barriers for cuneal inversion at sulfur(IV) may be obtainable in systems which are inert toward hydrolysis or with more rigorous exclusion of water.

Conclusion

Additional factors that influence sulfurane stability have been found. An increase in the electronegativity of the apical ligands is reflected in an increase in the stability of sulfuranes. Hydrolyses of spirosulfuranes are slowed by the presence of *gem*-dialkyl groups on the carbon α to the apical atoms, and sulfurane stability is enhanced by this structural feature.

A lower limit of 30 kcal mol^{-1} has been set for $\Delta G^*_{84°C}$ for the cuneal inversion at sulfur(IV), a process that interconverts a pair of diastereomeric spirosulfuranes. This value is the highest yet found for sulfuranyl sulfur but still represents only a lower limit to the value because inversion by another mechanism or catalysis by water, acids, or bases cannot rigorously be ruled out.

Acknowledgment. This research was supported in part by a grant from the National Science Foundation, CHE 75-17742.

Registry No.—**5,** 62220-51-3; **6,** 62750-57-6; **7,** 63743-90-8; **8,** 62750-58-7; **9,** 38059-09-5; **10,** 63743-91-9; **11,** 34400-24-3; **12,** 63743-92-0; **13,** 63743-93-1; **14,** 63743-94-2; **15,** 63731-54-4; **16,** 63743-95-3; **17a,** 63743-96-4; **17b,** 63813-46-7; **18,** 62750-61-2; **19,** 63743-97-5; **21,** 63743-98-6; **22a,** 63744-00-3; **22b,** 63744-01-4; **22c,** 63813-47-8; **24,** 63744-02-5; **25,** 63731-59-9; **26,** 63744-03-6; **27,** 63744-04-7; **28,** 63744-05-8; **29,** 63744-06-9; **30,** 24536-81-0; 2,2′-dicarboxydiphenyl sulfide, 22219-02-9; 2-bromo-2′-carboxydiphenyl sulfide, 20076-94-2; 2-bromothiophenol, 6320-02-1; 2-iodobenzoic acid, 88-67-5; methyl ethyl ketone, 78-93-3; L(−)-2,2,2-trifluoro-1-phenylethanol, 10531-50-7; fluoroboric acid, 14874-70-5; *d*-10-camphorsulfonic acid, 3144-16-9; triflic acid, 1493-13-6; acetyl chloride, 75-36-5; (*S*)-(+)-2,2,2-trifluoro-9-(anthryl)ethanol, 60646-30-2; hexafluoroacetone, 684-16-2.

References and Notes

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(35) It should be noted that the chemical-shift assignments for *exo*- and *endo*-methyl groups of **45** are inverted from those for the sulfuranes of this study, with the *endo*-methyl being found at higher field than the *exo*-methyl of **45.** Differences in geometry between the two systems may provide an explanation.

Synthesis of Methyl-Substituted *trans*- and *cis*-1-Thiadecalins

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Received May 4, 1977

Synthetic procedures for *trans*-1-thiadecalin (**1**), *cis*-1-thiadecalin (**11**), and 15 *trans*- (**2–10**) and *cis*-1-thiadecalins (**12–17**) with methyl substituents in various positions of the heterocyclic or the carbocyclic ring are described.

Interest in the conformational and configurational properties,[1] and in the rearrangement reactions[2] of thiane-1-*N*-arylimides motivated us to synthesize a number of methyl-substituted 1-thiadecalins. Configuration and conformational equilibria of the compounds were established by ^{13}C and ^{1}H NMR spectroscopy;[3] here the synthetic procedures are discussed in some detail. The formulas of the compounds prepared are collected in Schemes I and II; in Table I the compositions of the product mixtures are summarized.

The following procedures were used. **Method A.** Addition of a (methyl)allylmagnesium halide to a (methyl)cyclohexene sulfide[4] and ring closure of the resulting (methyl-substituted) 1-allyl-2-mercaptocyclohexane (Schemes III and IV).

Methods B and C. Cyclization of (methyl substituted) 1-(3′-mercaptopropyl)cyclohexene-1 and (methyl substituted) 3-(3′-mercaptopropyl)cyclohexene-1 (Schemes V and VI).

Method D. Reaction of (methyl substituted) 1-(3′-methylsulfonyloxypropyl)-2-methylsulfonyloxycyclohexane (cis and trans mixtures) with sodium sulfide, in 50% ethanol or in dimethylformamide (Scheme VII).

Table I. Composition of Products from the Syntheses of 1-Thiadecalins

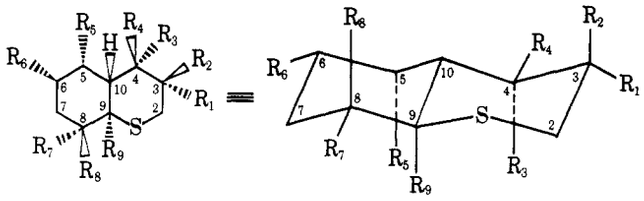
Starting material	Registry no.	Method[b]	Product[c]	%[a]
22a, 23a	286-28-2, 115-07-1	A	**1**	>97
22a, 23b[g]	115-11-7	A	**3**	97
			2	3
22a, 23c[g]	106-98-9	A	**4**	51
			5	49
cis-**22c, 23a**		A	**9**	90
cis-**22c**[g] (38%) +	40072-08-0,	A	**9**	63
trans-**22c**[g] (62%),	40072-07-9		**8**	13
23a			**6**	11
22b, 23a	7272-23-3	A	**10**	90
34a		B	**11**	68
			1	16
			18	16
34d		B	**12**	58.5
			13	17.5
			2	10
			19	14
34c[d]		B	**15**	70
			7	10
			20	14
34b[d]		B	**16**	70
			8	15
			17	7
			20	8
34b[d]		C	**16**	60
			8	15
			17	10
			20	14.5
30e	63714-74-9	C	**14**	>95
37a[d,e]		D	**11**	51
			1	8.5
			18	40.5
37a[d,f]		D	**11**	62
			1	7
			18	31
37d[d,e]	63714-75-0	D	**12**	45
			13	16.5
			2	<4
			3	<4
			19	34.5
37c[d,e]	63714-76-1	D	**15**	61
			20	24.5
			21	14.5
37b[d,e]	63714-77-2	D	**16**	46
			8	11
			20	27
			21	16
37b[d,f]		D	**16**	69
			8	11
			20	13
			21	8
16	63730-19-8	E	**8**	95
15	63730-18-7	E	**15**	<10
			7	>90

[a] Crude product mixtures were distilled from high-boiling material by distillation in a Kugelrohr apparatus and compositions of the resulting mixtures were determined by gas chromatography; differences to 100% result from small amounts of unidentified compounds. [b] See Text. [c] 1-Thiadecalin unless otherwise indicated. "α" means the substituent is on the opposite ring side as the substituent on C-10; "β" means the substituent is on the same ring side as the substituent on C-10. [d] Mixture of cis and trans isomers. [e] Solvent DMF. [f] Solvent 50% ethanol. [g] Registry numbers; *cis*-**22c**, 40072-08-0; *trans*-**22c**, 40072-07-9.

Method E. Equilibration of lithio derivatives of methyl *cis*-1-thiadecalin 1-oxides to methyl-*trans*-1-thiadecalin 1-oxides and reduction to the methyl-*trans*-1-thiadecalins (Scheme VIII).

Method A. Synthesis of compounds **1**,[4a] **4** and **5**,[4b] and **9**[4c] by this method has already been described, the trans fusion

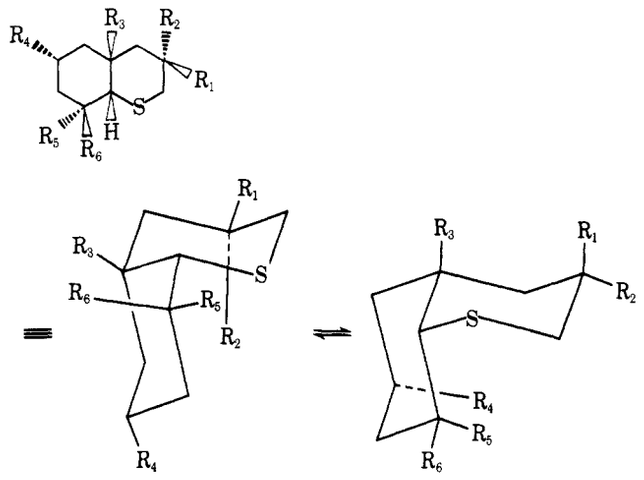
Scheme I



R = H unless indicated

1, all R's = H
2, $R_1 = CH_3$ (3α-CH_3)
3, $R_2 = CH_3$ (3β-CH_3)
4, $R_3 = CH_3$ (4α-CH_3)
5, $R_4 = CH_3$ (4β-CH_3)
6, $R_5 = CH_3$ (5α-CH_3)
7, $R_6 = CH_3$ (6α-CH_3)
8, $R_7 = CH_3$ (8α-CH_3)
9, $R_8 = CH_3$ (8β-CH_3)
10, $R_9 = CH_3$ (9-CH_3)

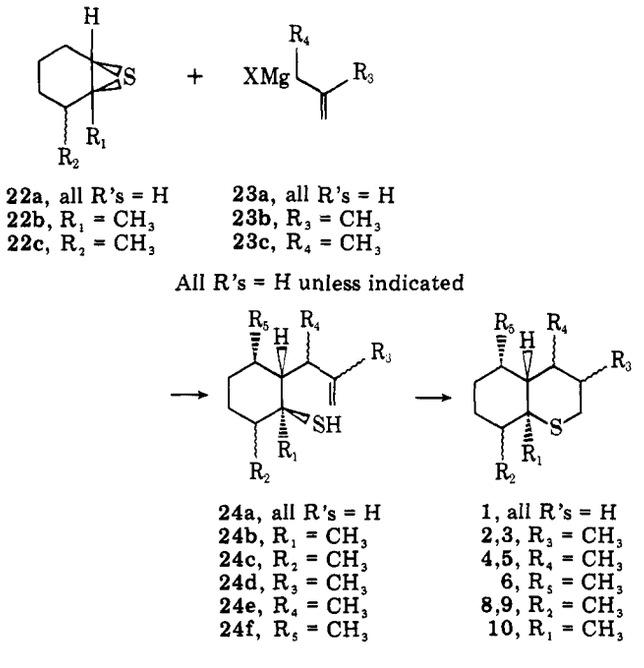
Scheme II



R = H unless indicated

11, all R's = H
12, $R_1 = CH_3$ (3β-CH_3)
18, $R_2 = CH_3$ (3α-CH_3)
14, $R_3 = CH_3$ (10-CH_3)
15, $R_4 = CH_3$ (6α-CH_3)
16, $R_5 = CH_3$ (8α-CH_3)
17, $R_6 = CH_3$ (8β-CH_3)

Scheme III



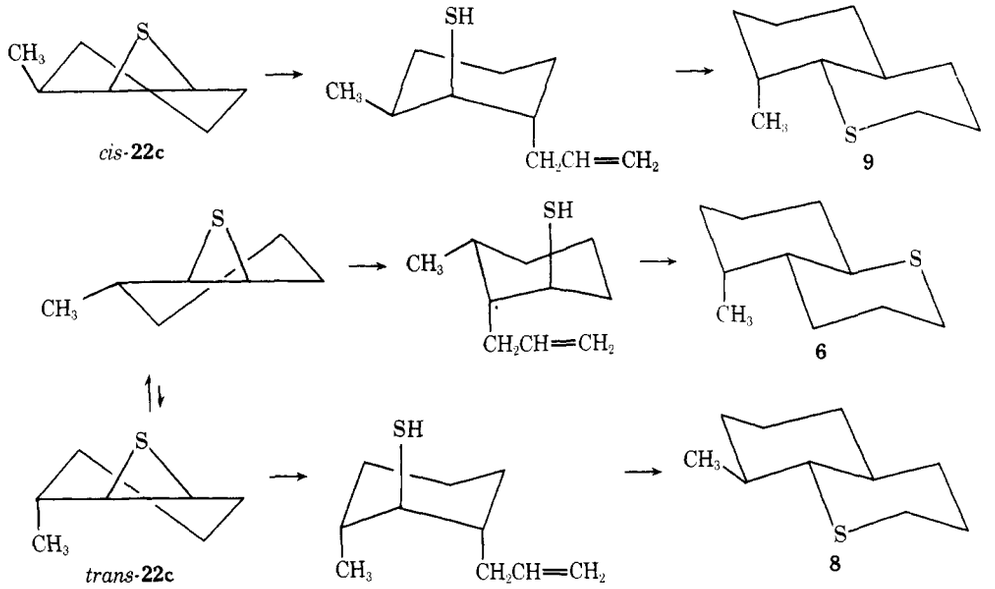
22a, all R's = H
22b, $R_1 = CH_3$
22c, $R_2 = CH_3$
23a, all R's = H
23b, $R_3 = CH_3$
23c, $R_4 = CH_3$

All R's = H unless indicated

24a, all R's = H
24b, $R_1 = CH_3$
24c, $R_2 = CH_3$
24d, $R_3 = CH_3$
24e, $R_4 = CH_3$
24f, $R_5 = CH_3$

1, all R's = H
2,3, $R_3 = CH_3$
4,5, $R_4 = CH_3$
6, $R_5 = CH_3$
8,9, $R_2 = CH_3$
10, $R_1 = CH_3$

Scheme IV



of the carbocyclic and heterocyclic rings being assumed.[4c] This assumption has now been verified by ^{13}C NMR[3], and the configuration of the methyl groups in **4** and **5**, previously not determined,[4b] has been established. When cyclohexene sulfide was allowed to react with methallylmagnesium chloride, a mixture of **2** and **3** was obtained; reaction of 3-methylcyclohexene sulfides (**22c**) with allylmagnesium bromide gave **9**, **6**, and **8**. Both the synthesis of the 3-methylcyclohexene sulfides and their reaction with the Grignard reagent require some discussion. It has been reported[5] that reaction of α-cyclohexene oxides with thiourea[6] leads to cyclohexene sulfides with retention of configuration. We found, however, that the reaction of pure *trans*-3-methylcyclohexene oxide with thiourea gave pure *cis*-3-methylcyclohexene sulfide, and reaction of a 1:1 mixture of *trans*- and *cis*-3-methylcyclohexene oxides with thiourea gave a mixture of *cis*- and *trans*-3-methylcyclohexene sulfides of the same composition. It is clear from these results that this reaction proceeds with clean inversion of configuration, not retention as claimed.[5] It also has been reported[5] that treatment of α-cyclohexene oxides with KSCN leads to mixtures of α- and β-cyclohexene sulfides (i.e., the reaction is nonstereospecific); thus, a 2:1 mixture of *cis*- and *trans*-3-methylcyclohexene oxides was reported to give a 1:2.5 mixture of *cis*- and *trans*-3-methylcyclohexene sulfides when treated with KSCN.[5] In our hands, reaction of a 1:1 mixture of *cis*- and *trans*-3-methylcyclohexene oxides with KSCN gave a mixture of *trans*- and *cis*-3-methylcyclohexene sulfides definitely richer in the trans product. However, this would seem to result not from the reaction being nonstereospecific but from the fact that the *trans*-3-methylcyclohexene oxide is much less reactive than the cis;[8] if the reaction was followed gas chromatographically the remaining starting material was seen to become gradually richer in the less reactive *trans*-3-methylcyclohexene oxide which could, in fact, be isolated in nearly pure form from the reaction mixture. ^1H NMR data of both epoxides and episulfides were found to differ from the previously reported values[5] and are listed together with the ^{13}C NMR data in Table III. The ^{13}C data confirm the configurational assignments (see ref 8 for the 3-methylcyclohexene oxides); the C-5s of the *trans*-3-CH_3 isomers are shifted upfield compared to the parent compounds due to the γ_a effect of the axial methyl group in one of the possible half-chair conformers (see Scheme IV), whereas the corresponding conformation for the cis isomers is depopulated because of sterical crowding between CH_3 and the heteroatom, as can be seen on a Dreiding model.

Reaction of *cis*-3-methylcyclohexene sulfide with allylmagnesium bromide, followed by cyclization of the intermediate **24**, gave only thiadecalin **9**. This agrees with the expected trans diaxial transition state, following an attack on the equatorially sulfur-substituted carbon atom 1 in the inverted conformation.

When mixtures of *trans*- and *cis*-3-methylcyclohexene sulfides were added to allylmagnesium bromide solutions, the major product after cyclization was **9**, even when *trans*-**22c** predominated in the starting material (see Table I), since, because of its greater stability, *trans*-**22c** reacts only partly and because two products (**6** and **8**) are formed from it in comparable amounts; attack on the preferred conformation of *trans*-**22c** (leading to **6**) is probably somewhat hindered for steric reasons.

Cyclization of the intermediate *trans*-1-allyl-2-mercaptocyclohexanes **24** was performed with 0.1 mol equiv of azobis(isobutyronitrile)[9] rather than by irradiation with UV light;[4] the reaction took place without changes in configuration, and only small amounts of thiahydrindanes (by addition to the less hydrogen-substituted carbon atom of the double bond) were formed as by-products.

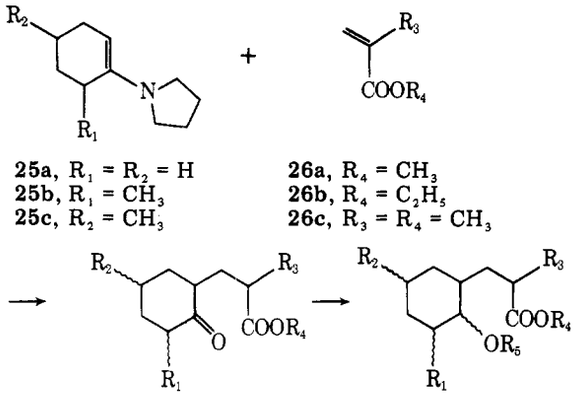
Products **2** and **3** (from **24d**) were found in very unequal amounts (~1:30). Model considerations show that formation of **3** must be preferred if the free-radical addition of the thiol to the double bond occurs trans, as it normally does.[10]

Method B. The condensation of pyrrolidino(methyl)cyclohexenes **25** with (meth-)acrylates to give (methyl substituted) 3-(2-oxocyclohexyl)propionates **27** has been described.[11] Reaction of **25b** with **26b** in anhydrous ethanol gave **27b** as the only product; no reaction at the methyl-substituted carbon atom occurred, while with dioxane as a solvent the formation of approximately equal amounts of the two products has been reported.[12a]

Reduction of the ketones with sodium borohydride gave mixtures of the cis and trans isomers of the cyclohexanols **28**. Temperatures during reaction were kept low to avoid the formation of the diols **36**.[12b] No attempts were made to separate the isomers, but the mixtures were converted into the methanesulfonates **29** and heated (without isolation of **29**) to induce elimination. Yields in this step were rather poor (<45%), since only methylsulfonyloxy groups cis to at least one of the other substituents of the cyclohexane ring could be expected to be suitably (i.e., axially) orientated for elimination.

The resulting 3-cyclohexenylpropionates (**30**) were mixtures

Scheme V



25a, $R_1 = R_2 = H$
25b, $R_1 = CH_3$
25c, $R_2 = CH_3$

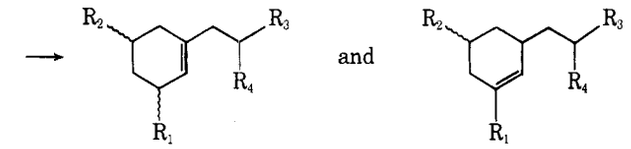
26a, $R_4 = CH_3$
26b, $R_4 = C_2H_5$
26c, $R_3 = R_4 = CH_3$

28, 29

27a, $R_4 = CH_3$
27b, $R_1 = CH_3$; $R_4 = C_2H_5$
27c, $R_2 = R_4 = CH_3$
27d, $R_3 = R_4 = CH_3$

28a, $R_4 = CH_3$
28b, $R_1 = CH_3$; $R_4 = C_2H_5$
28c, $R_2 = R_4 = CH_3$
28d, $R_3 = R_4 = CH_3$

29a, $R_4 = CH_3$; $R_5 = SO_2CH_3$
29b, $R_1 = CH_3$; $R_4 = C_2H_5$; $R_5 = SO_2CH_3$
29c, $R_2 = R_4 = CH_3$; $R_5 = SO_2CH_3$
29d, $R_3 = R_4 = CH_3$; $R_5 = SO_2CH_3$



30, 31, 32, 33, 34

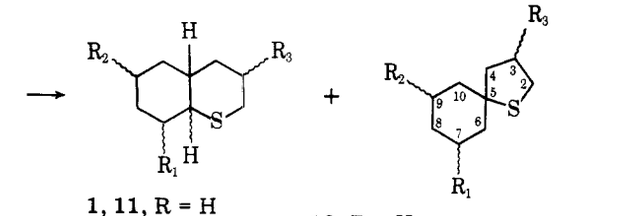
30a, $R_4 = COOCH_3$
30b, $R_1 = CH_3$; $R_4 = COOC_2H_5$
30c, $R_2 = CH_3$; $R_4 = COOCH_3$
30d, $R_3 = CH_3$; $R_4 = COOCH_3$

31a, $R_4 = CH_2OH$
31b, $R_1 = CH_3$; $R_4 = CH_2OH$
31c, $R_2 = CH_3$; $R_4 = CH_2OH$
31d, $R_3 = CH_3$; $R_4 = CH_2OH$

32a, $R_4 = CH_2OSO_2CH_3$
32b, $R_1 = CH_3$; $R_4 = CH_2OSO_2CH_3$
32c, $R_2 = CH_3$; $R_4 = CH_2OSO_2CH_3$
32d, $R_3 = CH_3$; $R_4 = CH_2OSO_2CH_3$

33a, $R_4 = CH_2SCN$
33b, $R_1 = CH_3$; $R_4 = CH_2SCN$
33c, $R_2 = CH_3$; $R_4 = CH_2SCN$
33d, $R_3 = CH_3$; $R_4 = CH_2SCN$

34a, $R_4 = CH_2SH$
34b, $R_1 = CH_3$; $R_4 = CH_2SH$
34c, $R_2 = CH_3$; $R_4 = CH_2SH$
34d, $R_3 = CH_3$; $R_4 = CH_2SH$



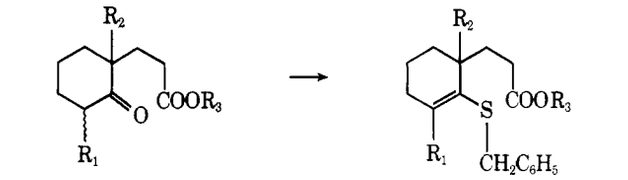
1, 11, R = H
8, 16, 17, $R_1 = CH_3$
7, 15, $R_2 = CH_3$
2, 12, 13, $R_3 = CH_3$

18, R = H
20, R_1 or $R_2 = CH_3$ (trans to S)
21, R_1 or $R_2 = CH_3$ (cis to S)
19, $R_3 = CH_3$

All R's = H unless indicated

of isomers as indicated in Scheme V. The ester groups were converted by a sequence of steps[13] into mercaptomethyl groups (see Scheme V), and the 3′-mercaptopropylcyclohexenes **34** were cyclized by heating with azobis(isobutyronitrile) in benzene as described for method A.

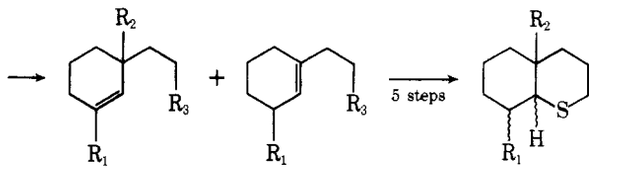
Scheme VI



27b, $R_1 = CH_3$, $R_3 = C_2H_5$
27e, $R_2 = R_3 = CH_3$

35b, $R_1 = CH_3$, $R_3 = C_2H_5$
35e, $R_2 = R_3 = CH_3$

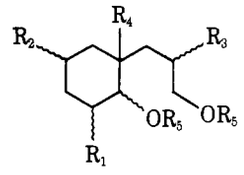
All R's = H unless indicated



30b, $R_1 = CH_3$, $R_3 = COOC_2H_5$
30e, $R_2 = CH_3$, $R_3 = COOCH_3$

8, 16, 17, $R_1 = CH_3$
14, $R_2 = CH_3$

Scheme VII

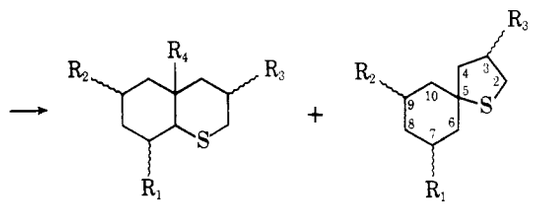


36, 37

36a, all R's = H
36b, $R_1 = CH_3$
36c, $R_2 = CH_3$
36d, $R_3 = CH_3$
36e, $R_4 = CH_3$

37a, $R_5 = SO_2CH_3$
37b, $R_1 = CH_3$, $R_5 = SO_2CH_3$
37c, $R_2 = CH_3$, $R_5 = SO_2CH_3$
37d, $R_3 = CH_3$, $R_5 = SO_2CH_3$
37e, $R_4 = CH_3$, $R_5 = SO_2CH_3$

All R's = H unless indicated

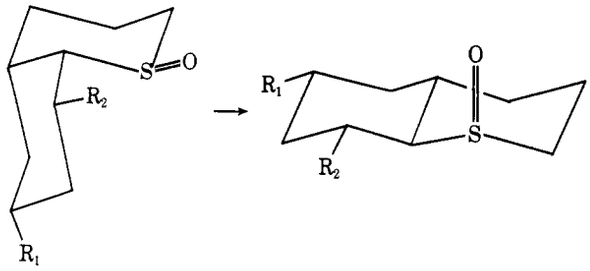


1,11, all R's = H
8,16, $R_1 = CH_3$
15, $R_2 = CH_3$
2,3,12,13, $R_3 = CH_3$
14, $R_4 = CH_3$

18, all R's = H
20, R_1 or $R_2 = CH_3$ (trans to S)
21, R_1 or $R_2 = CH_3$ (cis to S)
19, $R_3 = CH_3$

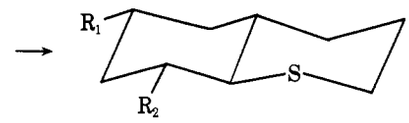
In addition to ring closure to give thiane derivatives, cyclization to give either thiepanes [from 3-(3′-mercaptopropyl)cyclohexene-1's] or thiolanes [from 1-(3′-mercaptopropyl)cyclohexene-1's] might be expected. No seven-membered ring products were isolated, the steric demand for such a reaction apparently being too high, but five-membered ring products (1-thiaspiro[4.5]decanes, **18–21**) were found in appreciable amounts. The mixtures of products were separated by precipitation and recrystallization of the $HgCl_2$ complexes, decomposition of the complexes with acid and steam distillation, and finally by preparative gas chromatography of the prepurified compounds or of the mother liquors. Configuration [cis or trans fusion of the rings, α or β position (see footnote *c*, Table 1) of the methyl groups] and conformation of the products were determined by ^{13}C and ^{1}H NMR spectroscopy.[3] From the data in Table I it is evident that formation of the cis-fused products is strongly preferred, in agreement with the

Scheme VIII



38a, $R_1 = CH_3$ **39a**, $R_1 = CH_3$
38b, $R_2 = CH_3$ **39b**, $R_2 = CH_3$

All R's = H unless indicated



7, $R_1 = CH_3$
8, $R_2 = CH_3$

known preference in addition of thio radicals to cyclohexenes to give axially substituted cyclohexanes.[13,14]

Method C. Since elimination of a methylsulfonyloxy group from 3-(1-methyl-2-methylsulfonyloxycyclohexyl)propionate was expected to be accompanied by skeletal rearrangements,[13] an alternative route, which had been successfully applied for the synthesis of 4-thia-5β-cholestanes,[13] was used to prepare 10-methyl-1-thiadecalin: 3-(1-methyl-2-oxocyclohexyl)propionate **27e** was converted into the benzyl thioenol ether **35e,** which was then desulfurized by treatment with Raney nickel previously partially deactivated by heating in acetone. Careful judgement of the time of deactivation is a somewhat crucial point of this method, or else the reaction does not go to completion; however, if the Raney nickel is properly prepared, yields in this step are excellent.

The reaction sequence from **30e** to **14** follows the procedure described above for method B (see also ref 13). An analogous synthesis starting with **27b** gave **8, 16, 17,** and **20** in the proportion listed in Table I, slightly different than in method B, presumably because different amounts of the two isomeric cyclohexenes **30b** are formed by the two paths. In general, method C is necessary for compounds with quaternary centers next to the carbonyl group on the cyclohexane ring, and the yields of compounds **30** are better than in method B; for large-scale synthesis, the large amount of Raney nickel required (see Experimental Section) poses a problem.

Method D. Reduction of the 3-(2-oxocyclohexyl)propionates **27** with lithium aluminum hydride afforded mixtures of cis and trans isomers of the diols **36.** The products were esterified with methanesulfonyl chloride without separation, and the bis(methanesulfonates) **37** were allowed to react with sodium sulfide in either dimethylformamide[4a] or 50% ethanol.[15,16]

The resulting (methyl-) 1-thiadecalins were admixed with very considerable amounts of 1-thiaspiro[4.5]decanes. Since the same products (**20** and **21**) are formed from **37b** and **37c,** the way of their formation may be inferred: instead of being replaced by S^-, the methylsulfonyloxy group on the cyclohexane ring reacts via elimination, and the sulfur on the propyl side chain subsequently adds to the resulting double bond. For the same reason, formation of the cis-fused thiadecalins is again strongly preferred, since the bis(methanesulfonate) with axial orientation of the CH_3SO_3 group on the cyclohexane ring (leading to trans products in case of nucleophilic displacement) is also oriented favorably for elimination.

An attempt to prepare 10-methyl-1-thiadecalins by this method gave a fraction of sulfides in only 9% theoretical yield, containing **14** and (by ^1H NMR spectrum) 10-methyl-*trans*-1-thiadecalin, but too little for positive identification. The low yield in this instance is explained by side reactions due to the quaternary carbon next to the methylsulfonyloxy group (see above).

Separation of the various product mixtures was accomplished in the manner described for methods A–C.

Method E. A number of *trans*-1-thiadecalins [especially the interesting 8α-methyl-*trans*-1-thiadecalin[1c] (**8**)] were obtained only in small amounts by the methods described above (see Table I). Moreover, the retention times of **8** and of *cis*-7-methyl-1-*r*-thiaspiro[4.5]decane (**21**) were practically identical on all available GC columns, which made purification of **8** nearly impossible.

Both **16** and **15,** on the other hand, were readily available in pure form: the mercuric chloride complex of **16** is not very soluble, allowing recrystallization, and **15** is a solid at room temperature and could itself be recrystallized. Since **16** and **15** are effectively locked in one conformation,[3] oxidation to the sulfoxides gave only one product in each case, the β-sulfoxides **38a** and **38b,** respectively, the α-sulfoxides being excluded because of severe syn–axial interactions in both possible conformations.

The sulfoxide oxygen in thiane 1-oxides is known[15,17] to prefer the axial position, and the *trans*-1-thiadecalin system has been calculated[18] to be more stable than the corresponding *cis*-1-thiadecalin by 1.7 kcal/mol. In addition, an interaction corresponding to a syn–axial interaction between oxygen and the methyl group in **38b** is absent in **39b.** Consequently, equilibration between **38** and **39** should lead to a high preference of the trans-fused system.

Equilibration was achieved by adding butyllithium to the benzene solutions of **38a** and **38b** and quenching with water after 2 h. Isolation of the sulfoxides **39** and reduction with phosphorus trichloride[19] indeed gave nearly pure **8,** and **7** containing less than 10% **15.**

The dideuterated analogue of **10** (9-methyl-*trans*-1-thiadecalin-2,2-d_2), which was needed to aid the identification of the signals of **10** in the ^{13}C NMR spectrum,[3] was also prepared via the sulfoxide: a mixture of the α- and β-1-oxides of **10** was reacted two times with butyllithium and with D_2O, and a mixture of mainly **10**-d_2, **10**-d_1, and **10** was obtained upon reduction of the sulfoxides.

Experimental Section

Melting points of compounds **1–21** and of their $HgCl_2$ complexes are summarized in Table II (for methods see footnotes *a* and *b*). Microanalyses were carried out by Dr. Zak, Physikalisch-Chemisches Institut der Universität Wien. Compounds **1, 3–5,** and **8–16** were further characterized by preparing their 1-*N*-*p*-chlorophenyl imides; melting points and elemental analyses of these compounds are reported elsewhere.[1c]

Analytical gas chromatography was carried out on a Varian Aerograph Series 1400 equipped with FID, on 0.125-in. columns. Columns used were 12-ft, 20% Carbowax 20M + 10% KOH, and a 12-ft, 20% SE 30, on Chromosorb W, 80–100 mesh. A Varian Aerograph Model 920 equipped with a thermal-conductivity detector, with 0.375-in. aluminum columns with matching phases, was used for preparative gas chromatography.

The ^1H and ^{13}C NMR spectra of compounds **1–17** are reported in the following paper of this issue.[3] The proton and variable temperature ^{13}C spectra of compounds **18–21** will be presented elsewhere.[20] 60-MHz ^1H spectra were recorded on a Varian EM-360 with internal lock facility; ^{13}C spectra were recorded in the pulsed mode at 25.16 MHz on a Varian XL-100 spectrometer. Solvent was $CDCl_3$, and the reference was Me_4Si.

Starting materials were purchased from various sources unless methods of preparation are indicated.

In the sequel, only one representative preparation of methods A–D

Table II. Characteristics of Thiadecalins 1–17 and Thiaspirodecanes 18–21

Compd	Registry no.	Mp (lit.)[a]	Mp of $HgCl_2$ complex (lit.)[b]	Registry no.
1	54340-73-7	17–18 (17.7[4a])	170–171 (172–173.5[4a])	63743-83-9
2	63702-90-9	*c*	172–176	63782-93-4
3	63730-12-1	8–10	152–153	63782-94-5
4	63730-13-2	9–11	176–177 (161–162[4b])	63782-95-6
5	63730-14-3	0–1	148–149 (141–142[4b])	63782-96-7
6	63702-91-0	2–3	*e*	
7	63702-92-1	8–10	161	63782-97-8
8	63702-93-2	*d*	132–133	63782-98-9
9	63730-15-4	6–8	145–146	63782-99-0
10	63702-94-3	*d*	153–154 (117.5–118.5[4c])	63714-81-8
11	57259-80-0	−1–1	176–177	63714-82-9
12	63730-16-5	12–14	187–188	63783-00-6
13	63730-17-6	31–32	158–159	63783-01-7
14	63702-95-4	−8 to −7	137–139	63714-83-0
15		46–47	154–155	63783-02-8
16		7–9	153–154	63783-03-9
17	63730-20-1	*c*	160–162	63783-04-0
18	53703-51-8	*d*	97–100	63714-84-1
19	63714-78-3	*d*	93–94	63714-85-2
20	63714-79-4	*d*	125–127	63714-86-3
21	63714-80-7	*d*	*e*	

[a] In °C. Melting points of sulfides melting below room temperature were determined by placing the crystalline compound in a sealed ampule into a stirred 2-propanol bath which was gradually warmed from −30 °C to room temperature. [b] In °C. Since some of the complexes showed a tendency to sublime the melting points were determined in sealed capillaries in an electrically heated Hoover type silicon bath. Differences to values previously reported (note for **10**[4c]) are probably due to this sublimation. [c] Sample contained small amounts of other isomers and did not crystallize. [d] Did not crystallize at −30 °C, although pure by GC. [e] Not determined because of very small amounts of material isolated. All compounds gave satisfactory elemental analysis, with exception of **6** and **21** where no analysis was attempted for the same reason.

Table III. ^{13}C[a] and Pertinent ^{1}H[b] Chemical Shifts of Cyclohexene Oxides[c] and Cyclohexene Sulfides[d]

	40[c]	*trans*-3-CH_3-**40**[g]	*cis*-3-CH_3-**40**[h]	**22a**	*trans*-**22c**	*cis*-**22c**
			^{13}C			
C-1	51.9[e]	52.6_8	52.8_6	36.7_2	37.7_6	36.4_3
C-2	51.9[e]	57.1_7	56.7_8	36.7_2	41.4_0	45.8_6
C-3	24.7[e]	29.1_1	30.2_1	25.8_9	31.7_4	30.9_0
C-4	19.7[e]	29.2_6	27.1_7	19.4_9	30.8_5	24.5_9
C-5	19.7[e]	17.1_4	20.3_3	19.4_9	16.8_9	21.2_2
C-6	24.7[e]	24.7_9	23.8_0	25.8_9	26.4_8	25.6_8
CH_3		19.1_6	18.5_3		22.8_0	22.5_6
			^{1}H			
H-1		3.08 ($w_{1/2}$ = 9)	3.08 ($w_{1/2}$ = 9)		3.18[f]	
H-2	3.08 ($w_{1/2}$ = 5)	2.78 (d, 4)	2.91 (d, 4 of d, 2)	3.18 ($w_{1/2}$ = 6)	2.77 (d, 6.5 of d, 1.5)	3.20 ($w_{1/2}$ = 5)
CH_3		1.06 (d, 7)	1.08 (d, 7)		1.15 (d, 7)	1.10 (d, 6.5)

[a] In ppm from Me_4Si; solvent $CDCl_3$. [b] H-1 and H-2 refer to the protons at C-1 and C-2, respectively. Ppm from Me_4Si, solvent $CDCl_3$. In parentheses: coupling constants, and half-width of not resolved signals, in Hz. Data are apparent values measured in spectra. [c] **40:** Cyclohexene oxide; registry no.: 286-20-4. [d] See Schemes III and IV. [e] Taken from the literature: S. G. Daves and G. H. Whitham, *J. Chem. Soc., Perkin Trans. 2,* 861 (1975). [f] Taken from a mixture of **22**c's. [g] Registry no.: 7443-54-1. [h] Registry no.: 7443-69-8.

is reported. More detailed procedures for the compounds prepared are given in the Supplemental Material.

Method A. 8α-Methyl-*trans*-1-thiadecalin (9), 8α-Methyl-*trans*-1-thiadecalin (8), 5α-Methyl-*trans*-1-thiadecalin (6). *trans*-3-Methylcyclohexene Sulfide (*trans*-22c) and *cis*-3-Methylcyclohexene Sulfide (*cis*-22c). (a) Thiourea Method.[6] 3-Methylcyclohexene oxide[8] (50% trans, 50% cis isomer, by NMR and GC; bp 42–47 °C/11 mm; bp lit.[8] 75 °C/6 mm) (11.2 g) was added to a suspension of 12 g of thiourea in 28 mL of water and 7.4 g of H_2SO_4 without external cooling; when addition was complete, the mixture was stirred for 2 h. A solution of 16 g of Na_2CO_3 in 100 mL of water was added dropwise, and the resulting (basic) solution was extracted repeatedly with petroleum ether. The organic solution was dried, and the solvent was distilled off. The product mixture was distilled (Kugelrohr, air bath ~85 °C/20 mm) and found free of starting epoxides by GC. Yield of **22c:** 10.6 g (83% of theory). Isomer ratio (by NMR): 50% *cis*-**22c,** 50% *trans*-**22c.**

(b) Thiocyanate Method[7]. 3-Methylcyclohexene oxide (mixture as for a) (11.2 g) was added to a solution of 20 g of KSCN in 13 mL of ethanol plus 15 mL of H_2O, and the mixture was stirred magnetically

at room temperature for 48 h. The mixture was extracted with petroleum ether, the extract was dried, and the solvent was distilled off. The residue was found by GC to consist of 42% epoxide (isomer ratio trans/cis = 65:35) and of 52% episulfide. The mixture was once more reacted with KSCN as above for 72 h. The product mixture consisted of 20% epoxide (trans/cis = 94:6) and of 80% episulfide. The epoxides were distilled from the mixture; pure *trans*-3-methylcyclohexene oxide was obtained from this fraction by preparative GC (Carbowax–KOH, 90 °C). The episulfides were distilled (Kugelrohr); composition (NMR): 62% *trans*-**22c**, 38% *cis*-**22c**. Yield 43%.

8β-Methyl-*trans*-1-thiadecalin (9). A solution of allylmagnesium bromide (from 5.7 g of magnesium turnings and 7.2 g of allyl bromide in anhydrous ether) was prepared and separated from excess magnesium by rapid decantation through a glass Büchner funnel. A solution of 1.1 g of pure *cis*-**22c** (prepared by the thiourea method from recovered *trans*-3-methylcyclohexene oxide, see above) in anhydrous ether was added slowly to the stirred Grignard solution. When the addition was complete, the mixture was heated to reflux for 12 h, and was then hydrolyzed with saturated NH_4Cl solution. The ether was decanted, the aqueous phase was repeatedly extracted with ether, and the ether solutions were united and dried. The solvent was distilled off at reduced pressure, and the residue (**24c**) was used without purification.

The crude **24c** was dissolved in 50 mL of anhydrous benzene and 100 mg of azobis(isobutyronitrile) was added. The solution was heated to reflux overnight. The solvent was distilled off at reduced pressure, and the residue was distilled in a Kugelrohr apparatus (~120 °C air bath temperature/10 mm). Gas chromatography of the product mixture showed one major product **9** and an unknown compound (presumably 2,7-dimethyl-1-thiahydrindane). No signals of **8** and **6** could be detected. Yield 410 mg (48% from *cis*-**22c**).

8β-Methyl- (9), 8α-Methyl- (8), and 5α-Methyl-*trans*-1-thiadecalin (6). A mixture of *trans*-**22c** (62%) and *cis*-**22c** (38%) (11.5 g) was added to a solution of allylmagnesium bromide (from 19 g of allyl bromide and 15 g of magnesium). The intermediates **24c** and **24f** were cyclized [500 mg of azobis(isobutyronitrile)] as described above. Yield of product mixture after distillation (Kugelrohr) 5.3 g; for composition, see Table I.

The mixture of products was dissolved in ethanol and added to a solution of 17 g of $HgCl_2$ in ethanol. The mixture was heated on a hot plate for 10 min and then brought to room temperature. The precipitate was collected and recrystallized three times from boiling ethanol. Decomposition of the recrystallized complex with 50% HCl and steam distillation and extraction of the distillate with petroleum ether gave pure **9**. Preparative gas chromatography (Carbowax–KOH, 145 °C) of the similarly treated mother liquor gave **6** and **8**.

Method B. *cis*-1-Thiadecalin (11). Methyl 3-(2-Hydroxycyclohexyl)propionate (28a). To a stirred solution of 14.7 g of **27a**[11] in 160 mL of anhydrous methanol, 3 g of $NaBH_4$ was slowly added, at 0 °C.[12b] When the addition was complete, the mixture was stirred for an additional 3 h at 0 °C and then was neutralized with CH_3COOH. After concentration to near dryness at reduced pressure, the residue was dissolved in CH_2Cl_2, the solution was washed with water and sodium bicarbonate solution, the organic solution was dried, and the solvent was distilled off. The residue was distilled in a Kugelrohr unit. Yield of **28a** 8.7 g; bp 120–130 °C/0.1 mm.

Methyl 3-Cyclohexen(1- or 2-)ylpropionate (30a). A solution of 8.7 g of **28a** in 150 mL of anhydrous pyridine was cooled to 0 °C, and 20 g of methanesulfonyl chloride was added gradually. The mixture was kept at +5 °C for 100 h and was then heated to reflux for 5 h. Most of the solvent was distilled off at reduced pressure, and the residue was poured on a mixture of ice, water, and HCl. The organic material was extracted with CH_2Cl_2, the extracts were washed with dilute HCl and sodium bicarbonate solution, and the solvent was distilled off. The residue was distilled in a Kugelrohr apparatus. Yield of **30a** 3.6 g; bp 120 °C/8 mm.

1-(3′-Hydroxypropyl)cyclohexene and 3-(3′-Hydroxypropyl)cyclohexene (31a). A solution of **30a** (8 g) in anhydrous ether was slowly added to 1.75 g of $LiAlH_4$ in anhydrous ether. The mixture was heated to reflux overnight and was then hydrolyzed with water. The ether was decanted, the precipitate was repeatedly washed with ether, the combined ether extracts were dried, and the solvent was distilled off. The residue was distilled in a Kugelrohr apparatus. Yield of **31a** 6 g; bp ~130 °C/8 mm.

1-(3′-Methylsulfonyloxypropyl)cyclohexene and 3-(3′-Methylsulfonyloxypropyl)cyclohexene (32a). To a solution of 6.5 g of **31a** in 200 mL of anhydrous pyridine at 0 °C, 30 g of methanesulfonyl chloride was added gradually. The resulting mixture was kept at +5 °C for 12 h and then poured on a mixture of ice, water, and HCl. The product was extracted with CH_2Cl_2, the extracts were washed with dilute HCl and sodium bicarbonate solution, the solvent was distilled off at reduced pressure, and the residue was used without further purification.

1-(3′-Thiocyanopropyl)cyclohexene and 3-(3′-Thiocyanopropyl)cyclohexene (33a). A solution of 8.7 g of **32a** and 50 g of KSCN in 200 mL of anhydrous acetone was heated to reflux overnight. The solvent was distilled off, the residue was extracted repeatedly with petroleum ether, the petroleum ether extracts were united and dried, and the solvent was distilled off. The residue was distilled in a Kugelrohr apparatus. Yield of **33a** 6.7 g; bp ~150 °C/8 mm.

1-(3′-Mercaptopropyl)cyclohexene and 3-(3′-Mercaptopropyl)cyclohexene (34a). A solution of 6.7 g of **33a** in anhydrous ether was added to 2 g of $LiAlH_4$ in anhydrous ether, and the mixture was stirred overnight at room temperature. After isolation of the product as described for **31a**, 5.22 g of **34a** (bp ~140 °C/8 mm) was obtained.

***cis*-1-Thiadecalin (11).** A solution of 5.1 g of **34a** and 0.5 g of azobis(isobutyronitrile) in dry benzene was reacted as described for method A. Distillation of the product in a Kugelrohr gave 4.8 g of a mixture; for composition, see Table I. Purification of **11** by repeated recrystallization of the $HgCl_2$ complex, or by preparative GC (Carbowax–KOH; 140 °C).

Method C. 8α-Methyl-*cis*-1-thiadecalin (16), 8β-Methyl-*cis*-1-thiadecalin, 8α-Methyl-*trans*-1-thiadecalin (8). Ethyl 3-(2-Oxo-3-methylcyclohexyl)propionate (27b). A solution of 66 g of **25b**[11] and 70 g of freshly distilled **26b** in 150 mL of anhydrous ethanol was heated to reflux for 48 h. Water (100 mL) was added, and the mixture was heated for 1 h. Most of the solvent was distilled off at reduced pressure, and the residue was worked up as described[11] for **27a**. Yield of **27b** 42.4 g; bp 147–149 °C/10 mm.

Ethyl 3-(2-Benzylthio-3-methylcyclohexen(1- or 2-)yl)propionate (35b). A solution of 39.6 g of **27b**, 40.9 g of benzyl mercaptan, and 2 g of toluenesulfonic acid in 500 mL of benzene was heated to reflux for 48 h, and the water formed was separated with a Dean–Stark trap. After the theoretical amount of water had been collected, the solvent was distilled off and the residue was distilled in a Kugelrohr distillation unit (air bath temperature 140–150 °C/10^{-3} mm). Yield of **35b** 53.6 g.

Ethyl 3-(3-Methylcyclohexen(1- or 2-)yl)propionate (30b). Raney nickel[21] from 300 g of alloy was washed with ethanol and acetone, and was heated in 1 L of acetone (Merck grade) to reflux for 45 min; 23.5 g of **35b** in 100 mL of acetone was rapidly added, and the mixture was heated to reflux, with stirring, for 18 h. The mixture was brought to room temperature, and the acetone was decanted. The solid was washed three times with acetone, and the combined acetone solutions were filtered through a bed of Celite. The solvent was distilled off, the residue was dissolved in petroleum ether, the solution was dried over Na_2SO_4, and the solvent was distilled off. The residue was distilled; yield of **30b** 13.4 g. Isomer ratio by GC 52:48. As was the case in method B, no attempt was made to determine which of the two isomers was the predominant one. The CH_3– signals in the ^1H NMR spectrum (–cyclohexen-1-yl: 1.63 ppm, s, half-width 6 Hz; –cyclohexen-2-yl: 0.93 ppm, d, J = 6.5 Hz) were superimposed with the rest of the molecule and could not be accurately integrated. The product composition of the thiadecalins indicates that more ethyl 3-(3-methylcyclohexen-2-yl)propionate is formed with method B, ultimately leading to the formation of less spiro-compound **20** (see Table I).

From the mixture of **30b, 16, 17,** and **8** were prepared analogously as described for **11,** method B. For composition of products, see Table I.

10-Methyl-*cis*-1-thiadecalin (14). Methyl 3-(1-Methyl-2-benzylthiocyclohexen-2-yl)propionate (35e). A solution of **27e**[12a] (39.6 g), 40.9 g of benzyl mercaptan, and 2 g of toluenesulfonic acid in 500 mL of benzene was reacted as described for **35b.** Kugelrohr distillation (bp ~150 °C/10^{-3} mm) gave 48.7 g of **35e.** Decomposition during distillation occurred if the bath temperature was raised above 160 °C.

Methyl 3-(1-Methylcyclohexen-2-yl)propionate (30e). From **35e** with Raney nickel as described for **30b.** Yield (from 23.5 g of **35e**) 10 g.

10-Methyl-*cis*-1-thiadecalin (14). From 9 g of **30e,** in an analogous procedure to **11** (see method B), 5.1 g of **14** was obtained after distillation. Purification was by recrystallization of the $HgCl_2$ complex.

Method D. *cis*-1-Thiadecalin (11). 2-(3′-Hydroxypropyl)cyclohexanol (cis and trans) (36a). A solution of 18.4 g of **27a**[11] in anhydrous ether was added to a stirred suspension of 5 g of $LiAlH_4$ in anhydrous ether. The mixture was heated to reflux overnight and

was hydrolyzed with water. The ether was decanted, the solid was washed repeatedly with ether, and the ether solutions were united and dried. The solvent was distilled off, and the residue was distilled in a Kugelrohr apparatus (bp lit.[12b] 119–120 °C/0.3 mm); yield15.4 g.

1-(3′-Methylsulfonyloxypropyl)-2-methylsulfonyloxycyclohexane (cis and trans) (37a). To a solution of 15.4 g of **36a** in 160 mL of dry pyridine cooled to 0 °C, methanesulfonyl chloride (36 g) was slowly added. The mixture was kept at +5 °C for 100 h and was then poured on ice, water, and HCl. The products were extracted with CH_2Cl_2, and the organic extracts were washed with dilute HCl and sodium bicarbonate solution and dried. The solvent was distilled off at low temperature, and the crude product was used for the next step without purification.

***cis*-1-Thiadecalin (11). (a) Solvent Dimethylformamide.**[4a] A solution of 58 g of $Na_2S·9H_2O$ in 250 mL of DMF was gradually heated to ~130 °C, and the water was distilled off. A solution of the crude **37a** in dry DMF was gradually added, and the mixture was kept at ~130 °C for 12 h. The mixture was brought to room temperature and poured on a fourfold volume of water. The aqueous mixture was extracted with petroleum ether, the extract was dried, the solvent was distilled off, and the residue was distilled in a Kugelrohr apparatus. Yield of product mixture 6.6 g; for composition, see Table I. Purification of **11** by recrystallization of the $HgCl_2$ complex and/or preparative GC (Carbowax–KOH, 140 °C).

(b) Solvent 50% Aqueous Ethanol. A solution of crude **37a** from 29.3 g of **36a** in the minimum amount of tetrahydrofuran was slowly added to a boiling solution of 61 g of $Na_2S·9H_2O$ in 800 mL of 50% ethanol, and the mixture was heated to reflux for 72 h. After that period, the mixture was steam distilled, and the distillate was diluted with water to a total volume of 3 L and was extracted with petroleum ether. The extracts were dried, the solvent was distilled off, and the residue was distilled in a Kugelrohr apparatus. Yield of product mixture 11.9 g; for composition, see Table I. Separation of products as reported above.

Method E. 8α-Methyl-*trans*-1-thiadecalin (8). 8α-Methyl-*cis*-1-thiadecalin 1β-Oxide (38b). To a solution of 10.3 g of **16** in CH_2Cl_2, 100 mL of an 0.59 M solution of *m*-chloroperbenzoic acid in CH_2Cl_2 was added at 0 °C, and the sulfoxide was isolated analogous to ref 15. Gas chromatography of the product mixture after separation from unreacted starting material showed one major (**38b**, >90%) and three minor products (SE 30, 230 °C). The product was used for the next step without purification: ^1H NMR 1.27 (d, CH_3, J = 6 Hz), 2.73 (s, H_9, half-width = 7 Hz), 3.42 ppm (d of m, H_{2e}, J = 11.5 Hz).

8α-Methyl-*trans*-1-thiadecalin 1β-Oxide (39b). A solution of 7.6 g of crude **38b** in dry benzene was cooled to <10 °C; a slow stream of dry nitrogen was passed through the reaction flask. A solution of butyllithium (17 mL of a 2.6 M solution in hexane, diluted with 20 mL of dry benzene) was added dropwise. When the addition was complete, the mixture was stirred at room temperature for 1.5 h and was then hydrolyzed with external cooling. The benzene layer was separated, and the aqueous layer was acidified and extracted with CH_2Cl_2. The organic solutions were united and dried, and the solvent was distilled off. The residue was distributed between an aqueous NaCl solution and petroleum ether; the aqueous solution was extracted with CH_2Cl_2, the extract was dried, and the solvent was distilled off. The residue consisted of one major (**39b**; >90%) and three minor unidentified products: yield 7 g; ^1H NMR 1.14 (d, CH_3, J = 5 Hz), 3.10 ppm (d of m, H_{2e}, J = 10 Hz).

8α-Methyl-*trans*-1-thiadecalin (8). A solution of 7 g of crude **39b** and of 18 mL of PCl_3 in 100 mL of CH_2Cl_2 was heated to reflux for 1 h. The mixture was poured on ice with stirring. After 2 h, the dichloromethane layer was separated, the aqueous layer was extracted with CH_2Cl_2, the dichloromethane solutions were united and dried, the solvent was distilled off, and the residue was distilled in a Kugelrohr apparatus. Yield of **8** 5.5 g.

6α-Methyl-*trans*-1-thiadecalin (7). 6α-Methyl-*cis*-1-thiadecalin 1β-Oxide (38a). From 1.9 g of **15**, analogous to **38b**: Yield 2.0 g of crude **38a**; ^1H NMR 0.95 (d, CH_3, J = 5 Hz), 2.68 (s, H_9, half-width = 9 Hz), 3.40 ppm (d of m, H_{2e}, J = 10 Hz).

6α-Methyl-*trans*-1-thiadecalin 1β-Oxide (39a). From 2.0 g of crude **38a**, analogous to **39b**: ^1H NMR 0.88 (d, CH_3, J = 5.5 Hz), 3.05 ppm (d of m, H_{2e}, J = 10 Hz).

6α-Methyl-*trans*-1-thiadecalin (7). From **39a**, as described for **8**. Composition >90% **7**, <10% **15**. Purification of **7** by recrystallization of $HgCl_2$ complex.

9-Methyl-*trans*-1-thiadecalin-2,2-d_2 (10-d_2). Crude **10** (see method A) (2 g) was oxidized as described for **38b**. The sulfoxides were distilled in a Kugelrohr apparatus; yield of approximately equal amounts of 1α- and 1β-oxide 1.4 g (by GC and ^1H NMR): ^1H NMR 1.25 (s, CH_3 1-α-oxide), 1.13 ppm (s, CH_3 1-β-oxide). The mixture was dissolved in benzene and treated with butyllithium as described for **39a** and **39b**. After 1.5 h, the mixture was hydrolyzed with a solution of 3 mL of D_2O and 1.6 g of acetyl chloride. The sulfoxides were recovered and the butyllithium–D_2O treatment was repeated. The recovered sulfoxides were reduced with PCl_3 as described above; yield of sulfides 0.5 g (mixture of **10**-d_2, **10**-d_1, and a little **10**).

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