J. Org. Chem. 1985, 50, 4218–4226

4-Nitro-1,3,5,7-tetraacetamidonaphthalene (23). Nitric acid (90%, 0.2 mL) was added to a stirring suspension of 1,3,5,7-tetraacetamidonaphthalene (**16b**, 300 mg, 0.842 mmol) in acetic acid (13 mL). After the reaction mixture was stirred at 25 °C for 3 days, it was poured into 50 mL of water and the product filtered to yield 273 mg (81%) of crude **23**; recrystallization from acetic acid gave yellow prisms, mp 336–338 °C (dec) (90% recovery); IR (KBr) 3100, 2900 (NH), 1625 (C=O), 1510 (NO_2) cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 10.33 (br s, 1 H, NH), 10.15 (br s, 1 H, NH), 9.78 (br s, 1 H, NH), 9.58 (br s, 1 H, NH), 8.25 (d, J = 2 Hz, 1 aryl CH), 7.72 (d, J = 2 Hz, 1 aryl CH), 7.67 (s, 1 aryl CH), 2.17 (s, 3 H, CH_3), 2.11 (s, 3 H, CH_3), 2.03 (s, 3 H, CH_3), 1.93 (s, 3 H, CH_3). Anal. Calcd for $C_{18}H_{19}.N_5O_6$: C, 53.86; H, 4.77; N, 17.45. Found: C, 53.69; H, 4.87; N, 17.34.

Acknowledgment. The authors are indebted to R. L. Atkins, E. D. Erickson, D. A. Fine, R. A. Hollins, M. P. Nadler, and D. W. Moore of this laboratory for technical assistance and helpful discussions. The support of L. A. Roslund and the Naval Sea Systems Command is gratefully acknowledged.

Bicyclic Vinyl Sulfides by Ring Expansions of Spirocyclic Dithioketal Systems

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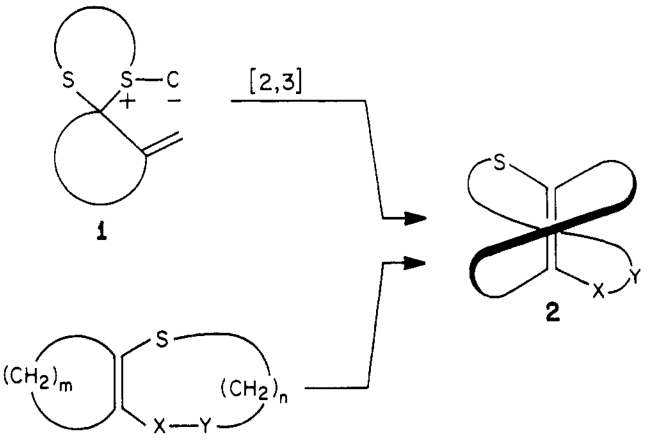
Our objective was to prepare sulfur-containing bicyclo[10.5.0]- and -[10.6.0]alkenes for future photochemical studies. Prototypes having a seven-membered heterocyclic ring with two sulfurs were obtained by one-atom ring expansion of a spirocyclic 1,3-dithiane 1-oxide (**11b**). A similar sequence applied to the homologous 1,3-dithiepine 1-oxide (**17**) enlarged it to its corresponding eight-membered heterocycle (**18**). A two-atom-ring growth of a β-hydroxy-1,3-dithiane promoted by P_2O_5 was developed with a monocyclic model compound (**23a**). The product (**24**) is a 1,5-dithiacyclooctene with one sulfur vinylic and the other allylic. When the scheme was applied to the appropriate spirocyclic 1,3-dithiane system (**29a**), P_2O_5 produced the corresponding 12/8 bicyclic alkene (**31a**) with a tetrasubstituted π bond. With $POCl_3$/Py, the 6 → 8 rearrangement afforded the trisubstituted olefin (**30a**), which separately could be isomerized to alkene **31a**. The action of P_2O_5 on a spirocyclic β-hydroxy-1,3-dithiolane (**29c**) gave the desired 12/7 ring system as a binary mixture of olefins (**30b, 31b**), which converted entirely to the more stable tetrasubstituted isomer when treated with HCl gas. One-atom (6 → 7) ring expansion in α-hydroxy-1,3-dithianes was tested on a monocyclic analogue (**32a**) and its acetate ester (**32b**). Hot $POCl_3$/Py successfully enlarged the alcohol to an alkene having a 1,4-dithiepane skeleton (**36**). Pyrolysis of the acetate (**32b**) effected the same ring expansion.

Recently, we described the first syntheses of doubly transoid, bicyclic olefins (i.e., "betweenanenes") having a heteroatom (sulfur) directly connected to the sheltered double bond (see **2**).[1,2] The approach involved multistep construction of unsaturated spirocyclic sulfur ylides of type **1**, which underwent [2,3]-sigmatropic rearrangement to the desired targets **2** (see Scheme I). Our studies of the chemistry of shielded alkenes make it necessary to develop other (potentially shorter) routes to such structures, and especially to those in which the transoid heterocyclic ring would be highly strained (e.g., eight membered or less).

Photic isomerization of bicyclic cisoid alkenes[3] could provide an entry to strained betweenanenes. One favorable feature of a vinylic sulfur is to shift the UV absorption of the alkene bathochromically to more accessible wavelengths.[4] But it is uncertain whether the heteroatoms would thwart the cis → trans photochemical change because the irradiation behavior of cycloalkenes carrying one or two vinylic sulfurs in unknown. Photochemical approaches to strained heterocyclic betweenanenes require prior syntheses of their appropriate fused bicyclic "cis" counterparts. The present paper describes routes to several "cis" prototypes with a 12-membered carbocyclic ring.

Scheme I



3 X = S; Y = CH_2
4 X = CH_2; Y = S

Some of these compounds have two vinylic sulfurs (i.e., type **3** whereas others have one vinylic and one allylic sulfur (i.e., type **4**).

Our first approach to type **3** used a transformation reported by Chen and Donatelli. They found that p-toluenesulfonic acid hydrate expands a 1,3-dithiolane 1-oxide (**5a**) to a dihydro-1,4-dithiine (**6a**), presumably via cationic intermediates like those shown in Scheme II.[5] We

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(1) (a) Nickon, A.; Rodriguez, A.; Shirhatti, V.; Ganguly, R. *Tetrahedron Lett.* **1984**, *25*, 3555–3558.

(2) Nickon, A.; Rodriguez, A. D.; Shirhatti, V.; Ganguly, R. *J. Org. Chem.* **1985**, *50*, 2767–2777.

(3) Nakazaki, M.; Yamamoto, K.; Yanagi, J. *J. Chem. Soc., Chem. Commun.* **1977**, 346–347.

(4) Whereas unstrained monoalkenes absorb around 200 nm or less, vinylic sulfurs can shift absorptions as high as 250–285 nm. For example, see Experimental Section for UV of compounds **12**, **14**, and **31a**.

(5) Chen, C. H.; Donatelli, B. A. *J. Org. Chem.* **1976**, *41*, 3053–3054.

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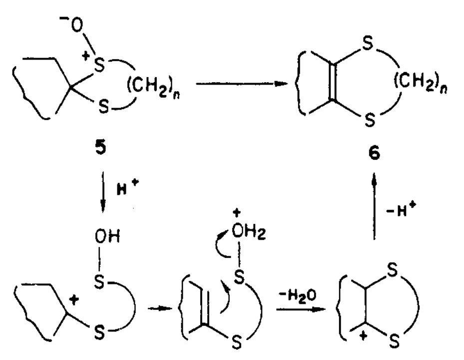
Scheme II[a]

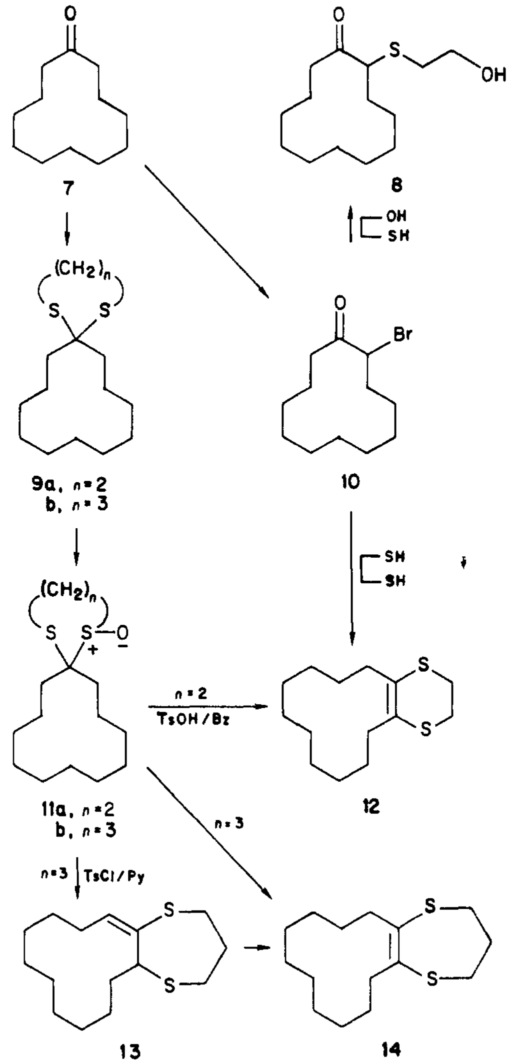


[a] a, n = 2; b, n = 3; c, n = 4.

wanted to apply their reaction not only to n = 2 but also to higher homologues (n = 3 and 4) in the hope it could enlarge such six- and seven-membered dithioketals to seven- and eight-membered rings, respectively.

Cyclododecanone (**7**) was converted conventionally to the 1,3-dithiolane **9a** and then to monosulfoxide **11a**.[5] Action of *p*-toluenesulfonic acid hydrate transformed **11a** to the ring-expanded 1,4-dithiine **12**. We also obtained **12** by a different route, namely action of 1,2-ethanedithiol on 2-bromocyclododecanone (**10**). This last reaction (**10** → **12**) proceeded in 67% yield and was modeled on an analogous change reported by Rubinstein and Wuerthele for an acyclic α-halo ketone.[6] In hope of extending this type of reaction to mixed heteroatoms, we also treated **10** with the monoanion from 2-mercaptoethanol. The product, however, was sulfide **8**, according to IR, ^{1}H NMR, and elemental analyses (see Scheme III).

Scheme III



Our next aim was to attempt the sulfoxide route on a higher homologue, specifically **9b**. We prepared this dithioketal from ketone **7** and oxidized it to its monosulfoxide **11b**. Both **9b** and **11b** are solids, whose NMR data (^{1}H and ^{13}C) fit their structures. When sulfoxide **11b** was subjected to the same ring-expansion conditions used for **11a**, we obtained parent ketone **7**, but no olefin. The literature describes instances where a dithioketal sulfoxide reverts to ketone on acid *hydrolysis*.[7] Therefore, it seemed likely that our ketone **7** arose from **11b** through capture of water by one of the ionic intermediates in Scheme II. Accordingly, we tried anhydrous *p*-toluenesulfonic acid in place of the hydrate. Ketone **7** was still a major product, but it was now accompanied by small amounts of olefins **13** (2.7%) and **14** (10.6%), which were separated. Wishing to minimize ketone formation, we explored various experimental conditions for the acidic ring expansion, but with limited success. Ultimately, we overcame the difficulties by modifying the reagent. Thus, *p*-toluenesulfonyl chloride in dry pyridine converted sulfoxide **11b** almost quantitatively to the liquid trisubstituted alkene **13** (one olefinic H), which gave a crystalline monomethiodide salt involving the allylic sulfur. Mechanistically, the **11b** → **13** change is probably akin to that depicted in Scheme II except that the departing group on sulfur is OTs and the final proton loss leads to a trisubstituted rather than a tetrasubstituted olefin. That kinetic and not thermodynamic factors determine the alkene produced is clear from the following experiment: olefin **13** (*Z* or *E* stereochemistry unassigned) was separately isomerized to the crystalline tetrasubstituted counterpart **14** by action of dry hydrogen chloride. In accord with its structure, the dihydro-1,4-dithiepine **14** showed no vinylic hydrogens and a ^{13}C NMR spectrum consistent with its symmetry (one sp^2 and seven sp^3 carbons). Interestingly, although dry HCl shifted the double bond smoothly, other acidic catalysts ($BF_3{\cdot}Et_2O$; $AlCl_3$; CF_3CO_2H; *p*-TsOH) proved ineffective. Comparing the outcome of sulfoxides **11b** and **11a** in the ring enlargements induced by *p*-TsOH, we conclude that expansion of the disulfur ring from six to seven is sufficiently slower than from five to six to allow the ketone-forming side reaction to compete seriously. The literature records very few precedents for transforming 1,3-dithianes to dihydro-1,4-dithiepines, so our success via TsCl/Py is welcome.[8]

With an effective route to the bicyclic 12/7 ring system **14** in hand, we wanted to apply the sequence to get the corresponding 12/8 analogue. When we tried to synthesize the requisite dithioketal of cyclododecanone routinely with 1,4-butanedithiol and $BF_3{\cdot}Et_2O$, the product was a high melting solid, sparingly soluble in most organic solvents. Its spectroscopic character, elemental analyses, and molecular weight indicated a dimeric structure, **15** (Scheme IV).[9] To try to preclude, or at least to minimize, dimer formation, we tested a variety of dithioketalization meth-

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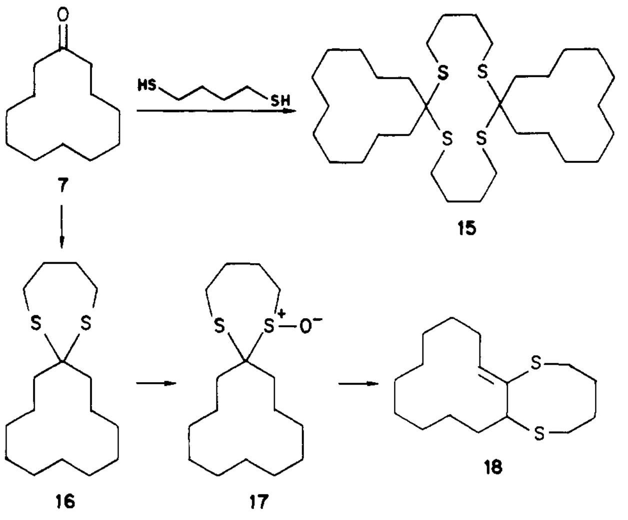
(6) Rubinstein, H.; Wuerthele, M. *J. Org. Chem.* **1969**, *34*, 2762–2763.

(7) Kuhn, R.; Neugebauer, F. A. *Chem. Ber.* **1961**, *94*, 2629–2644.

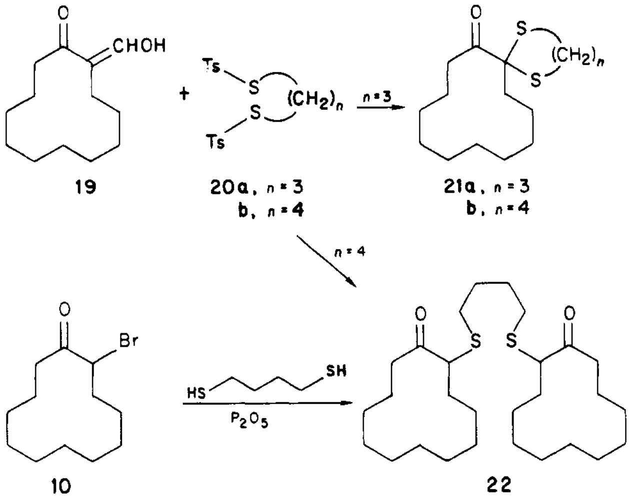
(8) Very recently, Salazar and co-workers have converted two steroidal 1,3-dithianes to dihydro-1,4-dithiepines by use of phenylselenyl chloride in methylene chloride. Francisco, C. G.; Freire, R.; Hernández, R.; Salazar, J. A.; Suárez, E. *Tetrahedron Lett.* **1984**, *25*, 1621–1624.

(9) Analogous dimers are known to arise when 1,5-pentanedithiol condenses with aldehydes and ketones under acid catalysis. Busby, R. E.; Huckle, D. *J. Chem. Soc., Perkin Trans. 1*, **1972**, 1705–1710.

Scheme IV



Scheme V

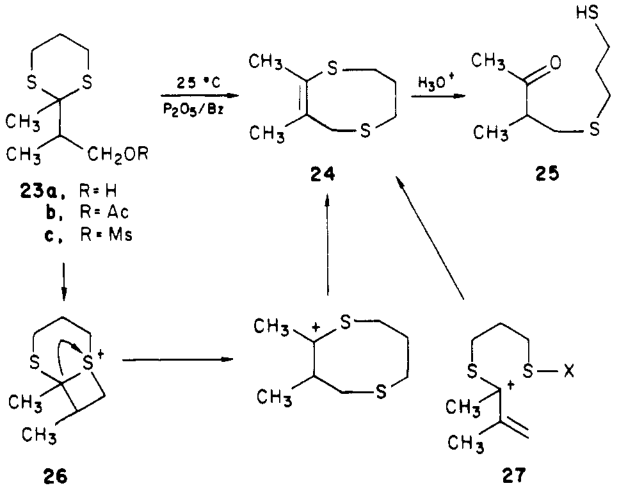


ods. Ultimately we found that AlCl$_3$/CH$_2$Cl$_2$[10] converted 7 to the desired spirodithioketal 16 (76%) without the accompanying dimer. Conventional oxidation produced monosulfoxide 17, and this in turn was subjected to the usual conditions for ring expansion (p-TsOH). In similarity with the behavior of **11b**, this treatment afforded only the parent ketone **7**. However, our alkaline milieu (TsCl/Py) handily transformed **17** to the trialkylated alkene **18**, a result that parallels the outcome with the lower homologue **11b**. Olefin **18** appears homogeneous, but we cannot specify whether it is a *Z* or *E* isomer. In harmony with the proposed structure **18**, this product displayed one vinylic hydrogen, two different olefinic carbons, and a weak IR band at 1605 cm^{-1}.

We hoped to move the double bond in **18** to the tetrasubstituted site. But treatment with dry HCl proved unsuccessful, and several other attempts under different acidic conditions also failed. Evidently for the 12/8 system, the double bond shuns the fully substituted position. Consequently, we looked for other possible routes to the tetrasubstituted 12/8 alkene.

One projected scheme required the spiroketone **21b** (Scheme V), and we strived to make it through a type of reagent originated by Woodward et al.[11] and used by

Scheme VI



Trost[12] and co-workers to synthesize the lower homologue **21a**. Specifically, Trost's team treated 2-(hydroxymethylene)cyclododecanone (**19**) with trimethylene dithiotosylate (**20a**) and obtained **21a**, a sequence that we successfully duplicated. To extend this approach to the next higher homologue required tetramethylene dithiotosylate (**20b**). We prepared this new reagent from 1,4-dibromobutane and potassium thiotosylate. However, action of this dithiotosylate on **19** did not produce **21b**; instead it gave a product, whose spectral and analytical data fit diketone **22**.[13] It melts sharply, so presumably it is a single diastereomer, but we do not know whether it is the pref (i.e., meso) or the parf (i.e., racemic) modification. Interestingly, when we treated **22** with 1,4-butanedithiol to try to join the rings with a second heteroatom chain, the product was dithioketal **16**. In one more attempt to get the tetrasubstituted isomer of **18**, we tried to force the same sort of reaction that earlier (Scheme III) successfully converted bromo ketone **10** to the dihydro-1,4-dithiine **12**.[6] In the event, treatment of 2-bromocyclododecanone (**10**) with 1,4-butanedithiol gave a complex mixture, from which one component crystallized out in 18% yield and proved to be the dimeric diketone **22**.

We now describe reaction sequences that provided bicyclic olefins having one sulfur allylic and the other sulfur vinylic (i.e., type **4**, Scheme I). Our approach was based on a skeletal rearrangement encountered during an attempted dehydration of the simple β-hydroxy dithioketal, **23a** (Scheme VI). To get this substrate, we treated the parent β-hydroxy ketone with 1,3-propanedithiol under mild conditions (0 °C) that did not acetylate the OH group. The dithioketal **23a** was then separately acetylated to give acetate **23b** with appropriate spectral and analytical properties. The corresponding mesylate **23c** was also obtained conventionally. It gave good spectra, but this derivative deteriorates quickly on standing.

From an attempted dehydration of alcohol **23a** with P$_2$O$_5$ in benzene, we isolated but one product (60%), which proved to be the eight-membered cycloalkene **24**.[14] The ^{1}H NMR spectrum of this homogeneous liquid showed no olefinic hydrogens, but sharp singlets at δ 2.0 and 1.9 indicated vinylic methyl groups. Also, a broad singlet ob-

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[10] Ong, B. S. *Tetrahedron Lett.* **1980**, 4225–4228.

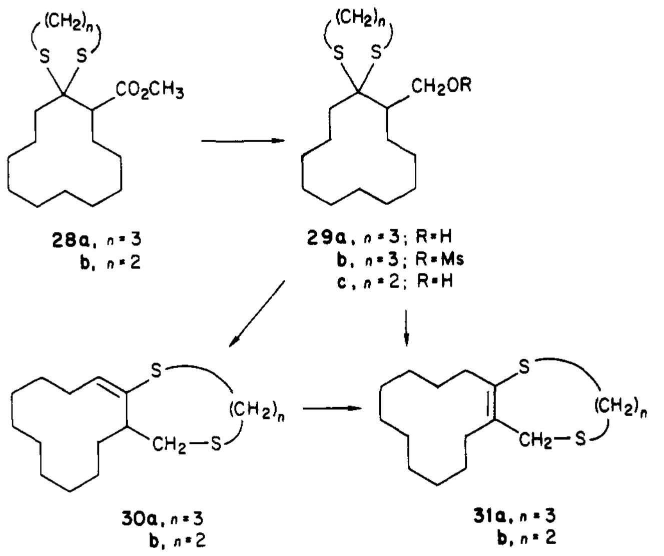
[11] (a) Woodward, R. B.; Pachter, I. J.; Scheinbaum, M. L. *J. Org. Chem.* **1971**, *36*, 1137–1139; (b) Woodward, R. B.; Pachter, I. J.; Scheinbaum, M. L. *Org. Synth.* **1974**, *54*, 33–37; 37–39.

[12] Trost, B. M.; Hiroi, K.; Jungheim, L. N. *J. Org. Chem.* **1980**, *45*, 1839–1847.

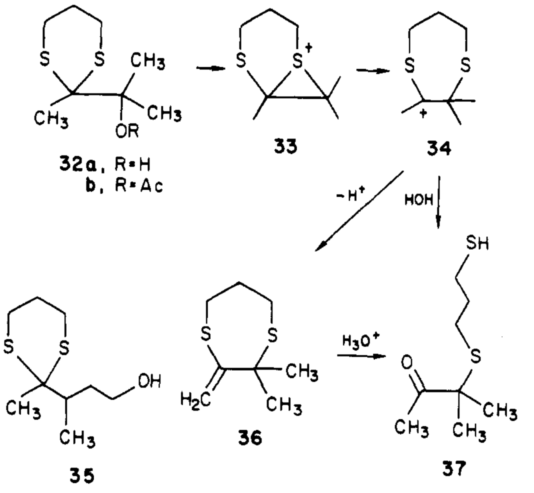
[13] The different outcome with reagents **20a** and **20b** may simply be related to the relative slowness of closing seven-membered vs. six-membered rings.

[14] We tried to effect the same ring expansion by thermolysis of acetate **23b**. In a Kugelrohr tube at 400 °C, the ester simply distilled. In a sealed tube at 280 °C, it produced an intractable mixture.

Scheme VII



Scheme VIII



served at δ 3.7 is typical for an allylic CH_2 joined to sulfur. That our alkene consisted of only one geometric isomer was confirmed by ^{13}C NMR, which indicated just two sp^2 carbons. We assign to alkene **24** the *Z* (rather than the highly strained *E*) geometry, because olefin isomerizations are likely in the acidic medium. One reasonable sequence for the **23a** → **24** rearrangement invokes sulfur participation via cation **26**. A ring-opened species like **27** (X = some electrophile) is also quite plausible.[15] Although olefin **24** appeared homogeneous, our efforts to get satisfactory combustion analyses were short of the mark, so we verified its structure chemically. Acid hydrolysis of the enol sulfide link converted **24** to a ketone (**25**) in 64% yield. This product gave appropriate C and H analyses, and its IR and ^1H NMR spectra were in full accord with structure **25**. In view of the novel six-membered → eight-membered ring expansion, encountered here with the monocyclic substrate **23a**, we sought to extend it to spirocyclic precursors to produce systems of type **4** in Scheme I.

Our prototype was the known 1,3-dithiane alcohol **29a** (see Scheme VII) synthesized from cyclododecanone via **28a** by a reported sequence.[1,2] Treatment of **29a** with phosphorus pentoxide rearranged it cleanly (82%) to the crystalline tetrasubstituted alkene **31a**. Its structure was deduced from elemental analyses, from ^1H NMR (no vinylic H; a methylene singlet for $=CCH_2S$—), and from ^{13}C NMR (two sp^2 carbons). Interestingly, when we used $POCl_3$/Py as the dehydrating milieu, the sole product (92%) was the trisubstituted olefin **30a** (one vinyl H and two sp^2 carbons). We have no reliable basis for knowing whether this isomer is *Z* or *E*, so the stereochemistry drawn in **30a** is arbitrary. Because **30a** was formed in pyridine solution, where double bond shifts are unlikely, we think this alkene arises from a kinetically regulated proton loss from cations like those discussed earlier in Scheme VI. Not surprisingly, when we simply heated mesylate **29b** in pyridine solution, it also rearranged to the same trisubstituted alkene **30a**. This double bond location is not favored thermodynamically because treatment of **30a** with $AlCl_3$/dry HCl produced the fully substituted isomer **31a**.

To explore further the generality of the two-atom ring expansion, we applied it to a 1,3-dithiolane, specifically **29c**. This new substrate was prepared from 2-(methoxycarbonyl)cyclododecanone by conventional thioketalization with 1,2-ethanedithiol to give **28b** followed by reduction to **29c** with lithium aluminum hydride. Both **28b** and **29c** showed the expected spectral and analytical properties. The action of P_2O_5/Bz on **29c** gave an oil whose ^1H NMR spectrum indicated it was a mixture (ca. 80:20, respectively) of trisubstituted olefin (**30b**; vinyl H as a double doublet) and tetrasubstituted olefin (**31b**; sharp singlet for $=CCH_2S$). When this mixture was treated with dry HCl, isomer **30b** converted to **31b** as evidenced by clean disappearance of the olefinic hydrogens in the ^1H NMR.[16]

Success with two-atom ring expansions led us to test whether cyclic dithioketals with an α-OH would undergo a corresponding one-atom ring enlargement. We explored this notion with the α-hydroxy-1,3-dithiane **32a**. This model compound was made by addition of an excess of CH_3Li to known[17] 2-(ethoxycarbonyl)-2-methyl-1,3-dithiane and was characterized spectrally and analytically. We investigated the behavior of **32a** under three different "dehydration" conditions.

The action of 20% aqueous sulfuric acid produced a liquid (95% yield) identified as the keto mercaptan **37** by IR (C═O and SH) and ^1H NMR ($COCH_3$ singlet and a sharp 6-H singlet for the geminal methyls). A logical sequence to **37** (Scheme VIII) invokes cations **33** and/or **34**. Ultimate capture by water would be expected to release ketone **37**.

In contrast, when the starting dithiane **32a** was treated with hot $POCl_3$ in dry pyridine, it gave the 1,4-dithiepane system **36** in 57% yield. This liquid showed IR absorption characteristic of olefinic C—H and C═C stretching, respectively. The ^1H NMR spectrum revealed two vinyl hydrogens and geminal methyls. Although alkene **36** was homogeneous by TLC and by GLC, our attempts to get acceptable C and H analyses were unsuccessful. However, we confirmed its structure by acid hydrolysis, which converted **36** quantitatively to the ketomercaptan **37**.

Our third assault on substrate **32a** involved P_2O_5 in dry benzene, which led to a mixture of two products in the ratio 40:60. The lesser component proved identical with the dithiepane **36**. The more abundant component re-

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(15) Various other cations and olefins might also be involved under the reaction conditions.

(16) Note that of the four trisubstituted bicyclic olefins in this study (**13**, **18**, **30a**, and **30b**) only in the case of **18** were we unable to isomerize the double bond to the fully substituted site. If these results are indicative of thermodynamic preference (rather than simply very slow rates of isomerization), then subtle factors other than ring size appear to influence relative stabilities in these bis-sulfur systems. See also: Nickon, A.; Zurer, P. St. J.; Hrnjez, B.; Tino, J. *Tetrahedron* **1983**, *39*, 2679–2690 and references cited there.

(17) Corey, E. J.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 1077–1078.

mains unidentified, but it is not the alkene from simple dehydration of **32a** because that olefin was available for direct comparison.[1,2]

We attempted to pyrolyze alcohol **32a**. At 320 °C in an open tube, the material distilled unchanged, and in a sealed tube, it produced a complex mixture. The acetate ester **32b** was prepared and pyrolyzed at 270 °C. It gave the rearranged alkene **36** in 92% yield. Therefore, we have in hand two good ways to expand the α-hydroxy dithioketal to **36**, viz. $POCl_3$/Py on **32a** or thermolysis of acetate **32b**.[18]

Finally, we examined briefly a γ-hydroxy dithioketal to look for a possible three-atom ring growth. To this end we synthesized **35** (by thioketalization of the corresponding ketone[19]) and treated this dithiane alcohol with P_2O_5/benzene. Even after 6 h at 100 °C, **35** was recovered on workup. Clearly, this γ-hydroxy dithioketal is not prone to rearrange as did its congeners with the OH closer to sulfur.

Experimental Section

General. Melting points and boiling points are uncorrected. Details for IR, UV, and NMR spectroscopy, separations by TLC, GLC, HPLC, drying of solvents, and purification of reagents are the same as those described earlier.[2] *p*-Toluenesulfonic acid refers to the monohydrate (Aldrich Chemical Co., 99% pure). To get the anhydrous acid, we dissolved the hydrate in methanol and removed the solvent at 50 °C on a rotary evaporator. This cycle was repeated twice. The final dried solid was recrystallized from chloroform and stored in a vacuum desiccator; mp 98–101 °C. *p*-Toluenesulfonyl chloride (Aldrich Chemical Co., 98% pure) in benzene was washed with 5% sodium hydroxide and with water. The organic layer was dried ($MgSO_4$) and evaporated. The residue was distilled at 4 torr; bp 85–90 °C. *m*-Chloroperoxybenzoic acid (Aldrich, Technical grade, 85% pure) and phosphorus trichloride oxide ($POCl_3$) (Alfa Products, 99% pure) were used without purification. Phosphorus pentoxide was Fisher Scientific Co. "Reagent Grade". THF refers to tetrahydrofuran.

1,4-Dithiaspiro[4.11]hexadecane (9a). This dithioketal was obtained from cyclododecanone as reported.[5] Because no elemental analyses were given, we prepared a pure sample by recrystallization from ethanol; mp 85–86 °C: IR (KBr) 1465 (s), 770 (m) cm^{-1}; 100-MHz ^1H NMR δ 2.8 (s, 4 H), 1.8–1.6 (m, 4 H), 1.15 (s, 18 H). Anal. Calcd for $C_{14}H_{26}S_2$: C, 65.04; H, 10.13. Found: C, 65.20; H, 10.39.

1,4-Dithiaspiro[4.11]hexadecane 1-Oxide (11a). We oxidized dithioketal **9a** with *m*-chloroperoxybenzoic acid as described by Chen and Donatelli[5] and obtained monosulfoxide **11a** in 82% yield, mp 107–107.5 °C (lit mp 107.2 °C): IR (KBr) 1465 (s), 1040 (s) cm^{-1}; 100-MH$_3$ ^1H NMR δ 3.8–3.4 (m), 3.4–3.15 (m), 2.2–1.85 (m), 1.65 (m), 1.35 (s).

2,3-Decamethylene-5,6-dihydro-1,4-dithiine (12). A. From Sulfoxide 11a. A solution of **11a** (2.57 g, 9.4 mmol) and *p*-toluenesulfonic acid monohydrate (0.25 g, 1.3 mmol) in dry benzene (75 mL) was refluxed 18 h while water was removed with a Dean–Stark trap. The cooled mixture was washed with saturated Na_2CO_3 solution and water, dried ($MgSO_4$), and evaporated in vacuo. The thick oil was chromatographed on 50 g of silica gel (10% CH_2Cl_2 in petroleum ether) to give a TLC-pure oil (1.82 g, 75%), which was dissolved in a 5:1 mixture of EtOH–petroleum ether (10 mL) and stored overnight at −10 °C; off-white crystals, mp 54–54.5 °C. Olefin **12** has been reported as an oil.[5] IR ($CHCl_3$) 1590 (w) cm^{-1}; 60-MHz ^1H NMR δ 3.12 (s, 4 H), 2.55–2.05 (m, 4 H), 1.9–1.5 (m), 1.4 (m, s, 16 H); 20-MHz ^{13}C NMR δ 124.9, 31.4, 29.2, 26.5, 24.9, 24.5, 22.4; UV (heptane) λ_{max} 276 (ϵ 3862), 231 (ϵ 6031), 210 (ϵ 5770) nm. Anal. Calcd for $C_{14}H_{26}S_2$: C, 65.56; H, 9.43. Found: C, 65.88; H, 9.38.

B. From Bromo Ketone 10. Our procedure was modeled on a related reaction.[6] A mixture of 2-bromocyclododecanone[20] (4.0 g, 0.015 mol), 1,2-ethanedithiol (1.3 g, 0.014 mol), and dry *p*-toluenesulfonic acid (0.8 g) in dry toluene (15 mL) under argon was refluxed for 3.5 h while water was removed with a Dean–Stark trap. The green mixture was cooled to room temperature, and the sulfonic acid that precipitated was removed. The clear filtrate was diluted with petroleum ether (30 mL) and washed with saturated Na_2CO_3 solution and water. The organic layer was dried (Na_2SO_4) and concentrated in vacuo to leave a yellow oil, which was dissolved in petroleum ether and then passed through a column of silica gel (15 g). The column was washed with more petroleum ether (300 mL), and the eluate provided a colorless oil, which was dissolved in chloroform (5 mL) and ethanol (30 mL). The solution stood at −10 °C overnight and deposited a white solid; mp 55–55.5 °C (2.65 g, 67%). This solid proved identical (by ^1H NMR, IR, TLC, and mixture mp) with olefin **12** from procedure A.

2-Hydroxyethyl 2-Oxocyclododecyl Sulfide (8). A 25 °C solution of 2-mercaptoethanol (59.8 mg, 0.765 mmol, Aldrich 98% pure) in 2 mL of anhydrous hexamethylphosphoric triamide (HMPT) under nitrogen was treated slowly with 1.6 M *n*-butyllithium (0.48 mL, 1 equiv) in hexane. The resultant solution was added over a period of 5 min to a 25 °C solution of 2-bromocyclododecanone[20] (0.20 g, 0.76 mmol) in dry HMPT (10 mL) under nitrogen. After being stirred vigorously for 24 min, the mixture was partitioned between water and pentane. The pentane layer was washed with water and brine and dried over Na_2SO_4. Evaporation in vacuo gave a white solid (0.29 g), which was recrystallized twice from methanol–water: mp 50.5–51.5 °C (0.14 g, 71%); IR ($CHCl_3$) 3660 (s), 3500 (br), 1700 (s), 1470 (m), 1450 (m), 1360 (m), 1050 (br) cm^{-1}; 100-MHz ^1H NMR δ 3.76 (m, 2 H), 3.56 (dd, 1 H), 2.68 (m, 5 H), 2.2–1.6 (br m, 4 H), 1.3 (br s, 14 H); GLC [SE-30] (120–300 °C, 40 psi, T_i = 5 min, 10°/min) T_R = 20 min; TLC (silica gel/$CHCl_3$), homogeneous. Anal. Calcd for $C_{14}H_{26}O_2S$: C, 65.07; H, 10.14. Found: C, 65.28; H, 10.18.

1,5-Dithiaspiro[5.11]heptadecane (9b). A 0 °C solution of cyclododecanone (3.0 g, 16.4 mmol) in a 3:1 mixture of acetic acid–THF (40 mL) and 1,3-propanedithiol (1.84 g, 17 mmol) under argon was treated with $BF_3{\cdot}Et_2O$ (4.3 g, 30 mmol) and was stirred vigorously at 0 °C for 1 h. The temperature was increased to 25 °C and stirring was continued for 48 h, during which a white, thick slurry formed. The mixture was cooled to 0 °C and filtered with suction. The white solid was rinsed repeatedly with cold THF and was recrystallized twice from ethanol: off-white beautiful crystals, mp 81–82 °C (4.01 g, 89.4%); IR (CCl_4) 1470 (m), 1445 (m), 1345 (w), 1275 (w), 1240 (w), 915 (w) cm^{-1}; 80-MHz ^1H NMR δ 2.8 (m, 4 H, $-SCH_2$), 2.0 (m, 6 H), 1.36 (br s, 18 H); GLC [OV-17](150–320 °C, 30 psi, T_i = 4 min, 10°/min), T_R = 15.4 min; TLC (silica gel/benzene), homogeneous. Anal. Calcd for $C_{15}H_{28}S_2$: C, 66.11; H, 10.35. Found: C, 66.36; H, 10.55.

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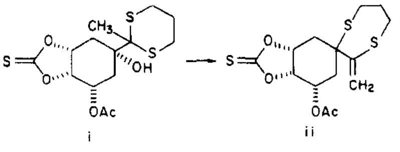
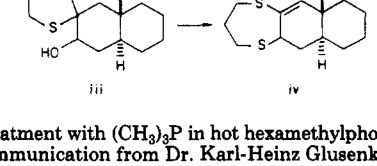
[18] We have found precedent for ring expansion of an α-hydroxy-1,3-dithiane. For example, R. Hermann [Ph.D. Dissertation, Westfälischen Wilhelms Universität, Münster, 1982] converted i to ii by



i ii



iii iv

prolonged treatment with $(CH_3)_3P$ in hot hexamethylphosphoric triamide (personal communication from Dr. Karl-Heinz Glusenkamp to A.D.R.). Also, the isolation of an alkene (thought to be iv) on attempted mesylation of iii may represent another example [Marshall, J. A.; Roebke, H. *J. Org. Chem.* **1969**, *34*, 4188–4891].

[19] (a) Grandberg, I. I.; Dashkevich, S. N. *Khim. Geterotsikl. Soedin.* **1971**, 7, 782–786; (b) Decor, J. P.; Descotes, G. *Bull. Soc. Chim. Fr.* **1970**, *6*, 2370–2376.

[20] Prepared in 90% yield from cyclododecanone as described by: Bauer, D. P.; Macomber, R. S. *J. Org. Chem.* **1975**, *40*, 1990–1992. Our melting point was 52–53 °C; lit. 53–54 °C (Zakharkin, L. T.; Korneva, V. V. *Izv. Akad. Nauk. SSSR, Otd. Khim Nauk.* **1962**, 1817–1871).

[21] Ainsworth, C. In "Organic Syntheses"; Rabjohn, N., Ed., Wiley: New York, 1963; Collect. Vol. IV, pp 536–539.

1,5-Dithiaspiro[5.11]heptadecane 1-Oxide (11b). A 0 °C solution of dithioketal **9b** (6.01 g, 0.022 mol) in anhydrous CH_2Cl_2 (45 mL) was treated with a solution of *m*-chloroperoxybenzoic acid (4.42 g, 0.026 mol) in dry CH_2Cl_2 (90 mL) with vigorous stirring over a period of 2 h. A saturated aqueous Na_2CO_3 solution was added, and stirring was continued for 10 min. The organic layer was washed with water, dried over $MgSO_4$, and concentrated in vacuo. Addition of petroleum ether followed by cooling at −10 °C overnight crystallized the pure sulfoxide, mp 123–124 °C (5.5 g, 88%): IR (KBr) 1030 (s) cm^{-1}; 100-MHz ^1H NMR δ 3.1–2.76 (m), 2.7–1.5 (m), 1.38 (s); 20-MHz ^{13}C NMR δ 64.8, 44.7, 32.0, 26.0, 25.9, 25.5, 24.1, 23.7, 23.3, 22.3, 22.0, 21.7, 19.8, 17.8, 15.8. Anal. Calcd for $C_{15}H_{28}OS_2$: C, 62.67; H, 9.82. Found: C, 62.71; H, 9.73.

2,3-Decamethylene-6,7-dihydro-5*H*-dithiepine (14). A solution of sulfoxide **11b** (6.01 g, 0.021 mol) and *anhydrous p*-toluenesulfonic acid (0.608 g) in dry benzene (150 mL) set up with a Dean-Stark trap was refluxed for 10 h. The cooled mixture was washed with saturated Na_2CO_3 (2 × 50 mL) and water (50 mL), dried ($MgSO_4$), and evaporated in vacuo. The brown oily residue (5.12 g) was chromatographed on 70 g of silica gel (petroleum ether, then gradual polarity increase by addition of $CHCl_3$). Only the main components were identified. Petroleum ether eluted the desired olefin **14** (0.60 g, 10.6%), mp 96.5–97 °C, and also the liquid trisubstituted olefin **13** (0.15 g, 2.7%). The material eluted with petroleum ether–$CHCl_3$ (2.6 g, 68.5%) was identified as cyclododecanone by ^1H NMR, IR, and TLC. Tetrasubstituted olefin **14** was characterized as follows: IR ($CHCl_3$) 1640–1630 (w) cm^{-1}; 100-MHz ^1H NMR δ 3.0–2.8 (m), 2.50–2.05 (m), 1.85–1.55 (m), 1.35 (s); 20-MHz ^{13}C NMR δ 139.2, 34.0, 32.2, 31.3, 26.7, 25.1, 24.5, 22.8; UV (heptane) λ_{max} 284 (ϵ 4148), 281 (ϵ 4173), 274 (ϵ 4011), 210 (ϵ 5558) nm. Anal. Calcd for $C_{15}H_{26}S_2$: C, 66.60; H, 9.68. Found: C, 66.43; H, 9.72.

13,17-Dithiabicyclo[10.5.0]heptadec-1-ene (13). A solution of *p*-toluenesulfonyl chloride (9.1 g, 0.048 mol) in dry pyridine (140 mL) was heated under nitrogen at 100–110 °C for 15–20 min. The solution was cooled to room temperature, and sulfoxide **11b** (6.5 g, 0.023 mol) was added at once. The resulting solution was stirred and heated at 110–120 °C under nitrogen for 4 h. More tosyl chloride (3.0 g, 0.016 mol) was added, and heating was continued another 1 h. The cooled mixture was poured into ice-cold water and was extracted with ether (3 × 100 mL). The combined ether was washed successively with aqueous 5% HCl solution (3 × 60 mL), saturated $NaHCO_3$ solution (2 × 60 mL), and water, dried ($MgSO_4$), and evaporated in vacuo to leave **13**. The oil (6.04 g, 99%) was homogeneous by TLC, but we do not know whether this alkene is *E* or *Z*: IR (neat) 2930 (s), 2850 (s), 2670 (w), 1605 (w), 1460 (s), 1440 (s), 800 (w) cm^{-1}; 80-MHz ^1H NMR δ 5.89 (dd, 1 H), 3.10–2.45 (m), 2.45–1.90 (m), 1.90–1.50 (m), 1.25 (br s).

13-Methyl-13-thionia-17-thiabicyclo[10.5.0]heptadec-1-ene Monomethiodide (Salt of 13). A mixture of olefin **13** (1.22 g, 0.0045 mol) and methyl iodide (2.28 g, 0.016 mol) in a 3:7 mixture of ethyl acetate–CH_3OH (20 mL) was stirred vigorously at room temperature for 18 h. The solution was evaporated in vacuo, and petroleum ether was added. When cooled to −10 °C, the crude sulfonium salt precipitated and was recrystallized from EtOH–petroleum ether; off-white solid, mp 119–121 °C (1.40 g, 75%). Its stereochemistry is unknown. IR (KBr) 1620 (m), 1460 (s), 1430 (s), 1390 (s), 1190 (m), 990 (m) cm^{-1}; 80-MHz ^1H NMR δ 6.85 (dd, 1 H, SC=C*H*), 5.15 (dd, 1 H, $^+$SC*H*CH_2), 4.17–3.76 (m, 2 H, $^+SCH_2$), 3.45 (s, 3 H, $^+SCH_3$), 3.0–1.5 (m), 1.24 (br s). Anal. Calcd for $C_{16}H_{29}O_2S_2I$: C, 46.59; H, 7.08. Found: C, 46.52; H, 7.06.

Isomerization of Alkene 13 to Alkene 14. A solution of **13** (6.04 g, 0.022 mol) in dry toluene (250 mL) was saturated with dry HCl gas and heated at 80–90 °C for 2 h with efficient stirring. The solution was resaturated with HCl gas and heated again for 2 h. This latter process was repeated three more times. After 10 h total, the mixture was cooled to room temperature, washed with saturated $NaHCO_3$ solution and water, dried ($MgSO_4$), and evaporated in vacuo. The dark oily residue was dissolved in $CHCl_3$ (10 mL), and ethanol (40 mL) was added. The solution stood at −10 °C overnight and gave white crystals; mp 93–94 °C (3.3 g, 54%). The TLC-pure solid was identical with tetrasubstituted olefin **14** by IR and ^1H NMR.

Formation of 13,18,31,36-Tetrathiadispiro[11.6.11.6]hexatriacontane (15). A solution of cyclododecanone (1.83 g, 0.01 mol), 1,4-butanedithiol (1.22 g, 0.01 mol), and $BF_3 \cdot Et_2O$ (1.15 g, 0.0081 mol) in acetic acid (25 mL) was stirred at room temperature for 22 h. The white solid was collected, washed with small portions of ethanol, and dried with suction. The crude product was recrystallized from boiling benzene, mp 246–247 °C (2.70 g, 94%): IR (KBr) 1465 (s), 765 (m) cm^{-1}; 80-MHz ^1H NMR δ 2.70–2.48 (m), 1.80–1.45 (m), 1.33 (s); MS, *m/e* 572 (M). Anal. Calcd for $C_{32}H_{60}S_4$: C, 67.07; H, 10.55. Found: C, 67.29; H, 10.59.

When oxidized at 0 °C with *m*-chloroperoxybenzoic acid (1.1 equiv, $CHCl_3$, 2 h), this dispiro compound afforded a crystalline sulfoxide (82%), mp 165–170 °C, which was not further purified or investigated.

1,6-Dithiaspiro[6.11]octadecane (16). To a stirred solution of 1,4-butanedithiol (0.25 g, 0.002 mol) and aluminum chloride (0.05 g, Fischer Scientific Co.) in anhydrous CH_2Cl_2 (5 mL) at room temperature was added over a period of 1 h a solution of cyclododecanone (0.36 g, 0.002 mol) in dry CH_2Cl_2 (10 mL). After 15 min, the mixture was washed with saturated Na_2CO_3 solution and water, dried ($MgSO_4$), and evaporated in vacuo. The oil was dissolved in ethanol (10 mL) and stored at −10 °C overnight during which the white dithioketal crystallized, mp 70–71 °C (0.43 g, 76%): IR ($CHCl_3$) 1040 (s) cm^{-1}; 100-MHz ^1H NMR δ 2.9–2.7 (m, 4 H), 2.1–1.75 (m, 8 H), 1.3 (broad s, 18 H); 20-MHz ^{13}C NMR δ 62.7, 37.4, 31.7, 27.5, 26.3, 25.8, 22.6, 22.3, 20.6. Anal. Calcd for $C_{16}H_{30}S_2$: C, 67.07; H, 10.55. Found: C, 67.31; H, 10.39.

1,6-Dithiaspiro[6.11]octadecane 1-Oxide (17). A 0 °C solution of dithioketal **16** (1.11 g, 0.0039 mol) in dry CH_2Cl_2 (8 mL) was treated with a solution of *m*-chloroperoxybenzoic acid (0.77 g, 0.0044 mol) in dry CH_2Cl_2 (16 mL) over a period of 2 h. The reaction was stopped by addition of saturated Na_2CO_3 (10 mL). The organic layer was washed with water, dried over $MgSO_4$, and evaporated in vacuo. The oily residue was dissolved in a 1:10 mixture of CH_2Cl_2–petroleum ether (20 mL). When stored at −10 °C overnight sulfoxide **17** crystallized out: off-white solid, mp 106–107 °C (0.99 g, 85%); IR (KBr) 1030 (s) cm^{-1}; 100-MHz ^1H NMR δ 3.3–2.35 (m), 2.0–1.5 (m), 1.3 (s); 20-MHz ^{13}C NMR δ 70.2, 44.1, 30.1, 28.1, 27.0, 26.3, 25.7, 22.5, 22.0, 19.7, 15.0. Anal. Calcd for $C_{16}H_{30}OS_2$: C, 63.62; H, 9.99. Found: C, 63.24; H, 10.08.

Attempted Ring Expansion of Sulfoxide 17 with *p*-Toluenesulfonic Acid. A solution of sulfoxide **17** (0.051 g, 0.17 mmol) and *p*-toluenesulfonic acid hydrate (0.0053 g) in dry benzene under nitrogen was refluxed for 8 h while water was removed by a Dean–Stark trap. The mixture, at room temperature, was washed with saturated Na_2CO_3 solution and water, dried ($MgSO_4$), and evaporated in vacuo. Examination of the residue by IR, ^1H NMR, and TLC revealed only one major product, identified as cyclododecanone (**7**).

13,18-Dithiabicyclo[10.6.0]octadec-1-ene (18). A solution of *p*-toluenesulfonyl chloride (4.5 g, 0.024 mol) in dry pyridine (60 mL) under nitrogen was heated to 110–120 °C for 15–20 min. The solution was cooled to room temperature, and then sulfoxide **17** (3.0 g, 0.01 mol) was added at once. The mixture was heated to 110–120 °C for 2.5 h under nitrogen, cooled to room temperature, poured into ice-cold water, and extracted with ether. The combined ether was washed successively with 5% HCl solution, saturated $NaHCO_3$ solution, and water, dried ($MgSO_4$), and evaporated in vacuo. The dark yellow oil was chromatographed on 20 g of silica gel (hexane) and provided TLC-pure **18** as a colorless oil (3.8 g, 89%), which may have either the *E* or *Z* geometry: IR (neat) 1605 (w), 1460 (w), 1435 (s) cm^{-1}; 80-MHz ^1H NMR δ 6.15 (dd, 1 H), 3.75–1.50 (m), 1.22 (br s); 20-MHz ^{13}C NMR δ 142.5, 134.4, 52.7, 33.0, 31.5, 29.2, 28.9, 27.8, 27.2, 25.8, 25.2, 24.6, 24.1, 23.6, 23.2, 22.3. Anal. Calcd for $C_{16}H_{28}S_2$: C, 67.54; H, 9.92. Found: C, 67.49; H, 9.91.

Attempted Double Bond Isomerization in Olefin 18. Treatment of **18** with dry HCl gas (as described earlier for **13**) failed to shift the double bond to the tetrasubstituted position. Other acidic catalysts also were unsuccessful, and some led to other products. For example, olefin **18** (3.0 g, 0.011 mol), anhydrous aluminum chloride (1.0 g, 0.0075 mol), and *p*-toluenesulfonic acid hydrate (0.3 g) in dry toluene (150 mL) were heated at 110–120 °C under nitrogen for 5 h. The cooled mixture was washed with saturated Na_2CO_3 solution and water, dried ($MgSO_4$), and evaporated in vacuo. The dark oily residue (1.7 g) was chromatographed on 40 g of silica gel (hexane) to elute first a crystalline compound, mp 146–146.5 °C (0.15 g, 5%). This solid was not the desired tetrasubstituted olefin as evidenced by its spectroscopic properties, but no definite structure has been assigned yet. IR ($CHCl_3$) 1470 (m), 1440 (m) cm^{-1}; 300-MHz ^1H NMR δ 2.75 (t, SCH_2), 2.55 (t, SCH_2), 1.85–1.25 (m, ring CH_2); 20-MHz ^{13}C NMR δ 137.3, 137.0, 30.3, 28.5, 26.0, 25.8, 25.5, 24.5, 24.2, 23.6, 22.5. Further elution (5% ether in hexane) gave cyclododecanone as a single minor component confirmed by IR, ^1H NMR, TLC, and melting point.

Synthesis of Spiroketone 21a. To have suitable reference compounds on hand and to calibrate our technique, we duplicated reported procedures to synthesize ketone **21a** (mp 88–89 °C)[12] by treatment of 2-(hydroxymethylene)cyclododecanone (**19**, bp 101–102 °C at 0.6 torr)[21] with trimethylene dithiotosylate (**20a**, mp 65–66 °C).[11]

Tetramethylene Dithiotosylate (20b). A mixture of potassium thiotosylate[11] (2.16 g, 0.0954 mol), 1,4-dibromobutane (10.8 g, 0.05 mol), and potassium iodide (ca. 0.01 g) was refluxed in 95% ethanol (75 mL) under nitrogen for 8 h away from light. The mixture was cooled to 0 °C, and the precipitate was collected. It was boiled with acetone (200 mL) and filtered hot to remove the precipitated KBr. The filtrate was cooled to room temperature, during which most of the product crystallized out. Petroleum ether (100 mL) was added, and the solution was cooled to 0 °C to force out more material. The dried crystals had mp 121–122 °C (11.9 g, 54%): 60-MHz ^1H NMR δ 7.80–7.10 (m, 8 H), 3.15–2.95 (m, 4 H), 2.47 (s, 6 H), 1.85–1.46 (m, 4 H). Anal. Calcd for $C_{18}H_{22}O_4S_4$: C, 50.20; H, 5.15. Found: C, 50.08; H, 5.11.

Attempted Synthesis of 8-Oxo-1,6-dithiaspiro[6.11]octadecane (21b). Formation of 1,4-Bis(2-oxocyclododecyl)dithiabutylene (22) from 19. A mixture of **20b** (4.38 g, 0.010 mol), **19**[21] (2.52 g, 0.012 mol), and potassium acetate (4.4 g, 0.045 mol) in methanol (80 mL) was refluxed for 3.5 h with vigorous stirring under nitrogen and in the dark. Evaporation of the solvent in vacuo gave a yellow solid, which was stirred with aqueous 2 N NaOH solution (40 mL) and filtered. The solid was dissolved in a 3:1 mixture of cyclohexane–benzene (50 mL), and the solution was filtered, concentrated in vacuo, and cooled at -10 °C overnight. The white crystals were recrystallized from 20% benzene in methanol; mp 131–132 °C (1.1 g, 26%). Spectral and analytical data fit the diketo structure **22** (stereochemistry not implied): IR (KBr) 1685 (s) cm^{-1}; 100-MHz ^1H NMR δ 3.55–3.00 (dd, 2 H), 2.80–2.55 (m, 4 H), 2.50–2.28 (m, 4 H), 1.70–1.48 (m), 1.3 (br s). Anal. Calcd for $C_{28}H_{50}O_2S_2$: C, 69.65; H, 10.44. Found: C, 69.97; H, 10.44.

Formation of 22 from 2-Bromocyclododecanone (10). A solution of **10**[20] (1.78 g, 0.0098 mol), 1,4-butanedithiol (0.82 g, 0.0067 mol), and P_2O_5 (0.065 g) in dry toluene (5 mL) was heated to 120 °C for 8 h under nitrogen. The mixture (several components) was cooled, diluted with methanol (10 mL), and kept at -10 °C overnight; white crystals, mp 131–132 °C (0.51 g, 18%). This solid proved to be diketo dimer **22** by IR, ^1H NMR, and melting point.

Conversion of Diketone 22 to the 1,3-Dithiepane 16. A solution of **22** (0.633 g, 0.0015 mol), 1,4-butanedithiol (0.185 g, 0.0015 mol), and *p*-toluenesulfonic acid hydrate (0.06 g) in dry toluene (5 mL) was refluxed for 3 h while water was removed with a Dean–Stark trap. The cooled mixture was washed with 1% NaOH solution and water, dried ($MgSO_4$), and concentrated in vacuo. The remaining oil was dissolved in petroleum ether and passed through a column of silica gel. Concentration of the eluate in vacuo gave an oil, which eventually crystallized (mp 70–71 °C) and was identified as dithioketal **16** by IR, ^1H NMR, and melting point.

2-Methyl-2-(2-hydroxy-1-methylethyl)-1,3-dithiane (23a). A solution of 4-hydroxy-3-methyl-2-butanone (1.86 g, 18.2 mmol, Aldrich) in a 3:1 mixture of glacial acetic acid–THF (40 mL) cooled at 0 °C under argon was treated with 1,3-propanedithiol (1.97 g, 18.22 mmol). To the mixture was added slowly $BF_3 \cdot Et_2O$ (3.7 g, 26 mmol), and the resulting solution was stirred at 0 °C for 2 h and then poured into ice-cold water. After ether extraction (3 × 40 mL), the combined ether was washed sequentially with water, saturated $NaHCO_3$ solution (2 × 50 mL), water, and brine, dried (Na_2SO_4), and evaporated in vacuo. Chromatography of the residue on 50 g of silica gel (benzene) gave the GLC-pure alcohol **23a** (2.76 g, 79%) as a colorless liquid: IR (neat) 3640–3060 (br), 1445 (s), 1425 (s), 1370 (m), 1280 (m), 1240 (m), 1025 (br), 910 (m) cm^{-1}; 80-MHz ^1H NMR δ 3.8 (m, 2 H, OCH_2), 2.85 (m, 4 H, SCH_2), 2.5–1.7 (br m, 4 H), 1.50 (s, 3 H, CH_3), 1.1 (d, 3 H, $CHCH_3$); GLC [OV-17] (100–200 °C, 30 psi, T_i = 4 min, 10°/min), T_R = 13.7 min; TLC (silica gel/50% petroleum ether–ether), homogeneous. Anal. Calcd for $C_8H_{16}OS_2$: C, 49.96; H, 8.38. Found: C, 49.88; H, 8.42.

2-Methyl-2-(2-acetoxy-1-methylethyl)-1,3-dithiane (23b). A vigorously stirred solution of alcohol **23a** (0.40 g, 2.1 mmol) in a 3:1 mixture of glacial acetic acid–THF (15 mL) and $BF_3 \cdot Et_2O$ (0.41 g, 2.9 mmol) under argon was heated at 40–50 °C for approximately 14 h. The cooled solution (25 °C) was poured into ice-cold water and extracted with ether (3 × 30 mL). The combined ether was washed with water, saturated $NaHCO_3$ solution, and brine, dried (Na_2SO_4), and evaporated in vacuo. The GLC-pure clear liquid acetate **23b** (0.42 g, 87.5%) showed these properties: IR (neat) 1740 (s), 1450 (br), 1425 (s), 1390 (m), 1380 (s), 1240 (br), 1035 (br), 990 (w), 915 (w) cm^{-1}; 60-MHz ^1H NMR δ 4.6 (dd, 1 H), 4.0 (dd, 1 H), 2.8 (m, 4 H), 2.2 (m, 3 H), 2.2 (s, 3 H, CH_3), 1.5 (s, 3 H, CH_3), 1.2 (d, 3 H); GLC[OV-17] (100–200 °C, 30 psi, T_i = 4 min, 10°/min), T_R = 15.2 min; TLC (silica gel/benzene), homogeneous. Anal. Calcd for $C_{10}H_{18}O_2S_2$: C, 51.25; H, 7.74. Found: C, 51.29; H, 7.92. In an open tube heated at 400 °C, acetate **23b** distilled without decomposition.

2-Methyl-2-(2-((methylsulfonyl)oxy)-1-methylethyl)-1,3-dithiane (23c). A solution of alcohol **23a** (0.27 g, 1.4 mmol) and methanesulfonyl chloride (0.32 g, 2.8 mmol) in dry pyridine (4 mL) under argon was stirred vigorously at room temperature for 6 h. The mixture was poured into water and extracted with ether, and the combined organic solution was washed with 1 M HCl (2 × 40 mL), water, and brine. The dried solution (Na_2SO_4) was evaporated in vacuo and the black oily residue was purified by PTLC (silica gel/50% petroleum ether–ether). The TLC-pure oil (0.21 g, 58%) was identified spectrally as mesylate **23c**. An elemental analysis was not attempted because this compound deteriorated quickly upon standing. IR (neat) 1450 (s), 1420 (s), 1350 (br), 1170 (br), 970 (br), 850 (s), 820 (s), 760 (s) cm^{-1}; 60-MHz ^1H NMR δ 4.8 (dd, 1 H), 4.2 (m, 1 H), 3.0 (s, 3 H, SO_2CH_3), 2.8 (m, 4 H), 2.1 (m, 3 H), 1.5 (s, 3 H), 1.2 (d, 3 H); GLC [OV-17] (100–200 °C) (*DECOMPOSITION!*); TLC (silica gel/50% petroleum ether–ether), homogeneous.

Dehydration of Alcohol 23a with Phosphorus Pentoxide. Formation of (*Z*)-2,3-Dimethyl-1,5-dithiacyclooct-2-ene (24). A mixture of alcohol **23a** (0.48 g, 2.5 mmol) and P_2O_5 (0.50 g, 3.5 mmol) in dry benzene (10 mL) was stirred vigorously at room temperature for 1.5 h. The mixture was partitioned between water and ether, and the combined organic solution was washed with water, saturated $NaHCO_3$ solution, and brine and dried over Na_2SO_4. Evaporation in vacuo gave a TLC-pure liquid **24** (0.26 g, 60%). The presence of only one isomer was confirmed by the ^{13}C NMR spectrum, which showed two olefinic carbon singlets: IR (neat) 1435 (s), 1420 (s), 1380 (m), 1275 (m), 1230 (m), 1065 (m), 855 (w), 785 (w) cm^{-1}; 60-MHz ^1H NMR δ 3.7 (br s, 2 H), 2.8 (m, 4 H), 2.2 (m, 2 H), 2.0 (s, 3 H, CH_3), 1.86 (s, 3 H, CH_3); 20-MHz ^{13}C NMR δ 140.00, 125.26, 37.37, 35.26, 34.83, 28.76, 28.59, 27.84; GLC [OV-17] (100–200 °C, 30 psi, T_i = 4 min, 10°/min), T_R = 10.5 min; TLC (silica gel/20:1 petroleum ether–ether), homogeneous. Elemental analyses for carbon were unacceptably high, so we verified the structure of olefin **24** by acid hydrolysis (see below).

Acid Hydrolysis of Olefin 24. Formation of 7-Mercapto-3-methyl-4-thia-2-heptanone (25). A mixture of olefin **24** (57.2 mg, 0.328 mmol) in benzene (10 mL) and aqueous 20% H_2SO_4 (10 mL) was refluxed for 19 h. The cooled mixture was poured into water and extracted with ether (3 × 20 mL). The combined organic solution was washed with water, saturated $NaHCO_3$ solution, and brine, dried (Na_2SO_4), and evaporated in vacuo. The liquid residue was purified by PTLC (silica gel/3:2 petroleum ether–ether) to afford pure mercapto ketone **25** (40 mg, 64%): IR (neat) 2560 (br), 1700 (s), 1445 (s), 1420 (s), 1355 (s), 1295 (m), 1250 (m), 1160 (s), 955 (w), 765 (w), 735 (w) cm^{-1}; 80-MHz ^1H NMR δ 2.6 (m, 7 H), 2.15 (s, 3 H, $COCH_3$), 1.85 (m, 2 H, CH_2S), 1.35 (m, 1 H, SH), 1.15 (d, 3 H, $CHCH_3$); GLC [OV-17] (100–320 °C, 30 psi, T_i = 0 min, 10°/min), T_R = 8.7 min; TLC (silica gel/3:2 petroleum ether–ether), homogeneous. Anal. Calcd for $C_8H_{16}OS_2$: C, 49.96; H, 8.38. Found: C, 50.24; H, 8.39.

Dehydration of Alcohol 29a with Phosphorus Pentoxide. Formation of 13,17-Dithiabicyclo[10.6.0]octadec-1(12)-ene (31a). A mixture of alcohol **29a**[1,2] (1.10 g, 3.66 mmol) and P_2O_5 (0.947 g, 6.67 mmol) in dry benzene (25 mL) was stirred vigorously for 15 min at room temperature. The mixture was diluted with benzene (25 mL), washed with water, saturated $NaHCO_3$, and brine, dried (Na_2SO_4), and evaporated in vacuo to give GLC-pure olefin **31a**. The oil was dissolved in 15% petroleum ether in ethanol and stored at −10 °C overnight; off-white crystals, mp 50–51 °C (0.824 g, 82%). The presence of only one isomer was confirmed by the ^{13}C NMR spectrum, which showed just two olefinic carbon singlets. IR (neat) 1470 (s), 1450 (s), 1425 (s) cm^{-1}; 60-MHz ^1H NMR δ 3.75 (s, 2 H, $C{=}CCH_2S$), 2.8 (m, 4 H), 2.2 (m, 2 H), 2.0–1.4 (broad s, 20 H); 20-MHz ^{13}C NMR δ 136.50, 135.90, 50.99, 39.28, 33.83, 32.73, 30.34, 30.08, 28.90, 26.24, 25.86, 25.54, 25.02, 24.91, 24.50, 23.93; UV (heptane) λ_{max} 247 (ϵ 1113), 212 (ϵ 12148) nm; GLC [OV-17] (150–320 °C, 30 psi, T_i = 4 min, 10°/min), T_R = 16.5 min; TLC (silica gel/20:1 petroleum ether–ether), homogeneous. Anal. Calcd for $C_{16}H_{28}S_2$: C, 67.49; H, 9.92. Found: C, 67.54; H, 9.92.

Dehydration of Alcohol 29a with $POCl_3$. Formation of 14,18-Dithiabicyclo[10.6.0]octadec-1-ene (30a). A mixture of alcohol **29a** (9.0 g, 0.03 mol), $POCl_3$ (20 mL), and dry pyridine (150 mL) was refluxed for 1 h under nitrogen. The mixture was cooled, poured into ice-cold water, and extracted with ether (4 × 70 mL). The combined ether was washed with 5% HCl solution, saturated Na_2CO_3 solution, and water, dried ($MgSO_4$), and evaporated in vacuo. The oil **30a** crystallized when seeded: mp 40–41 °C (7.8 g, 92%); IR (neat) 1605 (w), 1460 (s), 1440 (s), 1275 (m), 910 (m), 735 (s) cm^{-1}; 80-MHz ^1H NMR δ 5.95 (t, 1 H, $C{=}C\mathit{H}CH_2$), 3.5–1.85 (m), 1.25 (br s); 20-MHz ^{13}C NMR δ 155.62, 135.67, 50.67, 39.00, 33.54, 32.41, 30.03, 29.77, 28.60, 25.92, 25.51, 25.22, 24.69, 24.18, 23.39. Anal. Calcd for $C_{16}H_{28}S_2$: C, 67.54; H, 9.92. Found: C, 67.31; H, 9.98.

Conversion of Mesylate 29b to Alkene 30a. A solution of mesylate **29b**[1,2] (0.40 g, 1.05 mmol) in dry pyridine (10 mL) was heated to 100 °C for 3 h under nitrogen. The cooled solution was poured into crushed ice (15 g) and was extracted with ether. The combined ether was washed successively with 10% HCl, 5% $NaHCO_3$, and water, dried (Na_2SO_4), and evaporated in vacuo. Chromatography on 10 g of silica gel (50% petroleum ether–$CHCl_3$) gave a thick, colorless liquid (0.25 g, 84%), which proved to be trisubstituted olefin **30a** by IR, TLC, ^1H NMR.

Isomerization of Trisubstituted Olefin 30a to Tetrasubstituted Olefin 31a. A solution of olefin **30a** (7.0 g, 0.024 mol) and anhydrous aluminum chloride (0.20 g, 0.0015 mol) in dry toluene (150 mL) was saturated with dry HCl gas. The solution was heated to 90–100 °C for 25 h while it was resaturated with HCl gas every 2 h. The cooled mixture was washed with saturated Na_2CO_3 solution and water, dried ($MgSO_4$), and concentrated in vacuo. The colorless oil was dissolved in a 1:5 mixture of petroleum ether–ethanol (60 mL) and cooled to −10 °C overnight. The white crystals (mp 50–51 °C, 4.6 g, 66%) were shown to be **31a** by IR, ^1H NMR, TLC, and GLC.

6-(Methoxycarbonyl)-1,4-dithiaspiro[4.11]hexadecane (28b). A 0 °C solution of 2-(methoxycarbonyl)cyclododecanone[2] (6.27 g, 0.026 mol) and 1,2-ethanedithiol (2.5 g, 0.026 mol) in 3:1 mixture of acetic acid–THF (20 mL) under nitrogen was treated with $BF_3{\cdot}Et_2O$ (5.9 g, 0.041 mol) over a period of 15 min and then stirred at room temperature for 48 h. The mixture was poured into ice-cold water and was extracted with ether (3 × 100 mL). The combined ether was washed with saturated $NaHCO_3$ solution and water, dried ($MgSO_4$), and evaporated in vacuo. The white solid was recrystallized twice from ether–petroleum ether: mp 92–93 °C (6.4 g, 77.5%); 60-MHz ^1H NMR δ 3.68 (s, 3 H, OCH_3), 3.25 (s, 4 H, SCH_2), 2.70–1.58 (m), 1.37 (br s). Anal. Calcd for $C_{16}H_{28}O_2S_2$: C, 60.71; H, 8.92. Found: C, 60.75; H, 9.04.

6-(Hydroxymethyl)-1,4-dithiaspiro[4.11]hexadecane (29c). A solution of ester **28b** (3.0 g, 0.01 mol) in anhydrous ether (30 mL) was slowly added over a period of 1 h to a slurry of $LiAlH_4$ (1.0 g, 0.026 mol) in dry ether (60 mL). The mixture was stirred at room temperature for 4 h, and then the excess of $LiAlH_4$ was destroyed by slow addition of ethyl acetate until H_2 evolution ceased. The mixture was stirred with 10% HCl solution (50 mL) for 15 min. The ether layer was washed with saturated $NaHCO_3$ solution and water, dried ($MgSO_4$), and evaporated in vacuo. The colorless oil in petroleum ether (5 mL) was kept at −10 °C and deposited a white solid. Recrystallization from hexane gave pure spiro alcohol **29c**, mp 72–73 °C (1.75 g, 64.1%): IR ($CHCl_3$) 3450 (m), 3000 (m), 1470 (m), 1090 (m), 1030 (m), 610 (m) cm^{-1}; 60-MHz ^1H NMR δ 3.98 (br m, 2 H, $\mathit{CH_2}OH$), 3.30 (s, 4 H, SCH_2CH_2S), 3.0–2.0 (m), 1.4 (br s). Anal. Calcd for $C_{15}H_{28}OS_2$: C, 62.44; H, 9.78. Found: C, 62.20; H, 9.51.

Dehydration of Alcohol 29c with Phosphorus Pentoxide. Formation of 14,17-Dithiabicyclo[10.5.0]heptadec-1-ene (30b) and 13,16-Dithiabicyclo[10.5.0]heptadec-1(12)-ene (31b). Isomerization of 30b to 31b. A mixture of alcohol **29c** (0.303 g, 1.05 mmol) and P_2O_5 (ca. 0.10 g) in dry benzene (10 mL) was stirred vigorously at room temperature. The reaction was complete after 1 h (TLC) but was continued for 10 h. The mixture was washed with saturated $NaHCO_3$ solution and water, dried ($MgSO_4$), and concentrated in vacuo. The ^1H NMR spectrum of the colorless oil (0.23 g, 81%) showed a trisubstituted olefin as the major component (ca. 80%) as seen from the doublet of doublets at δ 5.95. However, the tetrasubstituted olefin **31b** (ca. 20%) was also evident from the sharp singlet at δ 3.60 (due to $C{=}CCH_2S$). No attempt was made to separate the two olefins. Instead, the mixture (0.23 g) dissolved in dry toluene (5 mL) was directly saturated with dry HCl gas and heated to 100 °C for 18 h. During this period the solution was resaturated with HCl gas every 2 h. The cooled solution was shaken with saturated $NaHCO_3$ solution and water, dried ($MgSO_4$), and evaporated in vacuo. The colorless oil (80% yield) consisted entirely of tetrasubstituted olefin by ^1H NMR, and showed no olefinic protons: 60-MHz ^1H NMR δ 3.60 (s, 2 H, $C{=}CCH_2S$), 3.25–2.5 (m), 2.5–1.9 (m), 1.38 (br s).

2-Methyl-2-(1-hydroxy-1-methylethyl)-1,3-dithiane (32a). A solution of 0.79 M methyllithium (36.53 mL, 28.85 mmol) in dry benzene (50 mL) at 25 °C under argon was treated over a period of 30 min with a solution of 2-(ethoxycarbonyl)-2-methyl-1,3-dithiane[17] (1.98 g, 9.62 mmol) in dry benzene (40 mL) while the temperature was increased slowly to 60 °C. After reflux for 1 h, the cooled solution (25 °C) was quenched with aqueous 1 M HCl (60 mL) and was partitioned between water and benzene. The organic layer was washed with water and brine, dried (Na_2SO_4), and evaporated in vacuo to give GLC-pure alcohol **32a** (1.7 g, 91%): IR (neat) 3460 (br), 1450 (s), 1420 (s), 1370 (s), 1330 (s), 1280 (m), 1240 (m), 1180 (s), 1140 (br), 1100 (s), 1070 (s), 960 (s), 915 (s), 880 (w), 860 (s), 760 (br) cm^{-1}; 80-MHz ^1H NMR δ 2.9 (m, 4 H, $S\text{-}CH_2$), 2.2 (br s, 1 H, OH), 2.0 (m, 2 H), 1.8 (s, 3 H, CH_3), 1.45 (s, 6 H, $C(CH_3)_2$); GLC [OV-17] (100–180 °C, 30 psi, T_i = 4 min, 10°/min), T_R = 7.6 min; TLC (silica gel/7:5 petroleum ether–ether), homogeneous. Anal. Calcd for $C_8H_{16}OS_2$: C, 49.96; H, 8.38. Found: C, 50.12; H, 8.44.

Dehydration of Alcohol 32a. A. With Sulfuric Acid. Formation of 7-Mercapto-3,3-dimethyl-4-thia-2-heptanone (37). A mixture of alcohol **32a** (0.43 g, 2.2 mmol) in benzene (5 mL) and aqueous 20% H_2SO_4 (20 mL) was heated at 60 °C for 3 h. The cooled mixture (25 °C) was poured into water and was extracted with ether (3 × 40 mL). The combined ether was washed with water, saturated $NaHCO_3$ solution, and brine (1 × 30 mL), dried over Na_2SO_4, and evaporated in vacuo to leave the GLC-pure liquid mercapto ketone **37** (0.41 g, 95%): IR (neat) 2970 (s), 2930 (s), 2860 (m), 2560 (w), 1700 (s), 1465 (s), 1440 (s), 1370 (m), 1355 (s), 1255 (br), 1140 (s), 1115 (s), 970 (m) cm^{-1}; 60-MHz ^1H NMR δ 2.8 (m, 4 H, SCH_2), 2.25 (s, 3 H, CH_3), 1.8 (br m, 3 H), 1.4 (s, 6 H, $C(CH_3)_2$); GLC [OV-17] (100–180 °C, 30 psi, T_i = 4 min, 10°/min), T_R = 6.9 min; TLC (silica gel/benzene), homogeneous. Anal. Calcd for $C_8H_{16}OS_2$: C, 49.96; H, 8.38. Found: C, 50.15; H, 8.20.

B. With $POCl_3$ in Pyridine. Formation of 2,2-Dimethyl-3-methylene-1,4-dithiepane (36). A mixture of alcohol **32a** (0.10 g, 0.54 mmol) and $POCl_3$ (0.247 g, 1.61 mmol) in dry pyridine (3 mL) under argon was stirred vigorously and heated to 80–90 °C for 4 h. The cooled reaction mixture (25 °C) was partitioned between water and ether, and the organic layer was washed with 1 M HCl (2 × 30 mL), water, and brine, dried (Na_2SO_4), and evaporated in vacuo. Chromatography of the dark oily residue on 5 g of silica gel (5% ether in petroleum ether) gave olefin **36** (52 mg, 57%) as a colorless liquid: IR (neat) 3090 (w), 1595 (s), 1460 (s), 1440 (s), 1410 (s), 1370 (m), 1360 (m), 1305 (m), 1270 (w), 1120 (br), 1100 (s), 920 (br), 860 (m), 760 (m) cm^{-1};

60-MHz ^{1}H NMR δ 5.6 (s, 1 H), 5.4 (s, 1 H), 3.0 (m, 4 H), 2.2 (m, 2 H), 1.6 (s, 6 H); GLC [OV-17] (100–180 °C, 30 psi, T_i = 4 min, 10°/min), T_R = 5.3 min; TLC (silica gel/benzene), homogeneous.

Although olefin **36** was homogeneous according to GLC and TLC, it probably had a slight residual impurity because our carbon analysis was not satisfactory. Therefore, we confirmed its structure by hydrolysis as follows. The olefin (40 mg, 0.23 mmol) in benzene (3 mL) and aqueous 20% H_2SO_4 (10 mL) was refluxed at 90–100 °C for 16 h. The cooled mixture (25 °C) was poured into water and extracted with ether. The combined ether was washed sequentially with water, saturated $NaHCO_3$, and brine, dried over Na_2SO_4, and evaporated in vacuo. The TLC-pure liquid (44 mg, 99%) was identical with our mercapto ketone **37** by IR, ^{1}H NMR, GLC, and TLC.

C. With Phosphorus Pentoxide. A mixture of alcohol **32a** (0.17 g, 0.89 mmol) and P_2O_5 (0.38 g, 2.7 mmol) in dry benzene (4 mL) was stirred vigorously at room temperature for 12 h. It was partitioned between water and ether, and the organic layer was washed with water and brine, dried (Na_2SO_4), and evaporated in vacuo to give an oily residue (0.13 g). Examination of the oil by GLC [OV-17] (100–200 °C, 30 psi, T_i = 4 min, 10°/min) showed no starting material and two major components at T_R = 5.3 min (40%) and T_R = 5.5 min (60%). The minor component was identified as olefin **36** by peak enhancement and from the ^{1}H NMR and IR spectra of the mixture. Although the major component has not yet been characterized, we know it is not 2-methyl-2-(1-methylvinyl)-1,3-dithiane, which we had on hand[1,2] for comparisons.

Attempted Pyrolysis of Alcohol 32a. Neat alcohol **32a** (66 mg) in a Kugelrohr tube was heated for 8 min in an oven at 320 °C. The colorless liquid (50 mg) that condensed in the receiving bulb (held at 0 °C) was starting alcohol according to IR, ^{1}H NMR, GLC, and TLC. An attempted pyrolysis of **32a** in a sealed tube at 330 °C for 15 min produced a complex mixture.

2-Methyl-2-(1-acetoxy-1-methylethyl)-1,3-dithiane (32b). Formation. A mixture of **32a** (0.13 g, 0.69 mmol) in dry benzene (10 mL) and 1 equiv of 0.79 M methyllithium in ether (0.87 mL) was stirred at 25 °C for 15 min under argon and then heated slowly to 70–80 °C. The hot solution was treated with freshly distilled acetyl chloride (0.078 g, 1 mmol) and maintained at 80 °C for 2.5 h. The cooled solution (25 °C) was partitioned between water and ether, and the organic layer was washed with water and brine, dried (Na_2SO_4), and evaporated in vacuo. Purification of the yellow oily residue by PTLC (silica gel/benzene) gave starting alcohol **32a** (63 mg, 47%) as a slow moving band and the acetate **32b** (68 mg, 42%) as a yellowish, fast moving band with these properties: IR (neat) 1740 (br), 1455 (s), 1425 (s), 1390 (s), 1370 (s), 1250 (br), 1220 (s), 1150 (br), 1020 (s), 950 (s), 915 (w), 830 (m), 765 (m) cm^{-1}; 60-MHz ^{1}H NMR δ 2.8 (m, 4 H, SCH_2), 2.4 (m, 2 H), 2.0 (s, 3 H, CH_3), 1.7 (s, 9 H); GLC [OV-17] (100–250 °C, 30 psi, T_i = 4 min, 10°/min), T_R = 8.9 min; TLC (silica gel/benzene), homogeneous. It was pyrolyzed directly.

Pyrolysis. Neat acetate **32b** (40 mg, 0.17 mmol) in a Kugelrohr tube (receiving bulb at 0 °C) was heated about 8 min in an oven preheated to 270 °C. Purification of the dark condensate by PTLC (silica gel/benzene) gave starting acetate (3 mg, 7.5%) and a TLC-pure colorless liquid (24 mg, 92%) identical with olefin **36** by IR, ^{1}H NMR, GLC, and TLC.

2-Methyl-2-(3-hydroxy-1-methylpropyl)-1,3-dithiane (35). A 0 °C solution of 5-hydroxy-3-methyl-2-pentanone[19] (0.70 g, 6.09 mmol) and 1,3-propanedithiol (0.66 g, 6.09 mmol) in a 3:1 mixture of glacial acetic acid–THF (20 mL) under argon was treated slowly with $BF_3 \cdot Et_2O$ (1.23 g, 8.68 mmol). The mixture was stirred vigorously at 0 °C for 5 h and then was poured into water and extracted with ether (3 × 40 mL). The combined ether was washed with water (2 × 30 mL), saturated aqueous $NaHCO_3$ solution (2 × 30 mL) to neutrality, water, and brine, dried (Na_2SO_4), and evaporated in vacuo. Chromatography of the residue on 10 g of silica gel (50% benzene–CH_2Cl_2) gave TLC-pure alcohol **35** (0.87 g, 70%) as a colorless oil: IR (neat) 3640–3100 (br), 1450 (s), 1420 (s), 1380 (s), 1280 (s), 1240 (m), 1055 (br), 1000 (br), 910 (s) cm^{-1}; 60-MHz ^{1}H NMR δ 3.8 (m, 2 H), 2.8 (m, 4 H), 2.4–1.8 (m, 6 H), 1.55 (s, 3 H), 1.1 (d, 3 H); TLC (silica gel/50% petroleum ether–ether), homogeneous.

Attempted Dehydration of Alcohol 35 with Phosphorus Pentoxide. A mixture of alcohol **35** (87 mg, 0.42 mmol) and P_2O_5 (0.12 g, 0.84 mmol) in dry benzene (5 mL) was stirred vigorously for 11 h at room temperature. After a conventional aqueous workup, we recovered starting alcohol (50 mg). The reaction was repeated at 100 °C for 6 h, but again the alcohol was recovered.

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Registry No. 8, 98051-49-1; **9a**, 16775-67-0; **9b**, 60719-91-7; **10**, 31236-94-9; **11a**, 59796-93-9; **11b**, 98051-50-4; **12**, 59796-96-2; **13**, 98051-51-5; **13**·MeI, 98051-75-3; **14**, 98051-52-6; **15**, 98051-53-7; **15** (sulfoxide), 98051-76-4; **16**, 98051-54-8; **17**, 98051-56-0; **18**, 98051-56-0; **19**, 949-07-5; **20a**, 3866-79-3; **20b**, 4010-05-3; **21a**, 73194-44-2; **21b**, 98051-57-1; **22**, 98051-58-2; **23a**, 98051-59-3; **23b**, 98051-60-6; **23c**, 98051-61-7; **24**, 98051-62-8; **25**, 98051-63-9; **28b**, 98051-64-0; **29a**, 93360-01-1; **29b**, 93360-02-2; **29c**, 98051-65-1; **30a**, 98051-66-2; **30b**, 98051-67-3; **31a**, 98051-68-4; **31b**, 98051-69-5; **32a**, 98051-70-8; **32b**, 98051-71-9; **35**, 98051-72-0; **36**, 98051-73-1; **37**, 98051-74-2; cyclododecanone, 830-13-7; 1,2-ethanedithiol, 540-63-6; 2-mercaptoethanol, 60-24-2; 1,3-propanedithiol, 109-80-8; 1,4-butanedithiol, 1191-08-8; potassium thiotosylate, 28519-50-8; 1,4-dibromobutane, 110-52-1; 4-hydroxy-3-methyl-2-butanone, 3393-64-4; 2-(methoxycarbonyl)cyclododecanone, 62939-87-1; 2-(ethoxycarbonyl)-2-methyl-1,3-dithiane, 4882-95-5; 5-hydroxy-3-methyl-2-pentanone, 1567-93-7.