Alkoxide-Promoted [1,3] Rearrangements of 1,3-Dithianes

Stephen R. Wilson,* Raj N. Misra, and Gregory M. Georgiadis

Department of Chemistry, Indiana University, Bloomington, Indiana 47405

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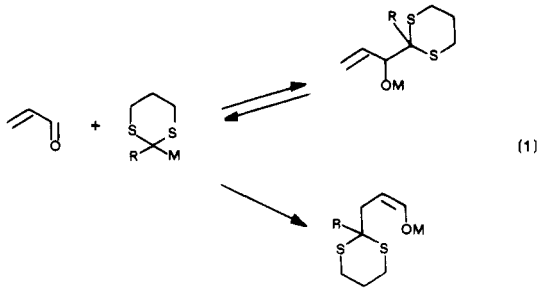
The allylic alcohols formed from 1,2-addition of 2-lithio-1,3-dithianes to α,β-unsaturated ketones have been shown to undergo [1,3] rearrangement to afford their respective Michael-addition products upon treatment with KH in HMPA/THF in some cases. The major side reaction and in some instances the sole reaction pathway was fragmentation. The rearrangement was applied to a two-carbon macrocyclic ring-expansion strategy which is illustrated in a synthesis of DL-muscone, a 15-membered-ring ketone, from cyclotridecanone. Attempts to induce a similar rearrangement by replacing the 1,3-dithiane group with a thiophenyl or 1,3-dithiolane group proved unsuccessful.

Molecular rearrangements[1] involving carbon–carbon bond cleavage and subsequent or concomitant carbon–carbon bond formation have been among the most important in developing a mechanistic understanding of chemical reactions. However, due in many instances to the necessity of high reaction temperatures, these thermal processes have limited synthetic potential. The reports by Evans and co-workers[2] that dissociated alkoxides significantly weaken adjacent carbon–carbon bonds and thus facilitate these rearrangements have recently prompted a number of investigations in this area.[3,4] We have been interested in alkoxide induced [1,3] rearrangements and their applications to general methods of synthesis.[4b,5] Recently, we reported the alkoxide-induced [1,3] rearrangements of 1,3-dithianes[5] and present the details of this study.

The addition of organometallic compounds to α,β-unsaturated ketones has provided an invaluable method of forming new carbon–carbon bonds.[6] In principle 1,2 and/or 1,4 addition may occur, and in many cases the reactions are completely regioselective. Recently, several reports involving stabilized carbanions[7] have indicated that in some instances this selectivity is a kinetic–thermodynamic phenomenon, and the initially formed 1,2-addition product equilibrates to the 1,4-adduct. Formally this isomerization is the result of a [1,3] sigmatropic rearrangement.[8]

Acyl anion equivalents,[9] particularly 1,3-dithianes,[10] have been widely used in organic synthesis. The addition of unstabilized 2-lithio-1,3-dithianes to α,β-unsaturated ketones occurs exclusively via 1,2-addition.[11] To our knowledge, there are no examples of Michael additions of unstabilized dithiane anions to α,β-unsaturated ketones although additional anion-stabilizing substituents (SPh, Ph, etc.)[12a-f] or the presence of HMPA[12g] may result in the formation of 1,4-adducts. The reasons for this selectivity are not completely clear; however, the 1,2-product may be the result of *irreversible* kinetic addition.[13] Subsequent isomerization to the 1,4-product requires cleavage of the newly formed carbon–carbon bond followed by readdition at the β position[14] (eq 1). Thus, it may be possible to effect



(1)

the initial carbon–carbon bond cleavage by prior generation of the potassium alkoxide in a dissociating medium.[15]

(1) (a) For a review of the Cope and Claisen processes see: Rhoads, S. J.; Raulins, N. R. *Org. React.* **1975**, *22*, 1. (b) Thermal [1,*j*] rearrangements: Spangler, C. W. *Chem. Rev.* **1976**, *76*, 187. (c) Claisen rearrangement: Ziegler, F. E. *Acc. Chem. Res.* **1977**, *10*, 227.

(2) (a) Evans, D. A.; Golob, A. M. *J. Am. Chem. Soc.* **1975**, *97*, 4765. (b) Evans, D. A.; Baillargeon, D. J. *Tetrahedron Lett.* **1978**, 3315, 3319.

(3) For some synthetic applications of anionic oxy-Cope rearrangements see: (a) Seebach, D.; Geiss, K.-H.; Phomakotr, M. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 437. (b) Still, W. C. *J. Am. Chem. Soc.* **1977**, *99*, 4186. (c) Jung, M. E.; Hudspeth, J. P. *Ibid.* **1978**, *100*, 4309. (d) Evans, D. A.; Baillargeon, D. J.; Nelson, J. V. *Ibid.* **1978**, *100*, 2242. (e) House, H. O.; Sayer, T. S. B.; Yau, C.-C. *J. Org. Chem.* **1978**, *43*, 2153. (f) Still, W. C. *J. Am. Chem. Soc.* **1979**, *101*, 2493. (g) Kozikowski, A. P.; Schmiesing, R. *J. Chem. Soc., Chem. Commun.* **1979**, 106. (h) Pohmakotr, M.; Geiss, K.-H.; Seebach, D. *Chem. Ber.* **1979**, *112*, 1420.

(4) For alkoxide promoted [1,3] rearrangements see: (a) Franzus, B.; Scheinbaum, J. L.; Waters, D. L.; Bowlin, J. B. *J. Am. Chem. Soc.* **1976**, *98*, 1241. (b) Wilson, S. R.; Mao, D. T.; Jernberg, K. M.; Ezmirly, S. R. *Tetrahedron Lett.* **1977**, 2559. (c) Thies, R. W.; Seitz, E. P. *J. Org. Chem.* **1978**, *43*, 1050. (d) Thies, R. W.; Seitz, E. P. *J. Chem. Soc., Chem. Commun.* **1976**, 846. (e) Wilson, S. R.; Mao, D. T. *Ibid.* **1978**, 479. (f) For a related rearrangement see: Dalton, J. C.; Stokes, B. G. *Tetrahedron Lett.* **1975**, 3179, and references cited therein.

(5) Wilson, S. R.; Misra, R. N. *J. Org. Chem.* **1978**, *43*, 4903.

(6) For reviews of Michael additions see: (a) Bergmann, E. D.; Ginsburg, D.; Pazpo, R. *Org. React.* **1959**, *10*, 179. (b) Posner, G. H. *Ibid.* **1972**, *19*, 1.

(7) (a) Schultz, A. G.; Yee, Y. K. *J. Org. Chem.* **1976**, *41*, 4044. (b) Deschamps, B.; Anh, N. T.; Seyden-Penne, J. *Tetrahedron Lett.* **1973**, 527. (c) Sauvetre, R.; Seyden-Penne, J. *Ibid.* **1976**, 3949. (d) Still, W. C.; Mitra, A. *Ibid.* **1978**, 2659. (e) Kaiser, E. M.; Knutson, P. L.; McClure, J. R. *Ibid.* **1978**, 1747. (f) Luchetti, J.; Krief, A. *Ibid.* **1978**, 2697. (g) Milzer, J.; Hartz, G.; Kühl, U.; Brüntrup, G. *Ibid.* **1978**, 2949. (h) Yamagiwa, S.; Hoshi, N.; Sato, H.; Kosugi, H.; Uda, H. *J. Chem. Soc., Perkin Trans. 1* **1978**, 214.

(8) Throughout this discussion the term "sigmatropic rearrangement" is used to indicate the overall bonding change and not to imply a concerted mechanism: Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Academic Press: New York, 1970.

(9) For a review see: Lever, O. W. *Tetrahedron* **1976**, *32*, 1943.

(10) (a) Seebach, D.; Corey, E. J. *J. Org. Chem.* **1975**, *40*, 231. (b) Seebach, D. *Synthesis* **1969**, *1*, 17. (c) Gröbel, B.-T.; Seebach, D. *Ibid.* **1977**, 357.

(11) Corey, E. J.; Crouse, D. *J. Org. Chem.* **1968**, *33*, 298.

(12) (a) Woessner, W. D. *Chem. Lett.* **1976**, 43. (b) Ostrowski, P. C.; Kane, V. V. *Tetrahedron Lett.* **1977**, 3549. (c) For 1,4-additions to butenolides see: Ziegler, F. E.; Schwartz, J. A. *Ibid.* **1975**, 4643. (d) Ziegler, F. E.; Schwartz, J. A. *J. Org. Chem.* **1978**, *43*, 985. (e) Asano, Y.; Kamikawa, T.; Tokoroyama, T. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3232. (f) For a comprehensive listing of Michael additions of metalated thioacetals and their derivatives see ref 10c. (g) For Michael additions in the presence of HMPA see: Brown, C. A.; Yamaichi, A. *J. Chem. Soc., Chem. Commun.* **1979**, 100; Binns, M. R.; Haynes, R. K.; Houston, T. L.; Jackson, W. R. *Tetrahedron Lett.* **1980**, 573.

(13) This suggestion was advanced by Stork and Maldonado a number of years ago. See: Stork, G.; Maldonado, L. *J. Am. Chem. Soc.* **1974**, *96*, 5272.

(14) During the course of this work a report appeared on the 1,2 → 1,4 isomerization of 2-phenyl-1,3-dithiane anions: Ostrowski, P. C.; Kane, V. V. *Tetrahedron Lett.* **1977**, 3549.

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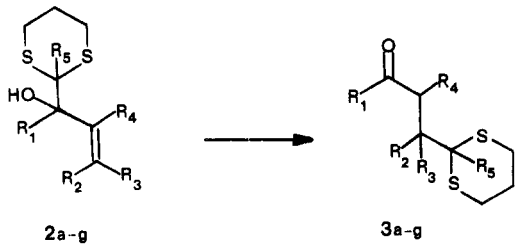
Scheme I



2a-g 3a-g

a. $R_1 = R_2 = -(CH_2)_3-$, $R_3 = R_4 = H$, $R_5 = CH_3$

b. $R_1 = R_2 = -(CH_2)_3-$, $R_3 = R_5 = CH_3$, $R_4 = H$

c. $R_1 = R_2 = -(CH_2)_2-$, $R_3 = R_4 = H$, $R_5 = CH_3$

d. $R_1 = R_2 = -(CH_2)_3-$, $R_3 = R_4 = R_5 = H$

e. $R_1 = R_5 = CH_3$, $R_2 = R_3 = R_4 = H$

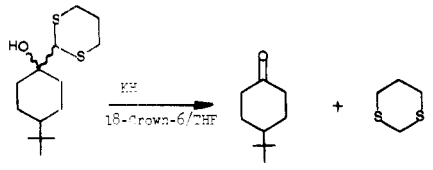
f. $R_1 = Ph$, $R_2 = R_3 = R_4 = H$, $R_5 = CH_3$

g. $R_1 = Ph$, $R_2 = R_3 = H$, $R_4 = trimethylsilyl$, $R_5 = CH_3$

Subsequent 1,4-addition affords the thermodynamically more stable Michael adduct.

Results and Discussion

Hydroxy dithiane **1** was obtained as a 2:3 mixture of



1

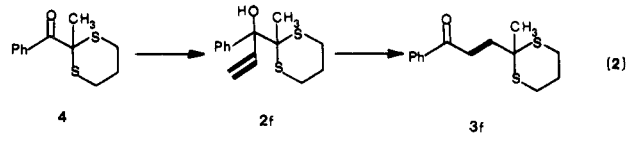
alcohol epimers by the addition of 2-lithio-1,3-dithiane to 4-*tert*-butylcyclohexanone. Treatment of **1** with 2 equiv of potassium hydride in THF solution in the presence of 18-crown-6 ether and warming to 45 °C for 6 h resulted in complete fragmentation of the ketone–dithiane adduct. The fragmentation products 4-*tert*-butylcyclohexanone and 1,3-dithiane were detectable in 10% and 60% yields (VPC), respectively. The fragmentation also occurred in warm HMPA solution at longer reaction times although it was necessary to add additional portions of potassium hydride as the reaction proceeded. The suspect stability of potassium alkoxides in HMPA for extended periods of time and at elevated temperatures may in part cause the consumption of base. Nevertheless, it was established that formation of the potassium alkoxide of ketone–dithiane adducts under dissociating conditions was sufficient to cause irreversible carbon–carbon bond cleavage. We next attempted to exploit this fragmentation as the initial step in [1,3] rearrangements of 1,2-addition products, derived from dithiane anions and α,β-unsaturated ketones, to the more stable 1,4-adducts.

Synthesis and Isomerization of 1,2-Adducts. The precursor allylic alcohols **2a–e** (Scheme I) were prepared by addition of the appropriate α,β-unsaturated ketone to the corresponding 2-lithio-1,3-dithiane in THF using literature procedures.[11] Exclusive 1,2-addition was observed in each case. No conjugate addition products were detectable by thin-layer chromatography or IR spectroscopy. Attempts to prepare allylic alcohol **2f** by an analogous route were unsuccessful. Thus addition of phenyl vinyl ketone to 2-lithio-2-methyl-1,3-dithiane at −20 °C in THF resulted in recovered 2-methyl-1,3-dithiane as the sole nonpolar product by TLC. Presumably facile base-catalyzed polymerization of phenyl vinyl ketone was the major side reaction. Alternatively, **2f** was prepared in 89% yield by addition of vinylmagnesium bromide to known ketone **4** (eq 2). Similarly **2g** was prepared from 1-lithio-1-(trimethylsilyl)ethylene and ketone **4**.

Table I. Potassium Alkoxide Induced Rearrangements[a]

allylic alcohol	product	yield, %
2a	3a	23[b]
		30[c]
2b		
2c	3c	53[b]
2d		
2e		
2f	3f	27[b]
2g	3f	25[d]
	2f	100[e]

[a] Allylic alcohols were treated with 1–1.5 equiv of KH. [b] HMPA/THF, 25 °C, 2 h. [c] TPPA/THF, 25 °C, 45 min. [d] THF/10 min. [e] HMPA/THF/1 min, VPC yield.



4 2f 3f (2)

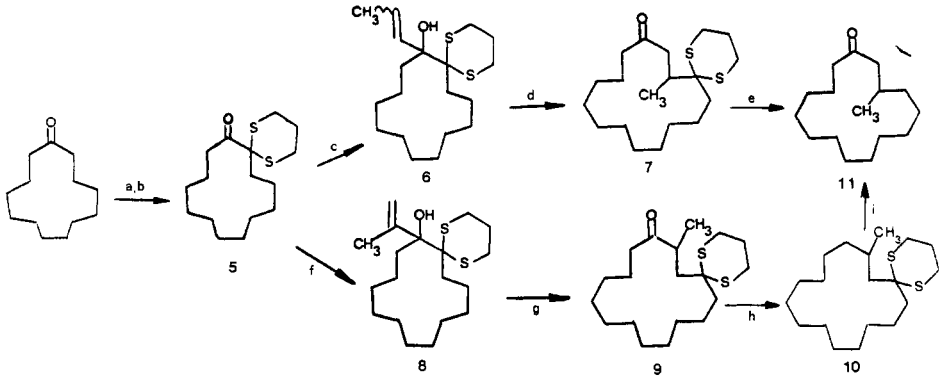
Treatment of allylic carbinol **2a** with 1.5 equiv of potassium hydride in 80% HMPA/THF solution resulted in the formation of a new substance of slightly lower R_f (ether–pentane) by TLC, whose IR spectrum showed a strong carbonyl absorption at 5.87 μm and the absence of a hydroxyl absorption band present in the starting material and whose ^1H NMR spectrum showed the absence of vinyl protons. On the basis of spectral data (IR, NMR, and mass spectra) the structure was assigned as rearranged dithiane **3a**. The isolated yield of **3a** was 23%. In general, allylic carbinols **2a–f** were treated with 1–1.5 equiv of potassium hydride in 80% HMPA/THF at 0 °C (Scheme I). The solutions were warmed to room temperature and worked up after 2–2.5 h, and the products were isolated by silica gel chromatography. The results are shown in Table I. The major side reactions and in some cases the sole reaction pathway was fragmentation, as evidenced by the recovery of either 1,3-dithiane or 2-methyl-1,3-dithiane in every case.[16] None of the corresponding α,β-unsaturated ketone was recovered from the crude reaction mixtures or detectable by ^1H NMR spectroscopy. Our attempts to suppress fragmentation in favor of rearrangement proved unsuccessful. Thus in the case of allylic alcohol **2a**, lowering the HMPA/THF ratio led to longer reaction times although no appreciable increase in yield of rearranged product **3a** was noted. The lithium and sodium salts of **2a** in 80% HMPA/THF afforded mostly recovered starting material while the potassium salt in THF/18-crown-6 or the sodium salt in refluxing DME led to only fragmentation. Isomerization of **2a** in 80% tris(pyrrolidinyl)phosphoramide (TPPA)/THF solution, a better coordinating solvent than HMPA,[17] led to a slight increase in yield, 23% vs. 30%, and a shorter reaction time, 45 min vs. 2 h. Interestingly, the trimethylsilyl derivative **2g** underwent rearrangement in THF with no added HMPA

(15) Solvent dependence reversal of phenyldithiane–ketone adducts has recently been reported: Juaristi, E.; Eliel, E. L. *Tetrahedron Lett.* **1977**, 543.

(16) In cases where the dithiane was isolated, the yield accounted for the material balance of product.

(17) Our measured $\Delta\delta$ value of TPPA was 2.18. The reported $\Delta\delta$ value of HMPA is 2.02; see: Normant, H. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 1046.

Scheme II

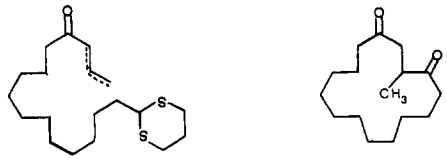


[a] NaH, HCO_2Et; 88%. [b] $TsSCH_2CH_2CH_2STs$; 41%. [c] $CH_3CH{=}CHLi$ (3 recycles); 48%. [d] KH, TPPA/THF; 21%. [e] Ra-Ni/EtOH; 40%. [f] $CH_3(Li)C{=}CH_2$ (5 recycles); 51%. [g] KH, HMPA/THF; 28%. [h] NH_2NH_2, KOH; 41%. [i] HgO, BF_3-OEt_2/aqueous THF; 72%.

at relatively short reaction times. It is possible that the increased steric congestion associated with a bulky trimethylsilyl group promotes carbon–carbon bond cleavage. The reaction of **2g** in the presence of HMPA results in immediate desilylation. Similar cleavage of carbon–silicon bonds has been previously observed in γ-hydroxy vinylsilanes by fluoride ion.[18] Presumably, nucleophilic displacement on silicon by the highly dissociated alkoxide is occurring in this case.

Two-Carbon Homologations. A number of suitable methods have been developed for the 1,4-addition of acyl anion equivalents to α,β-unsaturated ketones.[9] The [1,3] rearrangement here represents not only a limited extension of these methods but more importantly a *reorganization of the carbon skeleton*. Thus, the synthesis and rearrangement of **2f** (eq 2) is an interesting variation of the dithiane rearrangements of **2a–e**. The overall transformation of **4** to **3f** results in the insertion of two new carbons between two differentiated carbonyl groups.

Known methods for the synthesis of α-keto dithianes[19] from ketones allow the application of this methodology to a 2-carbon ring-expansion route in the case of cyclic carbonyl compounds. This approach is illustrated in the conversion of cyclotridecanone to 3-methylcyclopentadecanone (muscone, **11**) via a [1,3] sigmatropic rearrangement (Scheme II). In the first step, cyclotridecanone was converted to crystalline α-keto dithiane derivative **5** via the corresponding α-hydroxymethylene ketone in 40% overall yield.[19] Addition of 1-lithiopropene at 0 °C in ether after three recycles and chromatography resulted in 31% *trans*-**6**, 17% *cis*-**6**, and 48% recovered starting ketone **5**. Single treatment of ketone **5** with 1-lithiopropene resulted in only 15–20% addition to the hindered carbonyl. Attempts to add organolithiums to the corresponding cyclooctanone and cyclododecanone derivatives resulted in the recovery of only unreacted starting material. Similar results have been reported with the analogous cyclononanone system.[20] Apparently α-keto dithiane derivatives of the medium-sized rings are sufficiently hindered that enolization is the sole reaction pathway. Increasing the ring size beyond C_{12} allows for competitive addition to the carbonyl. Treatment of allylic alcohol **6** with potassium hydride in 80% HMPA/THF (2 h, 25 °C) afforded ring-expansion ketone **7** in 15% yield. The yield was increased to 21% in 80% TPPA/THF. Ring-cleaved product **12** was also isolated from the reaction

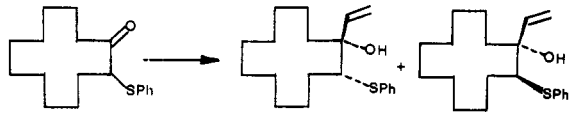


in 16% yield as a mixture of conjugated and nonconjugated double-bond isomers.[21] The remaining polar material was not characterized. Raney nickel (W-2) desulfurization in refluxing ethanol gave DL-muscone,[22] **11**, in 42% yield and diketone **13** in 34% yield. The facile hydrolysis of **7** can be explained by assuming participation by the neighboring carbonyl group. This type of participation has been previously postulated in the intramolecular transketalization of a dithiolane during mercuric chloride hydrolysis[23] and has been postulated to rationalize the facile hydrolysis of δ-hydroxy vinyl sulfides.[24]

An alternate route to **11** was also investigated, taking advantage of the dithiane moiety as a masked carbonyl group. Thus treatment of **5** with 2-lithiopropene in ether solution at 0 °C after five recycles afforded allylic alcohol **8** in 51% yield. Treatment with potassium hydride in 80% HMPA/THF solution resulted in a 28% yield of ring-expanded ketone **9**. Wolff–Kishner reduction (41%) and mercuric oxide hydrolysis (72%) again afforded DL-muscone (**11**).

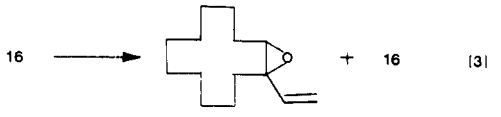
Attempted Rearrangements of α-Thiophenyl and Dithiolane Derivatives. We have also investigated several unsuccessful alternatives to 1,3-dithianes as migrating groups in an attempt to (1) improve additions to the ketone and (2) increase the yield of the rearrangement. Thus sulfenylation of cyclododecanone using Trost's procedure[25] gave a α-thiophenyl ketone **14**. Treatment of **14**

(18) Chan, T. H.; Mychajlowskij, W. *Tetrahedron Lett.* **1974**, 3479.
(19) (a) By the procedure of Woodward, R. B.; Pachter, I. J.; Scheinbaum, M. L. *J. Org. Chem.* **1971**, *36*, 1137. (b) Woodward, R. B.; Pachter, I. J.; Scheinbaum, M. L. *Org. Synth.* **1974**, *54*, 39.
(20) Trost, B. M.; Hiroi, K. *J. Am. Chem. Soc.* **1976**, *98*, 4313, footnote 8.
(21) The obtainment of **12** and fragmentation products from **2a–g** suggest a mechanism involving initial carbon–carbon bond cleavage. Such ring-opening reactions have been reported: (a) Marshall, J. A.; Roebke, H. *Tetrahedron Lett.* **1970**, 1555. (b) Cossement, E.; Biname, R.; Ghosez, L. *Ibid.* **1974**, 977. (c) Trost, B. M.; Preckel, M., Leichter, L. M. *J. Am. Chem. Soc.* **1975**, *97*, 2224. (d) Marshall, J. A.; Seitz, D. E. *J. Org. Chem.* **1974**, *39*, 1814.
(22) Identity was based on comparison to spectral data previously reported: Mookherjee, B. D.; Trenkle, R. W.; Patel, R. *J. Org. Chem.* **1971**, *36*, 3266.
(23) Matsumoto, T.; Schirahama, H.; Ichihara, A.; Shin, H.; Kagawa, S. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1144.
(24) Mura, A. J.; Majetich, G.; Grieco, P. A.; Cohen, T. *Tetrahedron Lett.* **1975**, 4437.



14 15 16

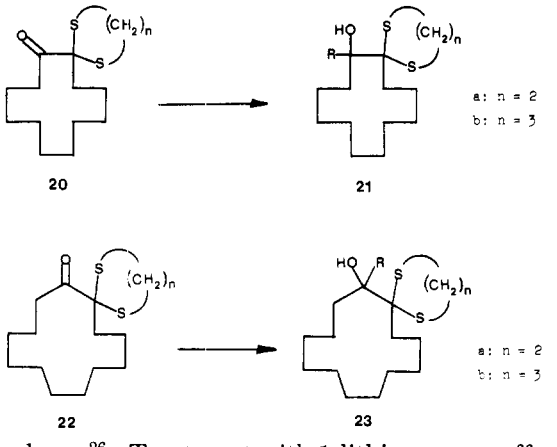
with vinylmagnesium bromide in THF at 0 °C afforded a yellow oil. Analysis of the crude product by VPC showed three components in a 59:16:25 area ratio, corresponding to **14**, **15**, and **16**, respectively. The stereochemistry of **15** and **16** was assigned on the assumption that the *cis*-α-hydroxy (thiophenyl) compound **15** was more mobile on TLC (ether–pentane). Employing vinyllithium in place of vinylmagnesium bromide substantially increased the yield of addition. Thus treatment of **14** with excess vinyllithium in THF at 0 °C gave a 19:8:73 mixture of **14**, **15**, and **16**, respectively. Two recycles afforded **16** in 80% isolated yield. Attempted isomerization of the potassium salt of **16** in 80% HMPA/THF at 25 °C for 24 h and isolation of the products by chromatography resulted in 54% recovered starting material (**16**) and a nonpolar UV-inactive product identified by ^{1}H NMR and mass spectroscopy as epoxide **17** in 30% yield (eq 3). Unfortunately,



17 [3]

no rearrangement or ring-cleaved products were isolated. Apparently, a single sulfur substituent is not sufficient to promote carbon–carbon bond cleavage under these conditions.

We next turned our attention to α-keto dithiolanes. It was anticipated that hindrance of an adjacent ketone by a five-membered dithiolane ring would be less severe than in the case of a six-membered dithiane ring. α-Keto dithiolanes **20a** and **22a** were obtained by using literature



20 21 22 23

procedures.[26] Treatment with 1-lithiopropene afforded

Table II. Addition of RLi to Cyclic α-Keto Dithianes[a]

compd	R	alcohol:ketone
18a	$CH=CH_2$	100:0
18b	CH_3	0:100[20]
18c	CH_3	0:100
20a	$CH=CHCH_3$	45:55
20b	$CH=CHCH_3$	3:97
22a	$CH=CHCH_3$	88:12
22b (5)	$CH=CHCH_3$	20:80

[a] Reactions were performed in ether solution at 0 °C by adding excess organolithium.

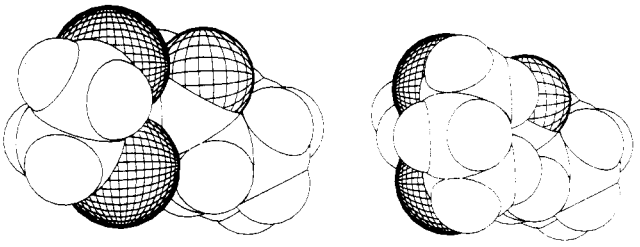
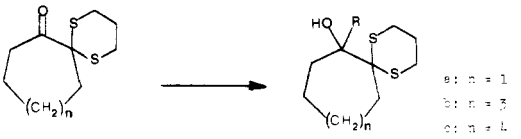


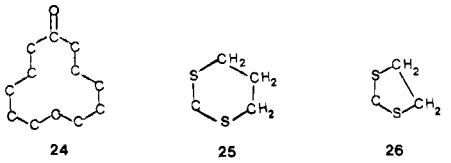
Figure 1. (a) Computer-generated space-filling model of molecule **20a** (left). (b) Computer-generated space-filling model of molecule **20b** (right).

alcohol (**21a**, **23a**):starting ketone in 45:55 and 88:12 ratios, respectively. In contrast, similar treatment of the corresponding α-keto dithianes **20b** and **22b** gave alcohol (**21b**, **23b**):starting ketone in 3:97 and 20:80 ratios, respectively.



18 19

A summary of these results is shown in Table II. A significant increase in the percentage of addition is apparent in the α-keto dithiolanes vs. the analogous α-keto dithianes. The steric hindrance can be seen by using *computer-generated* drawings obtained from the Cambridge Crystallographic Date File[41] by using a substructure search for **24**, **25**, and **26**. Computer models were constructed as de-



24 25 26

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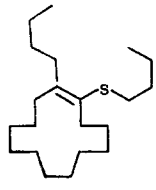
scribed in our paper on the Cambridge Data File.[41] The carbonyl carbon of dithiane **20b** is sterically protected by the macrocyclic ring on one side and two axial hydrogens of the spirocyclic ring on the other side. In contrast, the carbonyl of dithiolane **20a** is protected by the macrocyclic ring on one side but lacks the shielding effect of the axial hydrogens on the other side. The inaccessibility of the carbonyl carbon of **20b** relative to that of **20a** is dramatically seen in the computer-generated space-filling models[41,42] (Figure 1). Note that carbonyl carbon is barely visible between the axial hydrogens in Figure 1b.

Unfortunately, attempted rearrangement of **21a** (R = CH=CHCH$_3$) and **23a** (R = CH=CHCH$_3$) with potassium hydride in 80% HMPA/THF resulted in rapid and complete dissappearance of starting material but no isolable nonpolar products by TLC or significant peaks by VPC. In view of the reported instability of dithiolane anions,[27,43] which would result from heterolytic carbon–carbon bond cleavage, the results are not surprising.

An alternative mode of dithiolane reaction was also uncovered. When **22a** was reacted with excess (3.5 equiv) *n*-butyllithium in ether at 25 °C, **27** was formed in 55%



27

yield as the only nonpolar product. The mechanistic origin of this product and the synthetic consequences of the dithiolane cleavage leading to its formation are the subject of another report.[44]

Conclusions

We have demonstrated that it is possible to isomerize the 1,2-addition products of 1,3-dithiane anions and α,β-unsaturated ketones to the 1,4-adducts by the generation of the potassium salt in HMPA/THF in certain cases. The major side reaction was fragmentation. The rearrangement has been extended to a 2-carbon macrocyclic ring-expansion route[28] which was illustrated in a synthesis of DL-muscone. We are currently investigating other activating groups in the rearrangement and applications to synthesis.

Experimental Section

All reactions were carried out under a nitrogen or argon atmosphere. Melting points were obtained on a Thomas capillary melting point apparatus and are uncorrected. Boiling points are uncorrected.

Infrared (IR) spectra were obtained by using a Perkin-Elmer Infracord Model 137 spectrometer. Proton nuclear magnetic resonance (NMR) spectra were obtained by using a Varian T-60A and/or a Varian HR-220 spectrometer. All chemical shifts were measured relative to an internal standard, tetramethylsilane. Elemental combustion analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, MI. Mass spectral analyses were obtained on a Varian MAT CH-7 instrument and high-resolution mass spectra were obtained on an AEI MS-9 instrument at 70 eV unless otherwise specified.

Analytical TLC analyses were determined by using J. T. Baker Baker-flex (silica gel 1B-F) sheets. Preparative TLC separations were performed with Analtech precoated plates (silica gel GF, 2000 μm). Short-column chromatography was performed with EM Laboratories, Inc., Silica Gel G (type 60), containing a $CaSO_4$ binder. Vapor-phase (VPC) analyses were performed on a Varian Model 3700 with FID (5 ft × $^1/_8$ in. 5% OV-101 glass column).

All chemicals used were commercial samples unless reference is given to their purification or preparation. Potassium hydride was obtained as a 20% dispersion in oil from Ventron-Alfa Inorganics, Danvers, MA. HMPA was stirred over CaH_2 at 100 °C for 12 h, then distilled under reduced pressure, and stored under nitrogen. THF and ether were distilled from $LiAlH_4$.

4-*tert*-Butyl-1-(1,3-dithian-2-yl)cyclohexanol (1). To a solution of 251 mg (2.09 mmol) of 1,3-dithiane in 5 mL of THF cooled to −20 °C was added 0.80 mL (2.4 M in hexane, 1.9 mmol) of *n*-butyllithium. After 3 h the reaction mixture was cooled to −78 °C and a solution of 270 mg (1.75 mmol) of 4-*tert*-butylcyclohexanone in 2 mL of THF was added dropwise. The resulting solution was warmed to 0 °C over several minutes, poured into 30 mL of saturated aqueous NaCl solution, and extracted with 10 mL of ether. The organic layer was washed with two 30-mL portions of H_2O, dried (Na_2SO_4), and concentrated. The crude oil was purified by preparative TLC (25% ether–pentane), isolating the UV-active band of lower R_f, as 324 mg (68%) of 1, a white solid: mp 73–81 °C; IR (CCl_4) 2.73, 3.34, 6.89, 7.05, 7.85, 8.1 (br), 8.50, 9.48, 9.89, 9.95, 10.19, 10.42, 11.00 μm; NMR (CCl_4) δ 0.83 (s, 9 H), 1.0–2.4 (br m, 12 H), 2.67–3.00 (m, 4 H), 3.93 (s, 0.6 H), 4.25 (s, 0.4 H); mass spectrum, *m/e* (relative intensity) 274 (M^+, 3), 155 (19), 137 (9), 122 (25), 121 (21), 120 (100), 119 (37), 95 (13), 87 (16), 81 (25), 73 (10), 69 (10), 67 (13), 57 (50), 55 (23); exact mass calcd for $C_{14}H_{26}OS_2$ 274.14252, found 274.14236.

Fragmentation of Alcohol 1. To a solution of 25 mg (0.091 mmol) of alcohol 1 and 10 mg of *n*-tridecane in 3 mL of THF was added 36 mg (20% in oil, 0.18 mmol) of potassium hydride at room temperature. The reaction mixture was stirred for 5 min and then 53 mg (0.20 mmol) of 18-crown-6 ether was added, and the resulting solution was heated to 45 °C. VPC analysis (OV-101) of an aliquot removed after 6 h showed two significant peaks corresponding to 1,3-dithiane and 4-*tert*-butylcyclohexanone in 60% and 10% yields, respectively. None of the starting alcohol was detectable.

Preparation of 2a–e. The procedure of Corey and Crouse[11] was followed. The crude products were chromatographed on silica gel (ether–pentane) and recrystallized in the case of solids.

1-(2-Methyl-1,3-dithian-2-yl)-2-cyclohexen-1-ol (2a) was prepared in 52% yield as slightly yellow crystals (ether–pentane): mp 54–55 °C (lit.[11] mp 54.1–55 °C); IR (CCl_4) 2.78, 3.38, 6.01 (w), 7.10, 7.89, 8.55, 10.34, 11.00 μm; NMR (CCl_4) δ 1.60 (s, 3 H), 1.60–2.23 (br, 9 H), 2.63–3.20 (m, 4 H), 5.83–6.23 (m, 2 H).

1-(2-Methyl-1,3-dithian-2-yl)-3-methyl-2-cyclohexen-1-ol (2b) was prepared in 41% yield as oily white crystals (ether–pentane): mp 62.5–64.0 °C; IR (CCl_4) 2.78, 3.38, 6.02 (w), 6.94, 8.94, 10.35, 11.00 μm; NMR (CCl_4) δ 1.58 (s, 3 H), 1.59–2.13 (br, 12 H), 2.63–3.02 (m, 4 H), 5.67–5.83 (m, 2 H); mass spectrum, *m/e* (relative intensity) 244 (M^+, 1), 226 (16), 152 (15), 134 (34), 133 (100), 119 (22), 111 (75), 93 (17), 77 (13), 59 (40), 55 (16), 43 (16), 41 (22). Anal. Calcd for $C_{12}H_{20}OS_2$: C, 58.97; H, 8.25; S, 26.23. Found: C, 58.89; H, 8.31; S, 26.20.

1-(2-Methyl-1,3-dithian-2-yl)-2-cyclopenten-1-ol (2c) was prepared in 52% yield as large white crystals (ether-pentane): mp 40–41.5 °C; IR (CCl_4) 2.80, 3.36, 6.18 (w), 6.92, 7.05, 7.85, 8.93, 9.48, 10.98 μm; NMR (CCl_4) δ 1.60 (s, 3 H), 1.67–2.63 (m, 7 H), 2.65–3.07 (m, 4 H), 5.87 (s, 2 H); mass spectrum, *m/e* (relative intensity) 216 (M^+, 0.1), 135 (10), 134 (14), 133 (100), 95 (2), 83 (14), 59 (26), 55 (4), 53 (2), 45 (3), 43 (4), 41 (5), 39 (4). Anal. Calcd for $C_{10}H_{16}OS_2$: C, 55.51; H, 7.45; S, 29.64. Found: C, 55.66; H, 7.44; S, 29.55.

1-(1,3-Dithian-2-yl)-2-cyclohexen-1-ol (2d)[10b] was prepared in 83% yield as a pale yellow oil: IR (film) 2.83, 3.37, 6.10 (w), 7.10, 7.89, 8.50, 9.30, 10.22, 10.63, 11.00, 12.55, 13.63 μm; NMR (CCl_4) δ 1.37–2.23 (m, 9 H), 2.67–3.03 (m, 4 H), 4.05 (s, 1 H), 5.72 (m, 2 H); mass spectrum, *m/e* (relative intensity) 216 (M^+, 1), 121 (13), 120 (61), 119 (100), 97 (52), 85 (6), 79 (10), 77 (7), 75 (6), 73 (5), 67 (7), 55 (15), 47 (5), 45 (16), 43 (7), 41 (24), 39 (9).

2-(2-Methyl-1,3-dithian-2-yl)-3-buten-2-ol (2e)[40] was prepared in 36% yield as a pale yellow oil: IR (film) 3.82, 4.37, 6.93,

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(43) See, however: Yamashita, M.; Suemitsu, R. *J. Chem. Soc., Chem. Commun.* **1977**, 691.
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7.08, 7.33, 7.59, 7.85, 9.36, 10.05, 10.79 μm; NMR (CCl_4) δ 1.38 (s, 3 H), 1.63 (s, 3 H), 1.75–2.15 (m, 2 H), 2.28 (s, 1 H), 2.63–3.00 (m, 4 H), 5.07 (dd, 1 H, J_{ab} = 2, J_{ac} = 10 Hz), 5.30 (dd, 1 H, J_{ab} = 2, J_{bc} = 17 Hz), 6.18 (dd, 1 H, J_{ac} = 10, J_{bc} = 17 Hz); mass spectrum, *m/e* (relative intensity) 204 (M^+, 0.02), 135 (8), 134 (7), 133 (100), 105 (2), 101 (2), 83 (2), 75 (3), 71 (6), 59 (29), 55 (3), 43 (10).

1-(2-Methyl-1,3-dithian-2-yl)-1-phenyl-2-propen-1-ol (2f). To a solution of 4.0 mL (1.2 M in THF, 4.8 mmol) of vinylmagnesium bromide cooled to 0 °C was added a solution of 933 mg (3.92 mmol) of 2-benzoyl-2-methyl-1,3-dithiane (**4**)[30] in 5 mL of ether. The reaction mixture was warmed to room temperature and stirred for 2 h. H_2O (5 mL) was slowly added to the resulting solution which was then poured into 20 mL of ice-cold 5% aqueous NH_4Cl solution overlaid with 15 mL of ether. After the mixture was shaken, the organic layer was separated, washed with 20 mL of saturated $NaHCO_3$ solution and then 20 mL of H_2O, dried (Na_2SO_4), and concentrated. The crude material was purified by preparative TLC (10% ether–pentane), isolating the major mobile UV-active band as 923 mg (89%) of allylic alcohol **2f**, a colorless oil: IR (film) 2.80, 3.36, 6.24 (w), 6.73, 6.94, 7.08, 7.33, 7.52, 7.86, 8.56, 9.31, 9.41, 9.98, 10.79, 13.04, 14.20 μm; NMR (CCl_4) δ 1.47 (s, 3 H), 1.57–2.10 (m, 2 H), 2.48–2.90 (m, 4 H), 3.20 (s, 1 H), 5.14 (dd, 1 H, J_{ab} = 1, J_{ac} = 5 Hz), 5.39 (dd, 1 H, J_{ab} = 1, J_{bc} = 8.5 Hz), 7.05–7.37 (m, 3 H), 7.45–7.75 (m, 2 H); mass spectrum (22 eV), *m/e* (relative intensity) 266 (M^+, 1), 175 (1), 135 (10), 134 (7), 133 (100), 106 (1). Anal. Calcd for $C_{14}H_{18}OS_2$: C, 63.11; H, 6.81; S, 24.07. Found: C, 63.22; H, 6.70; S, 24.12.

1-Hydroxy-1-(2-methyl-1,3-dithian-2-yl)-1-phenyl-2-(trimethylsilyl)-2-propene (2g). To a solution of 860 mg (4.8 mmol) of (α-bromovinyl)trimethylsilane[37] in 20 mL of ether cooled to −78 °C was added dropwise 4 mL (1.8 M in pentane, 7.2 mmol) of *tert*-butyllithium. The reaction mixture was warmed to −20 °C and stirred for 1.5 h, and then a solution of 2-benzoyl-2-methyl-1,3-dithiane[30] in 5 mL of THF was added dropwise. After 1 h, the solution was warmed to room temperature and quenched with 2 mL of H_2O. The organic layer was separated, dried (Na_2SO_4), and concentrated, yielding 1.35 g of a yellow oil which solidified upon cooling. Recrystallization from aqueous ethanol yielded 1.01 g (80%) of **2g** as colorless crystals: mp 73.5–75.0 °C; IR (CCl_4) 2.92 (br), 3.40, 6.28 (w), 6.71, 6.94, 7.04, 7.09, 7.33, 7.58, 8.06, 9.66, 9.76, 14.49 μm; NMR (CCl_4) δ −0.13 (s, 9 H), 1.70 (s, 3 H), 2.07–2.57 (m, 6 H), 3.93 (s, 1 H), 5.65 (d, 1 H, *J* = 2 Hz), 6.75 (d, 1 H, *J* = 2 Hz), 7.07–7.30 (m, 3 H), 7.53–7.77 (m, 2 H); mass spectrum, *m/e* (relative intensity) 338 (M^+, 0.1), 323 (1), 205 (2), 189 (15), 159 (4), 133 (100), 115 (13), 75 (14), 73 (14), 59 (13). Anal. Calcd for $C_{17}H_{26}OS_2Si$: C, 60.30; H, 7.74; S, 18.84; Si, 8.29. Found: C, 60.32; H, 7.78; S, 18.95; Si, 8.17.

General Procedure for the Rearrangement of 2a–f. Method A (Noncrystalline Dithianes). A suspension of 1–1.5 equiv of potassium hydride in 4 mL of HMPA was added via syringe to 1 equiv of the dithiane (0.2–0.8 mmol) dissolved in 1 mL of THF cooled to 0 °C. After several minutes, the reaction mixture was warmed to room temperature and stirred for 2–2.5 h. The resulting dark solution was poured into 25 mL of saturated aqueous NaCl solution overlaid with 10 mL of ether. The organic layer was separated, washed with two 25-mL portions of H_2O, dried (Na_2SO_4), and concentrated. The crude material was purified by silica gel chromatography (ether–pentane).

Method B (Crystalline Dithianes). To a suspension of 1–1.5 equiv of potassium hydride in a solution of 1 mL of THF and 4 mL of HMPA cooled to 0 °C was added 1 equiv of the dithiane (0.2–0.8 mmol). After several minutes, the reaction mixture was warmed to room temperature and stirred for 2–2.5 h. The reaction mixture was worked up and the products were isolated as in method A.

3-(2-Methyl-1,3-dithian-2-yl)cyclohexanone (3a) from 2a. From 63 mg (0.29 mmol) of **2a** and 60 mg (22% in oil, 0.33 mmol) of potassium hydride was obtained 14 mg (23%) of a colorless oil, **3a**: IR (film) 3.49, 5.87, 6.94, 7.06, 7.89, 11.00, 12.71 μm; NMR (CCl_4) δ 1.20–2.58 (br, 11 H), 1.57 (s, 3 H), 2.60–2.97 (m, 4 H); mass spectrum, *m/e* (relative intensity) 230 (M^+, 8), 135 (10), 133 (100), 97 (5), 59 (22), 55 (6), 45 (5), 41 (17); exact mass calcd for $C_{11}H_{18}OS_2$ 230.0800, found 230.0779.

Attempted Rearrangement of 2b. From 95 mg (0.41 mmol) of **2b** and 90 mg (22% in oil, 0.50 mmol) of potassium hydride was obtained a crude yellow oil. TLC analysis (ether–pentane) showed a single nonpolar product corresponding to 2-methyl-1,3-dithiane.

3-(2-Methyl-1,3-dithian-2-yl)cyclopentanone (3c) from 2c. From 49 mg (0.23 mmol) of **2c** and 50 mg (22% in oil, 0.27 mmol) of potassium hydride was obtained 26 mg (53%) of a pale yellow oil, **3c**: IR (film) 3.38, 5.74, 7.07, 7.17, 8.55, 8.82, 11.00, 12.65, 13.10 μm; NMR (CCl_4) δ 1.70 (s, 3 H), 1.72–2.53 (br, 9 H), 2.67–3.07 (m, 4 H); mass spectrum, *m/e* (relative intensity) 216 (M^+, 14), 135 (9), 134 (6), 133 (100), 114 (8), 109 (6), 100 (10), 86 (7), 81 (8), 74 (26), 59 (35), 55 (9), 53 (8), 46 (10), 45 (11), 41 (19); exact mass calcd for $C_{10}H_{16}OS_2$ 216.0643, found 216.0634.

Attempted Rearrangement of 2d. From 133 mg (0.62 mmol) of **2d** and 120 mg (22% in oil, 0.66 mmol) of potassium hydride was obtained a crude oil. TLC and NMR showed a major nonpolar product corresponding to 1,3-dithiane. No rearrangement product was detectable. A residual amount of starting dithiane **2d** was present.

Attempted Rearrangement of 2e. From 22 mg (0.11 mmol) of **2e** and 26 mg (22% in oil, 0.14 mmol) of potassium hydride was obtained a crude yellow oil. TLC analysis (ether–pentane) showed a single nonpolar product corresponding to 2-methyl-1,3-dithiane.

3-(2-Methyl-1,3-dithian-2-yl)propiophenone (3f) from 2f. From 110 mg (0.41 mmol) of **2f** and 80 mg (22% in oil, 0.44 mmol) of potassium hydride was obtained 30 mg (27%) of light yellow oil, **3f**: IR (film) 3.37, 5.95, 6.28, 6.34, 6.94, 7.10, 7.33, 7.86, 8.29, 11.00, 13.35, 14.47 μm; NMR (CCl_4) δ 1.57 (s, 3 H), 1.68–3.32 (br, 10 H), 7.20–7.60 (m, 3 H), 7.75–8.05 (m, 2 H); mass spectrum, *m/e* (relative intensity) 266 (M^+, 2), 161 (10), 160 (39), 134 (19), 133 (100), 105 (63), 91 (14), 77 (31), 59 (10), 57 (11), 55 (76), 51 (12), 43 (22), 41 (16); exact mass calcd for $C_{14}H_{18}OS_2$ 266.0800, found 266.0805. 2-Methyl-1,3-dithiane (35 mg, 63%) was also obtained.

Attempted Rearrangement of 2g in HMPA. To a solution of 100 mg (0.30 mmol) of **2g** in 4 mL of HMPA and 1 mL of THF cooled to 0 °C was added 70 mg (20% in oil, 0.36 mmol) of potassium hydride. VPC (OV-101) and TLC analyses of an aliquot withdrawn immediately indicated the absence of starting material. The dark orange reaction mixture was warmed to room temperature, stirred for 5 min, and poured into 10 mL of H_2O overlaid with 10 mL of ether. After the mixture was shaken, the organic layer was separated, dried (Na_2SO_4), and concentrated. VPC and NMR, IR, and mass spectral analysis showed **2f** as the major product.

Rearrangement of 2g to 3f in THF. To a solution of 150 mg (0.44 mmol) of **2g** in 5 mL of THF at 0 °C was added 132 mg (20% in oil, 0.66 mmol) of potassium hydride. The reaction mixture was warmed to room temperature and after 10 min poured into 10 mL of H_2O overlaid with 10 mL of ether. After the mixture was shaken, the organic layer was separated, dried (Na_2SO_4), and concentrated. Preparative TLC (5% ether–pentane) afforded 30 mg (26%) of **3f** as a white solid, mp 46–48 °C.

α-(Hydroxymethylene)cyclotridecanone.[31] To a suspension of 2.50 g (57% dispersion in oil, 59.4 mmol) of sodium hydride in 100 mL of dry benzene was added 4.0 mL (3.7 g, 50 mmol) of ethyl formate and 4.40 g (22.4 mmol) of cyclotridecanone.[32] The reaction mixture was stirred at room temperature for 48 h. To the resulting semisolid gray mass was added 50 mL of 10% aqueous H_2SO_4, and the organic layer was separated. The aqueous layer was extracted with 20 mL of ether. The organic layers were combined, dried ($MgSO_4$), concentrated, and evaporatively distilled (oven temperature 120 °C (1 mm)), yielding 4.42 g (88%) of a light yellow oil, α-(hydroxymethylene)cyclotridecanone: IR (film) 3.10 (br), 3.34, 5.87, 6.11, 6.31, 6.87, 8.24 μm; NMR (CCl_4) δ 1.07–2.00 (br, 18 H), 2.00–2.58 (m, 4 H), 7.92 (d, 1 H, *J* = 7 Hz), 15.45 (d, 1 H, *J* = 7 Hz); mass spectrum, *m/e* (relative intensity) 224 (M^+, 8), 206 (8), 111 (23), 98 (30), 97 (21), 83 (31), 67 (27), 55 (94), 41 (100); exact mass calcd for $C_{14}H_{24}O_2$ 224.1776, found 224.1767.

1,5-Dithiaspiro[5.12]octadecan-7-one (5).[19] A solution of 4.05 g (18.1 mmol) of α-(hydroxymethylene)cyclotridecanone, 8.27 g (19.9 mmol) of trimethylene dithiotosylate,[37] and 5.10 g (52 mmol) of anhydrous potassium acetate in 150 mL of anhydrous methanol was refluxed for 10 h. The reaction mixture was cooled to room temperature and concentrated, and the residue was dissolved in 75 mL of H_2O overlaid with 50 mL of ether. The ether layer was

separated, washed with two 50-mL portions of H_2O, dried ($MgSO_4$), and concentrated. The resulting yellow oil was filtered through 50 g of silica gel. Short-column chromatography in three portions on 50 g of silica gel (5% ether–pentane) afforded 2.32 g (43%) of ketone **5** as a colorless oil which solidified upon cooling. Recrystallization from absolute ethanol yielded 2.21 g (41%) of **5** as white crystals: mp 51–53 °C; IR (CCl_4) 3.35, 5.86, 7.43, 7.86, 7.97, 11.00 μm; NMR (CCl_4) δ 1.05–1.58 (br, 16 H), 1.58–2.25 (m, 6 H), 2.25–3.23 (m, 6 H); mass spectrum, *m/e* (relative intensity) 300 (M^+, 11), 272 (41), 145 (100), 132 (32), 114 (26), 55 (36), 41 (60); exact mass calcd for $C_{16}H_{28}OS_2$ 300.1583, found 300.1607.

***trans*- and *cis*-7-Propenyl-1,5-dithiaspiro[5.12]octadecan-7-ols (6).** To a solution of 604 mg (2.01 mmol) of ketone **5** in 10 mL of ether cooled to 0 °C was added 2.0 mL (1.1 M in ether, 2.2 mmol) of 1-lithio-1-propene.[29] The reaction mixture was stirred for 30 min and then poured into 10 mL of H_2O. The ether layer was separated and the aqueous layer was extracted with 10 mL of ether. The ether layers were combined, dried (Na_2SO_4), and concentrated. The resulting crude oil was treated with 1-lithio-1-propene two additional times. Short-column chromatography on 50 g of silica gel (3% ether–pentane) yielded 214 mg (31%) of *trans*-**6**, a colorless solid: mp 70–73 °C; IR (film) 2.81, 3.37, 6.06 (w), 6.97, 7.57, 9.00, 13.1, 13.7 μm; NMR (CCl_4) δ 1.00–1.66 (br, 19 H), 1.67–2.25 (m, 5 H), 1.87 (crude d, 3 H, J = 6.5 Hz), 2.48–3.05 (m, 5 H), 5.32–5.77 (m, 2 H); mass spectrum, *m/e* (relative intensity) 342 (M^+, 13), 145 (23), 119 (86), 97 (15), 81 (18), 71 (21), 69 (91), 67 (27), 55 (54), 43 (36), 41 (100). Anal. Calcd for $C_{19}H_{34}OS_2$: C, 66.61; H, 10.00; S, 18.72. Found: C, 66.71; H, 9.96; S, 18.70. Also obtained was 118 mg (17%) of *cis*-**6**, a white solid: mp 64–67 °C; IR (film) 2.81, 3.37, 6.01 (w), 6.97, 7.57, 8.96, 13.7 (w) μm; NMR (CCl_4) δ 0.98–1.66 (br, 19 H), 1.67–2.18 (m, 5 H), 1.73 (crude d, 3 H, J = 6 Hz), 2.39–2.73 (m, 5 H), 5.43–5.93 (m, 2 H); mass spectrum, *m/e* (relative intensity) 342 (M^+, 18), 145 (26), 119 (99), 106 (20), 95 (18), 81 (26), 71 (22), 69 (100), 67 (31), 55 (52), 43 (41), 41 (92). Anal. Calcd for $C_{19}H_{34}OS_2$: C, 66.61; H, 10.00; S, 18.72. Found: C, 66.33; H, 9.95; S, 18.68. Recovered ketone **5** (289 mg, 48%) was also isolated.

7-Methyl-1,5-dithiaspiro[5.14]eicosan-9-one (7). To a solution of 127 mg (0.37 mmol) of allylic alcohol **6** in 1 mL of THF cooled to 0 °C was added a solution of 70 mg (22% in oil, 0.38 mmol) of potassium hydride in 4 mL of HMPA. The orange reaction mixture was warmed to room temperature and stirred for 2 h. The resulting solution was poured into 30 mL of saturated aqueous NaCl solution overlaid with 10 mL of ether. After the mixture was shaken, the ether layer was separated, washed with two 30-mL portions of H_2O, dried (Na_2SO_4), and concentrated. The crude product was purified by preparative TLC (7% ether–pentane), isolating the mobile UV-active band with highest R_f as 19 mg (15%) of **7**, a colorless oil which solidified upon cooling: mp 82–84 °C; IR (CCl_4) 3.35, 5.82, 6.89, 7.88, 8.95, 10.98 (w) μm; NMR (CCl_4) δ 0.92–1.58 (br, 17 H), 1.11 (d, 3 H, J = 7 Hz), 1.65–2.03 (m, 4 H), 2.66–2.99 (br m, 10 H); mass spectrum, *m/e* (relative intensity) 342 (M^+, 100), 236 (63), 235 (51), 145 (49), 106 (20), 81 (20), 69 (21), 55 (52), 41 (26); exact mass calcd for $C_{19}H_{34}OS_2$ 342.2053, found 342.2026. The mobile UV-active band with lower R_f was isolated as 20 mg (16%) of **12**, a colorless oil: IR (CCl_4) 3.38, 5.86, 5.99, 6.89, 7.98, 8.87, 9.51 μm; NMR (CCl_4) δ 1.10–1.38 (br with s at 1.28, 17 H), 1.83–2.60 (br m, 7 H), 2.60–3.00 (m, 4 H), 3.87 (crude t, 1 H, J = 6 Hz), 6–7 (scattered m); mass spectrum, *m/e* (relative intensity) 342 (M^+, 10), 133 (21), 121 (15), 119 (100), 107 (15), 106 (14), 95 (10), 87 (12), 84 (14), 81 (17), 73 (16), 69 (78), 67 (17), 57 (18), 55 (38), 45 (18), 43 (42), 41 (74).

DL-Muscone (11) from 7. A solution of 21 mg (0.61 mmol) of γ-keto dithiane **7** and 250 mg of a slurry of Raney nickel[33] in 5 mL of absolute ethanol was refluxed for 1 h. The reaction mixture was cooled, filtered through Celite, and concentrated. Short-column chromatography of the resulting oil on 10 g of silica gel (15% ether–pentane) yielded 6.1 mg (42%) of DL-muscone (**11**)[22] as a colorless oil: IR (CCl_4) 3.42, 3.51, 5.84, 6.86, 7.13, 7.28, 7.35, 7.42, 7.95, 8.92, 9.12, 9.84 μm; NMR (CCl_4) δ 0.92 (d, 3 H, J = 6.5 Hz), 1.05–1.76 (br, 23 H with s at 1.26), 1.80–2.17 (m, 2 H), 2.18–2.37 (m, 2 H). Also isolated was 5.3 mg (34%) of diketone **13** as a colorless oil: IR (CCl_4) 3.46, 3.55, 5.90, 6.92, 7.19, 7.35, 7.42, 7.45, 7.95, 8.01, 9.02 μm; NMR (CCl_4) δ 1.01 (d, 3 H, J = 8 Hz), 0.91–1.56 (br, 16 H with s at 1.23), 1.98–3.15 (br m, 7 H); mass spectrum, *m/e* (relative intensity) 252 (M^+, 80), 209 (26), 125 (54), 98 (30), 97 (44), 85 (87), 84 (33), 83 (35), 81 (31), 71 (48), 69 (72), 67 (28), 57 (34), 55 (100), 43 (64), 42 (31), 41 (92); exact mass calcd for $C_{16}H_{28}O_2$ 252.2091, found 252.2069.

7-Isopropenyl-1,5-dithiaspiro[5.12]octadecan-7-ol (8). To a solution of 512 mg (1.71 mmol) of ketone **5** in 10 mL of ether cooled to 0 °C was added 2.5 mL (0.75 M in ether, 1.9 mmol) of 2-lithiopropene.[29] The reaction mixture was stirred for 15 min and then poured into 10 mL of H_2O. The organic layer was separated, and the aqueous layer was extracted with 10 mL of ether. The organic layers were combined, dried (Na_2SO_4), and concentrated. The crude oil was treated with 2-lithiopropene and worked up as above four additional times. The resulting product was dissolved in 10 mL of ether, cooled to 0 °C, and treated with 100 mg (2.6 mmol) of lithium aluminum hydride.[39] After the mixture was stirred for 30 min, isopropyl alcohol was slowly added and then 1 mL of H_2O was added. The resulting slurry was filtered through Celite, dried (Na_2SO_4), and concentrated. The crude material was purified by preparative TLC (10% ether–pentane), isolating the UV-active band with highest R_f as 297 mg (51%) of allylic alcohol **8**, a colorless oil which solidified upon cooling: mp 52–55 °C; IR (film) 2.89, 3.44, 6.12, 6.94, 7.31, 7.51, 7.89, 8.70, 8.97, 11.12, 13.75 μm; NMR (CCl_4) δ 0.91–1.95 (br, 22 H), 1.97 (s, 3 H), 2.02–2.36 (m, 2 H), 2.55 (s, 1 H), 2.56–2.91 (m, 4 H), 4.98 (s, 1 H), 5.05 (s, 1 H); mass spectrum, *m/e* (relative intensity) 342 (M^+, 79), 267 (21), 257 (19), 145 (46), 132 (10), 121 (12), 119 (100), 107 (12), 106 (17), 97 (13), 95 (14), 81 (17), 73 (15), 71 (14), 69 (46), 67 (19), 55 (29), 43 (25), 41 (51); exact mass calcd for $C_{19}H_{34}OS_2$ 342.2053, found 342.2054. Isolation of the UV-active band of lower R_f afforded 163 mg (32%) of 1,5-dithiaspiro[5.12]octadecan-7-ol as a colorless oil: IR (film) 2.86, 3.41, 6.90, 6.96, 7.88, 11.00 μm; NMR (CCl_4) δ 1.09–1.80 (br, 22 H), 1.80–2.07 (m, 2 H), 2.48 (s, 1 H), 2.52–2.70 (m, 2 H), 2.77–3.00 (m, 2 H), 3.64–3.82 (m, 1 H); mass spectrum, *m/e* (relative intensity) 302 (M^+, 23), 199 (14), 145 (11), 121 (23), 119 (100), 117 (47), 106 (14), 95 (10), 82 (18), 81 (11), 75 (11), 73 (12), 67 (13), 55 (21), 47 (17), 43 (19), 41 (28); exact mass calcd for $C_{16}H_{30}OS_2$ 302.1740, found 302.1728.

8-Methyl-1,5-dithiaspiro[5.14]eicosan-9-one (9). To a solution of 100 mg (0.29 mmol) of allylic alcohol **8** in 1 mL of THF cooled to 0 °C was added a solution of 65 mg (22% in oil, 0.36 mmol) of potassium hydride in 4 mL of HMPA. The yellow reaction mixture was warmed to room temperature and after 2 h poured into 30 mL of saturated aqueous NaCl solution overlaid with 15 mL of ether. After the mixture was shaken, the organic layer was separated, washed with two 30-mL portions of H_2O, dried (Na_2SO_4), and concentrated. The crude material was purified by preparative TLC (5% ether–pentane), isolating the mobile UV-active band with highest R_f as 28 mg (28%) of **9**, a colorless oil: IR (film) 3.41, 5.85, 6.89, 7.08, 7.32, 7.90, 8.11, 9.01, 10.99 μm; NMR (CCl_4) δ 1.15 (d, 3 H, J = 7 Hz), 1.15–1.61 (br, 18 H with s at 1.28), 1.61–2.05 (m, 6 H), 2.42 (t, 2 H, J = 6 Hz), 2.50–2.93 (m, 5 H); mass spectrum, *m/e* (relative intensity) 342 (M^+, 22), 239 (17), 236 (62), 235 (60), 109 (22), 107 (16), 106 (20), 97 (22), 95 (27), 83 (18), 81 (43), 79 (18), 71 (17), 69 (44), 68 (17), 67 (47), 57 (30), 55 (95), 43 (76), 41 (100); exact mass calcd for $C_{19}H_{34}OS_2$ 342.2053, found 342.2058.

8-Methyl-1,5-dithiaspiro[5.14]eicosane (10).[34] A solution of 21 mg (0.061 mmol) of γ-keto dithiane **9** and 100 mg (1.8 mmol) of potassium hydroxide in 0.5 mL of hydrazine hydrate (85% in water) and 5 mL of triethylene glycol was heated to reflux (160 °C) for 2 h. The reaction flask was opened and heating continued until the pot temperature reached 180 °C. The condenser was replaced and heating was continued for an additional 4 h. The reaction mixture was cooled to room temperature, poured into 25 mL of 10% aqueous HCl solution, and extracted with 10 mL of pentane. The pentane layer was washed with 25 mL of saturated aqueous $NaHCO_3$ solution, and the aqueous layer was extracted with three 20-mL portions of pentane. The pentane layers were combined, dried (Na_2SO_4), and concentrated. The crude material was purified by preparative TLC (5% ether–pentane), isolating the mobile UV-active band with highest R_f as 8.2 mg (41%) of 8-methyl-1,5-dithiaspiro[5.14]eicosane (**10**), a colorless oil: IR (CCl_4) 3.40, 6.89, 7.98, 9.1 (br), 9.81, 11.00 μm; NMR (CCl_4) δ 0.85 (crude d, 3 H, J = 6.5 Hz), 1.09–1.60 (br, 23 H), 1.88–2.27 (m, 6 H), 2.50–2.89 (m, 4 H); mass spectrum, *m/e* (relative in-

tensity) 328 (M^+, 21), 253 (23), 145 (51), 119 (36), 111 (27), 109 (23), 107 (31), 106 (28), 97 (27), 95 (37), 83 (28), 81 (54), 79 (25), 73 (33), 71 (28), 69 (48), 67 (48), 57 (37), 55 (93), 43 (57), 41 (100); exact mass calcd for $C_{19}H_{36}S_2$ 328.22586, found 328.22519.

DL-**Muscone (11) from 10.**[35] To a solution of 5.6 mg (0.017 mmol) of 8-methyl-1,5-dithiaspiro[5.14]eicosane (**10**) in 2 mL of 15% aqueous THF was added 15 mg (0.069 mmol) of red mercuric oxide and then 3 drops of boron trifluoride etherate. The reaction mixture was rapidly stirred for 1.5 h at room temperature and then diluted with 10 mL of ether. The mixture was filtered through Celite. The filtrate was washed with 10 mL of saturated aqueous $NaHCO_3$ solution, dried (Na_2SO_4), and concentrated. The residue was filtered through silica gel to yield 2.9 mg (72%) of DL-muscone (**11**) as a colorless oil; IR and NMR spectra were similar to those of a sample prepared from **7**.

Tris(pyrrolidinyl)phosphoramide (TPPA).[36] To a solution of 10.0 mL (16.7 g, 109 mmol) of phosphorus oxychloride in 50 mL of ether cooled to 0 °C was added dropwise over 3 h 55 mL (46.9 g, 660 mmol) of pyrrolidine. A white precipitate formed upon addition. The reaction mixture was warmed to room temperature and stirred for 12 h. The resulting slurry was filtered and the filtrate was concentrated. The crude material was stirred at 100 °C over CaH_2 for 12 h and then distilled, yielding 15.1 g (54%) of TPPA, bp 131–133 °C (1 mm), a very hygroscopic pale yellow viscous liquid, which darkened upon standing: IR (CCl_4) 3.32, 3.44, 6.89, 7.49, 7.79, 8.25, 8.90, 9.30, 9.89, 10.95, 11.45 μm; NMR (CCl_4) δ 1.61–2.03 (m, 4 H), 2.92–3.30 (m, 4 H); mass spectrum, *m/e* (relative intensity) 257 (M^+, 15), 188 (9), 187 (30), 145 (5), 118 (8), 117 (6), 116 (6), 72 (13), 71 (29), 70 (100), 43 (7), 42 (7), 41 (7).

***cis*- and *trans*-2-(Thiophenyl)-1-vinyl-1-cyclododecanols (15 and 16). A. From Vinylmagnesium Bromide.** To a solution of 1.86 g (6.14 mmol) of 2-(thiophenyl)cyclododecanone[25] in 15 mL of THF cooled to 0 °C was added 5.6 mL (1.2 M in THF, 6.7 mmol) of vinylmagnesium bromide. After 30 min, the reaction mixture was poured into 50 mL of ice-cold 5% aqueous NH_4Cl solution and extracted with 25 mL of pentane. The organic layer was separated, washed with 50 mL of H_2O, dried (Na_2SO_4), and concentrated, yielding a yellow oil. VPC analysis (OV-101, 245 °C) showed three components in a 59:16:25 area ratio, corresponding to starting material, **15**, and **16**, respectively. The crude material was treated two additional times with vinylmagnesium bromide as described above and then dissolved in 15 mL of ether. The solution was cooled to 0 °C and 240 mg (6.3 mmol) of lithium aluminum hydride was added.[39] After 30 min, the reaction mixture was quenched with isopropyl alcohol followed by H_2O. The resulting slurry was filtered through Celite/$MgSO_4$. The filtrate was concentrated and the crude oily product was chromatographed on 100 g of silica gel (3% ether–pentane), yielding 402 mg (21%) of **15** as a colorless oil which solidified upon cooling: mp 42–44 °C; IR (film) 2.88, 3.42, 3.53, 6.33, 6.84, 6.96, 9.74, 10.06, 10.81, 13.46, 14.50 μm; NMR (CCl_4) δ 0.95–1.70 (br, 16 H), 1.72–2.09 (m, 5 H), 3.13 (d, 1 H, J = 10.5 Hz), 4.84 (dd, 1 H, J_{ab} = 10.5, J_{bc} = 1.5 Hz), 5.23 (dd, 1 H, J_{ac} = 17, J_{bc} = 1.5 Hz), 5.53 (dd, 1 H, J_{ac} = 17, J_{ab} = 10.5 Hz), 7.02–7.41 (m, 5 H); mass spectrum, *m/e* (relative intensity) 318 (M^+, 60), 209 (28), 123 (29), 111 (19), 110 (85), 109 (26), 95 (18), 83 (30), 81 (20), 69 (20), 67 (15), 59 (20), 57 (21), 55 (100); exact mass calcd for $C_{20}H_{30}SO$ 318.2019, found 318.2007. Also isolated was 590 mg (31%) of **16** as a colorless oil which solidified upon cooling: mp 55–57 °C; IR (film) 2.89, 3.43, 3.52, 6.33, 6.83, 6.94, 9.77, 10.02, 10.14, 10.90, 13.5, 14.29, 14.54, μm; NMR (CCl_4) δ 1.00–2.02 (br with s at 1.34, 20 H), 2.75 (s, 1 H), 3.38 (d, 1 H, J = 11 Hz), 5.07 (dd, 1 H, J_{ab} = 10.5, J_{bc} = 1.5 Hz), 5.50 (dd, 1 H, J_{ac} = 17, J_{bc} = 1.5 Hz), 5.84 (dd, 1 H, J_{ab} = 10.5, J_{bc} = 17 Hz), 7.02–7.27 (m, 3 H), 7.32–7.46 (m, 2 H); mass spectrum, *m/e* (relative intensity) 318 (M^+, 83), 209 (33), 123 (28), 111 (15), 110 (90), 109 (27), 95 (18), 83 (29), 81 (19), 69 (27), 67 (22), 57 (26), 55 (100); exact mass calcd for $C_{20}H_{30}SO$ 318.2019, found 318.1905.

B. From Vinyllithium.[38] To a solution of 101 mg (0.348 mmol) of α-(thiophenyl)cyclododecanone[25] in 5 mL of THF cooled to 0 °C was added 0.25 mL (1.7 M in THF, 0.42 mmol) of vinyllithium. The reaction was stirred for 10 min, and then poured into 20 mL of H_2O, and extracted with 10 mL of ether. The organic layer was washed with two 20-mL portions of H_2O, dried (Na_2SO_4), and concentrated, yielding a colorless oil. VPC analysis (OV-101, 245 °C) showed three components in a 19:8:73 area ratio, corresponding to starting material, **15**, **16**, respectively. The crude material was treated two additional times with vinyllithium as described above. VPC analysis showed 95% addition product and 5% starting ketone. Purification by preparative TLC (10% ether–pentane), isolating the UV-active band of lower R_f, afforded 88 mg (80%) of **16**.

1,2-Epoxy-1-vinylcyclododecene (17) from 16. To a suspension of 45 mg (22% in oil, 0.25 mmol) of potassium hydride in a mixture of 1 mL of THF and 4 mL of HMPA cooled to 0 °C was added 70 mg (0.22 mmol) of alcohol **16**. The reaction mixture was warmed to room temperature, stirred for 48 h, poured into 30 mL of saturated aqueous NaCl solution, and extracted with 10 mL of pentane. The organic layer was washed with two 30-mL portions of H_2O, dried (Na_2SO_4), and concentrated. The resulting oil was purified by preparative TLC (20% ether–pentane), isolating the band of higher R_f as 14 mg (30%) of epoxide **17**, a colorless oil: IR (film) 3.44, 3.54, 6.89, 6.98, 7.18, 10.15, 10.29, 10.82 μm; NMR (CCl_4) δ 0.91–1.68 (br, 20 H), 2.90 (dd, 1 H, J_{ab} = 10, J_{ac} = 3 Hz), 5.13–5.30 (m, 2 H), 5.91 (dd, 1 H, J_{ab} = 17, J_{ac} = 11 Hz); mass spectrum, *m/e* (relative intensity) 208 (M^+, 1), 109 (12), 98 (13), 97 (20), 96 (16), 95 (30), 93 (11), 83 (38), 81 (36), 79 (23), 71 (20), 70 (25), 69 (25), 68 (27), 67 (51), 57 (54), 55 (100), 54 (35), 53 (24); exact mass calcd for $C_{14}H_{24}O$ 208.1828, found 208.1811. The UV-active band of lower R_f was isolated as 38 mg (54%) of starting alcohol **16**.

α-(Hydroxymethylene)cyclododecanone[31] was prepared from 5.0 g (57% dispersion, 119 mmol) of sodium hydride, 8.5 mL (105 mmol) of ethyl formate, and 8.20 g (45 mmol) of cyclododecanone in 200 mL of benzene. After the mixture was stirred for 48 h at room temperature, it was worked up by a method similar to that for the preparation of α-(hydroxymethylene)cyclotridecanone. Evaporative distillation (135–140 °C (1 mm)) yielded 7.86 g (84%) of α-(hydroxymethylene)-cyclododecanone as a light yellow oil: IR (film) 3.3–2.75 (br), 3.40, 5.86, 6.25 (br), 6.80, 6.95, 7.35, 8.25, 9.8 μm; NMR (CCl_4) δ 1.18–1.86 (br s, 16 H), 2.09–2.55 (m, 4 H), 8.81 (s, 1 H), 15.43 (s, 1 H); mass spectrum, *m/e* (relative intensity) 210 (M^+, 17), 125 (16), 111 (33), 98 (58), 83 (43), 55 (100), 43 (55), 41 (94); exact mass calcd for $C_{13}H_{22}O_2$ 210.1621, found 210.1609.

1,4-Dithiaspiro[4.11]hexadecan-6-one (20a) was prepared from 7.80 g (37 mmol) of α-(hydroxymethylene)cyclododecanone, 12.1 g (30 mmol) of ethylene dithiotosylate,[37] and 8.33 (85 mmol) of anhydrous potassium acetate in 200 mL of refluxing absolute methanol for 10 h by a method similar to the preparation of **5**. Chromatography on 250 g of silica gel (10% ether–pentane) and recrystallization from absolute ethanol afforded 3.05 g (37%) of **20a** as white crystals: mp 101–103 °C; IR (CCl_4) 3.42, 5.85, 6.8, 6.92, 8.9 μm; NMR (CCl_4) δ 1.11–1.41 (br s, 14 H), 1.61–1.75 (m, 2 H), 2.11–2.23 (m, 2 H), 2.73 (t, 2 H, J = 5.5 Hz), 2.95–3.23 (m, 4 H); mass spectrum, *m/e* (relative intensity) 272 (M^+, 21), 244 (23), 216 (24), 183 (21), 131 (100), 55 (15), 41 (25); exact mass calcd for $C_{14}H_{24}OS_2$ 272.1270, found 272.1258.

***cis*- and *trans*-6-Propenyl-1,4-dithiaspiro[4.11]hexadecan-6-ols (21a).** To a solution of 500 mg (1.84 mmol) of **20a** in 10 mL of ether at 0 °C was added 3.2 mL (0.63 M in ether, 2 mmol) of 1-lithio-1-propene.[29] The reaction mixture was stirred for 45 min and then poured into 10 mL of H_2O. The organic layer was separated, dried (Na_2SO_4), and concentrated. VPC analysis (OV-101, 230 °C) showed the ketone:alcohol area ratio as 55:45. The resulting material was treated with 1-lithio-1-propene and worked up as above three additional times. This crude oil was dissolved in 15 mL of ether and 1.5–2.0 equiv of lithium aluminum hydride was added.[39] After 45 min, 2 mL of isopropyl alcohol and then 2 mL of H_2O were added. The solution was filtered through Celite; the organic layer was separated, dried (Na_2SO_4), and concentrated. Purification by preparative TLC (15% ether–pentane), isolating the UV-active band of higher R_f, yielded 230 mg (40%) of **21a** as a light yellow oil: IR (film) 2.88 (br), 3.45, 6.05 (w), 6.80, 6.95, 7.87, 10.45, 13.33 μm; NMR (CCl_4) δ 1.14–1.59 (br s, 18 H), 1.70 (d, 2 H, J = 6 Hz), 1.84 (d, 1 H, J = 6 Hz), 1.91–2.14 (m, 2 H), 2.16 (s, $^2/_3$ H), 2.36 (s, $^1/_3$ H), 3.02–3.18 (m, 4 H), 3.36–3.82 (m, 2 H); mass spectrum, *m/e* (relative intensity) 314 (M^+, 28), 255 (12), 253 (15), 131 (31), 105 (100), 97 (18), 69 (63), 55 (22), 41 (32); exact mass calcd for $C_{17}H_{30}OS_2$ 314.1740, found 314.1720. Also isolated was 52 mg (10%) of 1,4-dithia-

spiro[4.11]hexadecan-6-ol as a white solid: mp 105–110 °C; IR (CCl_4) 2.86, 3.42, 6.80, 6.94, 7.19 (w), 7.41 (w), 9.9 μm; NMR (CCl_4) δ 1.14–1.75 (br s, 19 H), 2.05–2.18 (m, 2 H), 3.05–3.36 (m, 4 H), 3.70–3.82 (m, 1 H); mass spectrum, *m/e* (relative intensity) 274 (M^+, 31), 213 (16), 131 (19), 105 (100), 92 (16), 61 (11), 55 (12), 41 (17); exact mass calcd for $C_{14}H_{26}OS_2$ 274.14252, found 274.14206.

1,4-Dithiaspiro[4.12]heptadecan-6-one (22a) was prepared from 2.61 g (11.7 mmol) of α-(hydroxymethylene)cyclotridecanone, 4.82 g (12.0 mmol) of ethylene dithiotosylate,[37] and 3.43 g (35.0 mmol) of anhydrous potassium acetate in 100 mL of refluxing absolute methanol for 15 h by a method similar to the preparation of **5**. Chromatography on silica gel (5% ether–pentane) and recrystallization from ethanol yielded 1.12 g (33%) of **22a** as pale yellow needles: mp 71.0–72.5 °C; IR (KBr) 3.40, 5.87, 6.86, 7.16, 7.40, 7.65, 7.90, 8.58, 9.10, 9.25, 9.75, 10.51, 11.31, 13.32, 14.00, 14.62 μm; NMR (CCl_4) δ 1.18–1.36 (br s, 16 H), 1.57–1.73 (m, 2 H), 2.10–2.22 (m, 2 H), 2.73 (t, 2 H, J = 6 Hz), 3.07–3.26 (m, 4 H); mass spectrum, *m/e* (relative intensity) 286 (M^+, 17), 258 (12), 230 (17), 197 (34), 131 (100), 118 (21), 105 (15), 55 (30), 41 (44); exact mass calcd for $C_{15}H_{26}OS_2$ 286.14252, found 286.14240.

***cis*- and *trans*-6-Propenyl-1,4-dithiaspiro[4.12]heptadecan-6-ols (23a)** were prepared by a single treatment of 370 mg (1.29 mmol) of ketone **22a** with 8.3 mL (0.18 M in ether, 1.5 mmol) of 1-lithio-1-propene[29] in ether solution as described for the preparation of **21a**. VPC analysis (OV-101, 230 °C) showed the alcohol:ketone ratio as 88:12. Purification by preparative TLC (10% ether–pentane) yielded 295 mg (70%) of **23a** as a colorless oil: IR (film) 2.75, 3.35, 5.95 (w), 6.80, 6.89, 10.25 μm; NMR (CCl_4) δ 1.18–1.39 (br s, 20 H), 1.41–1.55 (m, 2 H), 1.61 (d, 3 H, J = 5 Hz), 2.30 (s, 1 H), 3.09 (s, 4 H), 5.45–5.86 (m, 2 H); mass spectrum, *m/e* (relative intensity) 328 (M^+, 10), 300 (5), 267 (12), 250 (9), 137 (10), 131 (31), 105 (100), 97 (19), 69 (52), 55 (32); exact mass calcd for $C_{18}H_{32}OS_2$ 328.18945, found 328.18982.

Attempted Rearrangement of 23a. From 230 mg (0.70 mmol) of **23a** and 210 mg (20% in oil, 1.0 mmol) of potassium hydride by the rearrangement procedure described for **6** was obtained a yellow oil. VPC, TLC, and NMR analysis showed no detectable rearranged product or starting material.

1-(Butylthio)-2-butylcyclotridecene (27). To a solution of 200 mg (0.70 mmol) of ketone **21a** in 10 mL of ether was added 1 mL (2.4 M in hexane, 2.4 mmol) of *n*-butyllithium at room temperature. The reaction mixture was stirred for 5 h and then poured into 20 mL of water. The organic layer was separated, dried ($MgSO_4$), and concentrated to yield 210 mg of a yellow oil. The UV-active band at highest R_f was isolated by preparative TLC (hexane) to yield 124 mg (55%) of **27** as a colorless oil: IR (film) 3.42, 6.87, 7.30 (w), 7.43 (w), 9.26 (w), 14.10 μm; NMR (CCl_4) δ 0.91 (t, 6 H), 1.18–1.57 (br, 26 H), 1.91 (m, 2 H), 2.09 (m, 2 H), 2.25 (m, 2 H), 2.45 (t, J = 7 Hz, 2 H); mass spectrum, *m/e* (relative intensity) 324 (M^+, 44), 281 (17), 267 (100), 211 (5), 186 (4), 95 (32), 81 (41), 67 (51), 55 (81), 41 (95); exact mass calcd for $C_{21}H_{40}S$ 324.28506, found: 324.285.

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Registry No. *trans*-1, 40615-41-6; *cis*-1, 40615-42-7; **2a**, 15040-92-3; **2b**, 68984-50-9; **2c**, 68984-49-6; **2d**, 53178-46-4; **2e**, 62163-03-5; **2f**, 68984-53-2; **2g**, 73397-69-0; **3a**, 68984-52-1; **3c**, 68984-51-0; **3f**, 73397-70-3; **4**, 4883-01-6; **5**, 68984-55-4; (±)-*cis*-**6**, 73397-71-4; (±)-*trans*-**6**, 73397-72-5; (±)-**7**, 68984-58-7; (±)-**8**, 73397-73-6; (±)-**9**, 73453-96-0; (±)-**10**, 73453-97-1; **12**, 68914-27-2; (±)-**13**, 68984-60-1; **14**, 52190-43-9; **15**, 73397-74-7; **16**, 73465-26-6; **17**, 53601-11-9; **18a**, 51310-03-3; **18b**, 51310-07-7; **18c**, 73194-43-1; **20a**, 73454-01-0; **20b**, 73194-44-2; *cis*-**21a**, 73397-75-8; *trans*-**21a**, 73397-76-9; **22a**, 73397-77-0; **22b**, 68984-55-4; *cis*-**23a**, 73397-78-1; *trans*-**23a**, 73397-79-2; **23b**, 73397-80-5; **27**, 73397-81-6; 4-*tert*-butylcyclohexanone, 98-53-3; 1,3-dithiane, 505-23-7; vinyl bromide, 593-60-2; (α-bromovinyl)trimethylsilane, 13683-41-5; 2-methyl-1,3-dithiane, 6007-26-7; α-(hydroxymethylene)cyclotridecanone, 73397-82-7; ethyl formate, 109-94-4; trimethylene dithiotosylate, 3866-79-3; 1-lithio-1-propene, 29283-76-9; 2-lithiopropene, 3052-45-7; 1,5-dithiaspiro[5.12]-octadecan-7-ol, 73397-83-8; TPPA, 6415-07-2; phosphorus oxychloride, 10025-87-3; 2-(thiophenyl)cyclododecanone, 52190-43-9; vinyllithium, 917-57-7; cyclododecanone, 830-13-7; α-(hydroxymethylene)cyclododecanone, 949-07-5; ethylene dithiotosylate, 2225-23-2; pyrrolidine, 123-75-1.

Synthesis of the First Crystalline Thiaanthracenes, 9-Cyano- and 9-(Ethoxycarbonyl)-10-methyl-10-thiaanthracenes, and Their Reactions with Electrophiles[1]

Mikio Hori,* Tadashi Kataoka, Hiroshi Shimizu, and Sachio Ohno

Gifu College of Pharmacy, 5-6-1, Mitahora-Higashi, Gifu 502, Japan

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The isolable and crystalline thiaanthracene derivatives 9-cyano- (**9**) and 9-(ethoxycarbonyl)-10-methyl-10-thiaanthracene (**12**) were synthesized in high yield for the first time by proton abstraction from the corresponding thioxanthenium salts (**8a** or **8b** and **11**) with sodium hydride in THF under a nitrogen atmosphere. Upon standing in THF at 50 °C, thiaanthracenes **9** and **12** underwent thermal 1,4-rearrangement to give the corresponding thioxanthenes **13** and **14**, respectively. The ylidic property of the thiaanthracenes was manifested by spectral and chemical evidences. Reactions of the thiaanthracenes with electrophiles such as dimethyl acetylenedicarboxylate and tetracyanoethylene are also described together with the course of the reactions.

The chemistry of thiabenzenes[2] has attracted interest since Price et al. reported the synthesis of 1,2,4,6-tetraphenylthiabenzene from the reaction of 2,4,6-triphenylthiopyrylium perchlorate and phenyllithium.[3] In recent

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