maxima have been observed. The ϕ^{rel}_f and τ^{rel}_f changes can be attributed to the solvent effects on the rate of intersystem crossing caused by changes in relative energies of the $^1n,\pi^*$ (S_1) and $^3\pi,\pi^*$ (T_2) states. The dependency of λ^{fl}_{max} and ϕ^{rel}_f on the solvent character may make the fluorescence technique a useful probe for molecular environment of lasalocid and can be used conveniently for complexation, ionization, and other physicochemical studies that bring about a change in the molecular environment.

Experimental Section

Lasalocid sodium salt was obtained in a 99+% purity from Aldrich Chemical Co., Milwaukee, WI, and was used without further purification. All solvents were reagent grade and stored over molecular sieves prior to use.

Relative quantum yields of fluorescence for lasalocid were obtained by using an Aminco-Bowman spectrofluorometer. Ultraviolet spectra were recorded in a Bausch and Lomb Spectronic 2000 spectrophotometer.

A stock solution of 1×10^{-2} M lasalocid sodium was prepared in methanol. Appropriate dilutions were made in various solvents to give a final lasalocid concentration of 2 μM. In the final solutions, the concentration of methanol never exceeded 1% v/v. The fluorescence intensity–concentration relationship for lasalocid was linear at the final concentration in all of the solvents used.

Registry No. Sodium lasalocid, 25999-20-6.

Micelle-Mediated Organic Synthesis: The Synthesis and Characterization of Three New Polycyclic Dioxa Cage Compounds

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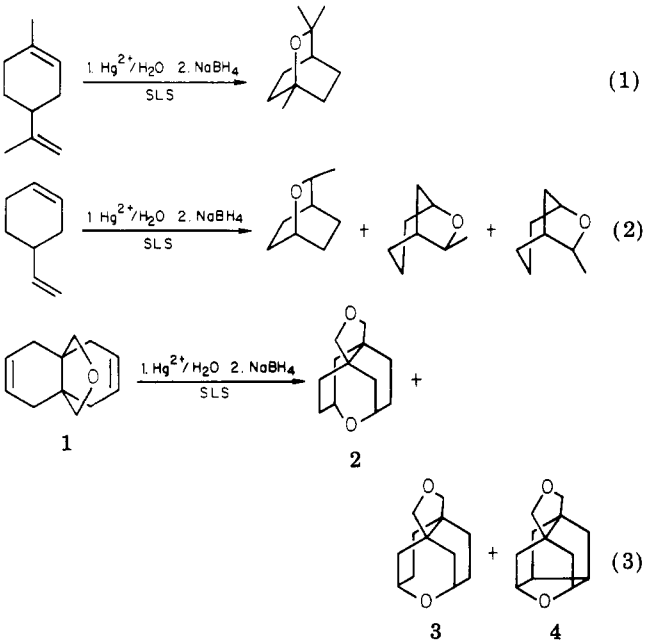
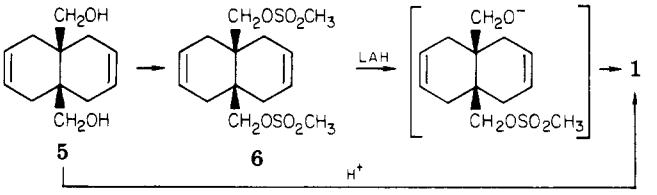
As part of our program in selective micellar catalysis of organic reactions,[2,3] we have identified a number of ways in which anionic micelles can direct the course of olefin hydroxymercuration.[2] One such perturbation is the ability of the micelle to favor the formation of cyclic ethers instead of diols in the reactions of various α,ω dienes. Examples of this cyclization are shown in eq 1 and 2.[2a] We have now applied this principle to propelladiene 1 and have succeeded in generating three new cage compounds as per eq 3. We report below a modified synthesis of 1 as well as the details of its conversion, in the presence of sodium lauryl sulfate (SLS), into cyclic ethers 2–4.[4]



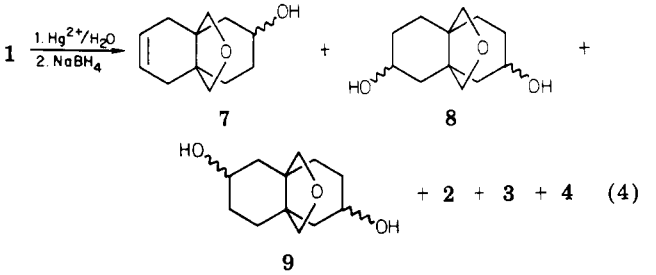
Scheme I



Results and Discussion

Synthesis of 1. The synthesis of diol 5 from butadiene and acetylenedicarboxylate, as well as its acid-catalyzed cyclization to 1 have been reported[5] (Scheme I). We have found that the conversion of 5 to its dimesylate 6 and treatment of 6 with LAH in THF gives an excellent yield of 1 via S–O bond cleavage and intramolecular trapping of the incipient alkoxide (Scheme I).

Hydroxymercuration of 1. When diene 1 is treated with aqueous $Hg(OAc)_2$, a variety of products are formed (eq 4). We have previously reported the successful con-



version of 1 to 7 by the use of 1 equiv of $Hg(OAc)_2$ in SLS solution.[2b] As expected, the use of more than 1 equiv of $Hg(OAc)_2$ leads to a mixture of diols and cyclic ethers. However, while excess $Hg(OAc)_2$ and long reaction times were used in eq 1 and 2 (to guarantee complete reaction), the preferential formation of 2–4 was adversely affected by the use of more than 3 equiv of $Hg(OAc)_2$. The best evidence for micelle-enhanced cyclization is found in reactions where a substantial amount of monoalcohol is recovered.

(1) NIH Research Career Development Awardee (1983–1988).

(2) (a) Link, C. M.; Jansen, D. K.; Sukenik, C. N. *J. Am. Chem. Soc.* **1980**, *102*, 7798. (b) Sutter, J. K.; Sukenik, C. N. *J. Org. Chem.* **1982**, *47*, 4174. (c) Sukenik, C. N.; Link, C. M. In "Solution Behavior of Surfactants"; Mittal, K. L., Fendler, E. J., Eds; Plenum Press: New York, 1982; Vol. 2, pp 1007–1015.

(3) Nikles, J. A.; Sukenik, C. N. *Tetrahedron Lett.* **1982**, *23*, 4211.

(4) (a) We have been informed by Dr. Robert W. White of Chemical Abstracts Service that "ring systems 2–4 have never before been encountered by Chemical Abstracts Service". Their names based on Chemical Abstracts Service nomenclature are as follows: 2, octahydro-2,6-epoxy-4a,8a-(methanoxymethano)naphthalene; 3, octahydro-2,7-epoxy-4a,8a-(methanoxymethano)naphthalene; 4, hexahydro-5*H*,7*H*-2,7a:3,4a-dimethanobenzo[1,2-*b*:4,5-*c*']difuran. (b) For an interesting recent paper on the synthesis of iceane derivatives that are reminiscent of 3 and 4, see: Spun, P. R.; Hamon, D. P. G. *J. Am. Chem. Soc.* **1983**, *105*, 4734.

(5) Altman, J.; Babad, E.; Itzchaki, J.; Ginsburg, D. *Tetrahedron* **1966**, *8*, 279. Also see an improved synthesis of 1 in ref 4b.

(6) Snatzke, G.; Zanati, G. *Ann.* **1965**, *684*, 62.

0022-3263/84/1949-1295$01.50/0

Table I

medium	[1], 10^2 M	[Hg(OAc)$_2$], 10^2 M	yield, % 1	2	3	4	7	8 + 9
SLS (3×10^{-2} M)	0.45	0.9	1	10	2	3	81	4
aqueous THF (50:50)	0.45	0.9	3	1	1		66	30
aqueous THF (50:50)	50.0	100.0	7	2	2	1	27	63

In nonmicellar experiments (50% aqueous THF,[7] no surfactant) the ratio of diols (8 + 9) to cyclic ethers (2 + 3 + 4) was typically >15:1. Moreover, the percentage of doubly reacted material (diols + cyclic ethers) that was accounted for by diols was never less than 90%. While there was some variability in the product ratios from the SLS reactions as well, the yield of cyclic ether could be optimized by the use of 2 equiv of Hg(OAc)$_2$ and a ratio of SLS to diene of 6:1.[8] Under these conditions, the percentage of doubly reacted material accounted for by cyclic ethers was never less than 75%. Thus the micellar medium is able to strongly enhance a delicately balanced and otherwise disfavored cyclization process. Our earlier arguments[2a] about the exclusion of water from the micellar pseudophase leading to a preference for cyclization are consistent with, and in fact strengthened by, these results.

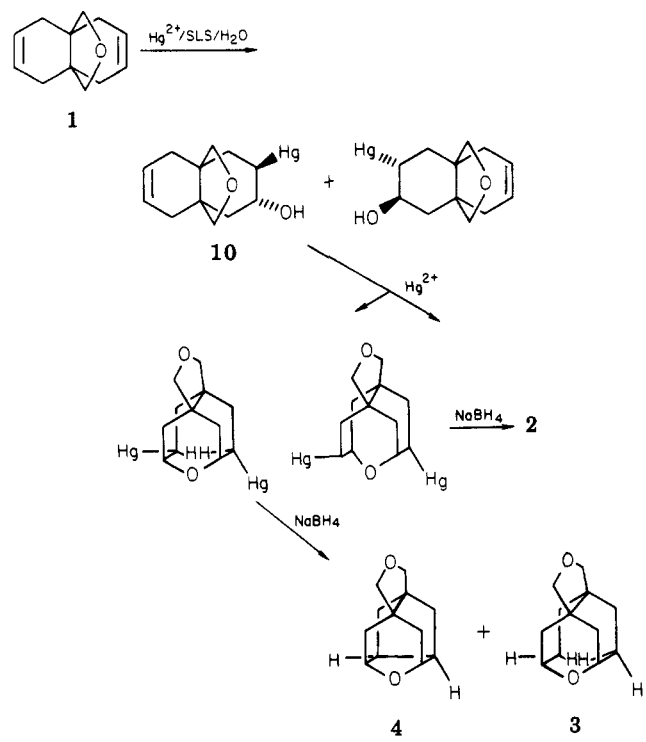
The analysis of the ratio of 2:3:4 by gas chromatography on a column of either OV-17 or OV-73 gave marginally useful separation of most of the reaction products. However, satisfactory analytical and preparative results were obtained by HPLC on silica gel using 2.5% 2-propanol in heptane as eluent. This allowed us to isolate pure samples of 2–4.

Structure Proofs for 2–4. The identities of these cyclic ethers were initially suspected on the basis of their GC elution between the starting diene and the monool products (as was the case for eq 1 and 2) and by the need for RI rather than UV detection (even at 210 nm) on HPLC. Confirmation of their composition was obtained by high-resolution mass spectroscopy at 20 eV. All three gave appropriate exact mass values.

Further evidence for the structures of these molecules and their unusual symmetry properties was obtained from their proton-decoupled ^{13}C NMR. The presence of a C_2 axis in 2 requires that it only show six different carbon signals: two different pairs of oxygen bearing carbons, one pair of quaternary carbons, and three pairs of CH_2 groups. This is consistent with the observed spectrum at 50 MHz. It is, however, in distinct contrast to the spectra observed for 3 and 4, where a plane of symmetry in each compound leads us to expect eight carbon lines (three ether carbons, two quaternary, three CH_2 and/or CH carbons). Spectra at both 50 and 125 MHz confirmed these expectations. The switch of one of the methylene carbons in 3 to a methine in 4 is confirmed by the APT pulse sequence.[9]

Proton NMR at 200 MHz confirmed the indicated structure assignments. In addition to the standard assignments of chemical shift values and peak intensities, the complete assignment of J_{HH} for 4 was achieved. We were able to obtain sufficient resolution of the alkyl proton signals between δ 1.15 and 1.65 to allow a clear assessment of all couplings. When taken together with the rigid, well-defined geometry of 4, this provides a clear example of some interesting long-range interactions (See Experimental Section).

Scheme II



Mechanism of Formation of 2–4. The basic pathway for the hydroxymercuration of both olefins and nonconjugated dienes is well understood.[7] Application of these ideas to the reaction of 1 leads to the steps shown in Scheme II, where those reactions leading to cyclic ether formation are illustrated.

The presumed anti stereochemistry in both the formation and further reaction of 10 is well precedented as is the formation of 2 and 3 by $NaBH_4$ reduction. The formation of 4 by $NaBH_4$-induced intramolecular coupling of two alkyl mercurials has only limited precedent.[10] It can be envisioned as a nucleophilic attack of hydride on one mercury leading to a successive intramolecular displacement of the second mercury. Alternatively, the normal mechanism for borohydride reduction of alkyl mercurials[10b] may be operative. The radical intermediate from the reduction of the first mercury partitions between radical displacement of the other mercury to give 4 and the normal abstraction of a hydrogen atom that would ultimately lead to 3.

The observation that the amount of 2 always exceeds the sum of 3 and 4 reflects the congestion on the inside of the cage leading to 3 and 4. This congestion is presumably also a factor in the balance between 3, where the internal hydrogens almost overlap, and 4 where the extra bond avoids this overlap at the expense of molecular flexibility. However, since the ratio of 3 to 4 is highly variable under both micellar and nonmicellar conditions,

(7) Brown, H. C.; Geoghegan, P. J.; Lynch, G. J.; Kurek, J. T. *J. Org. Chem.* **1972**, *37*, 1941.

(8) This optimization is not to suggest a maximum for the micellar effect. Rather, it is a reflection of a balance between classical micellar reaction conditions, convenience, and preparative utility.

(9) Le Cocq, C.; Lallemand, J. Y. *J. Chem. Soc., Chem. Commun.* **1981**, 150.

(10) Intramolecular C–C bond formation from the trapping of a mercurial-derived radical by a remote double bond has been reported: (a) Matsuki, Y.; Kodama, M.; Ito, S. *Tetrahedron Lett.* **1979**, 4081. (b) Quirk, R. P.; Lea, R. E. *J. Am. Chem. Soc.* **1976**, *98*, 5973.

the factors controlling the partitioning of this reduction are not clear.

Experimental Section

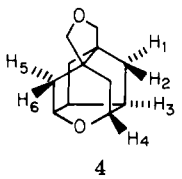
Synthesis of 1, 5, and 6. Compounds 1, 5, and 6 were obtained by literature[5,6] methodology. The conversion of 6 to 1 was effected by adding 6 (10 g, 28.5 mmol) as a solution in 50 mL of THF to a slurry of $LiAlH_4$ (1.05 g, 28 mmol) in 20 mL of dry distilled THF under N_2. This solution was refluxed for 3 h. The workup involved dropwise addition of 1 mL of H_2O, 1 mL of 15% NaOH, and 3 mL of H_2O. The granular precipitate was filtered and washed three times with 250-mL portions of diethyl ether. The combined organic layers were dried over $MgSO_4$ and concentrated. The isolated yield of 1 after bulb-to-bulb distillation was 4.50 g (96%, based on 6).

Mercuration of 1. Reactions in aqueous THF were done as per ref 7. The procedure in SLS was as follows. Diene 1 (100 mg, 0.57 mmol) was added to a solution of SLS (865 mg, 3 mmol) in 100 mL of doubly distilled H_2O and stirred vigorously until it was homogeneous (approximately 8 h). Warming the SLS/1 solution to 45 °C did not appreciably acclerate the dissolution of 1. $Hg(OAc)_2$ (362 mg, 1.1 mmol) in 1 mL of H_2O was added to the aqueous SLS/1 solution. Immediately after the Hg^{2+} solution was added, the SLS solution became slightly cloudy; after 10 min the combined solution was clear. The reaction mixture was allowed to stir at room temperature for 24 h. Addition of 2.0 mL of a 3.0 M NaOH solution gave a clear yellow solution. Upon addition of 2.0 mL of a 0.5 N $NaBH_4$ in 3.0 M NaOH, the solution turned black and was stirred for an additional 10 min to allow the Hg^0 to coagulate. The reduced solution was poured into four 50-mL centrifuge tubes, each containing 2.0 g of NaCl and 0.25 g of $BaCl_2$. These tubes were capped and vigorously agitated; a grey flocculent precipitate formed. Diethyl ether was added to each tube; they were shaken and then centrifuged for 3 min. The ether layer was removed, and this procedure was repeated three times. The combined ether extracts were dried with $MgSO_4$ and concentrated to yield an oily mixture of reaction products that were analyzed/isolated by chromatography.[11] GLC analysis (3% OV-73, 12 ft × $^1/_8$ in. on 100/120 Gas Chrom Q using Perkin-Elmer Model 3920B) provided ratios of **2 + 3 + 4** vs. **8 + 9**. HPLC analysis (Whatman 10 μPartisil, with 2.5% 2-propanol/97.5% heptane) provided ratios of **2:3:4**. Table I gives a few representative product ratios for the mercuration of 1.

Spectral Data for 2–4. MS (20 eV, AEI-MS 30 mass spectrometer). **2**: calcd. 194.1307, obsd. 194.1272. **3**: calcd 194.1307, obsd. 194.1311. **4**: calcd 192.1150, obsd 192.1146.

^{13}C NMR (50 MHz, $CDCl_3$) reported as δ values (no. attached protons). **2**: 80.68 (2), 69.16 (1), 43.47 (0), 35.78 (2), 29.95 (2), 29.26 (2). **3**: 84.33 (2), 81.87 (2), 68.71 (1), 43.55 (0), 36.23 (0), 35.32 (2), 30.80 (2), 29.79 (2). **4**: 79.23 (2), 77.08 (1), 73.26 (2), 51.09 (0), 42.65 (1), 42.16 (0), 35.24 (2), 32.59 (2). Spectra at 125 MHz confirmed these results.

^1H NMR (200 MHz, $CDCl_3$) reported as δ values (multiplicity, no. H). **2**: 1.47 (m, 4 H), 1.68–2.01 (m, 8 H), 3.74–3.83 (AB q, 4 H), 4.10–4.15 (m, 2 H). **3**: 1.49–1.63 (m, 8 H), 1.93–2.03 (m, 4 H), 3.51 (s, 2 H), 3.55 (s, 2 H), 4.24–4.32 (m, 2 H). **4**: 1.17 (dd, 2 H), 1.36 (d, 2 H), 1.46 (dd, 2 H), 1.60 (dt, 2 H), 2.72 (m, 2 H), 3.43 (s, 2 H), 3.76 (s, 2 H), 4.43 (m, 2 H). Assignments of chemical shifts and coupling constants (J_{HH}) for 4 are as follows. H_1: δ 1.17, J_{12} = 11.05, J_{13} = 2.35, J_{14} = 0.95. H_2: δ 1.46, $J_{23} \leq 0.9$. H_3: δ 2.72, J_{34} = 4.81, $J_{34'}$ = 1.80. H_4: δ 4.43, J_{45} = 2.33, $J_{46} \leq 0.9$. H_5: δ 1.60, J_{56} = 13.26. H_6: δ 1.36.



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Acknowledgment. Our initial sample of dimesylate 6 was a gift from Professor L. A. Paquette. NMR spectra on the Varian XL-200 at the Major Analytical Instrument Facility of Case Western Reserve University were made possible by an NSF Instrument Grant (CHE80-24633). ^{13}C NMR spectra at 125 MHz were obtained at the Northeast Regional NMR facility at Yale University (NSF CHE7916210). Funds for this work were provided by NIH (GM-27355).

Registry No. 1, 15405-67-1; 2, 88916-46-5; 3, 88916-47-6; 4, 88916-48-7; 5, 3642-42-0; 6, 3642-52-2; SLS, 151-21-3.

(11) Pure samples of 2–4 are low-melting, needle-like crystals.

Conformation of Seven- and Eight-Membered Organosilicon Heterocycles in Solution

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Recently the synthesis of the nine-membered dibenzophosphonin ring system has been reported, for which the ^{13}C NMR spectrum in solution indicated that the benzo groups severly restricted the conformational freedom of the ring.[1] We have suggested similar large barriers to ring inversion due to substituted benzo groups in derivatives of the eight-membered 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin and 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaborocin ring system to explain the observed ^1H NMR spectra.[2] The observed ^1H NMR spectra of seven-membered dibenzo[*d*,*f*][1,3,2]dioxaphosphepin ring derivatives did not provide information concerning their conformational freedom.[3]

Except for the pioneering work of Zuckerman et al.[4], the analogous silicon ring systems have received scant mention in the literature.[5] The synthetic utility of dibenzo[*d*,*f*][1,3,2]dioxasilepins for the preparation of cyclic fluorophosphoranes has been reported by Littlefield and Doak.[6] We report in this paper the synthesis and NMR conformational analysis of the tetrasubstituted dibenzo[*d*,*f*]-[1,3,2]dioxasilepin and 12*H*-dibenzo[*d*,*g*][1,3,2]dioxasilocin ring systems.

Results and Discussion

The reaction of the tetrasubstituted biphenyl-2,2′-diol 1 with the dihalosilane **2a** using triethylamine as an acid acceptor gave the dioxasilepin **3a** in 77% recrystallized

(1) (a) Quin, L. D.; Middlemas, E. D.; Rao, N. S. *J. Org. Chem.* **1982**, *47*, 905. (b) Quin, L. D.; Middlemas, E. D.; Rao, N. S.; Miller, E. W.; McPhail, A. T. *J. Am. Chem. Soc.* **1982**, *104*, 1893.

(2) (a) Odorisio, P. A.; Pastor, S. D.; Spivack, J. D.; Steinhuebel, L. P.; Rodebaugh, R. K. *Phosphorus and Sulfur* **1983**, *15*, 9. (b) Odorisio, P. A.; Pastor, S. D.; Spivack, J. D. *Ibid*; in press. (c) Pastor, S. D.; Spivack, J. D. *J. Heterocycl. Chem.* **1983**, *20*, 1311. (d) Odorisio, P. A.; Pastor, S. D.; Spivack, J. D.; Rodebaugh, R. K.; Bini, D. *Phosphorus and Sulfur*, in press.

(3) Pastor, S. D.; Spivack, J. D.; Steinhuebel, L. P.; Matzura, C. *Phosphorus and Sulfur* **1983**, *15*, 253.

(4) (a) Zuckerman, J. . *J. Chem. Soc.* **1962**, 873. (b) Zuckerman, J. J. *Ibid.* **1963**, 1322. (c) Emeleus, H. J.; Zuckerman, J. J. *J. Organomet. Chem.* **1964**, *1*, 328. (d) Silcox, C. M.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1966**, *88*, 168.

(5) (a) Schwarz, R.; Kuchen, W. *Z. Anorg. Allg. Chem.* **1955**, *84*, 279. (b) Ismail, Von R. M. *Ibid.* **1963**, *18b*, 1124. (c) Ismail, Von. R. M. *Z. Naturforsch. B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1964**, *19B*, 873. (d) Neth, Pat. Appl. 6611744, 1967 (Dynamite Nobel A.-G.); *Chem. Abstr.* **1967**, *67*, 65080*d*. (e) Allcock, H. R.; Nugent, T. A.; Smeltz, L. A. *Synth. Inorg. Met.-Org. Chem.* **1972**, *2*, 97.

(6) Littlefield, L. B.; Doak, G. O. *Phosphorus and Sulfur* **1977**, *3*, 35.

0022-3263/84/1949-1297$01.50/0