Ring Expansion by [2,3] Sigmatropic Shifts of Unstabilized Sulfonium Ylides. Synthesis of Eight- to Ten-Membered Thiacycloalk-4-enes

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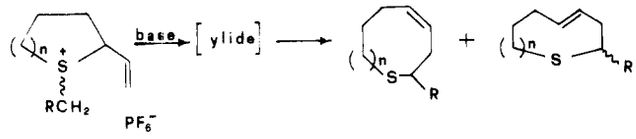
Vedejs' ring expansion procedure by a [2,3] sigmatropic shift of stabilized sulfonium ylides[1] has been extended to nonstabilized ylides. The more favorable conditions (≃90% yields) involve in situ ylide generation from sulfonium hexafluorophosphate salts (which are soluble in THF at low temperature) using *t*-BuOK as the base in the presence of *t*-BuOH. The geometry, *E* or *Z*, of the cyclic homoallylic sulfide product could not be related to that, cis or trans, of the 1-alkyl-2-vinyl cyclic sulfonium salt precursor, insofar as the latter was found to undergo rapid isomerization under the ring expansion conditions. A general synthesis is also reported of 2-vinylthiacycloalkanes, in particular the six- and seven-membered compounds **8b** and **8c**.

Vedejs[1] has recently reported the synthesis of thiacycloalk-4-enes by ring expansion of stabilized sulfonium ylides derived from 2-vinyl substituted cyclic sulfonium salts where $n = 1$ and 2[2] and R was an acid enhancing group such as



a, $n = 1$; **b**, $n = 2$; **c**, $n = 3$

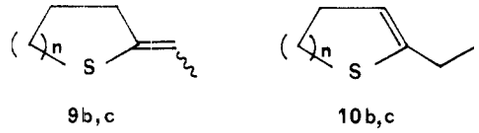
PhCO, EtOOC, or even CH_2=CH. In the latter case (i.e., when the starting sulfonium cation carries an *S*-allyl group), the ring expanded product has the 2-vinyl moiety already built in and may be further expanded in three-carbon unit steps (e.g., 5 → 8 → 11 → 14 . . .).[1c,3]

In this paper we wish to report the extension of Vedejs' ring expansion to nonstabilized ylides (R = H, Me, or Ph; $n = 1$–3). We also report a general synthesis of 2-vinyl derivatives of thiacycloalkanes, in particular 2-vinylthiane and -thiepane, which are the starting materials required to synthetize the whole series of meso- and macrocyclic thiacycloalkenes via the repeatable ring expansion procedure.[1-3] Furthermore, we report evidence indicating that the precursor 2-vinylsulfonium salts undergo rapid cis/trans isomerization under the reaction conditions. Therefore, no meaningful correlation can be made between the stereochemistry (cis or trans) of the starting sulfonium salt and that of the olefin product.

Results and Discussion

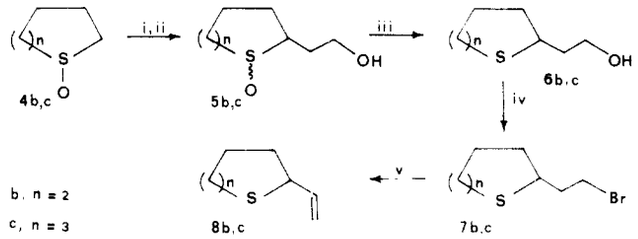
Synthesis of 2-Vinylcycloalkanes. Reaction Scheme I was found to give satisfactory results ($n = 2, 3$).[4] The overall yields were 34.5 and 29.5% for $n = 2$ and 3, respectively.

This procedure lends itself to the synthesis of functionalized derivatives through the use of substituted ethylene oxides and/or substituted thiacycloalkanes. All of the steps of the synthetic scheme are straightforward with the exception of the elimination step, v, which requires very careful temperature and time control to avoid extensive isomerization of **8** to the isomeric olefins **9** and **10.** Under the conditions indicated, the crude elimination product was essentially pure for $n = 2$, while for $n = 3$ it altogether contained ~12% of **9c** and **10c.**



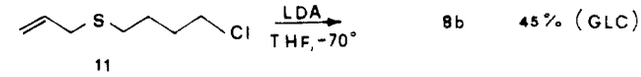
Although the stereochemistry and rate of the hydroxyethylation step iii are of no consequence as far as the overall synthetic scheme is concerned, they are nevertheless remarkable. For thiane 1-oxide the alkylation of the Li derivative proceeded rapidly at −70 °C, giving *trans*-**5b** as the sole product (see Experimental Section). On the other hand, for the higher homologue the reaction was sluggish even at 0 °C and gave a 9:1 mixture of *cis*- and *trans*-**5c,** where the cis isomer appears to predominate (see Experimental Section). The change in rate and stereochemistry as a function of ring size was not anticipated and is striking. Work is in progress in our laboratory to investigate this point further, particularly in relation to the recent work by Marquet[7] and Biellmann.[8]

Scheme I[a]



[a] Steps: i, BuLi, THF, −70 °C; ii, ethylene oxide, THF, −65 °C; for $n = 2$ the trans alkylation product was formed exclusively, and for $n = 3$ (−5 °C) both cis and trans isomers were formed, approximately 9:1; iii, $NaHSO_3$, H_2O, 100 °C; iv, PBr_3, pyridine, −5 °C; v, *t*-BuOK, THF–Me_2SO, −10 °C, 30 min.

The synthesis of 2-vinylthiane (**8b**) was also performed by base-catalyzed cyclization of allyl (4-chloro)butyl sulfide (**11**). This type of synthesis, which works very well for the preparation of the five-membered analogue,[1,6] turned out to be much less suitable in this case. The overall yield was low, and the olefin product was considerably contamined (~15%) by **9b** and **10b.** Separation of **8** from **9** and **10** was achieved by



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column chromatography. This operation, however, could be omitted if one is only interested in the ring expanded products since the ylides eventually generated from **9** and **10** are unable to undergo a [2,3] sigmatropic shift.

Ring Expansion by a [2,3] Sigmatropic Shift. Although various reaction conditions have been essayed, all involving in situ ylide generation by base treatment of sulfonium salts, the more favorable and general conditions for ring expansion involve (i) the use of sulfonium hexafluorophosphates, which being soluble in THF at low temperature allow the reaction to occur homogeneously, and (ii) the use of *t*-BuOK as the base in the presence of *t*-BuOH (1:10 ratio with respect to THF).

The presence of *t*-BuOH may not always be necessary, although it appears to be indispensable for successful ring ex-

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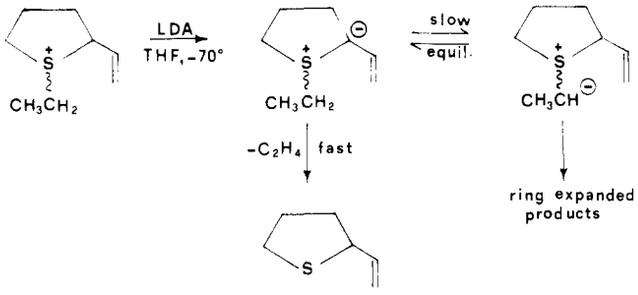
Table I. Ring Expansion by a [2,3] Sigmatropic Shift of 2-Vinyl Substituted Cyclic Sulfonium Alkylides

sulfonium salt precursor	reaction conditions	yield,[a] %	trans/cis[b]
1a,H	10:1 THF/*t*-BuOH, *t*-BuOK, −40 °C	90	0.17
1b,H		85	24
1c,H		85	50
1a,CH$_3$[c]		62	1.5
	THF, *t*-BuOK, −40 °C	*d*	
1a,H		91	0.17
	THF, LDA, −25 °C	70[e]	0.17
	10:1 toluene/*t*-BuOH, *t*-BuOK, −40 °C	90	0.17
	toluene, DBU, 110 °C	*f*	
	H$_2$O, 1 N NaOH, RT[i]	*g*	
1a,CH$_3$	THF, LDA, −70 °C	*h*	
1a,Ph	H$_2$O, 1 N NaOH, RT[i]	95	0.08

[a] Yield of isolated ring expanded product. [b] Ratio of trans to cis olefin in product. [c] Reference 6. [d] No reaction took place in 2 h. [e] GLC yield. [f] No ring expanded product was formed. [g] Rearranged sulfonium salt only (see text). [h] Product of β-elimination only (see text). [i] RT = room temperature.

pansion of the more unstable ylides, such as those derived from *S*-ethylsulfonium salts.[6]

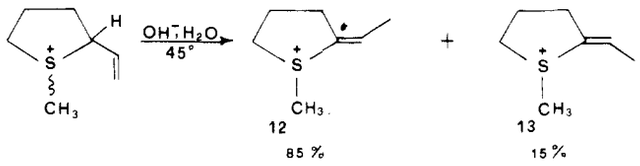
Whenever the starting sulfonium salt is crystalline and can be made into a fine dry powder, ring expansion can also be made to occur heterogeneously. Thus, a suspension of 1-methyl-2-vinylthiolanium hexafluorophosphate in toluene was successfully ring expanded (~90%) with *t*-BuOK/*t*-BuOH. On the other hand, no ring expanded products were found using diazabicycloundecene (DBU) in toluene at 110 °C.



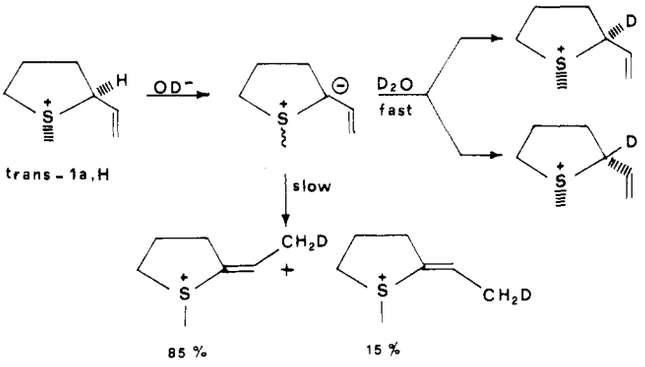
Ylide generation by LiN(*i*-Pr)$_2$ (LDA) appears to suffer from several disadvantages, and in certain cases ring expansion is not a major outlet. This is probably due to the endocyclic ylide being formed highly preferentially and lacking an easy pathway for rapid equilibration with the less stable exocyclic ylide required for ring expansion. Consequently, the product, or some of it, may evolve directly from the endocyclic ylide. Thus, when *cis*- and *trans*-1-ethyl-2-vinylthiolanium (PF_6^-) were reacted with LDA in THF at −70 °C, the only sulfide product was 2-vinylthiolane itself (80% by GLC), i.e., the β-elimination product, likely arising from the α′,β pathway.

However, when the exocyclic alkyl group was CH_3 (no β hydrogens), ring expansion did occur, though higher temperatures (−25 °C) were required. Under these conditions the yield was lower (70%; GLC) and a variety of products (three additional GLC peaks) was formed concurrently.

Ring expansion was also essayed in H$_2$O/OH$^-$. Rate data[9] indicate that the Me hydrogens of cyclic *S*-methylsulfonium cations undergo fairly rapid H–D exchange in aqueous base under mild conditions ($t_{1/2} \simeq 2$ h, D$_2$O, 1 N NaOD, 35 °C). Insofar as base-catalyzed H–D exchange requires the intermediacy of the ylide, there was a good chance to observe ring expansion under conditions where H–D exchange occurs. When mixtures of *cis*- and *trans*-1-methyl-2-vinylthiolanium PF_6^- (heterogeneous) or BF_4^- (homogeneous) were treated with aqueous 1 N NaOH at ~31 °C, no reaction occurred; on raising the temperature to 45 °C, ring expansion did not occur but the sulfonium salt rearranged essentially quantitatively (in ~6 h) to give an ca. 85:15 mixture of (*E*)- and (*Z*)-1-methyl-2-ethylidenethiolanium (PF_6^- or BF_4^-) (**12** and **13**).



To examine this prototropic shift more closely, the reaction was followed in the ^{1}H NMR starting with pure *trans*-**1a,H.** It was immediately apparent that in D$_2$O/1 N NaOD H–D exchange of both the methyne H at C$_2$ and the SMe H's occurs



faster than prototropic shift. Exchange occurs most rapidly at C$_2$; in 0.15 M Na$_2$CO$_3$ at 50 °C the resonance at δ 4.40 partially superimposed to the HDO singlet at δ 4.55 disappears rapidly while the intensity of the HDO singlet correspondingly increases. At the same time, the SCH_3 singlet at δ 3.02 decreases in intensity while another SCH_3 singlet appears at δ 2.75, characteristic of the *cis*-1-methyl-2-vinylthiolanium cation, whose intensity increases correspondingly. It then appears that exchange of the allylic proton is accompanied by epimerization at C$_2$, leading to isomerization and equilibration of the cis and trans thiolanium cations.

While this occurs, however, the SCH_3 protons appear not to undergo appreciable exchange. For this to occur measurably fast, the base concentration has to be raised substantially, and in 1 N NaOD the half-life of exchange is on the order of 4 h at the probe temperature (ca. 31 °C). The exchange of the SCH_3's protons is essentially complete much before the product arising from prototropic shift starts to show up in the NMR. The rearrangement occurs visibly, however, at 45 °C and may be easily followed in the NMR. The vinyl resonance [δ 4.25–5.25 (3 H)] begins to decrease in intensity and is replaced by a low field multiplet, centered at δ 6.55, and a broad high field doublet at δ 2.01, whose intensities eventually reach 1 H and 2 H, respectively. If the rearrangement is made to occur in D$_2$O containing a large amount of H$_2$O, a further characteristic change can be seen in the NMR; namely, the $SC(H,D)_3$ singlets at δ 3.02 and 2.75 are progressively replaced by another $SC(H,D)_3$ singlet at δ 2.98. The half-life of the rearrangement is on the order of 1.5 h at 45 °C (1 N NaOH). The ^{13}C NMR spectrum of the rearrangement product indicates that two isomers are formed approximately in a ratio of 85:15, which have been identified as the *E* and *Z* isomers, respectively (see Experimental Section for the configurational assignment).

It was reasoned that if the exocyclic α protons were made sufficiently acidic to compete favorably for base abstraction with the allylic proton at C_2, there was a chance for ring expansion to become the major route in aqueous solution also. This condition is fulfilled, for example, by *S*-benzylsulfonium cations. Accordingly, 1-benzyl-2-vinylthiolanium (**1a,Ph**) was synthesized as the fluoborate salt and tested for a [2,3] sigmatropic shift in H_2O and 1 N NaOH at room temperature. The ring expanded product separated out of the solution almost instantaneously and was recovered in over 90% yield without contamination from either Stevens or Sommelet products. From this result it appears likely that aqueous base may be used successfully also for 1-allylsulfonium cations.

The finding that base-catalyzed cis/trans isomerization of the starting sulfonium salt occurs much faster than exchange of the SCH_3 protons in aqueous solution prompted us to test whether such isomerization also occurs rapidly under the conditions where ring expansion occurs. To this end *trans*-**1a,H** was ring expanded with a 50% defect of *t*-BuOK in THF/*t*-BuOH at −40 °C. The excess sulfonium salt recovered was the ~1:1 equilibrium mixture of cis and trans salts. Apparently ring expansion does not compete favorably with reversible abstraction of the acidic methine at C_2, which results in rapid isomerization of the starting material. Under these conditions no meaningful correlation can be made between the stereochemistry of the starting sulfonium salt and that (*Z* or *E*) of the product olefin.

Experimental Section

^1H NMR spectra were recorded at 60 MHz on a JEOL C-60 HL instrument and at 100 MHz on a Varian XL-100 operating in the CW mode. Proton noise decoupled ^{13}C spectra were recorded at 25.15 MHz on a Varian XL-100 by the FT technique; single frequency off-resonance spectra were obtained by irradiation at δ − 4 in the proton spectrum. Analytical GLC analyses were carried out with a Hewlett-Packard 5700 instrument equipped with a flame ionization detector (1/8 in. × 3 m column, 10% XE 60 on Chromosorb W).

Solvents were reagent grade. Whenever required, they were obtained dry as follows. Benzene and methylene chloride were distilled from calcium hydride; tetrahydrofuran, dried over sodium and distilled, was redistilled from $LiAlH_4$ immediately before use; dimethyl sulfoxide (Merck, dry reagent) was further dried over molecular sieves (Union Carbide, A4, 1/16 in. rods, 4 Å); pyridine was distilled from KOH.

2-Vinylthiolane (8a) was prepared by ciclization of allyl 3-bromopropyl sulfide as previously described.[1b,6] In an attempt to synthesize it by Grignard coupling via the Tuleen[5] procedure, a freshly prepared benzene solution of 2-chlorothiolane[5] (0.05 mol in 60 mL) was reacted with 0.1 mol of vinylmagnesium bromide (Ventron) in 71 mL of THF. After workup, 0.7 g (12%) of 2-vinylthiolane was obtained, bp 60–62 °C (20 mm) [lit.[1b] bp 55–56 °C (16 mm)].

2-Vinylthiane (8b) was synthetized (method I) by dehydrobromination of 2-(2-bromoethyl)thiane (**7b**) (step v of Scheme I) and by base-catalyzed cyclization of allyl 4-chlorobutyl sulfide (**11**) (method II).

Method I. To a solution of **7b** (10.45 g, 0.05 mol, in 75 mL of THF) cooled at −30 °C was added 50 mL of 1 M *t*-BuOK (Fluka) in Me_2SO over a period of 5–7 min in a nitrogen atmosphere and under vigorous stirring. As the addition of the base resulted in a highly exothermic reaction, external cooling was necessary to prevent the temperature from rising above −10 °C. The suspension (KBr precipitate) was further stirred at −10 °C for 30 min, and then was poured into 350 mL of H_2O and thrice extracted with 100-mL portions of pentane. After solvent removal, the residue was distilled under reduced pressure to yield 4.7 g (74%) of **8b,** bp 76 °C (20 mm), uncontaminated by isomeric olefins (reaction conditions employing higher temperatures or longer reaction times caused extensive rearrangement of **8b** to **9b** and **10b;** see below): ^1H NMR (100 MHz, $CDCl_3$) δ 6.04–4.90 (m, 3 H, vinyl protons), 3.62 (m, 1 H, α-methine), 2.66 (m, 2 H, α-methylene), 2.18–1.12 (br m, 6 H, β- and γ-methylenes); ^{13}C NMR (δ_{Me_4Si}, $CDCl_3$) 139.2 (-**C**H=CH_2), 115.3 (-CH=CH_2), 44.5 (C_2), 33.6 (C_3), 29.0 (C_6), 26.8 (C_5), 25.6 (C_4).

Anal. Calcd for $C_7H_{12}S$: C, 65.56; H, 9.43. Found: C, 65.65; H, 9.21.

Method II. A solution of lithium diisopropylamide, prepared by adding BuLi in hexane (20 mL, 0.033 mol) to 0.033 mol of diisopropylamine in 20 mL of THF at −70 °C, was added under nitrogen to a solution of **11** (5 g, 0.03 mol) in 250 mL of THF at −70 °C. The reaction mixture was stirred for 3 h at −70 °C, and then was quenched with water. After warming to room temperature and removal of solvent in vacuo, the residue was extracted with pentane. The extracts were washed successively with dilute HCl and 10% aqueous $NaHCO_3$ and dried over $CaSO_4$. After solvent removal, the residue was distilled under reduced pressure to give 2.0 g (52%) of a crude sulfide, bp 73–76 °C (20 mm), which on TLC showed no less than three products. Separation by column chromatography (SiO_2, 4:1 *n*-pentane/benzene eluent) gave **8b** as the major product (85%). In the NMR the two minor components appeared to be isomeric olefins, most likely formed by base-catalyzed rearrangement. The first eluted material (~6%) appeared to be 2-ethyl-Δ^2-dihydrothiopyran (**10b**): ^1H NMR (60 MHz, $CDCl_3$) δ 5.40 (narrow unresolved m, 1 H, olefinic proton), 2.75 (m, 2 H, α-methylene), 2.0 (m, extending over 1.1 ppm, 6 H, β- and γ-methylenes), 1.06 (t, J = 7.0 Hz, CH_3).

The second eluted minor component (~9%) can be identified as either the *E* or the *Z* isomer of 2-vinylidenethiane: ^1H NMR (60 MHz, $CDCl_3$) δ 5.56 (q, J = 6.7 Hz, 1 H, olefinic proton), m centered at δ 2.5 extending over 0.6 ppm (4 H, α-CH_2 and C_3H_2), δ 1.9 (br m, partially superimposed on a doublet at δ 1.57, J = 6.7 Hz, 7 H overall, C_4H_2, C_5H_2, and methyl group).

2-(2-Bromoethyl)thiane (7b). Dry pyridine (1.39 mL, 0.0176 mol) was added dropwise during 15 min to a PBr_3 solution (9.26 g, 0.0342 mol, in 16 mL of benzene) and cooled at −5 °C. A mixture then was added of 2-(2-hydroxyethyl)thiane (**6b;** 13.6 g, 0.093 mol) and pyridine (0.3 mL) over a period of 45 min. Stirring was continued at −5 °C for another hour, and then the solution was allowed to warm to room temperature. After 24 h the reaction mixture was poured into 100 mL of H_2O and extracted with pentane. The extracts, washed with water and dried, gave, after evaporation of the solvent and distillation of the oily residue under reduced pressure, 12.8 g (66%) of the title compound: bp 92–93 °C (1 mm); ^1H NMR (60 MHz, $CDCl_3$) δ 3.59 (t, J = 6.8 Hz, 2 H, CH_2Br), 2.95 (br m superimposed on a more intense unresolved m at δ 2.80, 3 H overall, α-methine and α-methylene), 2.28–1.25 (m, 8 H overall, β- and γ-methylenes).

Anal. Calcd for $C_7H_{13}SBr$: C, 40.20; H, 6.26. Found: C, 40.22; H, 6.03.

2-(2-Hydroxyethyl)thiane (6b). Thiane 1-oxide[10] (11.8 g, 0.1 mol) was dissolved in THF (175 mL). After cooling at −70 °C (the material precipitated in part) butyllithium was added (0.1 mol in 61 mL of hexane), and after 15 min a freshly prepared THF solution of ethylene oxide (5.3 g, 0.12 mol in 20 mL) was added. A mildly exothermic reaction occurred immediately, raising the temperature to about −50 °C while the solution turned blue-green. The dry ice bath was removed, and the flask was kept at 0 °C for 7 h. The reaction mixture was then poured into 150 mL of H_2O and neutralized with dilute HCl.

The resulting aqueous and organic layers, unseparated, were evaporated under reduced pressure to remove the organic solvent, and the aqueous residue, containing **5b,** was diluted with H_2O to 280 mL. Sodium hydrogen sulfite (80 g, 0.76 mol) was added, and the solution was heated at 100 °C for 24 h.[11] After cooling, the solution was extracted four times with 100-mL portions of CH_2Cl_2; the solvent was evaporated and the crude, distilled under reduced pressure, gave 10.5 g (72.5%) of the title compound: bp 100 °C (1 mm); ^1H NMR (60 MHz, $CDCl_3$) δ 3.79 (t, J = 6.0 Hz, 2 H, CH_2OH), 3.41 (s, 1 H, OH), 2.94 (br m superimposed on a more intense unresolved m centered at δ 2.68, 3 H overall, α-methine and α-methylene protons), 2.25–1.20 (m, 8 H overall, β- and γ-methylenes).

Anal. Calcd for $C_7H_{14}SO$: C, 57.49; H, 9.65. Found: C, 57.61; H, 9.57.

***trans*-2-(2-Hydroxyethyl)thiane 1-Oxide (*trans*-5b).** The product of the ethylene oxide alkylation of α-lithiothiane 1-oxide was isolated by further evaporation of the aqueous layer (see above) and extraction with CH_2Cl_2. The residue, after solvent evaporation, was column chromatographed (SiO_2; 5:1 $CHCl_3$/absolute EtOH eluent) to give a colorless oil containing only one sulfoxide: ^{13}C NMR (δ_{Me_4Si}, $CDCl_3$) 60.1 (C_2), 59.0 (CH_2OH), 50.1 (C_6), 33.7 (C_3), 27.9 (CH_2CH_2OH), 24.0 (C_4), 22.1 (C_5). Based on the known ^{13}C shielding effects of the S–O function in six-membered rings,[12,13] the trans structure can be unambiguously assigned. No trace of the cis sulfoxide was detectable also in the ^{13}C spectrum of the crude. Therefore, trans alkylation of lithiothiane 1-oxide in THF occurs essentially exclusively, consistent with the results of alkylation studies with CH_3I.[7]

Allyl 4-Chlorobutyl Sulfide (11). To a 0.975 M solution of sodium ethoxide (232 mL, 0.226 mol) cooled at −10 °C was added allylthiol with stirring (17.0 g, 0.226 mol; Fluka, used without further purification) followed by addition of 4-bromo-1-chlorobutane[14] (39.5 g,

0.226 mol). After warming to room temperature, stirring was continued for 1 h, sodium bromide was filtered off, and the solution was neutralized with dilute HCl. The residue after evaporation of solvent was fractioned in a 100 plate column to obtain 15 g (40%) of the title compound: bp 84–85 °C (2 mm); ^{1}H NMR (60 MHz, $CDCl_3$) δ 6.17–4.93 (m, 3 H, vinyl protons), 3.58 (t, J = 6.2 Hz, 2 H, CH_2Cl), 3.16 (d, J = 6.7 Hz, 2 H, $CHCH_2S$), 2.50 (t, J = 6.6 Hz, 2 H, SCH_2CH_2), 2.25–1.50 (m, 4 H, β- and γ-methylenes).

Anal. Calcd for $C_7H_{13}SCl$: C, 51.05; H, 7.96. Found: C, 51.12; H, 8.06.

2-Vinylthiepane (8c) was prepared as described above for **9b** (method I) from **7c** (11.5 g, 0.05 mol) and 1 N t-BuOK in Me_2SO (50 mL, 0.05 mol). The crude olefin (5.8 g, 82%) appeared to contain ca. 88% of the title compound, which was separated by column chromatography (SiO_2; 4:1 pentane/benzene eluent): bp 108–109 °C (38 mm); ^{1}H NMR (100 MHz, $CDCl_3$) δ 6.0–4.8 (well-resolved m, 3 H, vinyl protons), 3.44 (m, 1 H, α-methine), 2.75 (m, 2 H, α-methylene), 1.8 (br m extending over 0.8 ppm, 8 H, β- and γ-methylenes).

Anal. Calcd for $C_8H_{14}S$: C, 67.54; H, 9.92. Found: C, 67.41; H, 10.03.

The rest of the crude olefin product consisted of two components (not separated from each other), which appeared likely to be the isomeric (*E*)- and (*Z*)-2-ethylidenethiepanes (**9c**). The ^{1}H NMR spectrum of the mixture was characterized by two broad quartets (J = 6.7 Hz) in a ca. 1.2:1 ratio, 1 H overall, centered at δ 5.74 and 5.36, respectively, and by a high field doublet (J = 6.7 Hz) at δ 1.65. Both the quartets and the doublet were further split into triplets ($J \simeq 0.5$ Hz), most likely as a consequence of long range coupling (allylic and homoallylic, respectively) to the methylene protons at C_3. The appearance of only one methyl doublet is doubtlessly due to accidental chemical shift coincidence. Other NMR features were δ 2.78 (m, 2 H, α-methylene) and 2.50 (br m, 2 H, C_3H_2).

2-(2-Bromoethyl)thiepane (7c) was obtained in 69% yield by the procedure outlined above for **7b**: bp 113 °C (2 mm); ^{1}H NMR (60 MHz, $CDCl_3$) δ 3.74 (t, 2 H, CH_2Br), 3.10 (br m partially superimposed on a δ 2.85 m, 3 H overall, α-methyne and α-methylene), 2.50–1.25 (m, 10 H, β- and γ-CH_2).

Anal. Calcd for $C_8H_{15}BrS$: C, 43.05; H, 6.77. Found: C, 42.89; H, 6.82.

2-(2-Hydroxyethyl)thiepane (6c). The α-lithio derivative of thiepane 1-oxide[10] (0.1 mol) was prepared and mixed with ethylene oxide at −65 °C as described above for **6b.** At this temperature, however, no reaction occurred. The dry ice bath was then removed, and the temperature was allowed to raise to −5–0 °C; in this temperature range the yellow solution turned blue, indicating that the reaction was taking place. Outside cooling was then restored to prevent a further temperature increase. A white precipitate formed as the reaction progressed, and the mixture was stirred at 0 °C for 10 h. Workup followed by hydrogen sulfite reduction, as described for **6b,** yielded 9.5 g (59.3%) of 2-(2-hydroxyethyl)thiepane [0.6 g (5.2%) of thiepane, from unreacted α-lithiothiepane oxide, was also recovered]: bp 128–129 °C (3 mm); ^{1}H NMR (60 MHz, $CDCl_3$) δ 3.82 (t, 2 H, CH_2OH), 3.50 (s, 1 H, OH), 2.87 (br m, 3 H, α-methine and α-methylene protons), 2.2–1.2 (m, 10 H, β- and γ-CH_2).

***cis*- and *trans*-2-(2-Hydroxyethyl)thiepane 1-oxide (5c)** were obtained from thiepane 1-oxide by the procedure described above for **5b** as a colorless oily mixture. The ^{13}C spectrum clearly indicated the presence of two isomers in an ca. 9:1 ratio. Their shifts (δ_{Me_4Si}, $CDCl_3$) were as follows (the first figure pertains to the major isomer); C_2, 56.2 (61.8); C_3, 34.8 (34.3); C_4 and C_5, interchangeable, 26.5 and 25.3 (24.9 and 24.7); C_6, 17.7 (19.7); C_7, 48.6 (51.8); CH_2CH_2OH, 24.1 (27.7); CH_2OH, 59.2 (58.8). The finding that all of the resonances which were expected[12] to be shielded by a quasi-axial S–O bond (C_2, C_7, C_6, CH_2CH_2OH) were upfield in the major isomer identifies the latter as the cis isomer (compare with the 1-methyl-2-vinylthiepanium salt (**1c,H**) below; the ^{13}C shielding by S–O and S–CH_3 is known to be qualitatively similar).[12]

1-Methyl-2-vinylthiolanium Hexafluorophosphate (1a,H). Neat **8a** (5.7 g, 0.05 mol) was added dropwise via syringe to a suspension of trimethyloxonium fluoborate[15] (7.75 g, 0.052 mol) in CH_2Cl_2 (65 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C and then for 2 more hours at room temperature. The residue, after evaporation of CH_2Cl_2, was dissolved in 50 mL of H_2O and ether extracted; aqueous ammonium hexafluorophosphate (8.7 g, 0.053 mol) was added to the separated aqueous layer, and the precipitate was collected (9 g, 65.6%), mp 60–65 °C. The filtrate, extracted with CH_2Cl_2, yielded 3.0 more grams (21.8%) as a viscous semisolid. ^{1}H NMR (CF_3COOH) showed two singlets at δ 3.02 and 2.77 (intensity ratio ca. 13:1 in the first crop and ca. 1:2 in the second). The first crystalline material, twice recrystallized, gave pure *trans*-1-methyl-2-vinylthiolanium hexafluorophosphate: mp 76–77 °C; ^{1}H NMR (60 MHz, CF_3COOH) δ 5.7 (m extending over 0.9 ppm, 3 H, vinyl protons), 4.5 (m, 1 H, α-CH), 3.62 (m, 2 H, α-CH_2), 3.02 (s, 3 H, CH_3), 2.62 (m, 4 H, β-CH_2); ^{13}C NMR [δ_{Me_4Si}, D_2O, dioxane as an internal reference (δ_{Me_4Si} 67.18)] 131.3 ($CH{=}CH_2$), 122.8 ($=CH_2$), 68.15 (C_2), 45.1 (C_5), 35.3 (C_3), 28.0 (C_4), 25.2 (CH_3).

Anal. Calcd for $C_7H_{13}SPF_6$: C, 30.66; H, 4.78. Found: C, 30.51; H, 4.67.

By heating (H_2O, 100 °C, 12 h),[16] the trans isomer isomerized to give an ca. 1:1 cis/trans equilibrium mixture. With respect to the trans isomer, the ^{1}H NMR spectrum (CF_3COOH) of the equilibrium mixture showed only one major new feature, namely, an S–CH_3 singlet at δ 2.77. The upfield shift with respect to the trans isomer (0.25 ppm) appeared to be the consequence of shielding by the cis double bond, a feature which is present in all of the cis/trans pairs (**1a–c, H;** see below). The ^{13}C spectrum of the cis/trans equilibrium mixture revealed the resonances of the cis isomer: 127.6 ($CH{=}CH_2$), 126.0 ($CH{=}CH_2$), 61.8 (C_2), 46.0 (C_5), 32.1 (C_3), 27.7 (C_4), 20.4 (CH_3). Comparison between the ^{13}C shielding of the two isomers (in particular C_2 and S–CH_3) leaves little doubt as to the configurational assignment.[12,17]

1-Ethyl-2-vinylthiolanium hexafluorophosphate (1a,Me) was prepared as described previously.[6]

1-Benzyl-2-vinylthiolanium Bromide (1a,Ph). Neat 2-vinylthiolane (1.14 g, 0.01 mol) was added to excess benzyl bromide (5.43 g, 0.03 mol) and stirred for 15 h at room temperature. The white precipitate was filtered, washed with ether, and dried in vacuo: 2.0 g (72%); mp 100–103 °C; recrystallized from ethanol/ether, mp 103–104 °C. Only one isomer appeared to be present: the ^{1}H NMR spectrum showed only one 2 H sharp singlet at δ 4.40 in CD_2Cl_2 and at δ 4.58 in Me_2SO-d_6. Apparently, in these solvents the diastereotopic benzyl protons have the same chemical shift. In CF_3COOH the benzyl CH_2 gave two resonances, δ 4.57 and 4.52, which are likely to be the central lines of the AB quartet. The rest of the ^{1}H NMR spectrum in CF_3COOH showed the following: δ 7.35 (br s, 5 H, aromatic protons), 6.02–4.77 (m, 3 H, vinyl protons), 4.35 (m, 1 H, α-CH), 3.55 (m, 2 H, α-CH_2), 2.32 (br m, 4 H, β ring CH_2).

Anal. Calcd for $C_{13}H_{17}SBr$: C, 54.74; H, 6.01. Found: C, 54.81; H, 6.12.

1-Methyl-2-vinylthianium hexafluorophosphate (1b,H) was prepared as described for **1a,H** from 2-vinylthiane (1.28 g, 0.01 mol). The hexafluorophosphate salt (2.6 g, 92%) was obtained by CH_2Cl_2 extraction as a viscous uncrystallizable material. NMR analysis of the crude fluoborate salt showed the presence of two isomers in a ca. 4:1 ratio. The isomeric mixture had the following ^{13}C resonances (δ_{Me_4Si}, D_2O, dioxane an an internal standard; the first figure refers to the major isomer): $-CH{=}CH_2$, 130.8 (129.6); $=CH_2$, 125.1 (126.8); C_2, 59.2 (50.6); C_3, 30.3 (23.5); C_4, C_5, and SCH_3, 23.2, 22.9, and 22.3, interchangeable (21.7, 17.7, and 14.6). These resonances unambiguously identify[17] the major product as the trans diequatorial isomer and the minor one as the cis isomer (SCH_3 axial, vinyl equatorial). This assignment is consistent with the ^{1}H NMR spectrum (D_2O), which showed two SCH_3 singlets (3 H overall) at δ 2.87 and 2.72, the former being more intense by a factor of about 4. No attempt was made to separate the isomers.

Anal. Calcd for $C_8H_{15}SPF_6$: C, 33.34; H, 5.25. Found: C, 33.41; H, 5.29.

1-Methyl-2-vinylthiepanium hexafluorophosphate (1c,H) was prepared in 98% yield as described for **1b,H** as a viscous noncrystallizable material. The crude fluorophosphate showed two SCH_3 singlets, 3 H overall, at δ 2.80 and 2.68 in the ^{1}H NMR; the former was more intense by a factor of about 5, suggesting that the major product is the trans isomer of the title compound and the minor the cis isomer. The ^{13}C NMR spectrum confirmed the presence of two isomers. The major isomer: (δ_{Me_4Si}, D_2O, dioxane as an internal standard) 131.6 (-CH=), 124.7 ($=CH_2$), 64.3 (C_2), 44.5 (C_7), 34.0 (C_3), 26.3, 24.8, 24.6, 24.2 (C_4, C_5, C_6, SCH_3, interchangeable). The minor isomer: 127.7 (-CH=), 126.9 ($=CH_2$), 56.6 (C_2), 38.6 (C_7), 31.5 (C_3), 27.4 (C_4 or C_5; a ^{13}C peak was missing, probably hidden below the group of three intense resonances of the major isomer at 24.8–24.2, 21.4 (C_6), 18.0 (SCH_3)). Although for the seven-membered ring the conformational situation is not as clear cut as in the six-membered one, there can be little doubt that the minor isomer has the cis structure. This follows from the observation that all carbons which are expected[17] to be shielded by a quasi-axial SCH_3 group (C_2, C_3, C_7, C_6, -CH=, S–CH_3) are upfield in the minor isomer.

Anal. Calcd for $C_9H_{17}SPF_6$: C, 35.76; H, 5.67. Found: C, 35.84; H, 5.61.

Ring Expansion of *cis*- and *trans*-1a,H. *cis*-Thiacycloct-4-ene (2a,H). Method I (*t*-BuOK in 10:1 THF/*t*-BuOH, −40 °C). The procedure was essentially the same as that previously described for ring expansion of **1a,Me.**[6] The title sulfonium salt (2.73 g, 0.01 mol,

trans/cis mixture about 13:1) was treated with *t*-BuOK (1.44 g, 0.013 mol) to give 1.16 g (91%) of a crude sulfide (>95% pure) which by GLC appeared to be a 6:1 mixture of two major products. The two components (GLC–MS) gave identical mass spectra, M^+ 128, indicating that isomeric compounds were converted to the same species upon electron impact. GLC monitoring revealed that the minor isomer was gradually and completely converted into the major isomer by heating the mixture at 120 °C. The direction of the isomerization suggests that the latter is the *E* olefin and the former the *Z* olefin.[18] Distillation under reduced pressure of the material obtained from thermal isomerization gave a liquid: bp 82 °C (18 mm); IR 720 cm^{-1} (cis double bond).

Anal. Calcd for $C_7H_{12}S$: C, 65.56; H, 9.43. Found: C, 65.48; H, 9.38.

^1H NMR (60 MHz, CCl_4) δ 5.8–5.0 (m, 2 H, olefinic protons), 2.8–2.0 (m, 8 H, methylene protons at C_2, C_3, C_6, and C_8), 1.9–1.4 (m, 2 H, C_7H_2). Irradiation (100 MHz) at δ 2.4 converted the low field multiplet into an AB quartet, $\Delta\nu$ = 21.3 Hz, J = 10.0 Hz, consistent with a cis double bond.[20] The ^{13}C spectrum (δ_{Me_4Si}, $CDCl_3$) is consistent with the assignment (the first figure pertains to the major isomer):[21] C_5, 130.6 (137.5); C_4, 129.8 (130.4); C_2, 34.0 (43.5); C_3, C_7, and C_8, interchangeable, 31.0, 30.9, and 30.4 (37.8, 36.8, and 35.2); C_6, 23.8 (34.8?). As shown, all corresponding carbons are upfield in the major isomer, consistent with the cis structure.[6,24]

Using *t*-BuOK as the base, ring expansion of **1a,H** may occur in high yield (ca. 90%) under conditions other than those described above; all of the variants are listed in Table I. Remarkably, however, the olefin distribution (cis/trans $\simeq$ 6) remained unchanged.

Method II (LDA in THF). To a solution of **1a,H** (1.37 g, 0.005 mol) in 40 mL of THF, cooled at −70 °C under an N_2 atmosphere, was added a cold solution (−70 °C) of lithium diisopropylamide in THF (0.005 mol in 5 mL) with stirring. The mixture was stirred at −70 °C for 2 h, during which time neither the yellow color was discharged nor GLC monitoring showed the formation of ring expanded product. The solution was then quenched with H_2O, and the sulfonium salt recovered was found to be the starting material essentially unchanged. In a second preparation, after mixing at −70 °C, the reaction mixture was allowed to slowly warm up; at −25 °C the color started to change and the solution was stirred for 2 h at this temperature. Quenching and workup as described under method I above yielded 0.440 g (70%) of a crude containing (GLC) ca. 80% of ring expanded product (in the same 6:1 proportion as obtained with method I) plus a variety of other unidentified products (five GLC peaks overall).

Method III. Ring expansion of **1a,H** (0.546 g, 0.002 mL) was attempted with diazabicycloundecene (DBU) (0.456 g, 0.003 mol) as the base in toluene (10 mL) as solvent at reflux for 4 h. Continuous GLC monitoring showed that no ring expanded product was formed during this time.

Method IV. Ring expansion of **1a,H** was also attempted with aqueous base. A suspension of the sulfonium salt (0.274 g, 0.001 mol) in 5 mL of 1 N NaOH was heated at 45 °C with stirring. The solid gradually turned into an oil and after 6 h was extracted with CH_2Cl_2. The residue, after removal of solvent, appeared to be a mixture of the two isomeric sulfonium salts **12** and **13** in ~6:1 ratio. Using the fluoborate salt, the reaction was repeated twice, in D_2O and in a 1:1 mixture of D_2O/H_2O, and followed in the NMR (see Results and Discussion). The two isomers have the following ^{13}C NMR data δ_{Me_4Si}, D_2O, internal reference dioxane; the first figure refers to the major isomer and that in parentheses to the minor one): C_2, 134.6 (135.1); C_3, 26.3 (33.5); C_4, 29.4 (28.8); C_5, 44.7 (45.2); SCH_3, 28.6 (26.8); $=CCH_3$, 138.6 (136.3); $=CCH_3$, 16.8 (18.1). The assignment was based on off-resonance experiments, specific deuteration (SCH_3 and $=CCH_2H$), and the known effects of substituents in thiolanium cations.[17e] The configurational assignment is essentially based on the differential chemical shift of C_3, 6 ppm upfield in the major isomer, consistent with the notion that in the *E* isomer the methyl group at the double bond should shield the γ carbon (C_3) by several parts per million. This configurational assignment is fully consistent with the evidence from ^1H NMR (100 MHz, CD_2Cl_2). The spectrum of the product mixture showed an intense high field methyl doublet (δ 1.92, J = 7.1 Hz), each line of which was split into a triplet (J = 1.6 Hz). The first, 7.1 Hz, is the vicinal coupling to the olefinic proton; the second is a long distance (five bonds) homoallylic coupling to the protons at C_3. Of the minor isomer, only the lower field triplet of the methyl doublet is visible (δ 2.10), showing a 2.0 Hz splitting. Thus, the homoallylic coupling is larger by 0.4 Hz in the minor isomer. Since transoid homoallylic couplings are usually higher than cisoid ones by ca. 0.3 Hz,[23] the CH_3 group ought to be trans to C_3 in the minor isomer, which hence has the *Z* configuration. All other resonances of the minor isomer are hidden below those of the major *E* isomer. The latter showed the following: δ 6.6 (q of *t*, 1 H, olefinic proton), 3.65 (m, 2 H, α-CH_2), 2.85 (s, superimposed on a multiplet, 5 H overall, SCH_3 and C_3H_2), 2.52 (m, 2 H, C_4H_2). Irradiation at δ 2.85 resolved the δ 6.6 multiplet into a quartet, J = 7.1 Hz (coupling to CH_3), and removed the 1.6 Hz splitting from the high field methyl doublet (as well as the 2.0 Hz splitting from the δ 2.10 resonance of the minor isomer). Irradiation of the doublet at δ 1.92 resolved the δ 6.6 m into a triplet, J = 2.4 Hz (allylic coupling to C_3H_2).

Ring Expansion of *trans*-1a,H with a 50% Defect of Base. The procedure was that of method I above expect that 0.005 mol of **1a,H** and 0.003 mol of *t*-BuOK were used. GLC analysis showed the formation of **2b,H** and **3b,H** in the usual 6:1 ratio. After quenching with H_2O and solvent removal in vacuo, the residue was diluted with H_2O and extracted successively with ether, to remove the olefins, and with CH_2Cl_2. The residue, after evaporation of CH_2Cl_2, was found to be (^1H NMR in CF_3COOH) an ca. 1:1 mixture of "unreacted" sulfonium salts *trans*- and *cis*- **1a,H.**

Attempted Ring Expansion of 1a,Me Using LDA. The reaction was carried out during 1 h at −70 °C under the conditions of method II above. Usual workup gave a sulfide product which proved to be (GLC, ^1H NMR) 2-vinylthiolane (70%).

Ring Expansion of 1b,H. *trans*-Thiacyclonon-4-ene (3b,H). The reaction was carried out according to method I. The sulfide material obtained (85%) was made up of two products in an ca. 24:1 ratio, whose composition was unchanged after distillation, bp 72 °C (2 mm). The product mixture showed the following: IR 960 cm^{-1} (s, trans double bond); ^1H NMR (100 MHz, $CDCl_3$), symmetrical m centered at δ 5.47 (2 H, olefinic protons), δ 3.1–1.1 (br m, 12 H, α-, β-, γ-, and δ-methylenes). Irradiation at δ 2.05 resolved the low field m into an AB quartet, $\Delta\nu$ = 41 Hz, J = 15.3 Hz, confirming that the major component (the only one visible in the proton spectrum) has the trans configuration at the double bond.[20] ^{13}C NMR: the major isomer has (δ_{Me_4Si}, $CDCl_3$) 134.6 (C_5), and 126.6 (C_4); the remaining resonances, unassigned, are at 37.6, 36.2, 33.2, 32.6, 26.0, and 25.6. The minor component also has eight resonances: 130.5 and 129.8 (olefinic carbons), 34.0, 31.0, 30.8, 30.5, 30.3, and 23.8. The fact that in the minor component the olefinic carbons resonate close together while all other resonances occur upfield with respect to those of the major component gives a strong indication that the former is the cis isomer.[6,24]

Anal. Calcd for $C_8H_{14}S$: C, 67.54; H, 9.92. Found: C, 67.61; H, 9.83.

Ring Expansion of 1c,H. *trans*-Thiacyclodec-4-ene. Under the reaction conditions of method I, a single (GLC, ^{13}C NMR) product was obtained in 85% yield (distilled under reduced pressure): bp 83 °C (1 mm); IR 965 cm^{-1} (s, trans double bond); ^1H NMR (100 Mz, $CDCl_3$) δ 5.77–5.27 (m, 2 H, olefinic protons), 2.71–1.96 (m, 8 H, C_2H_2, C_3H_2, C_6H_2, $C_{10}H_2$), 1.70–1.48 (m, 6 H, C_7H_2, C_8H_2, C_9H_2). Irradiation at δ 2.37 resolved the low field m into an AB quartet, $\Delta\nu$ = 13.2 Hz, J = 15.0 Hz (trans double bond). ^{13}C NMR (δ_{Me_4Si}, $CDCl_3$) 131.64 and 130.33 (olefinic carbons), 34.21 (two resonances), 33.50, 31.31, 27.19, 25.39, 23.55.

Anal. Calcd for $C_9H_{16}S$: C, 69.16; H, 10.32. Found: C, 69.23; H, 10.41.

Ring Expansion of 1a,Ph. *cis*-2-Phenylthiacyclooct-4-ene (2a,Ph). The reaction was accomplished according to method IV. To a solution of **1a,Ph** (2.85 g, 0.01 mol) in 25 mL of H_2O was added 35 mL of 2 M NaOH at room temperature. The solution became immediately cloudy, and then a white precipitate formed. The materials obtained by filtration and by pentane extraction were combined to give 3.8 g (95%) of a product, mp 60–64 °C, which (GLC and ^{13}C NMR) appeared to contain two substances in ca. 13:1 ratio, most likely *cis*- and *trans*-2-phenylthiacyclooct-4-ene, respectively. By heating the mixture at 150 °C, the minor product isomerized quantitatively to the major product (recrystallized from $EtOH/H_2O$): mp 67–68 °C; IR 725 cm^{-1} (s, cis double bond); ^1H NMR (60 MHz, $CDCl_3$) δ 7.15 (narrow m, 5 H, aromatic protons), 5.78 and 5.62 (m's, 2 H overall, olefinic protons), 3.62 (dd, J = 10.3 and 2.2 Hz, 1 H, C_2H), 3.30–1.50 (m's, 8 H overall, methylenes at C_6, C_3, C_7, and C_8). Irradiation at δ 2.14 changed the high field part of the olefinic resonances into an apparent triplet, J = 11 Hz. This must arise from two very nearly equal couplings being left, ca. 11 Hz, one of which is the vicinal coupling to the second olefinic proton. This value confirms the cis configuration of the double bond. ^{13}C NMR (δ_{Me_4Si}, $CDCl_3$): in the region of the aromatic and olefinic carbons, only four resonances are visible instead of six: 143.7, 130.9, 128.5, and 127.0. From their intensities, the latter two values appear to comprise two resonances each. Only the 143.7 resonance can be assigned unambiguously to C_1 of the Ph ring. Since, however, the maximum difference between the remaining ones is only 3.9 ppm, the cis structure is confirmed unambiguously.[6,24] The remaining resonances are at 51.8 (C_2), 37.2 (C_3), 31.2 and 30.4 (C_7

and C_8, interchangeable), and 23.8 (C_6).

Anal. Calcd for $C_{13}H_{16}S$: C, 76.41; H, 7.89. Found: C, 76.53; H, 7.95.

The ^{13}C NMR spectrum of the crude isomeric mixture showed five minor resonances in the aliphatic region: 63.1 (C_2), 43.6 (C_3), 35.9, 35.8, 34.9 (C_6, C_7, C_8, interchangeable). The occurrence of these resonances at low field with respect to those of the major component are consistent with the minor product being the trans isomer, **3a,Ph.**

Registry No.—*trans*-**1a,H,** 68013-66-1; *cis*-**1a,H,** 68013-68-3; **1a,Ph,** 68013-69-4; *trans*-**1b,H,** 68013-71-8; *cis*-**1b,H,** 68013-73-0; *trans*-**1c,H,** 68013-75-2; *cis*-**1c,H,** 68013-77-4; **2a,H,** 64945-38-6; **2a,Ph,** 64945-40-0; **2b,H,** 68013-78-5; **3a,H,** 64945-41-1; **3a,Ph,** 64945-42-2; **3b,H,** 68013-79-6; **3c,H,** 68013-80-9; *trans*-**5b,** 68013-81-0; *cis*-**5c,** 68024-68-0; *trans*-**5c,** 68013-82-1; **6b,** 68013-83-2; **6c,** 68013-84-3; **7b,** 68013-85-4; **7c,** 68013-86-5; **8a,** 57565-42-1; **8b,** 66120-24-9; **8c,** 66120-30-7; (*E*)-**9c,** 68013-87-6; (*Z*)-**9c,** 68013-95-6; **10b,** 68013-88-7; **11,** 68013-89-8; **12,** 68013-91-2; **13,** 68013-93-4; 2-chlorothiolane, 22342-03-6; vinylmagnesium bromide, 1826-67-1; 2-vinylidenthiane, 68013-94-5; thiane 1-oxide, 4988-34-5; ethylene oxide, 75-21-8; allylthiol, 870-23-5; 4-bromo-1-chlorobutane, 6940-78-9; trimethyloxonium fluoroborate, 420-37-1; benzyl bromide, 28807-97-8; 2-vinylthiane, 66120-24-9.

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(2) In the present paper the series of compounds where n = 1, 2, and 3 are identified by the letters a, b, and c, respectively; the nature of the R substituent is explicitly stated.

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(18) For eight-membered cyclic olefins, the trans isomer is considerably more strained than the cis isomer (9.3 kcal/mol in the cyclooctenes).[19]

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(20) L. M. Jackman and S. Sternell, "Applications of Nuclear Magnetic Resonance Spectroscopy", Pergamon Press, Oxford, 1969, p 301–303.

(21) The unambiguous chemical shift assignment for C_2, C_4, and C_5 has been made by position specific deuterium labeling.[22]

(22) Work in progress in this laboratory.

(23) Reference 20, p 326.

(24) J. B. Stothers, "Carbon-13 Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York, N.Y., 1972, p 69.

Ring Expansion of 2-Vinyl Derivatives of Thiane, *N*-Benzylpiperidine, and Thiepane by [2,3] Sigmatropic Shift

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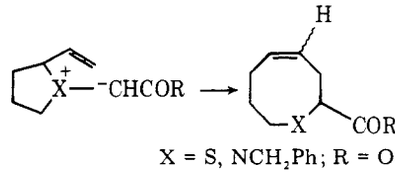
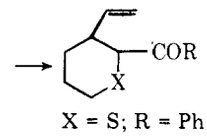
Syntheses of 2-vinylthiane, 2-vinylthiepane, and 2-vinyl-*N*-benzylpiperidine are described. The shortest routes involve addition of vinylmagnesium bromide to the α-chloro sulfides or to an *N*-benzylimmonium salt. Alkylation of the 2-vinyl heterocycles with carboethoxymethyl trifluoromethanesulfonate gives sulfonium or ammonium salts in good yield. Ring expansion occurs upon addition of DBU to the salts at 20 °C. Alkylation of 2-vinylthiane with allyl triflate followed by treatment with LDA affords 2-vinylthiacyclonon-4-ene. This substance can be converted into 2-carboethoxythiadodeca-4,7-diene by a second ring expansion sequence. The following medium-sized heterocycles have also been prepared: (*E*)-2-carboethoxythiacyclonon-4-ene, (*E*)-2-carboethoxy-*N*-benzylazacyclonon-4-ene, and (*Z*)-*N*-benzylazacyclonon-4-ene.

In a recent publication, we have described [2,3] sigmatropic ring expansions of five-membered nitrogen or sulfur heterocycles to give eight-membered heterocycles.[1] Typical rearrangements (eq 1) occur at room temperature or above with a time scale of the order of hours. Since similar acyclic ylide rearrangements are considerably faster,[2] the bicyclo[3.3.0] transition state for ring expansion apparently is destabilized relative to the monocyclic analogue. As a result, yields of eight-membered heterocycles are modest (65–80%) and side reactions such as Stevens rearrangement (eq 2) may compete in certain cases.



(1)

X = S, NCH_2Ph; R = OC_2H_5, Ph



(2)

X = S; R = Ph

We have also reported the ring expansions of six-membered heterocycles and related compounds.[3,4] Exocyclic ylides derived from α-vinylthianes or -piperidines resemble their acyclic relatives in qualitative rearrangement rates, and the yields of nine-membered products are uniformly excellent.

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