127.3, 105.2, 78.1 (COH); IR ($CHBr_3$) ν 3350 (NH), 3200 (OH), 1610, 1500, 740 cm^{-1}. Anal. Calcd for $C_{16}H_{14}N_2O$: C, 76.78; H,5.64; N, 11.19. Found: C, 76.46; H, 5.64; N, 11.26.

3-Benzylpyrazole (9l): ^1H NMR ($CDCl_3$) δ 7.32 (d, 1 H, C5-H), 7.25 (s, 5 H, Ph H), 6.12 (d, 1 H, C4-H), 3.98 (s, 2 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 141.8, 133.6, 129.1, 128.7, 127.5, 119.8, 116.5, 44.2; IR (neat) ν 3300 (NH), 1610, 950, 765, 720 cm^{-1}.

Acknowledgment. We thank the New Zealand Medical Research Council for a grant to G.W.R.

Registry No. 1, 288-32-4; 2, 23230-39-9; 3c, 50790-93-7; 3c·picrate, 107054-49-9; 3d, 116997-21-8; 3e, 5228-76-2; 3f, 117024-16-5; 3g, 116997-22-9; 3h, 79711-72-1; 5, 19213-18-4; 6a, 61233-51-0; 6b, 615-15-6; 6e, 1235-28-5; 6i, 13794-25-7; 6j, 13745-42-1; 6k, 5805-32-3; 7, 288-13-1; 8, 91272-98-9; 9a, 53848-78-5; 9b, 1453-58-3; 9b·picrate, 14710-76-0; 9e, 116997-23-0; 9l, 32251-82-4; $CH_3(CH_2)_3I$, 542-69-8; $CH_3(CH_2)_3Br$, 109-65-9; Ph_2CO, 119-61-9; p-$CH_3C_6H_4CHO$, 104-87-0; p-$CH_3C_6H_4CO_2Et$, 94-08-6; t-BuNCo, 1609-86-5; $(CH_3)_2CHCHO$, 78-84-2; PhNCO, 103-71-9; cyclohexanone, 108-94-1.

Transannular Addition of α-Thia Carbanions to Unactivated Double Bonds. 5. Synthesis of (9*R*,10*S*)-*trans*-1-Thiadecalin[1]

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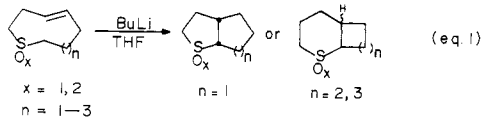
Received April 29, 1988

A synthesis of *trans*-1-thiadecalin in enantiomerically pure form is described that uses as the key step the recently discovered addition of α-thia carbanions (α-lithio sulfoxides or sulfones) to a transannular *E* double bond.[2] The required (*E*)-thiacyclodec-4-ene precursor was prepared by 2,3-sigmatropic rearrangement of a 7-membered cyclic sulfonium ylide[4] obtained in turn by elaboration of (*R*,*R*)-1,6-dibromo-3,4-hexanediol, a chiral synthon derived from D-mannitol. The product of the addition step was freed of the stereogenic diol unit, yielding the target compound. Its absolute configuration follows from straightforward NMR analysis of its diastereomeric precursors. The stereochemical aspects of the transannular cyclization (stereospecific in the sulfoxide case, 9:1 stereoselective in the sulfone) are briefly commented on.

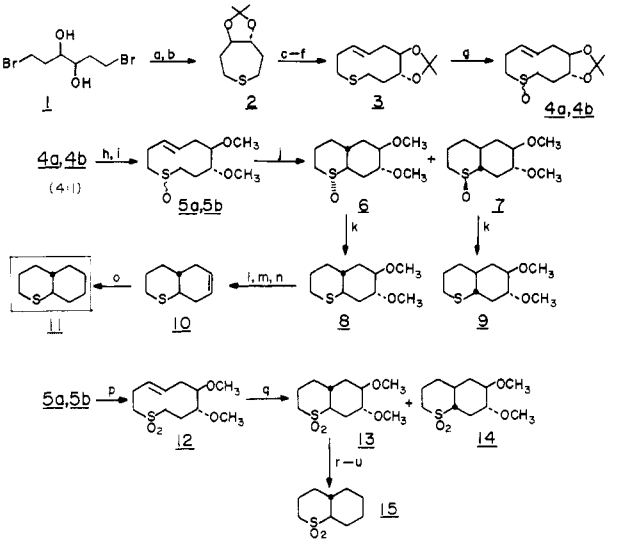
We have recently described a reaction of medium-ring homoallylic sulfoxides or sulfones whereupon, on treatment with a catalytic amount of butyllithium, transannular cyclization occurs leading to saturated bicyclics (eq 1).[2] The reaction occurs readily provided the double bond has the *E* configuration.



Since metalation induces carbanionic reactivity at the α carbons, the reaction may be described as a nucleophilic addition to an isolated double bond, a very rare process,[3] and, for what concerns C-nucleophiles, an unprecedented one.

Although the experimental evidence largely fits this description,[2c,d] several mechanistic facets remain to be elucidated, which are currently under investigation in our laboratory. The mechanistic ambiguities, however, do not hinder the exploitation of the reaction toward synthetic goals, and the present paper describes a synthesis that uses the transannular cyclization of a thiacyclodec-4-ene as the key step toward the preparation of *trans*-1-thiadecalin in enantiomerically pure form.

Scheme I[a]



[a] (a) $Me_2C(OMe)_2$, TsOH, benzene, 95.5%; (b) $Na_2S·9H_2O$, EtOH, 80%; (c) NCS, benzene; (d) CH_2=$CHMgBr$, THF; (e) CF_3SO_3Me, CH_2Cl_2; (f) t-BuOK, THF, −40 °C, 34.5% from 2; (g) MCPBA, CH_2Cl_2, −80 °C, 95%; (h) 0.1 N H_2SO_4, 83%; (i) MeI, NaH, DMF, 83%; (j) n-BuLi, THF, 0–20 °C, 77.8%, overall yield; (k) PCl_3, CH_2Cl_2, 75%; (l) Me_3SiCl, NaI, thiolane, ~3 equiv, 73%; (m) $MeSO_2Cl$, pyridine, 85.6%; (n) NaI, Zn, DMF, 150 °C, 75%; (o) RuO_2, MeOH/H_2O, 40 °C, H_2, 12 atm, 90%; (p) MCPBA, 0–20 °C, 96%; (q) n-BuLi, THF, 0–20 °C, 71%; (r) Me_3SiCl, NaI, CH_3CN, 77%; (s) $MeSO_2Cl$, pyridine, 90%; (t) NaI, Zn, DMF, 80%; (u) H_2, PtO_2, MeOH, 95%.

Results

Medium-size homoallylic thiacycloalkenes of *E* configuration can be conveniently obtained by 2,3-sigmatropic

(1) (a) Dedicated to the memory of Professor Gabriello Illuminati. (b) Financial support from CNR-Rome and Ministero Pubblica Istruzione is gratefully acknowledged.

(2) (a) Cerè, V.; Paolucci, C.; Pollicino, S.; Sandri, E.; Fava, A. *J. Chem. Soc., Chem. Commun.* **1981**, 764–765; (b) **1986**, 223–224; (c) *J. Org. Chem.* **1986**, *51*, 4880–4888; (d) *Pure Appl. Chem.* **1987**, *59*, 955–964.

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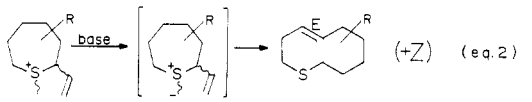
Table I. Carbon-13 NMR Shifts of 6,7-Dimethoxy-1-thiadecalin Derivatives[a]

compound	substituents at C_6, C_7	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	Me's
11[b]	H	29.96	28.10	34.25	34.45	26.20	26.62	32.48	46.98	44.20	
8	OMe	(29.94)	27.95	33.58	32.28	[76.23]	[76.38]	(29.85)	40.57	37.12	56.33, 56.25
9	OMe	29.38	27.40	33.24	37.24	(82.42)	(82.64)	35.25	42.99	41.33	57.34, 57.19
18[d]	OH	30.67	29.31	36.15	(34.94)	[70.27]	[70.35]	(34.27)	41.64	38.33	
trans-1-thiadecalin α-1-oxide[c]	H	51.47	21.75	32.89	33.14	25.39	25.45	27.01	67.11	38.74	
6	OMe	51.19	21.36	31.64	30.61	(74.44)	(75.21)	23.78	61.18	31.88	56.14, 56.04
7	OMe	51.05	21.65	31.88	36.26	(81.37)	(82.16)	30.14	64.07	36.69	57.66, 57.21
15[b]	H	51.54	22.96	32.07	32.71	24.62	24.95	20.10	65.27	39.60	
13	OMe	51.25	22.77	31.15	30.44	(74.53)	(74.69)	18.34	59.35	32.95	56.24, 56.15
14	OMe	51.17	23.12	31.27	36.09	(81.30)	(81.98)	23.71	62.23	37.79	57.87, 57.33
20[d]	OH	52.40	24.30	32.31	34.53	69.03	69.03	22.76	60.65	34.50	

[a] ppm from $(CH_3)_4Si$; $CDCl_3$ solvent; values in parentheses or in brackets may be interchanged. [b] This work. The differences with respect to previously reported shifts[15] are within 0.2 ppm. [c] From ref 15. [d] In methanol-d_4.

rearrangement of appropriate cyclic allylic sulfonium ylides.[4] Thus the (*E*)-thiacyclodec-4-ene ring system is accessible via ring expansion of a 2-vinylthiepanium 1-methylide (eq 2).[4d] The thiacyclodec-4-ene precursor used



in the synthesis of an enantiomerically pure thiadecalin needs to contain a stereogenic unit to be removed eventually. To this end a suitably protected vicinal diol grouping was chosen of known absolute configuration. The synthetic sequence (Scheme I) started from (*R*,*R*)-1,6-dibromo-3,4-hexanediol (**1**) obtained from D-mannitol by a published procedure.[5] The dibromide diol was protected as the acetonide and reacted with Na_2S in EtOH to give the corresponding thiepane (**2**). This was α-chlorinated with *N*-chlorosuccinimide and reacted with vinylmagnesium bromide in THF.[4c] The ~1:1.5 mixture of 2-vinylthiepane isomers thus obtained was treated with methyl triflate to yield a mixture of 1-methyl-2-vinylthiepanium salts, which was used as such in the subsequent ring expansion reaction. The sulfonium methylide was generated in THF/*t*-BuOH (9/1 v/v), by using *t*-BuOK as the base. These conditions are known to favor the formation of *E* products.[6] Indeed the ring-expanded olefinic material consisted essentially exclusively of the *E* isomer. This was quantitatively oxidized to a ~4:1 mixture of isomeric sulfoxides, **4a**,**b**. In our original plan the transannular addition reaction had been projected to take place at this stage. This could not be carried out, however, since the sulfoxide turned out to be unexpectedly resistant to cyclization. By monitoring the disappearance of the starting material, the cyclization was estimated to require drastic conditions (>24 h at room temperature) where the carbanion would largely not survive. It was reasonable to assume this behavior, at variance with respect to the parent ring,[2c] to arise from some (unspecified) conformational feature related to the presence of the dioxolane ring trans fused to the 10-membered ring. If this was the case the "normal" reactivity could have been restored simply by replacing the cyclic protection with an acyclic one. The isopropylidene derivative of the 4:1 sulfoxide mixture (**4a**:**4b**) was then deprotected[7] and reprotected as bis(methyl ether), **5a**, **5b**, a choice based on the presumption that the methoxy groups, because of their size, would exert a minimal conformational bias. Upon treatment with BuLi this material underwent smooth cyclization to a mixture of isomeric bicyclic sulfoxides **6**, **7** in the same 4:1 ratio as the starting material. They could be separated[8] by FC and their structure established unambiguously by ^{13}C (Table I) and ^1H NMR (see Discussion). From this point on the synthesis proceeded from the major isomer, **6**, whose bridgehead carbons appear to have the *R*,*R* configuration (see below). By PCl_3 reduction of **6**, sulfide **8** was obtained, which was deprotected with trimethylsilyl iodide in the presence of a large excess of thiolane.[9] The diol was dehydroxylated via mesylation followed by treatment with Zn/NaI, and finally the thiaoctalin **10** was hydrogenated in the presence of ruthenium catalyst[11] to give the target molecule, (9*R*,10*S*)-thiadecalin, **11**, in an overall yield of 3.76% over 14 steps.

The circumstance that the **6**:**7** diastereomer ratio is the same (within the limits of ^{13}C NMR analysis) as that of the **5a**:**5b** precursor suggests the cyclization to be essentially stereospecific. That this is so was confirmed by subjecting to BuLi-promoted cyclization a **5a**:**5b** mixture whose ratio had been changed by (partial) sulfur inversion[13] from ~4:1 to ~1:3. The product ratio **6**:**7** also changed to ~1:3.

In view of the stereospecificity of the sulfoxide cyclization it was interesting to examine the stereochemical behavior of the corresponding sulfone, a precursor that lacks

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(6) Cerè, V.; Paolucci, C.; Pollicino, S.; Sandri, E.; Fava, A. *J. Org. Chem.* **1981**, *46*, 3315–3321.

(7) Introducing the dimethyl ether protection at an earlier stage turned out to be of no advantage since the ylide rearrangement produced an inordinately large fraction of *Z* product.

(8) Alternatively, and more conveniently, the separation may be effected after reduction of the **6** + **7** mixture to the corresponding sulfides (**8** + **9**).

(9) To our knowledge no example has been reported where the Me_3SiI deprotection is applied to methyl ethers also containing a sulfide functionality. Although the fear that the reagent might cleave the C–S bond turned out to be unfounded, a problem arose from the methyl iodide byproduct alkylating the sulfide. Since the $LiAlH_4$ reduction of a sulfonium salt back to sulfide is known to occur in low yield,[10] it was found expedient to carry out the deprotection in the presence of a large excess of a reactive sulfide (thiolane) to scavenge methyl iodide.

(10) Cerè, V.; Guenzi, A.; Pollicino, S.; Sandri, E.; Fava, A. *J. Org. Chem.* **1980**, *45*, 261–264.

(11) Divalent sulfur compounds are notorious poisons for the more common hydrogenation catalysts;[12] these compounds do not affect ruthenium, however, and may be hydrogenated under moderate conditions of temperature and pressure. The scope of ruthenium catalysts in the hydrogenation of sulfur compound is being probed in our laboratory and will be reported elsewhere.

(12) See for example: Freifelder, M. *Catalytic Hydrogenation in Organic Synthesis. Procedures and Commentaries*; Wiley: New York, 1978; Chapter 14.

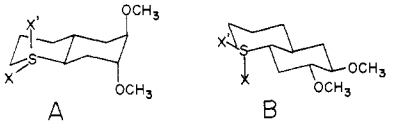
(13) Johnson, C. R.; McCants, D., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 5404–5409.

the sulfur chirality center. To this end sulfoxide **5a,b** was oxidized to sulfone **12**, which gave two diastereomers **13** and **14** in a ~9:1 ratio when treated with BuLi. From the NMR behavior their configuration could be unambigously assigned as depicted in the formulas. Similarly to the sulfoxide, the major isomer **13** appears to have the *R,R* configuration at the bridgehead carbons. When **13** was subjected to the sequence of methyl ether cleavage, mesylation, Tipson–Cohen elimination, and hydrogenation (on Pt catalyst) *trans*-(9*R*,10*S*)-thiadecalin 1,1-dioxide (**15**) was obtained, identical with the material obtained by oxidation of **11**.

Discussion

A few comments are appropriate concerning the configurational assignments and the stereochemical course of the cyclization.

The absolute configuration of the bicyclic sulfoxides (**6**, **7**), sulfides (**8**, **9**), and sulfones (**13**, **14**) follows from their NMR behavior on the basis of these premises: (a) the original 1,2-diol stereogenic unit has preserved its integrity throughout and (b) all these bicyclics have a trans ring fusion. While the former proviso is obvious, the second is obtained from the cyclizations of sulfoxide **5a,b** or sulfone **12** occurring under conditions leading to the thermodynamic product.[14] With these provisos it can be easily seen that the configuration of the bridgehead carbons is uniquely related to the conformational setting of the methoxy groups. With a trans ring junction, the configurations of bridgehead carbons may be either *R,R* or *S,S*. Therefore, neglecting for the moment the sulfoxide sulfur as a chirality center, the diastereoisomers of each pair have the configurations 6*R*,7*R*,9*R*,10*R* (A) and 6*R*,7*R*,9*S*,10*S* (B), respectively. Consequently the methoxy groups will be axial or equatorial according to whether the configuration of the bridgehead carbons is *R,R* or *S,S*, respectively. Hence the configuration may be assigned merely on the basis of the conformational setting of the methoxy groups. This is an easy task since, for a rigid molecular framework such as this, the ^{13}C NMR differential shieldings, axial vs equatorial, provide a clear cut criterion.



A B

6: X = O 7: X′ = O

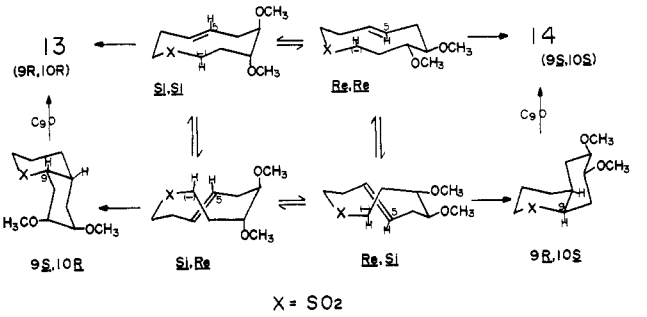
8: 9:

13: X, X′ = O 14: X, X′ = O

X, X′ = lone pairs unless specified otherwise

The ^{13}C NMR spectra of the above pairs are collected in Table I together with those of the parent ring sulfide, sulfone, and α-sulfoxide.[15] The data appear to be internally consistent: in each pair one diastereomer has all the carbons of the carbocyclic moiety (C_5–C_{10}) upfield with respect to the other diastereomer. Moreover the differential shieldings for corresponding carbons are largely independent of the nature of the sulfur functionality, be it sulfide, sulfone, or sulfoxide. This is expected if the differences arise from a combination of α, β, and γ effects of the methoxy substituents. From the known conformational dependence of these effects,[16] the more shielded diastereomer of each pair is deduced to have the MeO groups axial, hence to have the *R,R* configuration of the bridgehead carbons.

Scheme II



X = SO_2

That the sulfoxide pair, **6**, **7**, though having an additional chirality center, conforms to the sulfide and sulfone pairs implies that the sulfoxide oxygen has the same conformational setting in both **6** and **7**. That the setting is equatorial follows unambigously from the ^{13}C NMR shieldings of the carbons β or γ to the sulfoxide oxygen.[15,17] In particular, C_2 and C_3, which are essentially unaffected by the distal methoxy groups, have practically identical shieldings in either **6** or **7**, identical in turn with C_2 and C_3 in the parent *trans*-1-thiadecalin α-1-oxide.[15] Henceforth **6** and **7** are concluded to have the 1*R*,6*R*,7*R*,9*R*,10*R* and 1*S*,6*R*,7*R*,9*S*,10*S* configurations, respectively.

The above structural assignments are fully consistent with the ^1H behavior (see the Experimental Section): (i) Axial OCH_3 groups are known to resonate upfield relative to the equatorial ones,[18] and in fact the OCH_3 signals are upfield in **6** and **13** relative to **7** and **14**. (ii) The methyne protons at C_7 and C_8 will be equatorial or axial depending on whether the OCH_3 groups are axial or equatorial, respectively. Accordingly, in **6** and **13** they are found to resonate downfield (0.2–0.4 ppm) with respect to **7** and **14**, and their width is smaller, $W_H \simeq 8$ Hz in **6** and **13**, against $W_H \simeq 21$ Hz in **7** and >18 Hz in **14**.

A brief comment is in order about the steric course. A crucial role is played by the conformational properties of the monocyclic precursor. Consider the α-carbanion arising from sulfone **12**.[19] The formation of the transannular bond produces two new centers of chirality (the bridgehead carbons, C_9 and C_{10}). Their relative configuration depends on the relative topicity of the reacting two-dimensional stereogenic centers, C_5 and C_{10}. The four possibilities are depicted in Scheme II (X = SO_2). The *like* products, 9*R*,10*R* (**13**) and 9*S*,10*S* (**14**) arise from the *like* precursors, *Si,Si* and *Re,Re*, respectively. The *unlike* precursors, *Si,Re* and *Re,Si* give raise to the *unlike* products 9*S*,10*R* and 9*R*,10*S*, respectively. The latter, however, have a cis junction and under our reaction conditions are not ob-

(14) The kinetic product in the cyclization of the parent ring sulfoxide consists of a 1:1 mixture of cis and trans isomers, which on standing in base at room temperature convert to the more stable trans isomer essentially quantitatively.[2c]

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(16) (a) Schneider, H. J.; Hoppen, V. *Tetrahedron Lett.* **1974**, 579–582. (b) Grover, S. H.; Stothers, J. B. *Can. J. Chem.* **1974**, *52*, 870–878. (c) Wehrli, F. W.; Wirthlin, T. *Interpretation of Carbon-13 NMR Spectra*; Heyden: London, 1976; Chapter 2. (d) Ayer, W. A.; Browne, L. M.; Fung, S.; Stothers, J. B. *Can. J. Chem.* **1976**, *54*, 3272–3275. (e) Whitesell, J. K.; LaCour, T.; Lovell, R. L.; Pojman, J.; Ryan, P.; Yamada-Nosaka, A. *J. Am. Chem. Soc.* **1988**, *110*, 991.

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(18) (a) Lemieux, R. U.; Kullnig, R. K.; Bernstein, H. J.; Schneider, W. G. *J. Am. Chem. Soc.* **1958**, *80*, 6098–6105. (b) Baker, S. A.; Homer, J.; Keith, M. C.; Thomas, L. F. *J. Chem. Soc.* **1963**, 1538–1543.

(19) Assimilating the α-lithio sulfone to a free carbanion is an oversimplification as it ignores the presence of the metal atom. It is, however, equivalent to assuming, which is reasonable, the metalated carbon to be configurationally labile, at least in the timescale of the transannular addition reaction.

served but isomerize to their respective trans epimers 9*R*,10*R* and 9*S*,10*S*.[14]

The diastereoselectivity factor indicates cyclization occurs preferentialty (by a factor of 9) at the *Si* face of the doubly bonded carbon, C_5. Why this is so is not clear, however, since it results from the combination of two factors: conformer population and individual conformer reactivity, whose respective contributions cannot be easily dissected.

As to the sulfoxide (**5**) cyclization, the observation is that the configuration at sulfur and that at the distal bridgehead (C_{10}) are unequivocally correlated in the product: an *S* or *R* configuration at sulfur corresponds to an *S* or *R* configuration at C_{10}, respectively. Since the sulfoxide sulfur is not directly involved in the addition reaction (hence its configuration is retained), it must be concluded that the carbanion adjacent to the *S* or *R* sulfoxide, **5a** or, respectively, **5b**, attacks exclusively (within the limits of our ^{13}C NMR analytical method) the *Si* or, respectively, the *Re* face of C_5. Although this high degree of 1,3 induction is striking, no explanation can be offered at present aside from the trivial comment that it must arise from either conformer population or individual conformer reactivity or both.[20] There is no experimental basis for dissecting the two contributions, however.

Experimental Section

General Procedures. Proton NMR spectra were taken at 60, 200, or 300 MHz on Varian EM-360, Gemini 200, or Brucker CPX 300 instruments, respectively. Unless specified otherwise, 60-MHz spectra are reported. Proton noise decoupled ^{13}C NMR spectra were obtained at 25.15 and 50.3 MHz on Varian XL-100 and Gemini 200 instruments respectively. Single-frequency off-resonance spectra were obtained by irradiation at δ −4 in the proton spectrum. Proton and ^{13}C shifts are in ppm from $(CH_3)_4Si$ and, unless otherwise specified, refer to $CDCl_3$ solvent. The ^{13}C NMR spectral assignments were based on (i) off-resonance decoupling experiments, (ii) comparison with the ^{13}C NMR behavior of closely related systems, and (iii) the shielding effects of the oxygenated functions (sulfoxide and OCH_3 ether) and their conformational dependence.[16,17] These are so large and specific that they alone provide unequivocal configurational evidence. The few ambiguities that remain in the spectral assignments are of no consequence on the configurational assignments.

Solvents and reagents were obtained dry as follows: benzene, dichloromethane, *tert*-butyl alcohol, dimethylformamide, and acetonitrile by refluxing over, followed by distillation from, calcium hydride. Acetonitrile was stored over molecular sieves. Pyridine and tetrahydrofuran were distilled from KOH and sodium/benzophenone, respectively. Sodium iodide was dried in vacuo at 100 °C for 24 h before use. Melting points were determined on a Büchi apparatus and are uncorrected.

(3*R*,4*R*)-(+)-1,6-Dibromohexane-3,4-diol, 1, was prepared from 1,4:3,6-dianhydro-D-mannitol according to the Cope procedure:[5] mp 90–91 °C; $[\alpha]^{27}_D$ +58.4° (*c* 2.16, $CHCl_3$) [lit.[5] mp 89.5–90 °C; $[\alpha]^{27}_D$ +58.8° (*c* 2.2, $CHCl_3$)]; ^{13}C NMR δ 71.6 (C_3, C_4), 36.6 (C_1, C_6), 30.2 (C_2, C_5).

(4*R*,5*R*)-(+)-4,5-Bis(2-bromoethyl)-2,2-dimethyl-1,3-dioxolane, 16. A solution of **1** (42.8 g, 155 mmol), 2,2-dimethoxypropane (24.6 g, 236 mmol), and *p*-toluenesulfonic acid (0.08 g) in benzene (100 mL) was refluxed. Removal of the MeOH/benzene azeotrope was continued (2 h) until the vapor temperature had risen well above 57 °C. After neutralization with solid K_2CO_3, the solvent and unreacted dimethoxypropane were removed under reduced pressure, and the residue was distilled to give the title acetonide: 46.7 g (95.5%); bp 115 °C (1 mm); $[\alpha]^{27}_D$ +49.3° (*c* 2.13, $CHCl_3$); ^{13}C NMR δ 108.8 (C_2), 78.0 (C_4, C_5), 36.0 (CH_2Br), 29.4 (CH_2CH_2Br), 27.1 (CH_3); ^1H NMR δ 3.90 (m, 2 H, CHO), 3.56 (t, 4 H, CH_2Br), 2.13 (m, 4 H, CH_2CH), 1.36 (s, 6 H, CH_3's). Anal. Calcd: C, 34.20; H, 5.10. Found: C, 34.15; H, 5.12.

(1*R*,7*R*)-(−)-9,9-Dimethyl-8,10-dioxa-4-thiabicyclo[5.3.0]decane, 2. An ethanol solution of **16** (63 g, 0.2 mol in 1 L) and of $Na_2S{\cdot}9H_2O$ (58 g, 0.24 mol, in 1 L) were added dropwise under nitrogen, at the rate of 20 mL/h, to 2 L of vigorously stirred ethanol at reflux. The addition was conducted over 48 h, and reflux was continued for an additional 12 h. The residue after solvent evaporation was dissolved in petroleum ether, filtered, and extracted with water (3 × 50 mL). The dried organic layer, distilled under reduced pressure, yielded 30 g (80%) of the title compound: bp 92 °C (1 mm); $[\alpha]^{28}_D$ −85.5° (*c* 2.0, $CHCl_3$); ^{13}C NMR δ 108.2 (C_9), 80.2 (C_1, C_7), 33.0 (C_2, C_6), 30.7 (C_3, C_5), 27.0 (CH_3); ^1H NMR δ 4.07 (m, 2 H, CHO), 2.71 (m, 4 H, CH_2S), 2.40 and 1.85 (overlapping m's, 4 H overall, CH_2CH). Anal. Calcd: C, 57.41; H, 8.57; S, 17.03. Found: C, 56.8; H, 8.61; S, 17.21.

(*E*)-(1*R*,10*R*)-(−)-12,12-Dimethyl-11,13-dioxa-4-thiabicyclo[8.3.0]tridec-7-ene, 3. Compound **2** (8.67 g, 46 mmol, benzene 90 mL) was α-chlorinated with *N*-chlorosuccinimide by the procedure of Tuleen and Bennet.[21] After completing the addition of NCS, the solution was filtered and added dropwise over 30 min to an ice-cooled THF solution of vinylmagnesium bromide (0.1 mol in 150 mL). After being warmed to room temperature, the reaction mixture was quenched with 20% aqueous NH_4Cl and extracted with petroleum ether. The residue after solvent evaporation was distilled under reduced pressure to give a major fraction (7.3 g, bp 112–120 °C (1 mm), which by ^{13}C NMR analysis appears to contain two α-vinyl derivatives along with other unidentified products. Although this crude could be purified by FC (silica, 10% Et_2O in petroleum ether,[22] it was found expedient to omit purification. Methyl triflate (5.9 g, 36 mmol) was added dropwise to the crude product (7.3 g, 80%, 27 mmol in 170 mL of CH_2Cl_2) with stirring being continued for 3 h at room temperature. (The reaction was best performed in the presence of suspended $CaCO_3$ to neutralize any free acid.) After filtration, the solvent was evaporated and the viscous residue (a mixture of *S*-methyl salts) was dissolved in 270 mL of THF/*t*-BuOH, 10:1, cooled to −40 °C and treated portionwise with *t*-BuOK stirring being continued for 2 h at −35 °C. After the reaction was quenched with H_2O (5 mL), the usual workup[2c] followed by distillation gave 3.65 g (34.5% from **2**) of the title compound: bp 140 °C (2 mm); $[\alpha]^{24}_D$ −24.6° (*c* 1.8, $CHCl_3$); ^{13}C NMR δ 132.4 (C_7) 127.1 (C_8), 108.2 (C_{12}), 79.9, 79.4 (C_1, C_{10}, interchangeable), 37.1 (C_9), 32.4, 32.1, 31.9, 30.0 (C_2, C_5, C_3, C_6, interchangeable), 29.6 (CH_3); ^1H NMR δ 5.60 (m, 2 H, HC=CH), 4.3–3.6 (m, 2 H, CHO's), 3.0–1.7 (m, 10 H), 1.15 (s, 6 H, CH_3's). Anal. Calcd: C, 63.12; H, 8.83; S, 14.04. Found: C, 63.24; H, 8.71; S, 14.15.

(*E*)-(1*R*,10*R*)-12,12-Dimethyl-11,13-dioxa-4-thiabicyclo-[8.3.0]tridec-7-ene 4-Oxides, 4a,b. Low-temperature oxidation[2c] of 3 afforded (95%) a mixture of diastereomeric sulfoxides **4a** and **4b** in ~4:1 ratio. Their separation either by chromatography or by fractional crystallization was unsuccessful, and the mixture was used as such in the subsequent step. The major and (in parentheses) minor isomer have the following properties: ^{13}C NMR δ 130.7 (two signals) (130.8, 129.4) [C_7, C_8 interchangeable], 108.6 (106.9) [C_{12}], 80.6, 80.1 (83.8, 81.6) [C_1, C_{10} interchangeable], 51.7, 51.6 (54.1, 52.3) [C_3, C_5 interchangeable], 36.8 (36.5) [C_9], 27.2, 25.5 (27.2, 26.3) [C_2, C_6 interchangeable], 27.1 (26.9) [CH_3]; ^1H NMR δ 5.60 (m, 2 H, CH=CH), 3.93 (m, 2 H, CHO's), 3.7–1.9 (m, 10 H), 1.45, 1.39 (s, 6 H, CH_3). Anal. Calcd: C, 58.98; H, 8.25. Found: C, 58.93; H, 8.31.

(*E*)-(7*R*,8*R*)-7,8-Dihydroxy-1-thiacyclodec-4-ene 1-Oxides, 17a,b. The **4a,b** mixture (5.93 g, 25.3 mmol) was placed in 0.1 N aqueous H_2SO_4 (45 mL) and heated at 95 °C for 2 h. The solution was neutralized (Na_2CO_3) and brought to a small volume, the product being recovered after flash column chromatography (silica; MeOH/CH_2Cl_2, 10/90) and vacuum drying at 45 °C (4.29 g, 83%). (This procedure had to be adopted because the diol could not be extracted from H_2O.) In ^{13}C NMR (50 MHz, CD_3OD) this material displays a complex spectrum. Apparently each of the

(20) This matter has been discussed previously in relation to the cyclization of the 9- and 10-membered parent rings, yielding products of the α-series exclusively.[2c,d]

(21) Tuleen, D. L.; Bennett, R. H. *J. Heterocycl. Chem.* **1969**, *6*, 115.

(22) The material purified by FC had the following ^{13}C NMR (minor isomer in parentheses; numbering of bicyclic compounds) δ 138.1 (138.5) [CH=], 115.3 (115.0) [CH_2=], 107.9 (107.9) [C_9], 80.5, 79.0 (79.9, 79.1) [C_1, C_7], 47.4 (45.9) [C_3], 40.0 (36.6) [C_2], 35.2 (33.3) [C_6], 31.4, 30.7 [C_5], 27.9 [CH_3].

diol–sulfoxide diastereomers exists as a mixture of conformers whose lifetime is long enough to give raise to separate signals for some of the carbons. Similarly, the ^{1}H NMR spectrum shows extensive broadening at 200 MHz. The 60-MHz spectrum (CD_3OD) has δ 5.7 (m, 2 H, CH=CH), 4.84 (s, >2 H, OH), 3.1–1.6 (unresolved m, 10 H).

(*E*)-(7*R*,8*R*)-7,8-Dimethoxy-1-thiacyclodec-4-ene 1-Oxides, 5a,b. A DMF solution of diol **17a,b** (4.29 g, 21 mmol in 35 mL) was added dropwise to a stirred ice-cooled suspension of 50% NaH (2.17 g, 45 mmol) in DMF (17 mL). After warming to room temperature, further stirring for 45 min, and cooling at 0 °C, MeI was added dropwise (5.3 mL, 77 mmol in 7 mL of DMF). After the exothermic reaction had subsided, the mixture was warmed at 50 °C for 2 h and worked up by H_2O dilution and CH_2Cl_2 extraction. Purification by FC (silica, MeOH/Et_2O 15/85) gave 4 g (83%) of the title compounds as a 4:1 mixture of diastereomers. Their chromatographic separation was unsuccessful, and the mixture was used as such in the subsequent transannular addition step. The major and (in parentheses) minor isomer have the following properties: ^{13}C NMR δ 131.0, 128.3 (129.9, 129.0) [C_4, C_5, interchangeable], 81.5, 81.0, (82.0, 81.4) [C_7, C_8, interchangeable], 57.7, 56.8 (57.1, 56.9) [OCH_3's], 52.7 (49.7) [C_2], 49.1 (44.1) [C_{10}], 31.5 (31.0) [C_6], 24.8 (23.4) [C_3], 22.0 (20.2) [C_9]; ^{1}H NMR δ 5.57 (m, 2 H, CH=CH), 3.35 (s, 6 H, OCH_3). Anal. Calcd: C, 56.86; H, 8.68. Found: C, 56.33; H, 8.71.

(1*R*,6*R*,7*R*,9*R*,10*R*)-(−)-6,7-Dimethoxy-1-thiadecalin 1-Oxide, 6, and (1*S*,6*R*,7*R*,9*S*,10*S*)-(+)-6,7-Dimethoxy-1-thiadecalin 1-Oxide, 7. The 4:1 **5a:5b** sulfoxide mixture (2.63 g, 11.3 mmol) in 113 mL of freshly distilled dry THF at 0 °C was treated dropwise under argon with BuLi (1.6 M, in hexane, 3.6 mL, 5.75 mmol). The mixture was stirred for 3 h at room temperature and worked up.[2c] The crude mixture appears to contain (^{13}C NMR) three products in 12:3:1 ratio. The minor product shows olefinic carbon signals and probably arises from a competing eliminative ring fission. The two major products could be separated and freed from the olefinic side product by flash column chromatography (silica, CH_3OH/Et_2O, 15/85). The first eluted material (1.6 g, 60.8 %) was isomer **6** obtained as a viscous liquid: bp (Kugelrohr) 210 °C (0.01 mm), $[\alpha]^{28}_D$ −144.4° (*c* 4.24, $CHCl_3$); ^{13}C NMR (see Table I); ^{1}H NMR (300 MHz) δ 3.50 (m, $W_H \simeq$ 8 Hz, 1 H, CHO), 3.37 (m, 2 H, CHO and C_2H_{eq}), 3.28, 3.27 (s's, 6 H overall, OCH3's), 2.52 (m, 3 H), 1.95 (m, 1 H), 1.68 (m, 4 H), 1.48 (m, 2 H), 1.08 (m, 1 H). In C_6D_6 the whole spectrum is shifted upfield[23] and the OCH_3 signals become neatly separated: δ 3.32, 3.18 (m's, W_H = 8 Hz, 1 H each, CHO's), 3.05, 2.96 (s's, 3 H each, OCH_3's), 2.78 (m, 2 H), 2.51 (ddd, *J* = 12.8, 11.0, 3.8 Hz, 1 H), 2.24 (ddd, *J* = 13.5, 11.5, 3.0 Hz, 1 H), 1.78 (ddd, *J* = 14.0, 12.0, 2.0 Hz, 1 H), 1.58 (ddd, *J* = 12.0, 4.0, 4.0 Hz, 1 H), 1.46 (m, 2 H), 1.13 (m, 2 H), 0.94 (m, 1 H), 0.54 (m, 1 H). Anal. Calcd: C, 56.86; H, 8.68. Found: C, 56.60; H, 8.71.

After an intermediate fraction containing **6** together with the olefinic side product, the third fraction yielded a solid, **7** (0.45 g, 17%), recrystallized from hexane/benzene: mp 130–131 °C, $[\alpha]^{28}_D$ 36.9° (*c* 4.02, $CHCl_3$); ^{13}C NMR (see Table I); ^{1}H NMR (300 MHz) δ 3.43 and 3.42 (s's, 6 H overall, OCH_3's), 3.13 (m, 2 H, CHO and C_2H_{eq}), 2.92 (m, W_H = 21 Hz, 1 H, CHO), 2.62 (m, 1 H), 2.17 (m, 4 H), 1.74 (m, 2 H), 1.48, 1.33, 1.16 (m's, 1 H each). In C_6D_6: δ 3.36 (s, 3 H, C_7HOCH_3), 3.27 (s, C_6HOCH_3), 2.95 (m, 2 H), 2.84 (m, 2 H), 2.16, 1.84, 1.62 (m's, 1 H each), 1.23, 0.96, 0.75 (m's, 2 H each), 0.48 (m, 1 H). Anal. Calcd: C, 56.86; H, 8.68. Found: 56.89; H, 8.66.

A sample of the 4:1 **5a:5b** mixture was O-methylated (methyl triflate, CH_2Cl_2, 0 °C for 30 min, 12 h at room temperature), and the resulting oxysulfonium salt was hydrolyzed by dissolving it in 0.02 M NaOH.[13,2c] The sulfoxide recovered after CH_2Cl_2 extraction and solvent removal had **5a:5b** = 1:3 (corresponding to 90% configurational inversion). This mixture, treated with BuLi as described above, gave **6:7** in 1:3 ratio.

(6*R*,7*R*,9*R*,10*R*)-(−)- and (6*R*,7*R*,9*S*,10*S*)-(−)-dimethoxy-1-thiadecalin, 8 and 9, were obtained by reduction of the respective sulfoxides, **6** and **7**, with PCl_3 according to a published procedure.[24] Yields were 70 and 75%, respectively. The title compounds were also obtained by reduction of the crude 4:1 mixture of **6** and **7** obtained in the cyclization followed by FC separation (silica; petroleum ether/Et_2O, 85/15). The faster eluting isomer was **8**: bp 129–130 °C (1.5 mm); $[\alpha]^{27}_D$ −33.5° (*c* 5%, $CHCl_3$); ^{13}C NMR see Table I; ^{1}H NMR δ 3.4 (m) and 3.3 (s), overall 8 H, ($CHOCH_3$'s), 2.8–2.4 (m, 3 H), 2.1–1.0 (m, 9 H). Anal. Calcd: C, 61.07; H, 9.32. Found: C, 61.20; H, 9.27.

The slower eluting isomer **9** was crystallized from petroleum ether: mp 56–57 °C; $[\alpha]^{30}_D$ −109.5° (*c* 5.04, CH_3OH); ^{13}C NMR (see Table I); ^{1}H NMR (200 MHz) δ 3.43 and 3.42 (s's, 6 H overall, OCH_3's), 3.18 (m, 2 H, CHO's), 2.80–2.50 (m, 2 H), 2.40 (ddd, *J* = 12.5, 10.0, 3.5 Hz, 1 H), 2.20 (ddd, *J* = 12.5, 3.7, 3.7 Hz, 1 H), 2.02 (m, 2 H), 1.4–0.9 (m, 6 H). In C_6D_6 the CHO protons appear as an essentially symmetrical multiplet consistent with a AA'MM'XX' spin system, whose width (31.5 Hz) is in agreement with their axial setting. Anal. Calcd: C, 61.07; H, 9.32. Found: C, 61.23; H, 9.34.

(6*R*,7*R*,9*R*,10*R*)-(−)-Dihydroxy-1-thiadecalin, 18. To a solution of dimethoxythiadecalin **8** (0.785 g, 3.63 mmol), NaI (1.42 g, 9.5 mmol), and thiolane (0.9 mL, 10.2 mmol) in 15 mL of acetonitrile was added Me_3SiCl (1.5 mL, 9.5 mmol) slowly under argon at room temperature. The mixture was heated at reflux for 8 h, and the reaction progress was followed by GC. (The disappearance of the starting material was first accompanied by the build up of a peak, most likely the monohydroxy intermediates, which disappeared eventually.) After cooling, the reaction mixture was quenched with 1 mL of H_2O, diluted with MeOH until it became clear, neutralized with MeONa, and decolorized with aqueous $NaHSO_3$. Silica (4 g) was added to the solution, and the solvent was evaporated under reduced pressure. The silica residue was subjected to flash chromatography (FC) (silica; $CHCl_3$/MeOH, 92/8) to give 0.50 g (73%) of the title compound: crystallized from hexane–benzene; mp 111–112 °C; $[\alpha]^{27}_D$ −15.0° (*c* 5%, MeOH); ^{13}C NMR (see Table I); ^{1}H NMR (methanol-d_4) δ 3.82 (m, W_H = 6 Hz, 2 H, OCH's), 3.1–2.5 (m, 3 H), 2.2–1.0 (m, 9 H). Anal. Calcd: C, 57.41; H, 8.57. Found: C, 57.20; H, 9.02.

In the absence of thiolane the yield of **18** had been found to be considerably lower (~35%). Analysis of the crude product showed the presence of diol **18**, as well as two other major products, the ^{13}C NMR resonances of which were compatible with those of *S*-methyl sulfonium salts. The hypothesis that the CH_3I byproduct alkylates the sulfur atom receives support from the increased yields obtained in the presence of the CH_3I scavenger (thiolane).

(6*R*,7*R*,9*R*,10*R*)-(−)-6,7-Di-*O*-mesylthiadecalin, 19. Methanesulfonyl chloride (0.72 mL, 9.34 mmol) was added with stirring to a stirred ice-cold pyridine solution of **18** (0.75 g, 3.98 mmol in 11 mL). Stirring at room temperature was continued for 20 h. The precipitate, formed upon dilution with 70 mL of H_2O, was collected, washed with H_2O, and dried: 1.15 g (85.6%); mp 128–129 °C (from EtOH); $[\alpha]^{26}_D$ −40.0° (*c* 5.65, $CHCl_3$); ^{13}C NMR δ 75.3 (2 signals, C_6, C_7), 39.4 (C_9), 38.4 (2 signals, SCH_3's), 36.5 (C_{10}), 33.4, 33.0 (C_2, C_4, interchangeable), 31.7, 29.8 (C_5, C_8, interchangeable), 27.7 (C_3); ^{1}H NMR δ 4.92 (m, W_H = 7 Hz, 2 H, CHO's), 3.10 (s, 6 H, CH_3's), 3.0–2.6 (m, 4 H), 2.3–1.5 (m, 8 H). Anal. Calcd: C, 38.35; H, 5.85. Found: C, 38.41; H, 5.89.

(9*R*,10*R*)-(−)-6,7-Didehydro-1-thiadecalin, 10, was obtained by the Tipson-Cohen procedure.[25] A solution of the dimesylate **19** (1.1 g, 3.2 mmol) and dry NaI (12 g, 80 mmol) in 32 mL of DMF was refluxed for 5 h in the presence of zinc powder (5.2 g, 80 mmol). After cooling, the reaction mixture was filtered, diluted with 70 mL of H_2O and extracted with petroleum ether. The combined extracts were washed with H_2O and aqueous $NaHSO_3$ and dried. Evaporation of the solvent left a residue, which when purified by FC (silica; petroleum ether/Et_2O, 100/1) gave 0.370 g (75%) of the title compound as a low-melting waxy solid: $[\alpha]^{26}_D$ −71.1° (*c* 4.8, MeOH); ^{13}C NMR δ 126.5, 125.3 (C_6, C_7, interchangeable), 42.0 (C_9), 38.8 (C_{10}), 33.8, 32.9 (C_4, C_5, interchangeable), 32.0 (C_8), 29.6 (C_2), 27.8 (C_3); ^{1}H NMR (200 MHz) δ 5.62 (m, W_H < 1 Hz, 2 H, CH=CH), 2.76 (m, 2 H), 2.53 (m, 1 H), 2.3–1.6 (m, 8 H), 1.07 (m, 1 H). Anal. Calcd: C, 70.07; H, 9.15. Found: C, 70.12; H, 9.12.

(23) For aromatic solvent induced shifts of sulfoxides, see: Lett, R.; Marquet, A. *Tetrahedron* **1974**, *30*, 3379–3392 and references therein.

(24) Granoth, I.; Kalir, A.; Pelah, Z. *J. Chem. Soc. C* **1969**, 2424–2425.

(25) (a) Tipson, R. S.; Cohen, A. *Carbohydr. Res.* **1965**, *1*, 338–340. (b) Yamazaki, T.; Matsuda, K.; Sugiyama, H.; Seto, S.; Yamaoka, N. *J. Chem. Soc.* **1977**, 1981–1984.

(9*R*,10*S*)-(+)-1-Thiadecalin, 11. A suspension of $RuO_2 \cdot nH_2O$ (60% Ru, 0.075 g, 0.4 mmol) in 9 mL of MeOH/H_2O, 10/1 v/v, was stirred under H_2 (2 atm) for 12 h to activate the catalyst. To this suspension a solution was added of **10** (0.25 g, 1.62 mmol) in 3 mL of the same solvent mixture. The H_2 pressure was raised to 12 atm, and the hydrogenation continued for 24 h at 40 °C. The suspension was filtered through a Celite pad, and the filtrate was concentrated by distillation. Addition of H_2O to the aqueous methanolic residue precipitated a solid, which was extracted with petroleum ether. The extract was dried and evaporated to leave the title compound as a white solid (0.225 g, 90%), which was further purified by Kugelrohr distillation: bp 110 °C (1 mm); mp 34.5–35.0 °C;[26] $[\alpha]^{26}_D$ +24.4° (*c* 6.15, MeOH); ^{13}C NMR (see Table 1); ^1H NMR (300 MHz)[28] δ 2.66 (ddd, J = 13.5, 12.5, 3.0 Hz, 1 H, C_2H_{ax}), 2.48 (m, W_H = 21 Hz, 1 H, C_2H_{eq}), 2.37 (m, W_H = 26 Hz, 1 H, C_9H), 1.92 (m, W_H = 21 Hz, 1 H, C_3H_{eq}), 1.66, 1.50 (overlapping m's, 6 H overall), 1.25 (m, 4 H), 0.97 (m, 1 H). Anal. Calcd: C, 96.16; H, 10.32. Found: C, 69.31; H, 10.23.

(*E*)-(7*R*,8*R*)-(−)-7,8-Dimethoxy-1-thiacyclodec-4-ene 1,1-Dioxide, 12. Oxidation of the **5a,b** sulfoxide mixture (2.0 g in CH_2Cl_2) with *m*-chloroperbenzoic acid (1.2 equiv) added at 0 °C and stirred at room temperature for 6 h gave, after work up and FC purification (silica; MeOH/Et_2O, 2/98), the title compound (2.05 g, 96%) as a viscous uncrystallizable material: $[\alpha]^{26}_D$ −51.1° (*c*, 2.0, $CHCl_3$); ^{13}C NMR [In $CHCl_3$ at the probe temperature (~35 °C) the 23.15-MHz spectrum consists of 11 signals, several of which show broadening due to exchange between unequivalent sites] δ 130.2 (C_4), 129.3 (C_5), 81.5 and 81.2 (both br, C_7 and C_8, interchangeable), 57.8 and 57.4 (OCH_3's), 54.8, 50.4 (C_2 and C_{10}, interchangeable), 31.2 (br, C_6), 26.5 (C_3), 22.8 (br, C_9); ^1H NMR, at 200 MHz the spectrum shows extensive broadening due to exchange between unequivalent sites. The only sharp signals are at δ 3.42 and 3.36 (s's, OCH_3's) superimposed to a br m (8 H overall). The olefinic H's are centered at 5.8 and 5.6 (both br m's). Anal. Calcd: C, 53.20; H, 8.12. Found: C, 53.12; H, 8.16.

(6*R*,7*R*,9*R*,10*R*)-(−)- and (6*R*,7*R*,9*S*,10*S*)-(−)-6,7-Dimethoxy-1-thiadecalin 1,1-Dioxides, 13 and 14. Sulfone **12** (1.5 g, 6.04 mmol in 60 mL of THF) was treated with 0.5 equiv of BuLi under the conditions described above for the corresponding **5a,b** sulfoxide mixture. Workup as usual[2c] gave a crude product whose ^{13}C NMR contained three sets of signals (intensity ratio ~18:2:1), the minor of which has resonances in the olefinic region (probably a product of eliminative ring fission). The other two sets are assigned to the title compounds **13** (major) and **14** (minor) since they are identical with those of the products obtained by oxidation of the corresponding bicyclic sulfoxides **6** and **7**, respectively. The major product, **13**, was obtained by FC (silica, ether) as a crystalline material (1.065 g, 71%): mp 115–115.5 °C (from hexane–benzene); $[\alpha]^{27}_D$ −32.4° (*c* 5.1, MeOH); ^{13}C NMR (see Table I); ^1H NMR (300 MHz) δ 3.57, 3.34 (m's, both W_H = 8 Hz, 1 H each, CHO's, 3.30, 3.27 (s's, 6 H overall, OCH_3's), 3.02 (m, W_H = 20 Hz, 1 H, C_2H_{eq}), 2.84 (m, 2 H), 2.21 (ddd, J = 13.5, 3.0, 3.0 Hz, 1 H), 2.15–1.95 (m, 2 H), 1.86 (ddd, J = 13.0, 12.0, 2.5 Hz, 1 H), 1.75 (d,d,d, J = 13.0, 3.0, 3.0 Hz), 1.63 (m, 1 H), 1.52 (d,d,d, J = 13.5, 11.5, 3.0 Hz), 1.17 (m, 1 H). Anal. Calcd: C, 53.20; H, 8.12. Found: C, 53.5; H, 8.16.

The separation of the minor bicyclic product from the olefinic contaminant was not pursued. However, for identification purposes, sulfone **14** was obtained pure from **7** by oxidation (MCPBA, CH_2Cl_2), crystallized from hexane/benzene: mp 162–163 °C; $[\alpha]^{30}_D$ −83.2° (*c* 2, MeOH); ^{13}C NMR (see Table I); ^1H NMR (200 MHz) δ 3.47 (s's, 6 H overall, OCH_3's), 3.23–3.05 (m, 3 H, CHO's and C_2H_{eq}), 2.88 (m, 1 H), 2.58 (m, 2 H), 2.13 (m, 3 H), 1.86 (m, 2 H), 1.53, 1.18 (m's, 1 H each). In C_6D_6 the C_6H and C_7H protons appear at δ 2.83 as a symmetrical multiplet whose overall width, 37.5 Hz, is consistent with their axial setting. Anal. Calcd: C, 53.20; H, 8.12. Found: C, 53.14; H, 8.20.

(6*R*,7*R*,9*R*,10*R*)-(−)-6,7-Dihydroxy-1-thiadecalin 1,1-Dioxide, 20. The dimethyl ether **13** was cleaved by in situ generated Me_3SiI, as described above for sulfide **6**. In this case no scavenger was needed, sulfone sulfur being inert toward the CH_3I side product. The title compound was obtained in 77% yield after FC purification (silica; MeOH/CH_2Cl_2, 10/90): crystallized from EtOH; mp 208.5–209.5 °C; $[\alpha]^{25}_D$ −19.2° (*c* 5, MeOH); ^{13}C NMR (see Table I); ^1H NMR (200 MHz, methanol-d_4) δ 4.83 (s, >2 H, OH's), 3.93, 3.76 (m's, W_H = 8 Hz, 1 H each, CHO's), 3.07 (m, 3 H), 2.04 (m, 5 H), 1.57 (m, 3 H), 1.31 (m, 1 H). Anal. Calcd: C, 49.07; H, 7.32. Found: C, 48.59; H, 7.38.

(6*R*,7*R*,9*R*,10*R*)-6,7-Di-*O*-mesyl-1-thiadecalin 1,1-dioxide, 21, was obtained in 90% yield as a highly insoluble solid from diol **20** as described above for the preparation of **19**: crystallized from MeOH; mp 214–215 °C; ^{13}C NMR (in DMSO-d_6) δ 73.9, 73.8 (C_7, C_8, interchangeable), 56.8 (C_9), 50.4 (C_2), 37.5 (C_{10}), 32.7 (C_4), 31.1 (C_5), 29.4 (2 resonances, CH_3SO_2), 22.7 (C_3), 20.6 (C_8). (Because of low solubility the optical rotatory power was not determined.) ^1H NMR (DMSO-d_6) δ 5.02 (m, 2 H, CHO's), 3.35 (s overlapping a 3.2 m, 9 H overall), 2.5–1.3 (m, 9 H). Anal. Calcd: C, 35.09; H, 5.36. Found: C, 35.26; H, 5.29

(9*R*,10*R*)-(−)-6,7-Didehydro-1-thiadecalin 1,1-dioxide, 22, was obtained (80%) from **21** by the Tipson–Cohen procedure as described above for the corresponding sulfide **10**: purified by FC (silica, Et_2O); mp 74–76 °C; $[\alpha]^{27}_D$ −83.7° (*c* 5.07, MeOH); ^{13}C NMR δ 125.4, 123.5 (C_6, C_7, interchangeable), 61.2 (C_9), 51.7 (C_2), 35.3 (C_{10}), 31.9, 31.7 (C_4, C_5, interchangeable), 22.9 (C_3), 19.6 (C_8); ^1H NMR (200 MHz) δ 5.71 (m, $W_H \simeq 12$, CH=CH), 3.04 (m, 3 H), 2.48 (m, 2 H), 2.34–1.25 (overlapping m's, 7 H), 1.25 (m, 1 H). Anal. Calcd: C, 58.03; H, 7.57. Found: C, 57.61; H, 7.54.

(9*R*,10*S*)-(+)-1-Thiadecalin 1,1-dioxide, 15, was obtained by catalytic hydrogenation of **22** (0.560 g in 25 mL of MeOH, PtO_2 0.060 g, 3 atm, room temperature). The reduction was complete after 2.5 h. After filtration and solvent removal, the solid product (0.533 g, 95%) was crystallized from hexane, mp 103–103.2 °C;[29] $[\alpha]^{29}_D$ +3.5° and $[\alpha]^{29}_{435}$ +8.1° (*c* 6.39, MeOH); $[\alpha]^{29}_{435}$ −1.96° (*c* 2.8, $CHCl_3$); ^{13}C NMR (see Table 1); ^1H NMR (200 MHz) δ 3.11 (dddd, J = 13.5, 4.0, 3.5, 1.0 Hz, 1 H, C_2H_{eq}), 2.94 (m, 2 H), 2.61 (ddd, J = 12.5, 10.0, 3.5 Hz, 1 H), 2.14 (m, 2 H), 1.95–1.70 (m, 5 H), 1.58 (m, 1 H), 1.46–1.00 (m, 4 H). Anal. Calcd: C, 57.41; H, 8.57. Found: C, 57.20; H, 8.60.

A sample of the title compound was obtained by MCPBA oxidation of **11** and found to have identical properties.

Registry No. **1**, 82188-39-4; **2**, 116701-45-2; **3**, 116701-46-3; **4a**, 116701-47-4; **4b**, 116782-14-0; **5a**, 116701-48-5; **5b**, 116782-16-2; **6**, 116701-49-6; **7**, 116782-09-3; **8**, 116701-50-9; **9**, 116782-10-6; **10**, 116701-51-0; **11**, 116782-11-7; **12**, 116701-52-1; **13**, 116701-53-2; **14**, 116782-12-8; **15**, 116782-13-9; **16**, 116701-54-3; **17a**, 116701-55-4; **17b**, 116782-15-1; **18**, 116701-56-5; **19**, 116701-57-6; **20**, 116701-58-7; **21**, 116724-54-0; **22**, 116701-59-8.

(26) A mp of 17–18 °C has been reported for the racemic material.[27]

(27) Klaus, P. K.; Vierhapper, F. W.; Willer, R. L. *J. Org. Chem.* **1977**, *42*, 4016–4023.

(28) The 100-MHz spectrum has been previously reported: Vierhapper, F. W.; Willer, R. L. *J. Org. Chem.* **1977**, *42*, 4024–4029.

(29) A mp of 114–115.8 °C has been reported for the racemic material.[15]