 9-Oxide (7). To a stirred solution of 2.0067 g (0.0095 mol) of *anti,anti*-2,6-dichloro-9-thiabicyclo[3.3.1]nonane (I) in 30 mL of acetone was added 1 mL of 30% H_2O_2 and a catalytic amount of VSO_4 . The solution was stirred 24 h at room temperature and diluted with enough water to cause precipitation of 7 as a white solid. Filtration yielded 2.1 g of 7 (97.3%): mp 119–120 °C (lit.⁷ mp 121–122 °C); ^1H NMR 1.55–2.8 (m, 8 H), 3.3 (br s, 2 H), 4.3 (m, 1 H), 4.95 (m, 1 H); ^{13}C NMR 17.1 (C4), 20.9 (C8), 31.0 (C3, C7), 52.4 (C2), 54.2 (C1, C5), 56.1 (C6); IR (CHCl_3 reference cell) 2981, 1485, 1045 (S–O stretch) cm^{-1} ; mass spectrum, m/e (relative intensity) 239 (2.0) = M^+ , 223 (67.3), 221 (100), 203 (32.3), 117 (29.3), 91 (41.7), 79 (35.6), 77 (43.0).

anti,syn-2-Chloro-6-deuterio-9-thiabicyclo[3.3.1]nonane 9-Oxide (8). To a stirred solution of 1.502 g (0.0066 mol) of *anti,anti*-2,6-dichloro-9-thiabicyclo[3.3.1]nonane 9-oxide (7) in 15 mL of anhydrous tetrahydrofuran (THF) under nitrogen was added 30 mL of 1.0 M lithium triethylborodeuteride (Super-Deuteride) in THF. The mixture was refluxed for 7 days and then quenched cautiously with 5 mL of water. An additional 50 mL of water was added and the aqueous layer was extracted with ether (3 \times 50 mL). The combined ether extracts were dried (Na_2SO_4) and the solvent was stripped. The resulting yellow oil was dissolved in CHCl_3 and stirred over basic alumina to remove traces of boron compounds. The alumina was removed by filtration and the chloroform stripped to yield 0.31 g (58.6%) of 8: mp 117–118 °C; ^1H NMR 1.4–3.4 (br m, 11 H), 4.75–5.25 (m, 1 H); ^{13}C NMR 19.4, 21.9, 23.9, 27.3, 29.21, 29.18, 31.5, 47.5, 53.1; ^2H NMR 2.02; IR (CHCl_3 reference cell) 2985, 1485, 1035 (S–O stretch) cm^{-1} .

syn-2-Deuterio-9-thiabicyclo[3.3.1]nonane (9). To a stirred solution of 0.705 g (0.0036 mol) of *anti,syn*-2-chloro-6-deuterio-9-thiabicyclo[3.3.1]nonane 9-oxide (8) in 20 mL of anhydrous diethyl ether was added 0.7074 g (0.0168 mol) of lithium aluminum hydride. The mixture was stirred 24 h at room temperature under nitrogen and quenched by cautious addition of saturated Na_2SO_4 solution. The lithium salts were removed by suction filtration and the filtrate was dried over anhydrous Na_2SO_4 . Solvent was stripped and the crude residue was purified by sublimation (100 °C, 20–25 mmHg) to yield 0.306 g (58.6%) of 9, mp 164–166 °C (sealed capillary): ^1H NMR 1.5–2.3 (br m, 11 H), 2.85 (br s, 2 H); ^{13}C NMR 21.5 and 21.6 (C3, C7), 31.7 (C6, D-coupled triplet, J : 50 Hz), 32.1 (C2, C4, C8), 33.2 (C1, C5); ^2H NMR 2.14; IR (film) 2980, 1485 cm^{-1} .

anti,anti-2,6-Dideuterio-9-thiabicyclo[3.3.1]nonane (5). Reduction of 2.052 g (0.0097 mol) of 1 in 50 mL of dry diethyl ether with 0.233 g (0.0055 mol) of lithium aluminum deuteride

was conducted as described in the general procedure. The yield was 1.395 g (99.6%) of 5: mp 173 °C (sealed capillary); ^1H NMR 1.6–2.3 (m, 11 H) 2.8 (br s, 2 H); ^{13}C NMR 21.5 (C3, C7), 31.8 (C2, C6; D-coupled triplet; J = 45 Hz), 32.0 (C4, C8), 33.1 (C1, C5); ^2H NMR 1.9; IR (film) 2980, 1483 cm^{-1} ; mass spectrum, m/e (relative intensity) 144 (63.5 = M^+ , 143 (3.5), 142 (0.4), 115 (32.1), 102 (91.2), 88 (100), 68 (44.1).

Reduction of 0.813 g (0.0027 mol) of 2 in 20 mL of THF with 0.248 g (0.0059 mol) of lithium aluminum deuteride as described in the general procedure yielded 0.358 g (91.6%) of 5, mp 168–169 °C (sealed capillary). Spectral properties were the same as those reported above.

Reduction of 2.001 g (0.0095 mol) of 1 in 10 mL THF with 38 mL of 1.0 M Super-Deuteride in THF according to the general procedure gave an oil, the principle component of which, according to the ^{13}C NMR spectrum, was 9-thiabicyclo[3.3.1]nonadiene. Reduced material was isolated by crystallization from methanol and sublimation, leading to 0.095 g (6.9%) of 5, mp 164–165 °C (sealed capillary). Spectral properties were the same as those reported above.

Reduction of 4.023 g (0.134 mol) of 2 in 20 mL of THF with 50 mL of 1.0 M Super-Deuteride in THF according to the general procedure gave an oil containing diene. Pure reduction product was obtained by recrystallization for methanol–ether and sublimation: 0.0304 g (17%), mp 164–165 °C (sealed capillary). Spectral properties were the same as those reported above.

anti,anti-4,8-Dideuterio-2-thiaadamantane (6). Reduction of 0.603 g (0.0027 mol) of 3 in diethyl ether with 0.475 g (0.0113 mol) of lithium aluminum deuteride according to the general procedure gave 0.326 g (77.6%) of 6: mp 287–289 °C (sealed capillary); ^1H NMR 1.8–2.3 (m, 11 H), 2.8 (br s, 2 H); ^{13}C NMR 27.2 (C5, C7), 33.6 (C1, C3), 36.9 (C6), 38.5 (C9, C10), 38.1 (C4, C8; D-coupled triplet, J = 45 Hz); ^2H NMR 2.09; IR (film) 2900, 2840, 1300 cm^{-1} ; mass spectrum m/e (relative intensity) 156 (100) = M^+ , 155 (3.7), 154 (0.2), 98 (15.6), 81 (22.6), 80 (75.7), 79 (40.3).

Reduction of 1.000 g (0.0045 mol) of 3 in 16 mL of THF with 18 mL of 1.0 M Super-Deuteride in THF yielded 0.166 g (23.6%) of 6, mp 284–285 °C (sealed capillary). Spectral properties were the same as those reported above.

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