[3,3]Sigmatropic Ring Expansion of Cyclic Thionocarbonates. IV.[1] Relationship between Ring Size of Cyclic Thionocarbonates and Geometry of Created Double Bond in Medium- and Large-Membered Thiolcarbonates

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Medium- and large-membered cyclic thiolcarbonates containing an (*E*)- or (*Z*)-double bond were synthesized by two methods using [3,3]sigmatropic ring expansion of cyclic thionocarbonates. The [3,3]sigmatropic ring expansion proceeds exclusively *via* the transition state bearing the chain tethered in a *cis* relationship when the cyclic thionocarbonates are 8-membered or smaller. Importantly, the ring size of the cyclic thionocarbonate determines the double bond geometry of the thiolcarbonate.

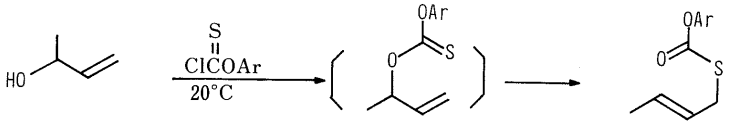
Conversion of the cyclic thiolcarbonates into (*E*)- or (*Z*)-allylic sulfides is also described.

Keywords [3,3]sigmatropic rearrangement; cyclic thionocarbonate; cyclic thiolcarbonate; ring expansion; (*Z*)-selectivity; (*E*)-selectivity; (*Z*)-allylic sulfide; (*E*)-allylic sulfide; 1,1′-thiocarbonyldi-2,2′-pyridone; sodium bis(trimethylsilyl) amide

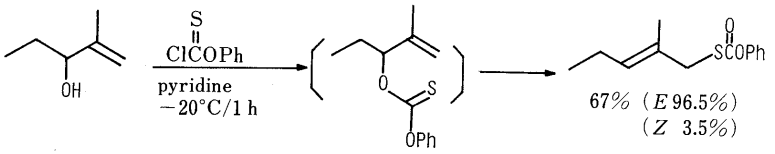
The exclusive (*E*)-selectivity of the double bond created by [3,3]sigmatropic rearrangement[2] has been extensively used for natural product synthesis.[3] However, few synthetic studies on the opposite (*Z*)-selective [3,3]sigmatropic rearrangement have been so far reported, probably owing to the lack of suitable methodology.[4] Garmaise and co-workers reported[5a] that the reaction of allyl alcohols with aryl chlorothionoformates yielded *S*-allyl aryl thiolcarbonates (Chart 1, Eq. 1). Faulkner and Peterson showed[5b] that treatment of 2-methyl-1-penten-3-ol with phenyl chlorothionoformate in pyridine at −20 °C afforded phenyl 2-methyl-2-pentenyl thiolcarbonate containing 96.5% (*E*)-olefin and 3.5% (*Z*)-olefin by rearrangement of the intermediate allylic thionocarbonate (Chart 1, Eq. 2).

Recently, we reported[6] that treatment of a diol monothionocarbonate (**5d**, $n=4$) with sodium hydride (NaH) or lithium diisopropylamide (LDA) resulted in the formation of an 8-membered thionocarbonate intermediate (**7d**) followed by spontaneous [3,3]-sigmatropic ring expansion to give a 10-membered heterocyclic thiolcarbonate (**8d**) containing a (*Z*)-double bond. This was easily converted into (*Z*)-allylic sulfides (**13** and **16**) of a type which has been widely used as intermediates for the formation of carbon–carbon bonds in organic synthesis.[7] We report herein the relationship between the ring size of cyclic thionocarbonates (**7**) and the geometry of the created double bond in medium- and large-membered thiolcarbonates (**8**), which could be prepared by two methods. We also present a full account of the work reported in a previous communication.[6] To our knowledge, there has been no previous report of a systematic study on [3,3]sigmatropic rearrangement applied in this fashion.[8]

Synthesis of Diol Monothionocarbonates (5a—g) The diol monothionocarbonates (**5c—g**) used in the present study were synthesized starting from commercially available ω-diols (**1**) *via* the three-step sequence outlined in Chart 2.



Eq. 1



Eq. 2

Chart 1

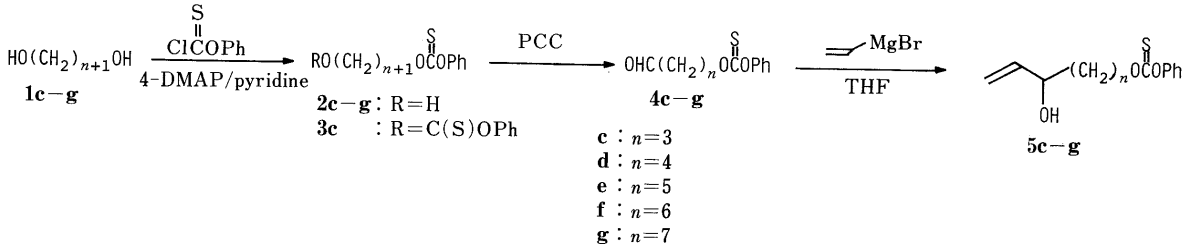


Chart 2

TABLE I. Yields and ^{1}H-NMR Spectral Data of Monothionocarbonates (**2**), Aldehydes (**4**), and Diol Monothionocarbonates (**5**)[a]

Compound No.	Yield (%)	^{1}H-NMR δ ($CDCl_3$, ppm)
2c	58	1.60—2.0 (4H, m, 2 × CH_2), 3.69 (2H, t, J=6.2 Hz, C$\underline{H}_2$OH), 4.54 (2H, t, J=6.4 Hz, CH_2O), 7.0—7.50 (5H, m, Ar-H)
2d	49	1.41—1.94 (6H, m, 3 × CH_2), 3.64 (2H, t, J=7.5 Hz, C$\underline{H}_2$OH), 4.51 (2H, t, J=7.5 Hz, CH_2O), 7.03—7.47 (5H, m, Ar-H)
2e	44	1.30—1.95 (8H, m, 4 × CH_2), 3.63 (2H, t, J=5.5 Hz, C$\underline{H}_2$OH), 4.50 (2H, t, J=5.5 Hz, CH_2O), 7.0—7.50 (5H, m, Ar-H)
2f	45	1.30—1.90 (10H, m, 5 × CH_2), 3.62 (2H, t, J=7.5 Hz, C$\underline{H}_2$OH), 4.49 (2H, t, J=8.0 Hz, CH_2O), 7.0—7.45 (5H, m, Ar-H)
2g	48	1.10—1.90 (12H, m, 6 × CH_2), 3.62 (2H, t, J=5.5 Hz, C$\underline{H}_2$OH), 4.49 (2H, t, J=5.5 Hz, CH_2O), 7.01—7.46 (5H, m, Ar-H)
4c	70	2.14 (2H, quint, J=5.5 Hz, CH_2), 2.64 (2H, t, J=6.0 Hz, C$\underline{H}_2$CHO), 4.54 (2H, t, J=5.5 Hz, CH_2O), 7.0—7.50 (5H, m, Ar-H), 9.81 (1H, s, CHO)
4d	68	1.68—1.96 (4H, m, 2 × CH_2), 2.51 (2H, t, J=5.0 Hz, C$\underline{H}_2$CHO), 4.52 (2H, t, J=5.0 Hz, CH_2O), 7.04—7.47 (5H, m, Ar-H), 9.78 (1H, s, CHO)
4e	63	1.35—1.95 (6H, m, 3 × CH_2), 2.44 (2H, t, J=6.0 Hz, C$\underline{H}_2$CHO), 4.51 (2H, t, J=5.5 Hz, CH_2O), 7.05—7.50 (5H, m, Ar-H), 9.77 (1H, s, CHO)
4f	58	1.18—1.92 (8H, m, 4 × CH_2), 2.45 (2H, t, J=9.0 Hz, C$\underline{H}_2$CHO), 4.51 (2H, t, J=8.0 Hz, CH_2O), 7.02—7.48 (5H, m, Ar-H), 9.77 (1H, s, CHO)
4g	63	1.13—1.92 (10H, m, 5 × CH_2), 2.41 (2H, t, J=6.0 Hz, C$\underline{H}_2$CHO), 4.48 (2H, t, J=6.0 Hz, CH_2O), 7.02—7.46 (5H, m, Ar-H), 9.76 (1H, s, CHO)
5a[b,c]	57	4.43 (1H, dd, J=11.4, 8.3 Hz, C$\underline{H}$OH), 4.59 (2H, dt, J=8.4, 3.2 Hz, CH_2O), 5.31 (1H, dt, J=10.6, 1.3 Hz, H⟩=⟨H), 5.46 (1H, J=17.2, 1.3 Hz, H⟩=⟨H), 5.92 (1H, ddd, J=17.2, 10.6, 5.3 Hz, =CH), 7.03—7.48 (5H, m, Ar-H)
5b[b]	76	1.90—2.15 (2H, m, CH_2), 4.32 (1H, br, C$\underline{H}$OH), 4.67 (2H, m, CH_2O), 5.17 (1H, d, J=11.0 Hz, H⟩=⟨H), 5.30 (1H, d, J=16.0 Hz, H⟩=⟨H), 5.92 (1H, ddd, J=16.0, 11.0, 7.0 Hz, =CH), 7.0—7.55 (5H, m, Ar-H)
5c	61	1.50—2.10 (4H, m, 2 × CH_2), 4.15 (1H, br, C$\underline{H}$OH), 4.55 (2H, t, J=5.5 Hz, CH_2O), 5.13 (1H, d, J=10.0 Hz, H⟩=⟨H),
	(47)[d]	5.23 (1H, d, J=16.0 Hz, H⟩=⟨H), 5.74 (1H, ddd, J=16.0, 10.0, 7.0, =CH), 7.0—7.50 (5H, m, Ar-H)
5d	70	1.40—1.60 (4H, m, 2 × CH_2), 1.85 (2H, quint, J=7.0 Hz, C$\underline{H}_2$CHOH), 4.12 (1H, br, C$\underline{H}$OH), 4.52 (2H, t, J=7.0 Hz,
	(75)[d]	CH_2O), 5.12 (1H, d, J=10.2 Hz, H⟩=⟨H), 5.21 (1H, d, J=18.0 Hz, H⟩=⟨H), 5.87 (1H, ddd, J=18.0, 10.0, 7.0 Hz, =CH), 7.05—7.50 (5H, m, Ar-H)
5e	55	1.30—1.95 (8H, m, 4 × CH_2), 4.10 (1H, br, C$\underline{H}$OH), 4.50 (2H, t, J=6.0 Hz, CH_2O), 5.10 (1H, d, J=10.5 Hz, H⟩=⟨H), 5.22 (1H, d, J=18.5 Hz, H⟩=⟨H), 5.83 (1H, ddd, J=18.5, 10.5, 6.0 Hz, =CH), 7.05—7.45 (5H, m, Ar-H)
5f	69	1.0—1.90 (10H, m, 5 × CH_2), 3.92—4.17 (1H, br, C$\underline{H}$OH), 4.49 (2H, t, J=8.0 Hz, CH_2O), 5.09 (1H, d, J=12.0 Hz, H⟩=⟨H), 5.20 (1H, d, J=18.0 Hz, H⟩=⟨H), 5.85 (1H, ddd, J=18.0, 12.0, 7.0 Hz, =CH), 6.9—7.48 (5H, m, Ar-H)
5g	61	1.15—1.98 (12H, m, 6 × CH_2), 4.08 (1H, br, C$\underline{H}$OH), 4.48 (2H, t, J=6.0 Hz, CH_2O), 5.08 (1H, d, J=12.0 Hz, H⟩=⟨H), 5.19 (1H, d, J=18.0 Hz, H⟩=⟨H), 5.85 (1H, ddd, J=18.0, 12.0, 7.0 Hz, =CH), 7.0—7.45 (5H, m, Ar-H)

a) Diol monothionocarbonates (**5**) showed an OH absorption band at 3380—3390 cm^{-1} in the IR spectra and did not give the expected MS peaks because of their thermal instability. b) Prepared from the diol (**6a** or **6b**). c) 4-Ethenyl-1,3-oxathiolan-2-one (**11**) (22%) was also obtained. d) Yield from the diol (**6c** or **6d**).

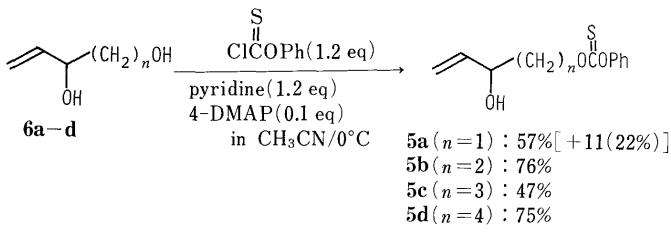


Chart 3

Thus, the diol (**1c**, n=3) was treated with phenyl chlorothionoformate (PCTF) (1 eq) in the presence of pyridine (1 eq) and 4-dimethylaminopyridine (4-DMAP) (0.1 eq) in acetonitrile at 0 °C to give a mixture of monothionocarbonate (**2c**) (58%) and bis-thionocarbonate (**3c**) (15%), which were separated by flash column chromatography (SiO_2). Formation of only **2c** could not be achieved in this reaction. The monothionocarbonate (**2c**) was then oxidized with pyridinium chlorochromate (PCC) in dichloromethane to give the aldehyde (**4c**) in 70% yield. Reaction of **4c** with vinylmagnesium bromide gave **5c** in 61% yield. Similarly, the diol monothionocarbonates (**5d—g**) were prepared. The yields and proton nuclear magnetic resonance (^{1}H-NMR) spectral data of the monothionocarbonates (**2**), aldehydes (**4**) and diol monothionocarbonates (**5**) are summarized in Table I. The monothionocarbonates (**5a—d**) were also prepared from unsaturated diols (**6**) by slow addition (7 h) of PCTF (1.2 eq) in the presence of pyridine (1.2 eq) and 4-DMAP (0.1 eq) in acetonitrile at 0 °C (Chart 3). The starting diols (**6a—d**) employed in this method were prepared according to the literature.[9]

Relationship between the Ring Size of Cyclic Thionocarbonates and the Geometry of the Created Double Bond in Medium- and Large-Membered Thiolcarbonates We have recently reported[6] that treatment of **5d** with LDA or NaH in tetrahydrofuran (THF) followed by refluxing for 1 h gives a 10-membered thiolcarbonate (**8d**) with a (*Z*)-double bond in 73% or 71% yield, respectively, *via* a spontaneous [3,3]sigmatropic rearrangement of the cyclic thionocarbonate (**7d**). We further found that the reaction proceeded at room temperature by the use of a sodium bis(trimethylsilyl)-amide [$(TMS)_2NNa$] (method A) as opposed to the elevated temperature often required for [3,3]sigmatropic rearrangement.[2] When a dry THF solution of $(TMS)_2NNa$ (1 eq) was rapidly added to a THF solution of **5d** (10 mM concentration) at room temperature, the reaction went to completion immediately and after usual work-up the

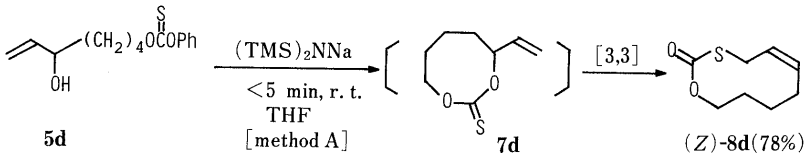


Chart 4

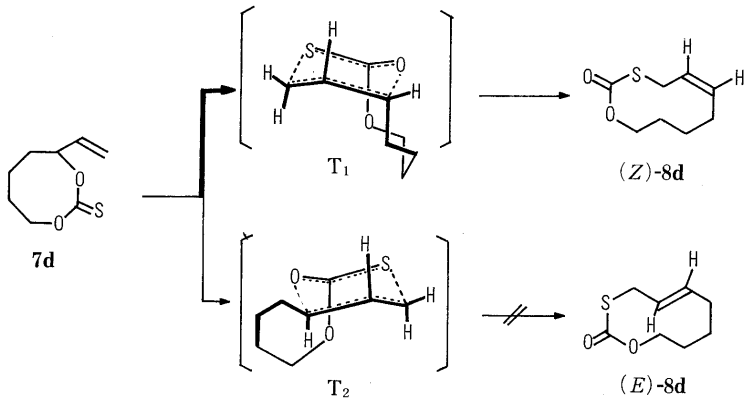


Chart 5

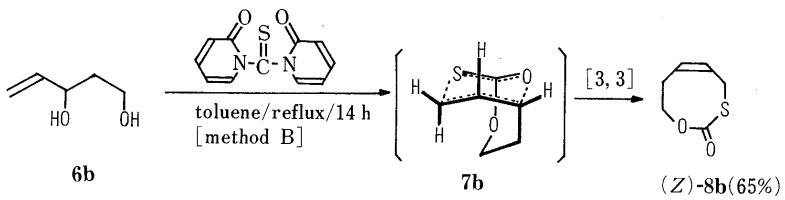


Chart 6

TABLE II. Synthesis of Cyclic Thiolcarbonates (**8**) Containing (*Z*)- or (*E*)-Double Bond

Compound		Yield (%)[a]	
8	*n*	Method A	Method B
a	1	—[b]	—[b]
b	2	—[c]	65 (*Z*)
c	3	(25)[b] (*E*)	—[c]
d	4	78 (*Z*)	46 (*Z*)
e	5	55[b] (*E*)	21 (*E*)
f	6	40 (*E*)	
g	7	—[b]	

a) Isolated yield. *b*) See text. *c*) Decomposed.

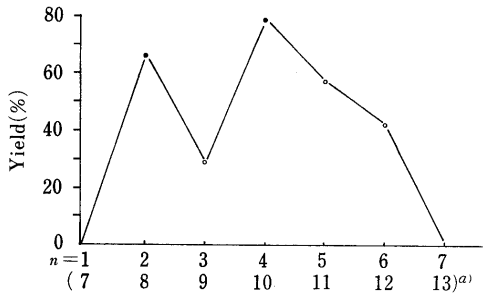


Fig. 1. Effect of the Ring Size on Selectivity of Double Bond Geometry of Cyclic Thiolcarbonates (**8**)

a) Number of atoms in cyclic thiolcarbonates (=*n*+6). ●, (*Z*)-double bond; ○, (*E*)-double bond.

product (**8d**) was isolated by flash column chromatography in 78% yield. Inspection of the ^{1}H-NMR [$CH_a=CH_bCH_2S$: δ 5.37 (H_a) (ddd, J=10.7, 8.4, 7.4 Hz), 5.57 (H_b) (dt, J=10.7, 8.2 Hz)] and carbon-13 (CH=CH: δ 126.1, 132.6 ppm) nuclear magnetic resonance (^{13}C-NMR) spectra of **8d** clearly showed the presence of a (*Z*)-double bond. Its stereochemical purity was also established by a vapor phase chromatography (VPC) analysis, using a 1.5% silicon OV-17 column. These results indicate that the reaction proceeds with high stereoselectivity. The cyclic thionocarbonates (**7d**) generated *in situ* were not isolated. The formation of a (*Z*)-double bond in **8d** can be rationalized as follows. In the [3,3]sigmatropic rearrangement, **7d** can adopt two possible conformations (T_1 and T_2) as the transition states, as shown Chart 5.[10] The T_1 with a 1,3-diaxial interaction would lead to the observed (*Z*)-olefin. On the other hand, the transition state (T_2) bearing the tethered chain in a *trans* relationship should be excluded because of the strain incurred in the four-carbon tether during proper alignment of the thiocarbonyl group and the double bond for the [3,3]sigmatropic ring expansion. Presumably, in the case of a larger membered thionocarbonate, the carbon bridge would be sufficiently long to allow the latter conformation.

In the case of **5b** (n=2), since the desired 8-membered thiolcarbonate (**8b**) was not obtained by method A, we employed an alternative approach using 1,1′-thiocarbon-

yldi-2,2′-pyridone (TCDP)[11] as the thiocarbonyl source. Refluxing 4-penten-1,3-diol (**6b**)[9a] with TCDP (1.1 eq) in toluene (method B) for 14 h cleanly gave an 8-membered thiolcarbonate (**8b**) containing a (*Z*)-double bond in 65% yield as shown in Chart 6. The (*Z*)-stereochemistry of **8b** was determined by ^{1}H-NMR [$CH_a=CH_bCH_2S$: δ 5.72 (H_a) (dt, J=11.2, 8.4 Hz), 5.98 (H_b) (dt, J=11.2, 9.1 Hz)]. The complete isomeric purity was confirmed by VPC analysis. The formation of the (*Z*)-olefin is reasonably accounted for by the all-chair transition state (**7b**). The remarkable ease of methods A and B is noteworthy and the results obtained are summarized in Table II and Fig. 1, making clear their characteristics in relation to the varying ring size of **8**. In these cases, the (*Z*)- and (*E*)-double bond in the cyclic thiolcarbonates (**8**) was distinguished clearly depending upon ring size. The [3,3]sigmatropic rearrangement of the 8-membered thionocarbonate (**7d**) was best carried out by method A and provided the 10-membered thiolcarbonate (**8d**) containing a (*Z*)-double bond in high yield.

Reaction of **5e** (n=5) with $(TMS)_2NNa$ by method A afforded an 11-membered thiolcarbonate (*E*-**8e**) in 55% yield. Inspection of the ^{1}H-NMR spectrum of the product (**8e**) showed an (*E*)-double bond [$CH_a=CH_bCH_2S$: δ 5.40 (H_a) (dt, J=15.0, 6.5 Hz), 5.51 (H_b) (dt, J=15.0, 6.5 Hz)]. Reaction of 7-octen-1,6-diol (**6e**) with TCDP by method B described above gave the product (**8e**) in 21% yield. The formation of the (*E*)-olefin shows that [3,3]sigmatropic ring expansion of **7e** proceeded through a relatively strain-free transition state (T_3) bearing the tethered chain in a *trans* relationship. Therefore, these observations have revealed that the [3,3]sigmatropic ring expansion proceeds exclusively *via* the transition state bearing the chain tethered in a *cis* relationship when the cyclic thionocarbonate (**7**) is 8-membered or smaller ($n \leqq 4$).

When **5f** (n=6) was similarly treated with $(TMS)_2NNa$, a mixture of a 12-membered thiolcarbonate (**8f**) and an unexpected product (**9f**) was obtained in 40% and 19% yields, respectively. The ^{1}H-NMR spectrum of **8f** showed an (*E*)-double bond [$CH_a=CH_bCH_2S$: 5.43 (H_a) (dt, J=15.4, 6.0 Hz), 5.58 (H_b) (dt, J=15.4, 6.0 Hz)]. Although the ^{1}H-NMR [δ 5.47 (2H, dt, J=14.8, 6.7 Hz), 5.64 (2H, dt, J=14.8 Hz, 6.7 Hz)] and infrared (IR) (960 cm^{-1}) spectra of **9f** closely resembled those of (*E*)-**8f**, the structure of **9f** was finally determined to be a dimer having two (*E*)-allylic thiolcarbonate moieties and a 24-membered cyclic system by examination of its mass spectrum (MS), which exhibited a parent peak at m/z 400. The similar reaction of **5g** (n=7) gave a dimer **9g** having a 26-membered cyclic system in 39% yield, together with decomposed materials. The structure of **9g** was supported by the MS (M^+, 428), ^{1}H-NMR ([δ 5.48 (2H, dt, J=15.2, 6.9 Hz), 5.66 (2H, dt, J=15.2, 6.9 Hz)] and IR (960 cm^{-1}) spectra. The presence of (*E*)-double bonds in the dimer **9g** was ultimately clarified by conversion of **9g** into an (*E*)-allylic thiolcarbamate (**10g**) (75%) by alkaline hydrolysis followed by treatment of the resulting allylic thiol with dimethylcarbamoyl chloride in

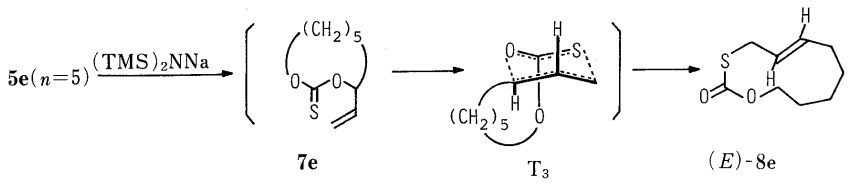


Chart 7

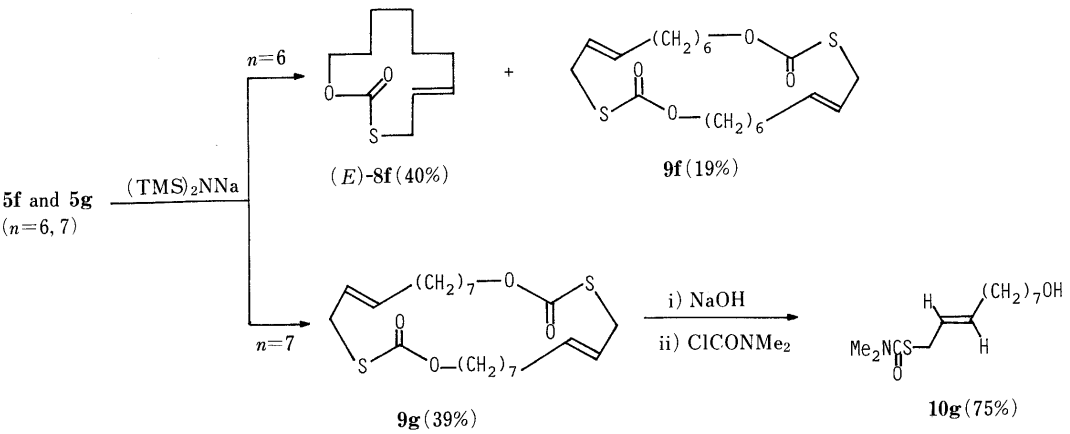


Chart 8

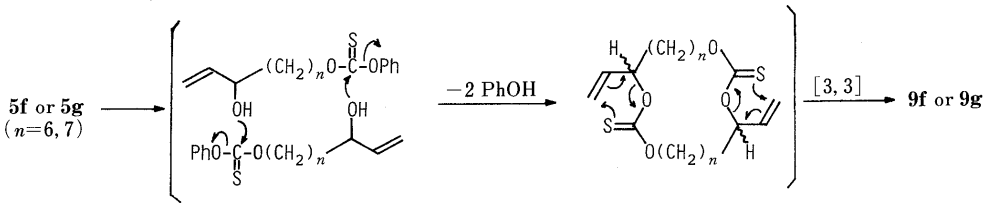


Chart 9

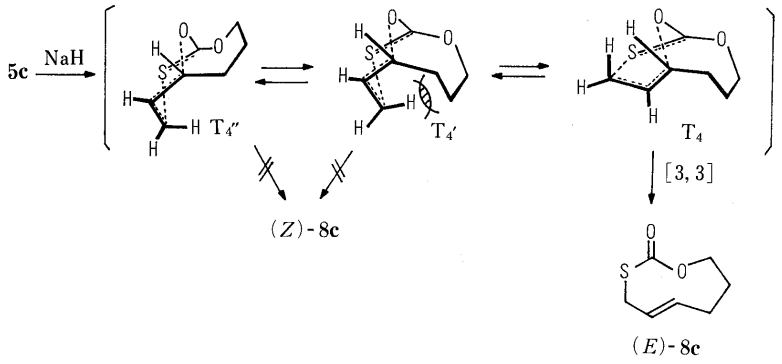


Chart 10

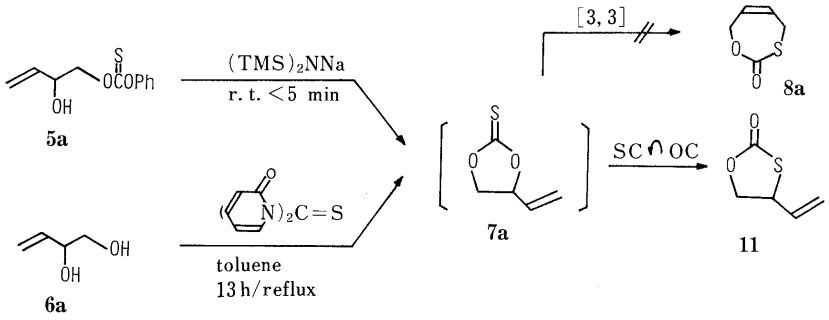
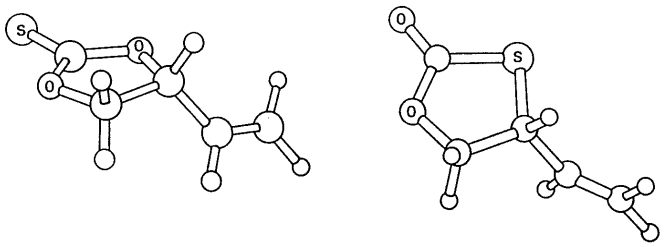


Chart 11



7a, $H_f = -47.13$ kcal/mol 11, $H_f = -64.14$ kcal/mol

Fig. 2. MNDO-Optimized Structures for **7a** and **11**

the presence of triethylamine and 4-DMAP. The formation of **9f** and **9g** may be easily explained by dimerization of the substrates (**5f** and **5g**) followed by a [3,3]sigmatropic ring expansion as depicted in Chart 9. Meanwhile, although **5c** ($n=3$) did not give a satisfactory result by method A or B, refluxing of **5c** with NaH[6] in THF for 20 min gave a 25% yield of (*E*)-**8c**. The formation of the (*E*)-isomer may be accounted for by the conformational preference of a boatlike transition state (T_4) over the more congested chairlike transition state ($T_{4'}$) or a boat 1,3-dioxepane ring ($T_{4''}$) leading to the (*Z*)-isomer.[10] The low yield of (*E*)-**8c** may be a consequence of the known difficulty in synthesis of medium rings and the inclusion of the (*E*)-double bond in the 9-membered ring.

In the case of **5a** ($n=1$), the methods A and B gave only 4-ethenyl-1,3-oxathiolan-2-one (**11**) (65% and 68% yields, respectively), which is an O,S-rearrangement product of the 5-membered thionocarbonate (**7a**), and the corresponding **8a** was not produced at all. The product **11** was also obtained as a by-product at the stage of preparation of the diol monothionocarbonate (**5a**) (Chart 3). In order to evaluate this isomerization, we carried out a molecular modeling study. Energy calculations[12] on **7a** and **11** were performed using the modified neglect of diatomic overlap (MNDO) program[13] in MOPAC.[14] The value of the calculated heat of formation energy (H_f) for each optimized conformer (**7a** and **11**) is shown with the molecular graphics in Fig. 2, wherein the ethenyl π-orbital in **7a** is restricted to a location perpendicular to the thiocarbonyl group. The energy of the conformer of **11** was lower by 17.01 kcal/mol than that of **7a**. The large difference of H_f value between **7a** and **11** is consistent with ease of isomerization.

Conversion of the Cyclic Thiolcarbonates [(*Z*)- or (*E*)-8] into (*E*)- or (*Z*)-Allylic Sulfides (10, 13 and 16) Allylic sulfides and their oxidation products, *i.e.*, sulfoxide or sulfones, play an important role in organic reactions, in particular carbon skeletal construction, because of the diversity of their chemical reactions.[6] (*E*)-Allylic sulfides are synthesized by a variety of methods involving [3,3]-sigmatropic rearragement.[15] On the other hand, the existing method[16] for the (*Z*)-allylic sulfides still relies on Lindlar hydrogenation of the corresponding acetylenes.[16a,b] Hayashi and co-workers[16a] derived (*Z*)-2-alkenyl *N,N*-dimethylthiolcarbamates from propargyl alcohol *via* several steps. However, hydrolysis of cyclic thiolcarbonates (**8**) containing a (*Z*)- or (*E*)-double bond with sodium hydroxide in aqueous methanol at room temperature easily gave the (*Z*)- or (*E*)-allylic thiols (**12b—e**) in quantitative yields, respectively. To avoid the undesirable formation of bisallylic sulfide in air, the products have been characterized by their conversion of allylic thiolcarbamates (**10b—e**) with dimethylcarbamoyl chloride in the presence of triethylamine and 4-DMAP. The reaction of the allylic thiol (**12d**) with electrophiles (methyl iodide, 2-bromocyclopentanone, 2-cyclopentenone, dimethylthiocarbamoyl chloride) led to the corresponding (*Z*)-allylic sulfides (**13a—d**), having a

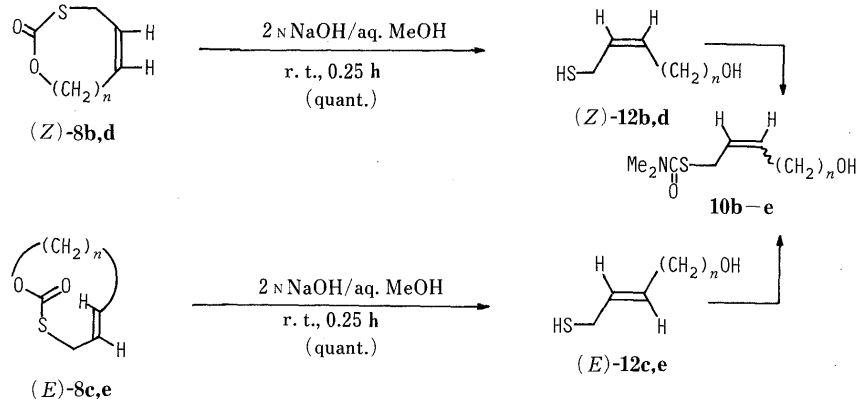


Chart 12

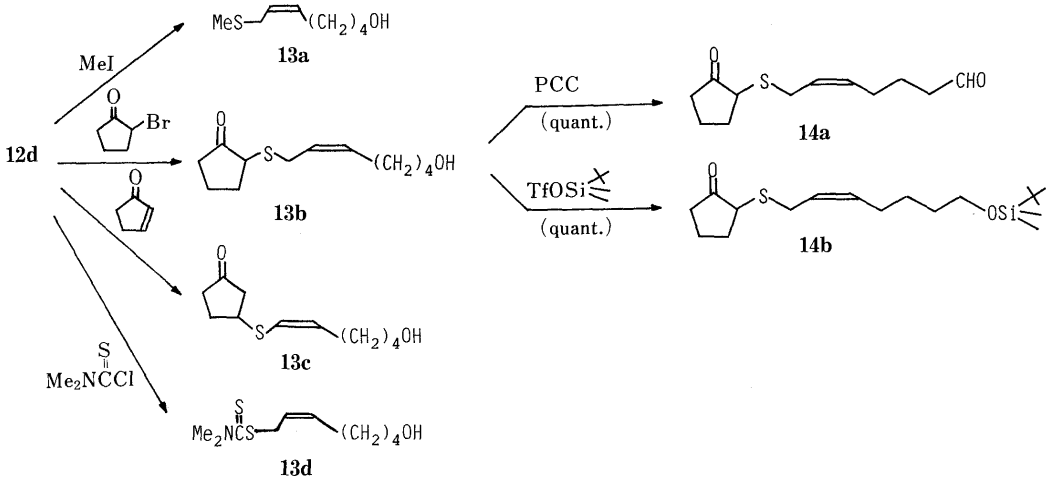


Chart 13

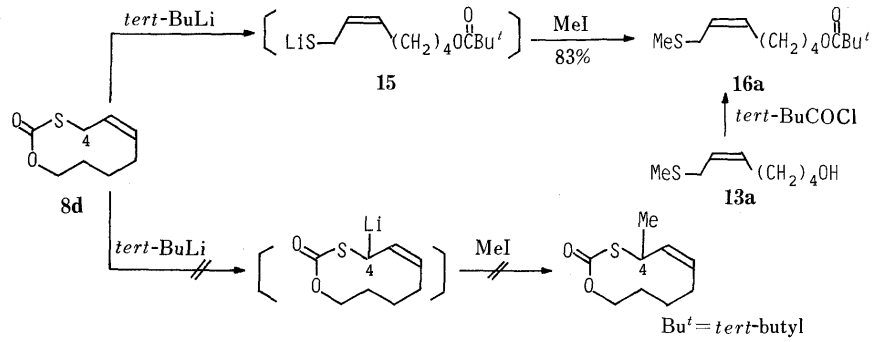


Chart 14

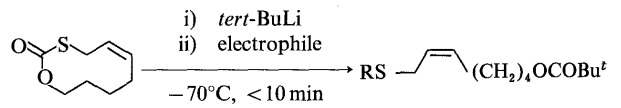
versatile alcohol function at the terminal position. The alcohol function of **13b** was easily converted into an aldehyde (**14a**) or silyl ether (**14b**) in quantitative yield, as shown in Chart 13.

We were further interested in a carbon–carbon bond formation reaction at the C-4 allylic position in the 10-membered thiolcarbonate (**8d**), as illustrated in Chart 14. However, treatment of **8d** with *tert*-butyllithium (*tert*-BuLi) at −78 °C in THF followed by addition of methyl iodide gave an unexpected (*Z*)-allylic sulfide (**16a**) with a pivaloate ester function in 83% yield. The structure of **16a** was established by an alternative synthesis from (*Z*)-allyl methylsulfide (**13a**) with pivaloyl chloride. This obviously means that *tert*-BuLi attacks the carbonyl group of **8d** to cleave the carbon–sulfur bond, followed by spontaneous coupling of the generated thiol anion (**15**) with methyl iodide. The thiol anion (**15**) was coupled with various alkyl halides as well as cyclolkenones to give the corresponding (*Z*)-allylic sulfides (**16**) containing a pivaloate moiety in good yield. The results are summarized in Table III. The method described here would provide new routes for (*Z*)-allylic sulfides.

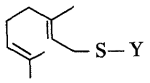
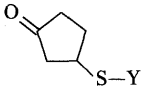
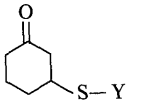
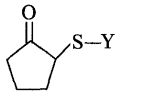
Conclusion

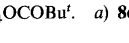
Diol monothionocarbonates employed in this study could be prepared by two different routes. Methods A and B are useful for the preparation of medium- and large-membered thiolcarbonates (**8**) containing a (*Z*)- or (*E*)-double bond.

TABLE III. Yields of (*Z*)-Allylic Sulfides (**16**) Containing a Pivaloate Moiety



8d **16**

Electrophile	Product No.	Product	Yield (%)
MeI	**16a**	MeS–Y	83
Benzyl bromide	**16b**	$C_6H_5CH_2S$–Y	76
Geranyl bromide	**16c**		81
Propyl iodide	**16d**	$Me(CH_2)_2S$–Y	40
2-Cyclopentenone	**16e**		77
2-Cyclohexenone	**16f**		89
2-Bromocyclopentanone	**16g**		44[a]

Y =  *a*) **8d** (33%) was recovered.

This study has revealed that [3,3]sigmatropic ring expansion proceeds *via* the transition state bearing the chain tethered in a *cis* relationship when the cyclic thionocarbonate is 8-membered or smaller. This observation may provide an interesting insight into the factors influencing the transition state of the [3,3]sigmatropic rearrangement. Moreover, the ring size of cyclic thionocarbonates (**7**) is claimed to be an important factor for stereocontrolled olefin synthesis *via* [3,3]sigmatropic ring expansion. Further, conversion of cyclic thiolcarbonates (**8**) containing a (*Z*)- or (*E*)-double bond into **10**, **12**, **13** and **16** may provide a versatile and flexible approach for (*Z*)- or (*E*)-allylic sulfides. Further synthetic applications of cyclic thiolcarbonates (**8**) containing a (*Z*)- or (*E*)-double bond are being investigated in our laboratory.

Experimental

The IR spectra were recorded on a Shimadzu IR-435, and MS on a Hitachi M-80 spectrometer. ^{1}H- and ^{13}C-NMR spectra were taken with tetramethylsilane as an internal standard on a Varian Gemini-200 spectrometer in $CDCl_3$. Vapor-phase chromatographic analyses were performed with a Shimadzu GC-4BMPF gas chromatograph with a flame ionization detector using a 1.5% silicon OV-17 column (3 mm i.d. × 3 m, programed at 140—270 °C, 10 °C/min). For column chromatography, SiO_2 (Merck 9385) was used. All reactions were carried out under a nitrogen stream unless otherwise noted.

Synthesis of Diol Monothionocarbonate (5c) Method i (General Procedure): A solution of phenyl chlorothionoformate[17] (0.98 ml, 7 mM) in acetonitrile (10 ml) was added dropwise to a solution of 1,4-butanediol (**1c**) (630 mg, 7 mM) in acetonitrile (70 ml) in the presence of pyridine (0.56 ml, 7 mM) and 4-DMAP (85 mg, 0.7 mM) over 3 h at 0 °C under argon. After being stirred for 1 h, the mixture was evaporated under reduced pressure. The oily residue was dissolved in EtOAc–hexane (1 : 1). The organic layer was washed with H_2O and brine, dried over anhydrous Na_2SO_4, and then evaporated under reduced pressure. The residue was purified by column chromatography using hexane–EtOAc (1 : 1) as the eluent to give butane-1,4-bis (*O*-phenylthionocarbonate) (**3c**) (380 mg, 15%) [^{1}H-NMR spectrum: δ 1.55 (4H, m, 2 × CH_2), 4.52 (4H, t, J = 6.5 Hz, 2 × OCH_2), 7.10—7.55 (10H, m, Ar-H)] from the first fraction and *O*-4-hydroxybutyl *O*-phenyl thionocarbonate (**2c**) (920 mg, 58%) from the second fraction, each as an oil. Compound **2c** (920 mg, 4.3 mM) in dichloromethane (2 ml) was added to a suspension of PCC[17] (965 mg, 4.5 mM) in dichloromethane (3 ml) and the mixture was stirred at room temperature for 2 h. The mixture was filtered through a Celite pad and the filtrate was concentrated *in vacuo* to give a crude oil, which was purified by column chromatography (eluent: 20% EtOAc in hexane) to give *O*-3-formylpropyl *O*-phenyl thionocarbonate (**4c**) (638 mg, 70%) as an oil. A solution of vinylmagnesium bromide[17] (0.93 M in THF) (1.42 ml, 1.33 mM) was added dropwise to a solution of **4c** (298 mg, 1.33 mM) in THF (15 ml) over 10 min at 0 °C and the mixture was stirred for 20 min at the same temperature. The reaction was quenched by the addition of H_2O, and the mixture was extracted with EtOAc–hexane (1 : 1). The extract was washed with brine, dried over anhydrous Na_2SO_4, and then evaporated under reduced pressure. The residue was purified by column chromatography using 20% EtOAc in hexane for elution to give *O*-(4-hydroxy-5-hexenyl) *O*-phenyl thionocarbonate (**5c**) (206 mg, 61%) as an oil.

Similar treatments of **1d**—**g** afforded the monothionocarbonates (**2d**, **2e**, **2f** and **2g**) [no attempt was made to isolate the corresponding undesired bis-thionocarbonates (**3d**—**g**)], aldehydes (**4d**, **4e**, **4f** and **4g**) and diol monothionocarbonates (**5d**, **5e**, **5f** and **5g**), of which yields and ^{1}H-NMR spectral data are shown in Table I.

Synthesis of Diol Monothionocarbonate (5d) Method ii (General Procedure): A solution of phenyl chloroformate (2.46 g, 14.2 mM) in acetonitrile (8 ml) was added slowly over 7 h to a solution of 6-heptene-1,5-diol (**6d**)[9b] (1.54 g, 11.8 mM) in acetonitrile (70 ml) in the presence of pyridine (1.12 g, 14.2 mM) and 4-DMAP (0.144 g, 1.18 mM) at 0 °C under argon by a syringe pump technique. The solvent was evaporated off under reduced pressure to give an oil, which was subsequently diluted with EtOAc–hexane (1 : 1). The organic layer was washed with H_2O, and brine, dried over anhydrous Na_2SO_4, and then evaporated *in vacuo*. The residue was purified by column chromatography using 20% EtOAc–hexane for elution to give *O*-(5-hydroxy-6-heptenyl) *O*-phenyl thionocarbonate (**5d**) (2.33 g, 75%) as an oil.

Similar treatments of the diols (**6a**—**c**) gave the diol monothionocarbonates (**5a**, **5b** and **5c**), of which the yields and spectral data are shown in Table I.

General Procedure for the Preparation of Cyclic Thiolcarbonates (8) Method A (General Procedure): A 1M solution of $(TMS)_2NNa$[17] in THF (0.5 ml) was added rapidly to a solution of a diol monothionocarbonate (**5**) (0.5 mM) in THF (50 ml) at room temperature, and the mixture was stirred for 5 min. The reaction was quenched by the addition of H_2O and the solvent was evaporated off under reduced pressure. The residue was extracted with EtOAc–hexane (1 : 1) and the extract was washed with brine, dried over anhydrous Na_2SO_4, and then evaporated under reduced pressure. The residual oil was purified by column chromatography using 5% or 10% EtOAc in hexane of elution to give the corresponding cyclic thiolcarbonate as an oil. Reaction of **5f** with $(TMS)_2NNa$ afforded **8f**, accompanied with a dimeric product (**9f**, 19%).

Method B (General Procedure): TCDP[17] (0.55 mM) was added to a solution of a diol (**6**)[9b] (0.5 mM) in toluene (50 ml), and the mixture was refluxed for 14 h. The solvent was evaporated off under reduced pressure. The residue was purified by column chromatography to give the corresponding cyclic thiolcarbonate as an oil.

(*Z*)-7,8,9,10-Tetrahydro-4*H*-1,3-oxathiecin-2-one (**8d**): IR (film) cm^{-1}: 1690 (C=O). ^{1}H-NMR δ: 1.5—1.8 (4H, m, 2 × CH_2), 2.37 (2H, br q, $CH=CH_2$), 3.40 (2H, br, SCH_2), 4.39 (2H, br s, OCH_2), 5.37 (1H, ddd, J = 10.7, 8.4, 7.4 Hz, C_6-H), 5.57 (1H, dt, J = 10.7, 8.2 Hz, C_5-H). ^{13}C-NMR δ: 26.0, 27.2, 27.3, 29.8, 68.7, 126.1, 132.6, 169.8. MS *m/z*: 172 (M^+). HRMS Calcd for $C_8H_{12}O_2S$: 172.0558. Found: 172.0556. VPC analysis: t_R = 6.0 min.

(*Z*)-7,8-Dihydro-4*H*-1,3-oxathiocin-2-one (**8b**): IR (film) cm^{-1}: 1700 (C=O), 1100 (C–O–C), 1060, 965. ^{1}H-NMR δ: 2.47 (2H, m, OCH_2CH_2), 3.55 (2H, d, J = 8.8 Hz, SCH_2), 4.26 (2H, t, J = 4.8 Hz, OCH_2), 5.72 (1H, dt, J = 11.2, 8.4 Hz, C_6-H), 5.98 (1H, dt, J = 11.2, 9.1 Hz, C_5-H). MS *m/z*: 144 (M^+). HRMS Calcd for $C_6H_8O_2S$: 144.0243. Found: 144.0239. VPC analysis: t_R = 3.7 min.

(*E*)-1-Oxa-3-thia-5-cycloundecen-2-one (**8e**): IR (film) cm^{-1}: 1690 (C=O), 1140, 965. ^{1}H-NMR δ: 1.30—1.85 (6H, br, 3 × CH_2), 2.10 (2H, quint, J = 5.0 Hz, $=CHCH_2$), 3.40 (2H, d, J = 5.0 Hz, SCH_2), 4.23 (2H, t, J = 5.0 Hz, OCH_2), 5.40 (1H, dt, J = 15.0, 6.5 Hz, C_6-H), 5.51 (1H, dt, J = 15.0, 6.5 Hz, C_5-H). ^{13}C-NMR δ: 21.8, 25.9, 28.7, 33.1, 36.2, 67.9, 127.1, 135.0, 170.1. MS *m/z*: 186 (M^+). HRMS Calcd for $C_9H_{14}O_2S$: 186.0714. Found: 186.0717.

(*E*)-1-Oxa-3-thia-5-cyclododecen-2-one (**8f**): IR (film) cm^{-1}: 1685

(C=O), 960. ^{1}H-NMR δ: 1.20—1.90 (8H, m, 4×CH_2), 2.10 (2H, br s, =CHC$\underline{H}_2$), 3.38 (2H, d, J=8.0 Hz, SCH_2), 4.32 (2H, t, J=8.0 Hz, OCH_2), 5.43 (1H, dt, J=15.4, 6.0 Hz, C_6-H), 5.58 (1H, dt, J=15.4, 6.0 Hz, C_5-H). MS m/z: 200 (M^+). HRMS Calcd for $C_{10}H_{16}O_2S$: 200.0870. Found: 200.0871.

(*E,E*)-1,13-Dioxa-3,15-dithia-5,17-cyclotetracosandien-2,14-dione (**9f**): IR (film) cm^{-1}: 1695 (C=O), 960. ^{1}H-NMR δ: 1.10—1.50 (16H, m, 8×CH_2), 2.0 (4H, m, 2× =CHC$\underline{H}_2$), 3.41 (4H, d, J=8.0 Hz, 2×SCH_2), 4.21 (4H, t, J=7.0 Hz, 2×OCH_2), 5.47, 5.64 (each 2H, each dt, J=14.8, 6.7 Hz, 2×CH=CH). MS m/z: 400 (M^+). HRMS Calcd for $C_{20}H_{32}O_4S_2$: 400.1739. Found: 400.1740.

(*E*)-7,8-Dihydro-4*H*,9*H*-1,3-oxathionin-2-one (8c) A suspension of **5c** (172 mg, 0.68 mM) and 60% NaH (33 mg, 0.82 mM) in THF (70 ml) was refluxed for 20 min. The reaction mixture was cooled and quenched by the addition of H_2O and extracted with hexane–EtOAc (2 : 1). The extract was washed with H_2O, brine, and dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography using 5% EtOAc in hexane for elution to give **8c** (27 mg, 25%). IR (film) cm^{-1}: 1695 (C=O), 1150, 965. ^{1}H-NMR δ: 1.75 (2H, quint, J=5.5 Hz, CH_2), 2.13 (2H, q, J=5.5 Hz, =CHC$\underline{H}_2$), 3.30 (2H, d, J=5.5 Hz, SCH_2), 4.10 (2H, t, J=6.0 Hz, OCH_2), 5.42 (1H, dt, J=15.0, 6.9 Hz, C_5-H), 5.55 (1H, dt, J=15.0, 6.9 Hz, C_6-H). MS m/z: 158 (M^+). MRMS Calcd for $C_7H_{10}O_2S$: 158.0401. Found: 158.0408.

4-Ethenyl-1,3-oxathiolan-2-one (11) When treated according to the method A (or B), **5a** (or **6a**) gave **11** in 65% (or 68%) yield as an oil. IR (film) cm^{-1}: 1790 (C=O). ^{1}H-NMR δ: 4.32 and 4.75 (each 1H, each t, J=8.2 Hz, OCH_2), 5.32 (1H, q, J=8.0 Hz, SCH), 5.46 (1H, d, J=10.2 Hz, H⟩=⟨H), 5.51 (1H, d, J=17.2 Hz, H⟩=⟨H), 5.89 (1H, ddd, J=17.2, 10.2, 7.2 Hz, =CH). MS m/z: 130 (M^+). HRMS Calcd for $C_5H_6O_2S$: 130.0088. Found: 130.0093.

(*E,E*)-1,14-Dioxa-3,16-dithia-5,18-cyclohexacosandien-2,15-dione (9g) A 1 M solution of $(TMS)_2NNa$ (0.5 ml, 0.5 mM) in THF was added over 1.5 h to a solution of **5g** (154 mg, 0.5 mM) in THF (50 ml) at room temperature by a syringe pump technique. The ordinary work-up afforded **9g** (41 mg, 39%) as an oil. IR (film) cm^{-1}: 1695 (C=O), 1140, 960. ^{1}H-NMR δ: 1.10—1.80 (20H, m, 10×CH_2), 2.0 (4H, m, 2×CH=C$\underline{H}_2$), 3.42 (4H, d, J=8.0 Hz, 2×OCH_2), 4.19 (4H, t, J=8.0 Hz, 2×SCH_2), 5.48, 5.66 (each 2H, each dt, J=15.2, 6.9 Hz, 2×CH=CH). MS m/z: 428 (M^+). HRMS Calcd for $C_{22}H_{36}O_4S_2$: 428.2053. Found: 428.2052.

General Precedure for Hydrolysis of Cyclic Thiolcarbonates (8b—e) Aqueous 2 N sodium hydroxide solution (0.8 ml) was added to a thiolcarbonate (**8**) (1 mM) in MeOH (4 ml) at 0°C, and the mixture was stirred for 15 min at room temperature. The solvent was removed by evaporation and the residue was neutralized with 5% HCl. Extraction with CH_2Cl_2 by a salting-out technique gave almost pure allylic thiol as an oil in almost quantitative yield.

(*Z*)-5-Mercapto-3-penten-1-ol (**12b**): IR (film) cm^{-1}: 3400 (OH). ^{1}H-NMR δ: 2.30 (2H, q, J=7.5 Hz, =CHC$\underline{H}_2$), 3.16 (2H, t, J=7.5 Hz, SCH_2), 3.62 (2H, t, J=7.5 Hz, OCH_2), 5.41 (1H, dt, J=10.5, 10.0 Hz, C_4-H), 5.68 (1H, dt, J=10.5, 9.0 Hz, C_3-H). MS m/z: 118 (M^+).

(*E*)-6-Mercapto-4-hexen-1-ol (**12c**): IR (film) cm^{-1}: 3400 (OH). ^{1}H-NMR δ: 1.55—1.75 (2H, m, CH_2), 1.95—2.20 (2H, m, SCH_2), 3.09 (2H, t, J=5.5 Hz, SCH_2), 3.63 (2H, t, J=5.5 Hz, OCH_2), 5.5—5.6 (2H, br, CH=CH). MS m/z: 132 (M^+).

(*Z*)-7-Mercapto-5-hepten-1-ol (**12d**): IR (film) cm^{-1}: 3400 (OH). ^{1}H-NMR δ: 1.30—1.65 (4H, m, 2×CH_2), 2.10 (2H, q, J=7.0 Hz, =CHC$\underline{H}_2$), 3.16 (2H, t, J=8.0 Hz, SCH_2), 3.66 (2H, t, J=6.0 Hz, HOC$\underline{H}_2$), 5.31—5.65 (2H, m, CH=CH). MS m/z: 147 (M^+). HRMS Calcd for $C_7H_{15}OS$: 147.0843. Found: 147.0841.

(*E*)-8-Mercapto-6-octen-1-ol (**12e**): IR (film) cm^{-1}: 3400 (OH). ^{1}H-NMR δ: 1.10—1.70 (6H, m, 3×CH_2), 2.0 (2H, br, =CHC$\underline{H}_2$), 3.08 (2H, br, SCH_2), 3.59 (2H, t, J=6.5 Hz, OCH_2), 5.50 (2H, br, CH=CH). MS m/z: 160 (M^+).

General Procedure for Preparation of Thiolcarbamates (10b—e and 10g) A mixture of **12** (0.27 mM), dimethylcarbamoyl chloride (0.32 mM), triethylamine (0.32 mM) and 4-DMAP (0.054 mM) in THF (1 ml) was stirred overnight at room temperature under argon. The solvent was evaported off and the residue was diluted with EtOAc–hexane (1 : 1). The organic layer was washed with H_2O and brine, and dried over anhydrous Na_2SO_4. Evaporation of the solvent left a crude oil, which was purified by column chromatography using 30% EtOAc in hexane for elution to give **10** as an oil.

(*Z*)-*S*-(5-Hydroxy-2-pentenyl)*N*,*N*-Dimethylcarbamothioate (**10b**): Yield 59%, IR (film) cm^{-1}: 3400 (OH), 1630 (NC=O), 1095, 1040. ^{1}H-NMR δ: 2.41 (2H, q, J=5.5 Hz, =CHC$\underline{H}_2$), 2.93 (6H, s, 2×CH_3), 3.53 (2H, d, J=6.0 Hz, SCH_2), 3.64 (2H, t, J=6.5 Hz, OCH_2), 5.40—5.65 (2H, m, CH=CH). MS m/z: 189 (M^+). HRMS Calcd for $C_8H_{15}O_2NS$ Calcd: 189.0822. Found: 189.0830. VPC analysis: t_R=8.5 min.

(*E*)-*S*-(6-Hydroxy-2-hexenyl) *N*,*N*-Dimethylcarbamothioate (**10c**): Yield 41%, IR (film) cm^{-1}: 3400 (OH), 1630 (NC=O). ^{1}H-NMR δ: 1.61 (2H, quint, J=6.0 Hz, CH_2), 2.08 (2H, q, J=5.5 Hz, =CHC$\underline{H}_2$), 2.95 (6H, s, 2×CH_3), 3.49 (2H, d, J=6.0 Hz, SCH_2), 3.60 (2H, t, J=5.5 Hz, OCH_2), 5.48 (1H, ddd, J=15.3, 6.6, 6.3 Hz, C_3-H), 5.65 (1H, ddd, J=15.3, 6.3, 5.9 Hz, C_2-H). MS m/z: 203 (M^+). HRMS Calcd for $C_9H_{17}NO_2S$: 203.0979. Found: 203.0981. VPC analysis: t_R=10.6 min.

(*Z*)-*S*-(7-Hydroxy-2-heptenyl) *N*,*N*-Dimethylcarbamothioate (**10d**): Yield 92%, IR (film) cm^{-1}: 3400 (OH), 1630 (NC=O). ^{1}H-NMR δ: 1.30—1.60 (4H, m, 2×CH_2), 2.05—2.25 (2H, m, =CHC$\underline{H}_2$), 2.93 (6H, s, 2×CH_3), 3.55 (4H, m, SCH_2 and OCH_2), 5.45 (2H, m, CH=CH). VPC analysis: t_R=11.3 min.

(*E*)-*S*-(8-Hydroxy-2-octenyl) *N*,*N*-Dimethylcarbamothioate (**10e**): Yield 40%, IR (film) cm^{-1}: 3450 (OH), 1635 (NC=O), 1095, 965. ^{1}H-NMR δ: 1.10—1.70 (6H, m, 3×CH_2), 2.0 (2H, q, J=6.5 Hz, =CHC$\underline{H}_2$), 2.95 (6H, s, 2×CH_3), 3.48 (2H, d, J=6.5 Hz, SCH_2), 3.60 (2H, t, J=6.0 Hz, OCH_2), 5.45 (1H, dt, J=16.0, 7.5 Hz, C_3-H), 5.62 (1H, dt, J=16.0, 6.0 Hz, C_2-H). MS m/z: 231 (M^+).
HRMS Calcd for $C_{11}H_{21}O_2NS$: 231.1292. Found: 231.1291. VPC analysis: t_R=12.4 min.

(*E*)-*S*-(10-Hydroxy-2-decenyl) *N*,*N*-Dimethylcarbamothioate (10g) Aqueous 2 N NaOH (0.35 ml) was added to a solution of **9g** (30 mg, 0.07 mM) in MeOH (5 ml) and the mixture was stirred for 20 min at room temperature. Evaporation and extractive work-up gave a thiol (**12g**) (26 mg), which was subsequently treated with dimethylcarbamoyl chloride as described above (general procedure) to give **10g** (27 mg, 75%) as an oil. IR (film) cm^{-1}: 3450 (OH), 1630 (NC=O), 1360, 1100, 960. ^{1}H-NMR δ: 1.16—1.38 (8H, m 2×CH_2), 1.44—1.55 (2H, br, CH_2), 1.94 (2H, q, J=6.6 Hz, =CHC$\underline{H}_2$), 2.93 (6H, s, 2×CH_3), 3.46 (2H, d, J=7.2 Hz, SCH_2), 3.57 (2H, t, J=7.2 Hz, OCH_2), 5.41 (1H, dt, J=15.0, 7.2 Hz, C_3-H), 5.58 (1H, dt, J=15.0, 7.2 Hz, C_2-H). MS m/z: 259 (M^+). HRMS Calcd for $C_{13}H_{25}NO_2S$: 259.1604. Found: 259.1602.

(*Z*)-7-Methylthio-5-hepten-1-ol (**13a**) Methyl iodide (60 mg, 0.42 mM) was added to a solution of **12d** (21 mg, 0.14 mM) and MeONa (23 mg, 0.42 mM) in MeOH (8 ml), and the mixture was stirred for 20 min at room temperature. The solvent was evaporated and the residue was diluted with H_2O and CH_2Cl_2. The organic layer was washed with brine and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by column chromatography using 40% EtOAc in hexane for elution to give **13a** (20 mg, 90%) as an oil. ^{1}H-NMR δ: 1.30—1.70 (4H, m, 2×CH_2), 2.02 (3H, s, CH_3), 1.95—2.18 (2H, m, =CHC$\underline{H}_2$), 3.12 (2H, d, J=7.0 Hz, SCH_2), 3.65 (2H, t, J=6.5 Hz, OCH_2), 5.38—5.63 (2H, m, CH=CH). MS m/z: 160 (M^+). HRMS Calcd for $C_8H_{16}OS$: 160.0921. Found: 160.0913.

(*Z*)-2-(7-Hydroxy-2-heptenyl)thiocyclopentanone (13b) 2-Bromocyclopentanone (137 mg, 0.84 mM) was added to a solution of **12d** (120 mg, 0.70 mM) and MeONa (45 mg, 0.84 mM) in MeOH (4 ml), and the mixture was treated as described for the preparation of **13a** to give **13b** (92 mg, 58%) as an oil. IR (film) cm^{-1}: 3700—3100 (OH), 1725 (C=O). ^{1}H-NMR δ: 1.30—2.55 (13H, m, 6×CH_2 and OH), 3.10 (2H, m, SCH_2), 3.45 (1H, dd, J=12.0, 9.0 Hz, SCH), 3.65 (2H, t, J=7.0 Hz, OCH_2), 5.50 (2H, m, CH=CH). MS m/z: 228 (M^+). HRMS Calcd for $C_{12}H_{20}O_2S$: 228.1183. Found: 228.1185.

(*Z*)-3-(6-Hydroxy-1-hexenyl)thiocyclopentanone (13c) 2-Cyclopentenone (4 mg, 0.05 mM) was added to a solution of **12d** (8 mg, 0.05 mM) and MeONa (3 mg, 0.06 mM) in MeOH (1 ml), and the mixture was treated as described above to give **13c** (9 mg, 86%) as an oil. IR (film) cm^{-1}: 3600—3000 (OH), 1725 (C=O). ^{1}H-NMR δ: 1.30—2.67 (13H, m, 6×CH_2 and OH), 3.21 (2H, d, J=7.0 Hz, SCH_2), 3.40 (1H, quint, J=7.0 Hz, SCH), 3.64 (2H, t, J=7.0 Hz, OCH_2), 5.50 (2H, m, CH=CH). MS m/z: 228 (M^+). HRMS Calcd for $C_{12}H_{20}O_2S$: 228.1183. Found: 228.1185.

(*Z*)-Dimethyl 7-Hydroxy-2-heptenylcarbamodithioate (13d) A mixture of **12d** (136 mg, 0.93 mM), dimethylthiocarbamoyl chloride (149 mg, 1.2 mM), triethylamine (121 mg, 1.2 mM) and 4-DMAP (24 mg, 0.2 mM) in THF (1 ml) was treated as described for the preparation of **10** to give **13d** (152 mg, 70%) as an oil. ^{1}H-NMR δ: 1.30—1.60 (4H, m, 2×CH_2), 1.70 (1H, br s, OH), 2.05—2.25 (2H, q, J=8.0 Hz, =CHC$\underline{H}_2$), 3.30, 3.35 (each 3H, each s, 2×CH_3), 3.59 (2H, q, J=6.0, SCH_2), 3.90 (2H, d, J=8.0 Hz, OCH_2), 5.40—5.65 (2H, m, CH=CH). MS m/z: 233 (M^+). HRMS Calcd for $C_{10}H_{19}NOS_2$: 233.0908. Found: 233.0904.

(*Z*)-7-(2-Oxocyclopentyl)thio-5-hexenal (14a) A suspension of **13b** (7 mg, 0.031 mM) and PCC (10 mg, 0.047 mM) in dichloromethane (1 ml)

was stirred for 13 h at room temperature. The reaction mixture was diluted with ether and filtered through a Celite pad. The filtrate was evaporated to give a brown oil, which was purified by column chromatography using EtOAc–hexane (1 : 1) for elution to give **14a** (7 mg, 100%) as an oil. IR (film) cm^{-1}: 1725 (C=O). ^{1}H-NMR δ: 1.60—2.60 (12H, m, $6\times CH_2$), 3.10 (2H, m, SCH_2), 3.45 (1H, m, SCH), 5.50 (2H, m, CH=CH), 9.75 (1H, s, CHO). MS *m/z*: 226 (M^+). HRMS Calcd for $C_{12}H_{18}O_2S$: 226.1027. Found: 226.1029.

(*Z*)-2-(7-*tert*-Butyldimethylsilyloxy-2-heptenyl)thiocyclopentanone (14b) *tert*-Butyldimethylsilyl trifluoromethanesulfonate[17] (1 drop) was added to a solution of **13b** (4 mg, 0.018 mM) in pyridine (1 ml) at −10 °C, and the mixture was stirred for 10 min. The reaction was quenched by the addition of H_2O at this temperature and the mixture was diluted with EtOAc–hexane (1 : 1). The organic layer was washed with H_2O and brine, and dried over anhydrous Na_2SO_4. Evaporation of the solvent left a crude oil, which was purified by column chromatography using 20% EtOAc in hexane for elution to give **14b** (6 mg, 100%) as an oil. IR (film) cm^{-1}: 1725 (C=O). ^{1}H-NMR δ: 0.03 (6H, s, $2\times CH_3$), 0.86 (9H, s, *tert*-Bu), 1.30—2.55 (12H, br, $6\times CH_2$), 3.10 (2H, m, SCH_2), 3.44 (1H, dd, J=13.0, 7.0 Hz, SCH), 3.60 (2H, t, J=7.0 Hz, OCH_2), 5.50 (2H, m, CH=CH). MS *m/z*: 342 (M^+). HRMS Calcd for $C_{18}H_{34}O_2SSi$: 342.2047. Found: 342.2045.

General Procedure for Reaction of 8d with Electrophiles in the Presence of *tert*-BuLi An electrophile (methyl iodide, benzyl bromide, geranyl bromide, propyl iodide, 2-cyclopentenone, 2-cyclohexenone or 2-bromocyclopentanone) was added to a solution of **8d** (0.1 mM) and 1.5 M *tert*-BuLi (0.11 mM) in THF (4 ml) at −78 °C under argon, and the mixture was stirred for 10 min at this temperature. The reaction was quenched by the addition of H_2O and the solvent was evaporated off under reduced pressure. The residue was extracted with CH_2Cl_2 and the extract was washed with H_2O and brine, and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave a crude oil, which was purified by column chromatography using 5% EtOAc in hexane for elution to give **16** as an oil.

(*Z*)-7-Methylthio-5-heptenyl 2,2-Dimethylpropionate **(16a)**: IR (film) cm^{-1}: 1720 (C=O). ^{1}H-NMR δ: 1.18 (9H, s, *tert*-Bu), 1.43 and 1.64 (each 2H, each q, J=7.5 Hz, $2\times CH_2$), 2.0 (3H, s, CH_3), 2.07 (2H, q, J=7.5 Hz, $=CHC\underline{H}_2$), 3.11 (2H, d, J=7.5 Hz, SCH_2), 4.03 (2H, t, J=7.5 Hz, OCH_2), 5.43 (1H, dt, J=10.5, 6.2 Hz, C_6-H), 5.52 (1H, dt, J=10.5 Hz, 6.8 Hz, C_5-H). MS *m/z*: 244 (M^+). HRMS Calcd for $C_{13}H_{24}O_2S$: 244.1496. Found: 244.1494.

This compound **(16a)** was alternatively prepared as follows: A mixture of **13a** (18 mg, 0.12 mM) and pivaloyl chloride (17 mg, 0.14 mM) was allowed to stand overnight in the presence of triethylamine (15 mg, 0.14 mM) and 4-DMAP (1.5 mg, 0.012 mM) in THF (4 ml). Extractive work-up and purification by column chromatography gave **16a** (10 mg, 35%).

(*Z*)-7-Benzylthio-5-heptenyl 2,2-Dimethylpropionate **(16b)**: IR (film) cm^{-1}: 1720 (C=O). ^{1}H-NMR δ 1.16 (9H, s, *tert*-Bu), 1.40—1.65 (4H, m, $2\times CH_2$), 1.97 (2H, q, $=CHC\underline{H}_2$), 3.05 (2H, d, J=7.0 Hz, SCH_2), 3.66 (2H, s, $ArCH_2$), 4.0 (2H, t, J=7.0 Hz, OCH_2), 5.46 (2H, m, CH=CH), 7.2—7.4 (5H, m, Ar-H). MS *m/z*: 320 (M^+). HRMS Calcd for $C_{19}H_{28}O_2S$: 320.1809. Found: 320.1810.

(*Z,E*)-7-(3,7-Dimethyl-2,6-octadienyl)thio-5-heptenyl 2,2-Dimethylpropionate **(16c)**: IR (film) cm^{-1}: 1720 (C=O). ^{1}H-NMR δ: 1.18 (9H, s, *tert*-Bu), 1.55—1.67 (13H, $3\times CH_3$ and $2\times CH_2$), 1.98—2.12 (6H, br, $3\times =CHC\underline{H}_2$), 3.10 (4H, d, J=7.5 Hz, CH_2SCH_2), 4.02 (2H, t, J=7.3 Hz, OCH_2), 5.06, 5.24 (each 1H, each m, $2\times$ =CH), 5.48 (2H, m, CH=CH). MS *m/z*: 366 (M^+). HRMS Calcd for $C_{22}H_{38}O_2S$: 366.2591. Found: 366.2597.

(*Z*)-7-Propylthio-5-heptenyl 2,2-Dimethylpropionate **(16d)**: IR (film) cm^{-1}: 1725 (C=O). ^{1}H-NMR δ: 0.95 (3H, t, J=8.0 Hz, $CH_2C\underline{H}_3$), 1.17 (9H, s, *tert*-Bu), 1.36—1.66 (6H, m, $3\times CH_2$), 2.02—2.12 (2H, q, J=7.5 Hz, $=CHC\underline{H}_2$), 2.43 (2H, t, J=7.5 Hz, SCH_2), 3.10—3.15 (2H, d, J=7.5 Hz, $SC\underline{H}_2CH=$), 4.03 (2H, t, J=7.2 Hz, OCH_2), 5.46 (2H, m, CH=CH). MS *m/z*: 272 (M^+). HRMS Calcd for $C_{15}H_{28}O_2S$: 272.1809. Found: 272.1814.

(*Z*)-7-(3-Oxocyclopentyl)thio-5-heptenyl 2,2-Dimethylpropionate **(16e)**: IR (film) cm^{-1}: 1720 (C=O). ^{1}H-NMR δ: 1.17 (9H, s, *tert*-Bu), 1.30—2.65 (12H, m, $5\times CH_2$ and $=CHC\underline{H}_2$), 3.21 (2H, d, J=7.0 Hz, SCH_2), 3.40 (1H, quint, J=7.0 Hz, SCH), 4.04 (2H, t, J=7.0 Hz, OCH_2), 5.50 (2H, m, CH=CH). MS *m/z*: 312 (M^+). HRMS Calcd for $C_{17}H_{28}O_3S$: 312.1758. Found: 312.1780.

(*Z*)-7-(3-Oxocyclohexyl)thio-5-heptenyl 2,2-Dimethylpropionate **(16f)**: IR (film) cm^{-1}: 1710 (C=O). ^{1}H-NMR: 1.16 (9H, s, *tert*-Bu), 1.37—2.15 (12H, m, $6\times CH_2$), 2.25—2.39 (2H, m, $=CHC\underline{H}_2$), 3.0 (1H, m, SCH), 3.20 (2H, d, J=7.5 Hz, SCH_2), 4.03 (2H, t, J=7.2 Hz, OCH_2), 5.45 (2H, m, CH=CH). MS *m/z*: 326 (M^+). HRMS Calcd for $C_{18}H_{30}O_3S$: 326.1914. Found: 326.1921.

(*Z*)-7-(2-Oxocyclopentyl)thio-5-heptenyl 2,2-Dimethylpropionate **(16g)**: IR (film) cm^{-1}: 1720 (C=O). ^{1}H-NMR δ: 1.17 (9H, s, *tert*-Bu), 1.35—2.60 (12H, m, $5\times CH_2$ and $-CHC\underline{H}_2$), 3.10 (2H, m, SCH_2), 3.43 (1H, dd, J=14.0, 8.1 Hz, SCH), 4.02 (2H, t, J=7.0 Hz, OCH_2), 5.50 (2H, m, CH=CH). MS *m/z*: 312 (M^+). HRMS Calcd for $C_{17}H_{28}O_3S$: 312.1758. Found: 312.1782.

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