followed by column chromatography (SiO_2; hexane/AcOEt, 5/1) gave **8b**: 48.5 mg (92%); mp 82–84 °C, IR (Nujol) 3055, 1312, 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.75 (s, 3 H, CH_3), 1.95 (s, 3 H, CH_3), 3.71 (dd, J = 15, 9 Hz, 1 H, CH_2) 4.29 (dd, J = 15, 2 Hz, 1 H, CH_2), 4.51 (dd, J = 9, 2 Hz, 1 H, CH), 7.46–8.08 (m, 5 H, Ph).

Anal. Calcd for $C_{14}H_{14}Br_2O_2S$: C, 35.70; H, 3.81. Found: C, 35.99; H, 3.73.

Electrochemical Conversion of Dimethyl 4,5-Epoxycyclohexane-1,2-dicarboxylate (2) into Dimethyl 2,3-Bis(2,2-dimethoxyethyl)succinate (10). A mixture of **2** (150 mg, 0.70 mmol) and H_2SO_4 (0.15 mL) in MeOH (10 mL) was electrolyzed at 17 mA/cm^2 by using two glassy carbon electrodes (1.5 × 2 cm^2) for 6.75 h. Usual workup gave **10**: 187 mg (87%); IR (neat) 1725 (C=O), 1260, 1160, 1130, 1070, 955 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.40–2.32 (m, 4 H), 2.60–2.89 (m, 2 H, HCC=O), 3.31 (s, 12H, CH_3O), 3.72 (s, 6 H, CH_3OCO), 4.38 (t, J = 6 Hz, 2 H, OCHO).

Anal. Calcd for $C_{14}H_{26}O_8$: C, 52.16; H, 8.13. Found: C, 51.88; H, 8.34.

Hydrolysis of Dimethyl 4,5-Epoxycyclohexane-1,2-dicarboxylate (2). A suspension of **2** (500 mg, 2.33 mmol) in H_2O (50 mL) was heated to reflux for 3 h. The usual workup yielded **11** (531 mg, 98%).[9]

Electrochemical Cleavage of Dimethyl 4,5-Dihydroxycyclohexane-1,2-dicarboxylate (11). A mixture of **11** (103 mg, 0.44 mmol) and H_2SO_4 (0.15 mL) in MeOH (10 mL) was electrolyzed at 10 mA/cm^2 for 7.3 h by using two glassy carbon electrodes (1.5 × 2 cm^2). The usual workup gave **10** (119 mg, 83%), which was identifical in all respects with **10** obtained above.

Registry No. **1**, 4841-84-3; **2**, 51349-92-9; **3a**, 77743-51-2; **3b**, 77743-52-3; **3** chlorohydrin, 77743-53-4; **4**, 77841-42-0; **5a**, 29171-21-9; **5b**, 15874-80-3; **6a**, 77743-54-5; **7a**, 77743-55-6; **7b**, 77743-56-7; **8a**, 77743-57-8; **8b**, 77743-58-9; **9**, 77743-59-0; **10**, 77743-60-3; **11**, 61825-80-7; NaBr, 7647-15-6.

Ring Enlargement by [2,3] Sigmatropic Rearrangement of Cyclic Sulfonium Ylides. 2. Conformational Control of Product Stereochemistry

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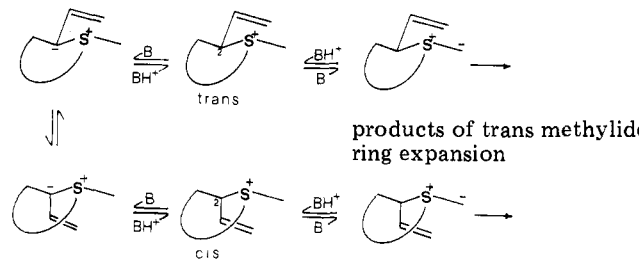
The geometry of the cyclic homoallylic sulfides produced by [2,3] sigmatropic ring enlargement of cyclic sulfonium ylides[5] is largely determined by configurational and conformational factors. Thus "trans" ylides (vinyl and S^+–CH_2^- moieties on opposite sides of the ring) can only attain a transoid transition state and rearrange to *E* products exclusively. "Cis" ylides, on the other hand, may attain both a cisoid and a transoid transition state whose relative energy depends on conformational factors which may be assessed merely by inspection of the ground state. Thus it is possible to direct the rearrangement toward one or the other steric course by appropriate substitutions on the ring or on the appended vinyl group. Wherever the sulfonium salt precursor has a H atom at the α allylic position, a certain extent of stereochemical control may be achieved by the method of ylide generation. Under "reversible" conditions (*t*-BuOK in THF/*t*-BuOH) the ring-expanded product largely arises from the "cis" ylide,[8] while under "irreversible" conditions (lithium diisopropylamide in THF) the product merely reflects the diastereoisomer population of the starting sulfonium salts, where the trans isomer often prevails.

Allylic sulfonium ylides rearrange to homoallylic sulfides in a concerted [2,3] sigmatropic process occurring via a five-membered transition state.[1] The geometry of the newly formed double bond is of interest. In acyclic systems there appears to be a strong preference for formation of the *E* olefin,[1b,2] a tendency which has been explained in terms of the conformational requirements of the R group:[3]

Because of its relative bulk, R will tend to set itself equatorial in the envelope conformation of the five-center transition state and end up trans to the substituent carrying the thioether group in the product olefin.[3]

When the S–C_2 bond is part of a ring,[4] however, the geometrical properties of the latter (configuration and conformation), as well as the properties (strain) of the product ring, may be expected to play a key role in determining the geometry of the cyclic olefin product.[6]

Scheme I



The study of the stereochemistry of the sulfonium ylides' ring enlargement is complicated by the sulfonium salt precursors existing as diastereomeric cis–trans pairs which, under the conditions required for ylide generation, may

(1) (a) Baldwin, J. E.; Hackler, R. E.; Kelly, D. P. *J. Chem. Soc., Chem. Commun.* **1968**, 538. (b) Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147 and references therein.

(2) (a) Baldwin, J. E.; Patrick, J. E. *J. Am. Chem. Soc.* **1971**, *93*, 3556. (b) Grieco, P. A. *J. Chem. Soc., Chem. Commun.* **1972**, 702. (c) Grieco, P. A.; Boxler, D.; Hirsi, K. *J. Org. Chem.* **1973**, *38*, 2572.

(3) Trost, B. M.; Melvin, L. S., Jr. "Sulfur Ylides"; Academic Press: New York, 1975; Chapter 7.

(4) The [2,3] sigmatropic rearrangement of cyclic sulfonium ylides brings about a three-carbon ring expansion, leading to thiacycloalk-4-enes.[5]

(5) Vedejs, E.; Hagen, J. P. *J. Am. Chem. Soc.* **1975**, *97*, 6878.

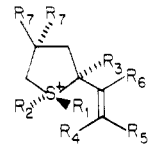
(6) Indeed, for six-membered ammonium ylides Vedejs and co-workers have brought to light dramatic evidence of the effects that relatively minor structural changes in the starting material may have on the geometry of the ring-expanded product.[7]

(7) (a) Vedejs, E.; Arco, M. J.; Renga, J. M. *Tetrahedron Lett.* **1978**, 523. (b) Vedejs, E.; Arco, M. J.; Powell, D. W.; Renga, J. M.; Singer, S. P. *J. Org. Chem.* **1978**, *43*, 4831.

0022-3263/81/1946-3315$01.25/0

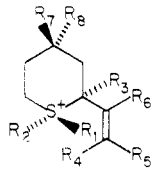
interconvert via an endocyclic ylide intermediate[8] (Scheme I).

This difficulty was circumvented by replacing the acidic H at C_2 by a CH_3 group, a structural feature which effectively prevents isomerization of the sulfonium salt precursors, thus allowing for meaningful stereochemical information to be drawn.[9] Only two pairs of cyclic sulfonium salts were investigated [five-membered (**1b,i**) and



1

All R's = H unless otherwise noted; **a**, $R_1 = CH_3$, R_2 = lone pair; **b**, $R_1 = R_3 = CH_3$, R_2 = lone pair; **c**, $R_1 = R_5 = CH_3$, R_2 = lone pair; **d**, $R_1 = R_4 = CH_3$, R_2 = lone pair; **e**, $R_1 = R_4 = R_5 = CH_3$, R_2 = lone pair; **f**, R_1 = lone pair, $R_2 = R_4 = R_5 = CH_3$; **g**, $R_1 = R_6 = CH_3$, R_2 = lone pair; **h**, $R_1 = R_7 = CH_3$, R_2 = lone pair; **i**, R_1 = lone pair, $R_2 = R_3 = CH_3$



2

All R's = H unless otherwise noted; **a**, $R_1 = CH_3$, R_2 = lone pair; **b**, R_1 = lone pair, $R_2 = CH_3$; **c**, $R_1 = R_3 = CH_3$; R_2 = lone pair; **d**, R_1 = lone pair, $R_2 = R_3 = CH_3$; **e**, $R_1 = R_3 = R_6 = CH_3$, R_2 = lone pair; **f**, R_1 = lone pair, $R_2 = R_3 = R_6 = CH_3$; **g**, $R_1 = R_7 = R_8 = CH_3$, R_2 = lone pair; **h**, R_1 = lone pair, $R_2 = R_7 = R_8 = CH_3$; **i**, $R_1 = R_8 = CH_3$, R_2 = lone pair; **j**, R_1 = lone pair, $R_2 = R_8 = CH_3$; **k**, $R_1 = R_6 = CH_3$, R_2 = lone pair; **l**, R_1 = lone pair, $R_2 = R_6 = CH_3$; **m**, $R_1 = R_4 = CH_3$, R_2 = lone pair; **n**, R_1 = lone pair, $R_2 = R_4 = CH_3$; **o**, $R_1 = R_5 = CH_3$, R_2 = lone pair; **p**, R_1 = lone pair, $R_2 = R_5 = CH_3$

six-membered (**2c,d**)] and were found to undergo highly stereoselective but not stereospecific ring enlargement.[9] In particular, **1by**,[10] in which the termini of the sigmatropic transition state are on the same side of the ring ("cis" ylide), expands to a largely *Z* homoallylic sulfide (*Z*/*E* ratio $\simeq$17), while **1iy**[10] (the "trans" ylide) cannot reach a geometry suitable for [2,3] sigmatropic shift and, rather, undergoes (α', β) β-elimination.[9] On the other hand, both "cis" and "trans" six-membered ylides, **2cy** and **2dy**, rearrange stereoconvergently to (*E*)-5-methylthiacyclonon-4-ene.[9]

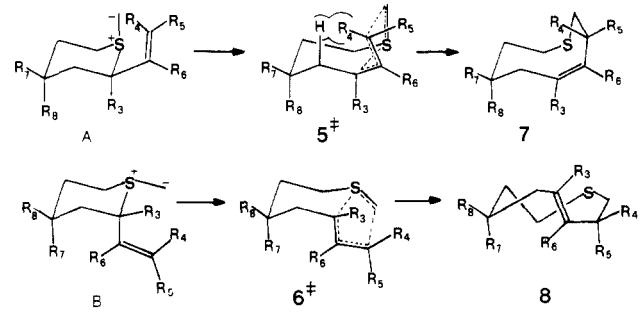
An explanation for this behavior was offered in terms of the ground-state conformational effect[9] and, for the rearrangement of the five-membered ylide, of competing conformational and ring strain effects.[5,9]

In this paper we develop further these arguments and report a number of observations pertaining to changes in steric course brought about by reasoned structural changes in the sulfonium salt precursors.

These observations strengthen the notion that the stereochemistry of the rearrangement is largely determined by conformational factors, the steric course being predictable on the basis of ground state considerations in accord with an early transition state.

(8) Ceré, V.; Paolucci, C.; Pollicino, S.; Sandri, E.; Fava, A. *J. Org. Chem.* **1978**, *43*, 4826.
(9) Ceré, V.; Paolucci, C.; Pollicino, S.; Sandri, E.; Fava, A. *J. Org. Chem.* **1979**, *44*, 4128. This paper is considered to be part 1.
(10) Methylides are denoted in the text by a y; thus the notation **1ay** indicates the methylide corresponding to sulfonium salt **1a**.

Scheme II[a,b]

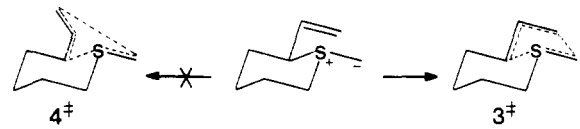


[a] a, all R's = H; c, $R_3 = CH_3$; e, $R_3 = R_6 = CH_3$; g, $R_7 = R_8 = CH_3$; i, $R_8 = CH_3$; k, $R_6 = CH_3$; m, $R_4 = CH_3$; o, $R_5 = CH_3$. [b] Note that B is represented as the mirror image of the desired conformational isomer of A for ease of viewing the desired stereochemical interactions.

Results and Discussion

Conventions. "Cis" and "trans" methylides refer to the stereochemistry of reactants (e.g., see Scheme I); "cisoid" and "transoid" refer to the stereochemistry of the developing double bond (e.g., "cisoid" transition state **5** leading to the cis olefin **7**, Scheme II); "y" stands for methylide such as A in Scheme II (e.g., **1ay** indicates the methylide corresponding to sulfonium salt **1a**).

Six-Membered Ylides. It was pointed out in part 1[9] and by Vedejs[7a] that "trans" methylides, while easily forming a transoid transition state (**3**‡), are prevented from reaching a cisoid transition state (**4**‡) as this would be of prohibitively high energy. Thus, *trans methylides unfailingly rearrange stereospecifically to E olefins.*



"Cis" ylides on the other hand may, in principle, attain both a cisoid (**5**‡) and a transoid (**6**‡) transition state (Scheme II). These may be reached, respectively, from conformer A (vinyl group equatorial, S–CH_3 axial) and B (vinyl axial, S–CH_3 equatorial). The finding that the product from **2cy** contained no *Z* olefin[9] had to be explained by postulating some kind of unfavorable interaction in the cisoid transition state. This was suggested to arise from the steric compression of the axial H at C_3 on to one of the vinyl H's (R_4) which is required to draw close in the cisoid (**5c**‡) but not in the transoid (**6c**‡) transition state. This interaction would raise the energy of **5c**‡ enough for the reaction to occur entirely via the transoid transition state, **6a**‡, which does not experience any comparable steric crowding.

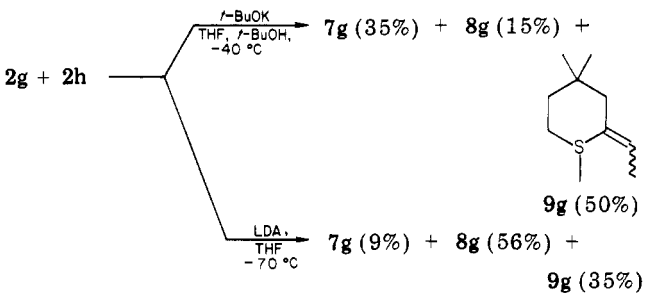
If this picture is correct, it is easy to see how the steric course of the rearrangement of cis ylides may be influenced by appropriate substitution in the ring and/or in the vinyl moiety. In fact, if transition state **6c**‡ is reached at least 50 times more readily than **5c**‡, it means the interaction depicted in **5c**‡ contributes at least 2.4 kcal/mol to the activation energy of the cisoid with respect to the transoid transition state. Inspection of models, however, suggests that merely by placing a CH_3 group at either R_6 or R_7 or at both positions the transoid transition state energy may be raised substantially, perhaps to the point where the reaction will take the cisoid course preferentially. This turns out to be the case (Table I). Methylation of 2-methyl-2-(1-methylvinyl)thiane with methyl triflate gave a 2.4:1 mixture of diastereomeric *S*-methyl sulfonium salts **2f** (trans) and **2e** (cis), whose configurations were assigned

Table I. Stereochemistry of Ring Expansion of Six-Membered Sulfonium Methylides

sulfonium salt	cis/trans[a]	method[b]	yield,[c] %	E/Z ratio[d]
2a,b[e]	0.075	I	85	24
2c,d[f,g]	1.5	I	89	≤0.02
2d[f]		I	70	≥50
2e,f[g]	0.4	I	90	≤0.02
2f		I	85	≥50
2g,h	0.18	I	50	0.4
2g,h	0.18	II	65	5.5
2i,j	1	I	80	≥50
2k,l	0.18	I	70	0.23
2k,l	0.18	II	75	6.0
2m,n,p	0.17	I	90	50

[a] Diastereoisomer ratio in the starting sulfonium salt. The cis and trans descriptors indicate the relation between the *S*-methyl and vinyl groups. [b] Method I uses *t*-BuOK base in THF/*t*-BuOH (10:1 v/v) solvent at −70 to −40 °C. Method II uses lithium diisopropylamide in THF at −70 °C. [c] Percent yield of three-carbon ring-expanded products. [d] Ratio of (*E*)- to (*Z*)-thiacyclonon-4-ene derivatives. [e] Reference 8. [f] Reference 9. [g] Base deficit corresponding to the trans sulfonium salt.

Scheme III



on the basis of their *S*-methyl shieldings.[8] Treatment of the mixture with 0.25 equiv of *t*-BuOK in THF/*t*-BuOH (10:1 v/v) at −70 °C (method I, "reversible" ylide generation) brought about ring expansion of the cis salt, **2e**, with essentially exclusive formation of *Z* olefin **7e**. The residual salt was treated first with 0.1 equiv of base at −70 °C to scavenge any cis salt left and subsequently with 0.65 equiv of *t*-BuOK at −40 °C to yield pure *E* olefin **8e**. Therefore the rearrangement of the **2ey,fy** pair is stereospecific (cis ylide → *Z* olefin; trans ylide → *E* olefin) in contrast to the **2cy,dy** pair which rearranges stereoconvergently (cis ylide → *E* olefin ← trans ylide). Thus a simple substitution of CH_3 for H at the R_6 position suffices for switching the steric course of the cis ylide from transoid to cisoid.

The same stereochemical result can be expected for a sulfonium salt in which $R_7 = CH_3$ [a condition which can be met by placing a *gem*-Me_2 grouping at C_4 (**2g,h**)] since the transoid transition state from the cis ylide **6g‡** would experience a repulsive interaction very similar to that prevailing in **6e‡**. This appears to be the case: methylation of 4,4-dimethyl-2-vinylthiane afforded a 5:1 mixture of diastereomeric sulfonium salts **2h** (trans, major) and **2g** (cis) which when treated with 1 equiv of base under the "reversible" conditions of method I gave a 2.3:1 mixture of ring-expanded olefins **7g** and **8g** together with rearranged sulfonium salt **9g** (Scheme III).

Of course the paradox that the ring-expanded product from a largely trans sulfonium salt has predominantly the *Z* configuration is only apparent, since, as we pointed out above, under the basic conditions required for ylide formation, diastereomeric sulfonium salts carrying a H atom at C_2 ($R_3 = H$) are known to interconvert easily.[8] Moreover, it was proven that "cis" ylides (such as **2cy**) rearrange somewhat more rapidly than their "trans" counterparts (**2dy**).[9] Thus olefin **7g** must originate from cis ylide **2gy**, in turn arising, for the largest part, from base-catalyzed isomerization of **2h**.

That this behavior is related to the presence of the axial methyl at C_4 (R_8) and not merely to the presence of a methyl group at C_4 is shown by the results obtained with the **2i,j** pair, which rearrange stereoconvergently to the *E* olefin **8i**. In this case the transoid transition state **6i‡** is easily accessible (R_8 is equatorial and out of the way of R_6 = H) while the cisoid transition state still suffers the same type of steric compression (C_3H–R_4) present in **5c‡** (see above).

The question may arise as to whether the minor olefin, **8g**, formed from the **2g,h** pair under conditions of reversible ylide generation, also originates from the cis ylide **2gy**. Although this cannot be ruled out, **8g** is likely to arise from the trans ylide **3hy** which in this particular system appears not to rearrange much slower than the cis ylide. This view is consistent with the results obtained in an experiment where the 5:1 mixture of **2g**/**2h** was ring expanded with lithium diisopropylamide (LDA) base in the absence of a protic cosolvent (method II, essentially "irreversible" ylide generation). The ring-expanded product was a mixture of **8g** and **7g** in a 5.5:1 ratio, i.e., close to the ratio of the starting sulfonium salts. This result shows that while they do not equilibrate, ylides generated under the above conditions rearrange stereospecifically and at rates not too different from each other.[11] A further, useful consequence of this result is that by changing reaction conditions (method I or II) it may be possible to exert a certain extent of stereochemical control. In fact, the products formed with method I (reversible ylide generation) arise largely from the "cis" ylide, while those generated with method II (substantially irreversible ylide generation) merely reflect the diastereomers population of the starting sulfonium salt, where the trans isomer normally prevails.

The remaining results reported in Table I are also consistent with the above principles. Thus the **2k,h** pair, though made up largely (6.5:1) of the trans isomer, **2l**, rearranged (method I) to a predominantly *Z* olefin (**7k**/**8k** ratio of 4) while under the conditions of method II the stereochemistry was inverted (**8k**/**7k** ratio of 7).

Finally, the results obtained with the mixture of sulfonium salts derived from 2-(2-methylvinyl)thiane are worth considering in some detail. Alkylation of 2-chlorothiane with (2-methylvinyl)magnesium bromide gave a 4:1 mixture of (*Z*)- and (*E*)-2-(2-methylvinyl)thianes whose configurations could be unambiguously assigned by ^{13}C NMR on the basis of the C_2 and CH_3 shieldings which were expected to be upfield in the *Z* isomer (γ effects). Thus the major isomer (δ_{C_2} 39.0, δ_{CH_3} 13.1) was assigned the *Z* and the minor one (δ_{C_2} 44.2, δ_{CH_3} 17.8) the *E* configuration. Methylation of the above mixture afforded three (out of the four possible) sulfonium salts in an ~6:2:1 ratio (identified as **2n,p,m**, respectively; see Experimental Section) which under the conditions of method I ring expanded to a single product, (*E*)-3-methylthiacyclonon-4-ene (**8m** (or **8o**).[12] This stereoconvergent course is fully

(11) The rearrangement rate shows a dichotomy: when C_2 is quaternary ($R_3 = CH_3$), the trans salts appear to rearrange considerably more slowly than cis salts (cf. the pairs **2c,d** and **2e,f** above), while for tertiary C_2 (R_3 = H) the rate differential seems to almost vanish under the conditions of method II. Systematic investigation of this unexpected behavior is under way.

(12) The two structures **8m** and **8o** represent diastereomeric conformers which rapidly interconvert at ambient temperature and are indistinguishable except at low temperature.[13]

(13) Cerè, V.; Paolucci, C.; Pollicino, S.; Sandri, E.; Fava, A.; Lunazzi, L. *J. Org. Chem.* **1980**, *45*, 3613.

Table II. Stereochemistry of Ring Expansion of Five-Membered Sulfonium Methylides[a]

sulfonium salt[b]	yield,[c] %	E/Z ratio[d]	ref
1a	91	0.17	8
1b	78	0.06	9
1c + 1d[e]	85	0.43	16
1e	70	50	this work
1g	85	0.02	16
1h	80	0.14	16

[a] Ylide generation by *t*-BuOK in THF/*t*-BuOH (10:1 v/v). [b] Only "cis" salts are mentioned since only they can ring expand. The actual diastereomer population of starting salt can be obtained from the pertinent part of the Experimental Section. [c] Percent yield of ring-enlarged products. [d] Ratio of (*E*)- to (*Z*)-thiacyclooct-4-ene derivatives. [e] 85:15 mixture of 1c/1d.

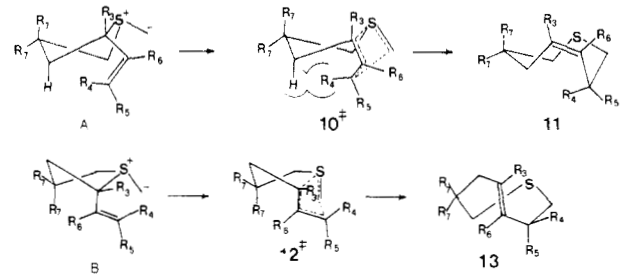
understandable: the cis ylide from the *E* isomer, **2py** ($R_5 = CH_3$; if any is formed by epimerization of **2o**), has no problem forming the transoid transition state **6o‡**, while the corresponding cisoid transition state, **5p‡**, would suffer the same hindrance discussed above in relation to **2cy**. The steric hindrance effect would be even stronger (much more so) in **5m‡**, the cisoid transition state from **2my** ($R_4 = CH_3$), while the transoid transition state **6m‡** appears to have no special problem.

Five-Membered Ylides. Of five-membered sulfonium salts, only those where the *S*-CH_3 and vinyl moieties are cis to each other ("cis" isomers) give methylides capable of ring expansion.[9] However, under reversible ylide-generation conditions, trans salts carrying a H atom at C_2 are rapidly equilibrated with their cis isomers and may undergo 2,3-shifts, through this route.[8] In any case, ring-expansion products arise from the cis ylide, independent of the isomer distribution of the starting salt. [For this reason Table II reports only the cis sulfonium salts, although the actual starting materials were normally mixtures of cis and trans salts (see the pertinent Experimental Sections).]

Five-membered sulfonium ylides expand to eight-membered homoallylic sulfides, and, in view of the strain attending the inclusion of a trans double bond in a eight-membered ring,[14] the *E* product might have expected not to form to any appreciable extent. The evidence instead is that sizeable (and variable) proportions of *E* olefin are formed along with the generally predominant *Z* isomer.[4,7a,8,9] To account for this behavior, the above ring-strain factor was suggested to be counterbalanced, to a certain extent, by another steric factor, this one disfavoring the *Z* product.[9] As for six-membered ylides, this was suggested to be the interaction arising in the cisoid transition state **10a‡** from one of the vinyl H's (R_4) being pushed against and past the axial H at C_3 (Scheme IV).

Since such interaction does not exist in the transoid transition state **12a‡**, the possibility is envisioned of rendering the latter relatively more accessible merely by hindering the cisoid transition state further. Within the framework of the steric interaction hypothesis, this goal may be achieved simply by replacing one or both the interacting H's by bulkier groups such as CH_3. Suggestive evidence that the hypothesis may be sound can be found in previous data on the rearrangement of 1-methyl-2-(2-methylvinyl)thiolanium salts **1c** and **1d**[16] (Table II). The starting materials was a 85:15 mixture of *E* (**1c**) and *Z* (**1d**) isomers, and the attending ring-expanded product was a 70:15:15 mixture of (*Z*)-, (*RS,SR*)-(*E*)-, and (*RR,SS*)-(*E*)-3-methylthiacyclooct-4-ene.[16] From Scheme IV, transition state **10d** ($R_4 = CH_3$) appears to be severely hindered, to the point where no *Z* olefin may be formed from **1dy**; the latter instead would give (*SS,RR*)-**13d** via transition state **12d‡**.[17] On the other hand, the *E* isomer **1c** ($R_5 = CH_3$) may have access to both transition states, **10c** and **12c‡**, to form, respectively, **11c** and (*RS,SR*)-**13c** (only the first enantiomer is represented in Scheme IV). If the latter has to be formed in a 15% overall population, **1c** must distribute itself ~5:1 toward **10c‡** and **12c‡**, a reasonable ratio.

Scheme IV[a]



[a] **a**, all R's = H; **b**, $R_3 = CH_3$; **c**, $R_5 = CH_3$; **d**, $R_4 = CH_3$; **e**, $R_4 = R_5 = CH_3$; **g**, $R_6 = CH_3$; **h**, $R_7 = CH_3$.

If the above interpretation is correct, it follows that compound **1e**, where both R_4 and R_5 are methyls, should be unable to attain the cisoid transition state but should ring expand to the *E* isomer exclusively. The evidence shows this to be the case: treatment of 1-methyl-2-(2,2-dimethylvinyl)thiolanium triflate (**1e** and **1f**, 1:2.3 mixture of trans/cis isomers) with base (method I) gave a single ring-expansion product which proved to be (*E*)-3,3-dimethylthiacyclooct-4-ene (**13e**). Apparently, not a trace (≤2%) of *Z* isomer was produced, showing that the postulated steric interaction has enough repulsion energy (≥4 kcal/mol) to switch the stereochemical course from predominantly cisoid to exclusively transoid.

The remaining data in Table II offer somewhat conflicting evidence. Sulfonium salt **1g** rearranges to the *Z* olefin **11g** exclusively, a result which fits the overall picture since the transoid transition state **12g** would appear to be especially destabilized by the compression of R_6 (CH_3) onto the axial H at C_4, while the corresponding cisoid transition state does not derive any special steric problem from the presence of the methyl substituent. If correct, this interpretation would seem to require **1hy** to be unable to reach the transoid transition state by virtue of the compression of R_6 (H) on to the quasi-axial R_7 (CH_3) at C_4. The evidence instead shows that **1h** rearranges to a 7:1 *Z*/*E* mixture, a ratio close to that of the parent salt, **1a**. A plausible explanation of this result is that the *gem*-Me_2 grouping distorts the half-chair conformation and flattens the ring enough to relieve the R_6–R_7 compression in the ground state as well as in the transoid transition state. That a *gem*-M_2 grouping may distort the thiolane ring is quite reasonable in view of the known flexibility of five-membered rings in general.[18] For the thiolane ring in

(14) The energy difference between (*E*)- and (*Z*)-thiacyclooct-4-ene must be of the same order as that of the homocyclic counterpart, i.e., ~10 kcal/mol.[15]

(15) Benson, S. W.; Cruikshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279.

(16) Calderoni, C.; Cerè, V.; Paolucci, C.; Pollicino, S.; Sandri, E.; Fava, A.; Guerra, M. *J. Org. Chem.* **1980**, *45*, 2641.

(17) Formula **13** represents (*E*)-thiacyclooct-4-ene of *S* configuration at the chiral plane and of *S* or, respectively, *R* configuration at the chiral center (C_3) according to whether $R_4 = CH_3$ and $R_5 = H$ (**13d**) or $R_4 = H$ and $R_5 = CH_3$ (**13c**). The first descriptor indicates the configuration of C_3.

particular, suggestive evidence is provided by the unprecedented, anomalously large ^{13}C NMR α effect (11.9 ppm in 3,3-dimethylthiolane[19] and 16.0 ppm in 1,3,3-trimethylthiolanium[20]) that may well be indicative of severe geometrical ring distortions relative to the respective parent compound.

In this paper we have shown that the stereochemistry of cyclic sulfonium ylides rearrangement is primarily determined by the geometrical properties of the starting sulfonium salt precursor. "Trans" ylides (from six-membered sulfonium salts) may only reach a transoid transition state and evolve to (*E*)-thiacyclonon-4-enes stereospecifically. "Cis" ylides (from five- and six-membered sulfonium salt precursors) may attain both a cisoid and a transoid transition state; their relative energy depends on conformational factors whose importance may be qualitatively evaluated simply by inspection of the ground state. Thus it is possible, by appropriate substitutions on the ring and/or on the appended vinyl group, to address the rearrangement toward one or the other stereochemical course specifically.

Experimental Section

Proton NMR spectra were recorded at 60 or at 100 MHz on Varian EM-360 and XL-100 instruments, respectively. The latter was used for obtaining proton noise decoupled ^{13}C NMR spectra at 25.15 MHz by the FT technique. Single-frequency off-resonance spectra were obtained by irradiation at δ −4 in the ^1H spectrum. Unless otherwise stated, ^1H and ^{13}C shifts are given in parts per million from Me_4Si in $CDCl_3$ solvent. GLC analyses were carried out with a Hewlett-Packard 1700 instrument equipped with a flame-ionization detector ($^1/_8$ in. × 3 m column, 10% Xe-60 on Chromosorb W).

Solvents and reagents were obtained dry as follows. Benzene, dichloromethane, *tert*-butyl alcohol, and diisopropylamine were distilled from calcium hydride; ethyl ether was distilled from $LiAlH_4$. Tetrahydrofuran, dried over sodium and distilled, was redistilled from $LiAlH_4$ before use. All reactions involving organolithium reagents were carried out under nitrogen, the reagent being introduced by syringe through a rubber stopper.

Ring expansion was effected on sulfonium hexafluorophosphate salts (soluble in THF at low temperature) by using either one of two methods. Method I involves *t*-BuOK as the base in THF/*t*-BuOH (10:1 v/v) at −70 to −40 °C. Method II employed lithium diisopropylamide in THF at −70 °C.

2-(1-Methylvinyl)thiane was obtained by coupling 2-chlorothiane with (1-methylvinyl)magnesium bromide by the procedure previously described for 2-vinylthiane.[7b] A benzene solution of 2-chlorothiane, freshly prepared by the method of Tuleen and Bennett[21] from thiane (3 g, 29 mmol in 60 mL) and *N*-chlorosuccinimide (4.62 g, 35 mmol), was added dropwise over 45 min to an ice-cooled solution of the Grignard reagent [prepared from 65 mL (75 mmol) of 2-bromopropene and 1.92 g (79 mmol) of magnesium in 90 mL of THF]. After warming to room temperature, the reaction mixture was decomposed with ice/20% sulfuric acid and extracted with pentane. The residue after solvent evaporation was fractionally distilled to give 2.0 g (48%) of the title compound: bp 97–98 °C (25 mm); ^1H NMR δ 4.94 and 4.86 (2 m, 2 H overall, $=CH_2$), 3.30 (q, J = 10.0, 3.0 Hz, 1 H, C_2H), 1.81 (s, 3 H, CH_3), ^{13}C NMR δ 146.2 (>C=), 111.8 ($=CH_2$), 49.1 (C_2), 33.2 (C_3), 30.1 (C_6), 27.1 and 26.8 (C_4 and C_5, interchangeable), 20.7 (CH_3). Anal. Calcd for $C_8H_{14}S$: C, 67.54; H, 9.92. Found: C, 67.45; H, 9.87.

2-(1-Methylvinyl)thiane 1-oxide was prepared (90%) by aqueous $NaIO_4$ oxidation[22] of 2-(1-methylvinyl)thiane. The ^{13}C spectrum displays 16 lines of roughly equal intensity, indicating a ca. 1:1 isomeric mixture. No attempt was made to separate the isomers, and the material was used as such in the subsequent methylation step (see below).

2-Methyl-2-(1-methylvinyl)thiane 1-oxide was obtained (75%) by methylation (MeI) of the α-lithio derivative(s) (LDA, THF, −70 °C)[9] of the crude mixture of *cis*- and *trans*-2-(1-methylvinyl)thiane 1-oxides. By GLC and ^1H and ^{13}C NMR the material appears to be a single isomer. It was purified by column chromatography (SiO_2, CH_3OH–$CHCl_3$, 15:85 v/v): ^1H NMR δ 5.15 and 5.07 (2 br s, 1 H each, $=CH_2$), 1.93 (s, 3 H, $CH_3C=$), 1.32 (s, 3 H, C_2CH_3); the remaining 8 H's occur as complex absorptions spread in the 3.1–1.4 region; ^{13}C NMR δ 145.3 (C=), 115.6 ($CH_2=$), 58.5 (C_2), 41.9 (C_6), 25.9 (C_3), 20.4 and 19.6 (C_4 and C_5, interchangeable), 18.3 (C_2CH_3), 14.6 ($=CCH_3$). The configurational assignment of this material cannot be made simply on the basis of NMR; however, previous evidence indicates that in the alkylation of α-lithiothiane 1-oxides the Me group enters trans to S–O.[23] Little can be said about the steric course of alkylation, except that one isomer must react with complete retention and the other with complete inversion of configuration. This matter is being further investigated.

2-Methyl-2-(1-methylvinyl)thiane was obtained by $NaBH_4$ reduction in EtOH of the corresponding 1-methoxysulfonium derivative [prepared by methyl triflate alkylation of 2-methyl-2-(1-methylvinyl)thiane 1-oxide] according to the Johnson and Phillips procedure,[24] and distilled: 80% yield; bp 105 °C (25 mm); ^1H NMR δ 5.42 and 4.96 (2 br s, $w_h \simeq 3$ Hz, 1 H each, $CH_2=$), 2.53 (m, 2 H, α-CH_2), 1.83 (s, 3 H, $CH_3C=$), 1.34 (s, 3 H, C_2CH_3), the remaining six H's appear as two multiplets centered at δ 2.1 and 1.7; ^{13}C NMR δ 147.9 (>C=), 113.0 ($CH_2=$), 48.1 (C_2), 38.2 (C_3), 28.2, 27.0, 26.9, 22.6, 19.6 (unassigned). Anal. Calcd for $C_9H_{16}S$: C, 69.17; H, 10.32. Found: C, 69.02; H, 10.40.

***r*-1,*t*-2- and *r*-1,*c*-2-Dimethyl-2-(1-methylvinyl)thianium Hexafluorophosphates (2e,f).** Methyl trifluoromethanesulfonate (triflate) alkylation of 2-methyl-2-(1-methylvinyl)thiane (1.72 g, 11 mmol), followed by metathesis with aqueous ammonium hexafluorophosphate, CH_2Cl_2 extraction, and solvent evaporation, gave 3.15 g (95%) of a waxy solid. By ^1H NMR this appears to be a 30:70 mixture of isomers: the respective *S*-CH_3 singlets are at δ 2.77 and 2.85, indicating the minor and major isomer have their *S*-methyl and vinyl groups cis (**2e**) and trans (**2f**) to each other, respectively. No attempt was made to separate the isomers; however, a fairly pure sample of **2f** was obtained by recovering the sulfonium salt left unreacted after ring expansion with a deficit of base (see below): ^1H NMR (acetone d_6) δ 5.45 (s, 1 H, olefinic H), 5.40 (d, J = 1.0 Hz, 1 H, olefinic H), 3.56 (m, 2 H, C_6H_2), 2.86 (t, 3 H, SCH_3); 2.00 (s, 3 H, $CH_3C=$), 1.75 (s, 3 H, C_2CH_3), the remaining 6 H's appear as a complex multiplet in the region 2.4–1.8; ^{13}C NMR (acetone-d_6) δ 143.0 (>C=), 118.6 ($CH_2=$), 60.4 (C_2), 35.9 and 33.7 (C_6 and C_3, interchangeable), the remaining five carbons occur at 21.1, 20.1, 19.5, 18.9, and 18.0. From the ^{13}C spectrum of the isomeric mixture, the shieldings of the minor isomer, **1e**, could be obtained: δ 142.9 (>C=), 119.4 ($CH_2=$), 59.2 (C_2), 32.7 (C_6), 28.1 (C_3), the remaining five carbons occurring at 21.3, 19.3, 18.7, 16.6, and 16.2.

Ring Expansion of 2e and 2f with a Deficit of Base. (*Z*)- and (*E*)-4,5-Dimethylthiacyclonon-4-enes (7e and 8e). A solution of 0.98 g (3.1 mmol) of the 30:70 mixture of **2e** and **2f** in 28 mL of THF–*t*-BuOH (10:1 v/v, method I) was treated at −70 °C with *t*-BuOK [0.087 g, 0.77 mmol (75% deficit)]. After 2 h at −70 °C the mixture was quenched with 3 mL of H_2O and extracted with pentane/water. Evaporation of the pentane extract gave 0.12 g (23% based on total salt) of a sulfide which appears to be (*Z*)-4,5-dimethylthiacyclonon-4-ene (**7e**): ^{13}C NMR δ 129.8 and 127.9 (C_4 and C_5, interchangeable), 35.5, 32.6, 30.4, 30.1, 25.0, and 24.5 (C_2, C_3, C_6, C_7, C_8, and C_9, interchangeable), 19.4 and 18.0 (C_4 CH_3 and C_5 CH_3, interchangeable); ^1H NMR δ 2.52 (m, 8 H, C_2 H_2, C_3 H_2, C_6 H_2, and C_9 H_2), 1.69 and 1.63 (2 s, 3 H each, CH_3's). The remaining four H's occur as a multiplet in the δ 1.9–1.3 region.

The aqueous phase, after evaporation of organic solvents under reduced pressure, was twice extracted with CH_2Cl_2 to recover the

(18) For a recent account of the conformational properties of five-membered rings see: Fuchs, B. *Top. Stereochem.* **1978**, *10*, 1.
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(22) Leonard, N. J.; Johnson, C. R. *J. Org. Chem.* **1962**, *27*, 282.
(23) (a) Biellmann, J. F.; Vicens, J. J. *Tetrahedron Lett.* **1978**, 467. (b) Bory, S.; Marquet, A. *Ibid.* **1978**, 471. (c) Ceré V.; Pollicino, S.; Sandri, E.; Fava, A. *Ibid.* **1978**, 5239.
(24) Johnson, C. R.; Phillips, W. G. *J. Org. Chem.* **1967**, *32*, 3233.

unreacted salt (0.75 g, 2.2 mmol). By ^{1}H NMR this appears to largely consist of **2f** with only ~10% of **2e**, indicating **7e** was formed by reaction of **2e**. The unreacted salt was treated a second time with *t*-BuOK [0.02 g, 0.2 mmol (90% deficit)] for 30 min at −40 °C and worked up. The pentane extract was discarded while from the aqueous phase unreacted salt was recovered (0.64 g, 2.02 mmol) which proved to be isomerically pure **2f** (see above). The salt was finally treated with a slight excess of base (method I) at −40 °C to give a single product (0.29 g, 85%) which appears to be (*E*)-4,5-dimethylthiacyclonon-4-ene (**8e**): ^{13}C NMR δ 130.1 and 127.6 (C_4 and C_5, interchangeable), 38.1, 35.9, 35.4, 34.3, 29.7, and 28.0 (C_2, C_3, C_6, C_7, C_8, C_9, interchangeable), 23.1 and 21.5 (C_4 CH_3 and C_5 CH_3, interchangeable); ^{1}H NMR δ 2.8 (complex m, 4 H, probably C_3 H_2 and C_6 H_2); 1.90 and 1.84 (2 s, 3 H each, CH_3's); the remaining eight H give raise to a highly complex multiplet extending in the δ 2.4–1.1 region. The comparison between the NMR features of the two isomers leave little ambiguity about their stereochemical assignment. Strong support is provided by the aliphatic resonances which are all downfield in the olefin from **1f** with respect to that from **1e**, as expected for a *E*/*Z* pair.[25] The comparison between the methyl resonances is especially significant in this respect.[26]

4,4-Dimethyl-2-vinylthiane was prepared from 4,4-dimethylthiane[27] via NCS chlorination[21] and coupling with vinylmagnesium bromide as described for 2-vinylthiane.[7b] The crude product was purified by distillation at reduced pressure: 65% yield; bp 77 °C (20 mm); ^{1}H NMR δ 6.0–5.0 (m, 3 H, vinyl H's), 3.53 (octet, J = 11, 7, 3 Hz, 1 H, C_2 H), 2.87 (m, 1 H, C_6 H_{eq}), 2.50 (m, 1 H, C_6 H_{ax}), 0.95 and 0.91 (2 s, 3 H each, CH_3's), the remaining four H appear as a complex multiplet in the δ 1.8–1.3 region; ^{13}C NMR δ 139.1 (CH=), 115.5 (CH_2=), 46.2 (C_3), 40.6 (C_2), 38.9 (C_5), 33.3 [CH_3(eq) (cis to the vinyl group)], 30.1 (C_4), 25.2 (C_6), 23.6 (CH_3(ax)). Anal. Calcd for $C_9H_{16}S$: C, 69.17, H, 10.32. Found: C, 69.23; H, 10.39.

1,4,4-Trimethyl-2-vinylthianium Hexafluorophosphates (2g,h). Methylation ($CH_3OSO_2CF_3$) of the sulfide followed by metathesis with aqueous NH_4PF_6 gave (85%) the title salts in a 15:85 mixture, as estimated from the intensities of the respective *S*-CH_3 ^{1}H NMR signals at δ 2.98 (major, **2h**) and 2.75 (minor, **2g**). The major isomer has the following in addition: δ 5.90–5.50 (m, 3 H, vinyl H's), 4.15 (q, 1 H, C_2 H), 3.9–3.1 (m, 2 H, C_6 H_2), 1.94 (m, 4 H, β-CH_2's), 1.17 and 1.11 [2 s, 6 H overall, *gem*-$(CH_3)_2$]. Of the minor isomer, besides the *S*-CH_3 singlet, only the *gem*-methyls are visible at δ 1.18 and 1.12. In the ^{13}C NMR (acetone d_6) the major isomer could be assigned as follows: δ 131.1 (CH=), 125.1 (CH_2=), 55.0 (C_2), 42.8 (C_3), 36.9 (C_6), 35.3 (C_4 CH_3(eq)), 31.7 (C_5), 28.9 (C_4), 23.6 (C_4 CH_3(ax)); 22.4 (*S*-CH_3).

Ring Expansion of 2g and 2h: (*Z*)- and (*E*)-7,7-Dimethylthiacyclonon-4-enes (7g and 8g). Method I. Treatment of the 15:85 mixture of **2g** and **2h** with *t*-BuOK under the conditions of method I and a workup as usual gave a sulfide fraction (60%) consisting of two isomers (*m*/*e* 170) in a ~2.5:1 ratio (^{13}C NMR estimate) and a rearranged sulfonium salt. The two sulfides were separated by exploiting their differential reactivity toward $HgCl_2$. In practice this was achieved by adding 0.5-mL portions of 6% (w/v) aqueous $HgCl_2$ to a pentane solution (0.20 g in 20 mL) of the crude sulfide until GLC monitoring of the supernatant revealed that the minor component had been removed. From the precipitate, the sulfide was recovered by treatment with aqueous KI (50% w/v) and pentane extraction. Evaporation of the solvent left a residue (0.05 g) whose ^{1}H NMR indicated the olefin had the *E* configuration (**8g**): δ 5.8–5.2 [m, 2 H, CH=CH; irradiation at 2.2 resolved the high-field part of an AB q, J = 16 Hz (*E* double bond)]. Another significant feature of the spectrum is provided by a broad absorption (indicative of slow exchange between nonequivalent sites) at δ 2.5 and 1.9 (overall 8 H, α- and β-protons). Other features: δ 1.57 (m, 2 H, C_6H_2), 0.94 (s, 6 H, CH_3's); ^{13}C NMR δ 131.7 and 129.4 (C_4 and C_5, interchangeable), 46.9, 40.8, 36.2, 32.3, 32.4 (unassigned), 34.3 (C_7). There are in addition two broad resonances (at 28 °C) at δ 33.1 and 26.1 (unassigned), indicative of slow exchange, as expected for a nine-membered *E* olefin.[13]

The major component of the sulfide mixture, recovered (0.135 g) from the filtrate of the $HgCl_2$ precipitation, appears to be the *Z* isomer **7g**: ^{1}H NMR δ 5.65 (m, 2 H, CH=CH; irradiation in the 2.8–2.2 region gave rise to a relatively narrow singlet, indicating the two olefinic protons have very close shieldings), 2.5 (m, 8 H, C_α H_2 and C_β H_2); 1.50 (m, 2 H, C_6 H_2), 0.94 (s, 6 H, CH_3's); ^{13}C NMR δ 129.8 and 129.5 (C_4 and C_5, interchangeable), 38.4 and 38.2 (C_6 and C_8, interchangeable), 34.0 (C_7), 30.0, 27.5, and 25.7 (C_2, C_3, and C_9, interchangeable), 28.7 (CH_3). As a whole, the aliphatic carbon shieldings are upfield with respect to the minor isomer, consistent with the major and minor isomers having the *Z* and *E* configurations, respectively.[25]

The aqueous phase from the initial workup, after evaporation of the organic solvents under reduced pressure, was extracted with CH_2Cl_2 to yield a sulfonium salt mixture which, however, did not contain the starting salts **2g** and **2h** in any appreciable amount. This material was not investigated in detail; its ^{1}H NMR, however, was consistent with a mixture of (*Z*)- and (*E*)-1,4,4-trimethyl-2,2-ethylidenethianium salts (**9g**) arising from a prototropic rearrangement of the ylide at C_2, in analogy with previous findings on five-membered salts.[8]

Method II. A cold (−70 °C) solution of lithium diisopropylamide in THF (1.1 mmol in 2.5 mL) was added under nitrogen to a stirred solution of the 15:85 mixture of **2g** and **2h** (0.35 g, 1.1 mmol, in 9 mL of THF). After 2 h of being stirred at −40 °C, the mixture was quenched with water and extracted with pentane. The residue after solvent evaporation (0.12 g, 65%) was found to be (GLC, ^{13}C NMR) a 5.5:1 mixture of **8g** and **7g**.

The aqueous phase yielded a rearranged sulfonium salt residue, **9g** (see above).

***trans*-4-Methyl-2-vinylthiane** was prepared from 4-methylthiane[27] as described above for 2-(1-methylvinyl)thiane. The crude product was fractionally distilled to give (62%) the title compound: bp 85 °C (20 mm); ^{1}H NMR (60 MHz) δ 6.25–5.70 (m, 1 H, =CH), 5.40–4.95 (m, 2 H, $=CH_2$), 3.44 (m, 1 H, C_2H), 2.85 (m, 2 H, C_6H_2), 1.03 (d, 3 H, CH_3); ^{13}C NMR δ 138.9 (=CH), 115.0 ($=CH_2$), 40.2 (C_2), 39.8 (C_3), 34.6 (C_5), 26.4 (C_4), 24.3 (C_6), 21.5 (CH_3). By combination of the known spectra of 2-vinylthiane,[8] 4-methylthiane,[27,28] and *cis*-[27] and *trans*-2,4-dimethylthiane,[27] the trans structure can be unambiguously assigned. Anal. Calcd for $C_8H_{14}S$: C, 96.09; H, 9.92. Found: C, 96.20; H, 9.85.

***r*-1,*t*-4-Dimethyl-2,*c*-vinyl- and *r*-1,*c*-4-Dimethyl-2,*t*-vinylthianium Hexafluorophosphates (2i,j).** Methylation of the sulfide gave (90%) the title salts in a ca. 1:1 ratio, as evinced from the relative intensities of the *S*-CH_3 singlets at δ 3.13 (**2j**) and 2.85 (**2i**). The rest of the ^{1}H NMR (acetone-d_6) of the mixture shows multiplets at δ 6.5–5.6 (3 H, CH=CH_2), 4.4 (1 H, C_2 H), 3.6 (2 H, C_6 H_2), and 2.1 (superimposed on acetone-d_5) and two doublets at δ 1.14 and 1.07 (3 H overall, CH_3). The ^{13}C spectrum showed the expected 18 lines, whose assignments were not attempted.

Ring Expansion of 2i and 2j: (*E*)-7-Methylthiacyclonon-4-ene (8i). Ring expansion was effected with method I by using 1 equiv of base as well as a 50% deficit. In either case the crude sulfide (80% based on *t*-BuOK) consisted of a single species which was identified as the title compound: ^{1}H NMR δ 5.7 and 5.3 (2 m, 1 H each, HC=CH; irradiation of the allylic H's in the δ 2.5–2.1 region resolved the multiplet into an AB q, J = 15.5 Hz, thus establishing the *E* setting of the H's involved), 2.9 (m, 2 H), 2.3 (m, 4 H, allylic H's), 2.2–1.8 (m, 1 H), 1.6 (m, 4 H), 0.98 (d, 3 H, CH_3); ^{13}C NMR 134.8 (C_5), 126.5 (C_4), 41.8, 36.4, 36.0, 35.0, 32.6 (unassigned), 33.2 (C_7), 23.5 (CH_3).

2-(1-Methylvinyl)thianium Hexafluorophosphates (2k,l) were obtained (85%) from the corresponding sulfide as described above for **2e,f** in an ~15:85 mixture. This proportion was evinced from the intensity of the respective *S*-CH_3 singlets at δ 3.05 (major, **2l**) and 2.85 (minor, **2k**). Other ^{1}H NMR features of the major isomer are as follows (acetone-d_6, 60 MHz): 5.35 (m, 2 H, $=CH_2$), 4.4–3.4 (m, 3 H, C_2H and C_6H_2); 2.05 (unresolved m, superimposed on the acetone-d_5 resonances and on a s at 1.95 ($=CCH_3$)); ^{13}C

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(26) Reference 19b, p 80.
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NMR δ 138.4 (=CH), 120.7 (=CH_2), 63.1 (C_2), 40.8 (C_6), 30.0 (C_3), 24.1 (C_4 or C_5), 23.3 (S-CH_3, superimposed to either C_4 or C_5), 18.4 (=CCH_3).

Ring Expansion of 2k and 2l: (*Z*)- and (*E*)-4-Methylthiacyclonon-4-enes (7k and 8k). Method I. Ring expansion of the 15:85 mixture of **2k** and **2l** with *t*-BuOK yielded after workup a sulfide fraction (70%) which by GLC (10% Xe-60 on Chromosorb W) appeared to consist of three products in the ratio 1:4.8:1.1 (increasing retention time). The three products were (partially) separated by fractional precipitation with $HgCl_2$ as described above. The material with the shortest retention time precipitated first and was regenerated as a 27:1 mixture with the material of longest retention time. The latter which precipitated second was regenerated as a 1.5:1 mixture with the material of intermediate retention time. The latter could be obtained essentially free of contaminants by evaporation of the supernatant after separation of the second crop. The more abundant product appears to be (*Z*)-4-methylthiacyclonon-4-ene (**7g**): ^1H NMR δ 5.30 (td, *J* = 8, ~1 Hz, =CH), 2.63 and 2.39 (2 m, 8 H overall, allylic CH_2's and α-CH_2's), 1.75 (d, *J* = 1 Hz, 3 H, CH_3), 1.65 (m, 4 H, C_7H_2 and C_8H_2). The proton spectrum does not show any appreciable temperature dependence in the −55 to +60 °C range: ^{13}C NMR 134.8 (C_4), 126.5 (C_5), 33.2 (C_3), 29.9, 29.4, 26.5, 26.1, 25.7, and 24.5 (unassigned).

The second abundant product, with the longest retention time, was obtained in a pure form by fractional precipitation of the sulfide fraction produced by ring expansion with method II (see below). Its features identify it as the *E* isomer **8k**. The ^1H NMR spectrum at the probe temperature (28 °C) has three broad absorptions in the δ 2.2 region which sharpen considerably on warming at 64 °C or on cooling at −54 °C, as expected for a nine-membered *E* olefin.[7,13] The assignment is supported by the ^{13}C NMR spectrum: δ 130.2 (C_4), 128.0 (C_5), 40.8 (C_3), 37.2, 35.4, 29.7, 27.8, 27.2, 27.1 (unassigned), showing the aliphatic carbons resonances to be consistently downfield with respect to the major isomer.

The third product, of shortest retention time, could not be obtained in sufficiently pure form and in a sufficient amount to warrant a detailed structural study and went unidentified.

From the aqueous phase from the initial workup a mixture of sulfonium salts was recovered (30%), the main component (90%) of which appears to be a 1-methyl-2,2-isopropylidenethianium salt whose ^1H NMR (acetone-d_6) is characterized by δ 3.10 (s, 3 H, SCH_3), 2.08 and 2.00 (2 s, 3 H each, CH_3's).

Method II. Ring expansion of **2k** and **2l** (15:85) with LDA produced the same materials, though in a quite different ratio (1:1:6, in order of increasing retention time). From the second crop of the fractional precipitation with $HgCl_2$ was obtained the major product free of contaminants, and it was identified as **8k** (see above).

(*Z*)- and (*E*)-2-(2-Methylvinyl)thianes were obtained as a 4:1 mixture by coupling 2-chlorothiane with 1-propenylmagnesium bromide [prepared from commercial (Fluka) 1-propenyl bromide in THF]. The crude product was fractionally distilled [bp 76 °C (4 mm)] to give a material which by ^{13}C NMR appears to consist of two isomers in a ca. 4:1 ratio. The major and minor isomer (in parentheses) have the following ^{13}C shieldings (δ): C_2CH=, 131.3 (132.1); =$CHCH_3$, 125.9 (126.5); C_2, 39.0 (44.2); C_3, 34.4 (34.3); C_6, 29.3 (29.8); C_4 and C_5 interchangeable, 26.7 and 25.9 (26.8 and 25.9); CH_3, 13.1 (17.8). (For the assignment see the Results and Discussion.)

Ring Expansion of 1-Methyl-2-(2-methylvinyl)thianium Hexafluorophosphates (2m,n,p). (*E*)-3-Methylthiacyclonon-4-ene (8m). Methylation of the (*Z*)- and (*E*)-2-(2-methylvinyl)thiane mixture (see above) followed by metathesis with NH_4PF_6 gave a mixture of at least three of the four possible sulfonium salts in a 1:2:6 ratio. The ^{13}C spectrum is very helpful for assigning their structures, on the basis of the known effects of equatorial and axial S-CH_3.[28,29] Thus the major component, which has C_2 and C_6 at δ 53.1 and 40.2, respectively, may be assigned structure **2n**; the minor component (C_2, δ 45.3; C_6, δ 35.7) and the intermediate one (C_2, δ 58.9; C_6, δ 40.6) are assigned structures **2m** and **2p**, respectively. Base treatment of these sulfonium salts with method I (at −70 °C) gave a single product: 90% yield; ^1H NMR δ 5.55 (m, 1 H, C_5 H), 4.90 (q, *J* = 15.0, 7.0 Hz, 1 H, C_4 H; irradiation at 2.1 changes the q into the upfield part of an AB q, *J* = 15.0 Hz, indicating that the olefin has the *E* configuration), 2.8–1.2 (complex absorption, overall 11 H); 1.03 (d, *J* = 6.5 Hz, 3 H, CH_3; irradiation at 2.1 changes the d in to a s); ^{13}C NMR δ 133.0 and 132.4 (C_4 and C_5, interchangeable), 43.6 (C_2), 39.8 (C_3), 37.4, 32.4, 26.0, and 25.4 (unassigned), 19.6 (CH_3).

3-Bromopropyl 3-Methylbut-2-en-1-yl Sulfide. Thietane (2.35 g, 31.8 mmol) and 1-bromo-3-methyl-2-butene[30] (4.78 g, 32 mmol, prepared from commercial 3-methylbut-2-en-1-ol and PBr_3) were heated at 45–50 °C for 24 h. Distillation of the reaction mixture gave the title compound: 6.0 g (84%); bp 96–98 °C (2 mm); ^1H NMR δ 5.17 (t, 1 H, =CH), 3.45 (t, 2 H, SCH_2CH=), 3.06 (d, SCH_2CH_2), 2.53 (t, 2 H, CH_2Br), 2.06 (q, 2 H, $CH_2CH_2CH_2$), 1.73 and 1.67 (2 s, 3 H each, CH_3's). Anal. Calcd for $C_8H_{15}SBr$: C, 96.09; H, 15.12. Found: C, 96.19; H, 15.25.

2-(2,2-Dimethylvinyl)thiolane was obtained by LDA cyclization of 3-bromopropyl 3-methylbut-2-en-1-yl sulfide by the procedure previously described for 2-(2-methylvinyl)thiolane. The product was purified by distillation: 75% yield; bp 78 °C (8 mm); ^1H NMR δ 5.15 (d, 1 H, =CH), 4.15 (m, 1 H, C_2 H), 2.86 (m, 2 H, C_5H_2), 2.0 (m, 4 H, C_3H_2 and C_4H_2), 1.70 (s, 6 H, CH_3's, accidental coincidence of chemical shifts; ^{13}C NMR δ 133.0 (>C=), 127.0 (=CH), 46.3 (C_2), 38.5 (C_3), 32.9 (C_5), 30.9 (C_4), 25.7 ((*E*)-CH_3), 18.0 ((*Z*)-CH_3). Anal. Calcd for $C_8H_{14}S$: C, 67.54; H, 9.92. Found: C, 67.39; H, 9.87.

1-Methyl-2-(2,2-dimethylvinyl)thiolanium Hexafluorophosphates (1e,f). Methyl triflate methylation and methatesis gave (95%) a viscous oil whose ^1H NMR spectrum indicated the presence of two isomers in a 3:7 ratio which were characterized by the S-CH_3 singlets at δ 3.01 (minor, **1f**) and 2.72 (major, **1e**). The rest of the spectrum has relatively wide absorption regions consistent with the presence of two isomers: δ 5.4 (1 H, CH=), 5.0 (1 H, C_2 H), 3.7 (2 H, C_5H_2), 2.5 (4 H, β-CH_2's), 1.85 (br s, 6 H, CH_3's).

Ring Expansion of 1e and 1f. (*E*)-3,3-Dimethylthiacyclooct-4-ene (13e). Base treatment (method I) of the 30:70 mixture of **1e** and **1f** gave after the workup a single sulfide product (70%) whose ^1H NMR clearly indicates its *E* configuration: the olefinic region shows a multiplet at δ 5.8 (1 H, C_5 H) and a doublet (*J* = 16.5 Hz, 1 H, C_4 H) which establishes the *E* setting of the double bond. That the molecule is chiral and rigid is also evinced by the methyl groups occurring as separate resonances at δ 1.19 and 1.06. Other features are as follows: δ 3.0 (m, 1 H), 2.57 (br s, 2 H, C_2H_2, coincidental identity of chemical shifts), 2.5 and 1.6 (m, s, 5 H overall); ^{13}C NMR 139.4 (C_4), 132.2 (C_5), 56.6 (C_2), 40.8 (C_3), 38.0, 35.4 and 34.9 (C_8, C_7, and C_6, interchangeable), 28.0 and 21.2 (CH_3's). The large differential shielding of the methyl groups (6.8 ppm) is worth noting; on the basis of the configurational assignment of the diastereoisomers of 3-methylthiacyclooct-4-ene,[16] the high-field and low-field methyl resonances can be assigned to R_4 and R_5, respectively, in the enantiomer of *S* configuration at the chiral plane (see structure **13** and footnote 17).

Registry No. **1e**, 77743-62-5; **1f**, 77743-64-7; **2e**, 77743-66-9; **2f**, 77743-68-1; **2g**, 77743-70-5; **2h**, 77743-72-7; **2i**, 77743-74-9; **2j**, 77841-44-2; **2k**, 77743-76-1; **2l**, 77743-78-3; **2m**, 77743-80-7; **2n**, 77841-46-4; **2p**, 77841-48-6; **7e**, 77743-81-8; **7g**, 77743-82-9; **7k**, 77743-83-0; **8e**, 77743-84-1; **8g**, 77743-85-2; **8i**, 77743-86-3; **8k**, 77743-87-4; **8m**, 77743-88-5; (*E*)-**9g**·PF_6^-, 77743-90-9; (*Z*)-**9g**·PF_6^-, 77743-92-1; **13c**, 77841-49-7; **13d**, 77841-50-0; **13e**, 77743-93-2; 2-(1-methylvinyl)thiane, 77743-94-3; *cis*-2-(1-methylvinyl)thiane 1-oxide, 77743-95-4; *trans*-2-(1-methylvinyl)thiane 1-oxide, 77743-96-5; *cis*-2-methyl-2-(1-methylvinyl)thiane 1-oxide, 77773-55-8; 2-methyl-2-(1-methylvinyl)thiane, 77743-97-6; 4,4-dimethyl-2-vinylthiane, 77743-98-7; *trans*-4-methyl-2-vinylthiane, 77743-99-8; 1-methyl-2-isopropylidenethianium hexafluorophosphate, 77744-01-5; (*Z*)-2-(2-methylvinyl)thiane, 77744-02-6; (*E*)-2-(2-methylvinyl)thiane, 77744-03-7; 3-bromopropyl 3-methylbut-2-en-1-yl sulfide, 77744-04-8; 2-(2,2-dimethylvinyl)thiolane, 77744-05-9.

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