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[3,3]SIGMATROPIC RING EXPANSION OF CYCLIC THIONOCARBONATES. 8.[1] HIGHLY STEREOSELECTIVE SYNTHESIS OF (*Z*)- OR (*E*)-DOUBLE BONDS BY CONTROLLING CHAIRLIKE-BOATLIKE TRANSITION STATES IN THE [3,3]SIGMATROPIC REARRANGEMENT OF 8-MEMBERED THIONOCARBONATES[2]

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Abstract: A highly stereoselective synthesis of (*Z*)- or (*E*)-double bonds in 10-membered thiolcarbonates (**3**) was successfully conducted by controlling the chairlike-boatlike transition states in the [3,3]sigmatropic rearrangement of 8-membered thionocarbonates (**2**). The geometry of the product appeared to be highly dependent on the substituent pattern in the allylic system of the substrates (**1**). The 10-membered thiolcarbonates (**3**) were readily converted to (*Z*)- or (*E*)-allylic thiolcarbonates (**11**). Treatment of (*Z*)-**3j** or **3i** with lithium in liquid ammonia afforded (*Z*)-trisubstituted or tetrasubstituted olefins (**12j** and **12i**) in high yields.

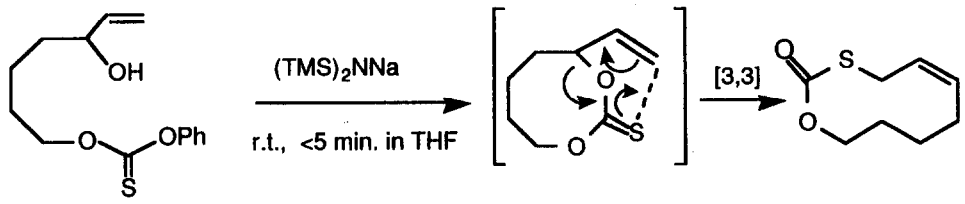
Introduction

[3,3]Sigmatropic rearrangements represented by Cope and Claisen rearrangements are very useful for the construction of desired molecules and many variations have been developed.[3] The strong preference for a chairlike conformation in the transition state for the rearrangement of acyclic systems serves as a basis for predicting product stereochemistry.[3a, d]

The exclusive (*E*)-selectivity of the double bond geometry by [3,3]sigmatropic rearrangement has been extensively used for natural products synthesis.[3c),4] However, only few synthetic studies on the opposite (*Z*)-selective [3,3]sigmatropic rearrangement have so far been reported owing to the lack of suitable methodology.[5] Consequently, it is difficult to obtain the (*Z*) selectivity using conventional methodologies. [3,3]Sigmatropic rearrangements of allylic thion-esters[6] have proven exceedingly useful for the (*E*)-selective construction of unsaturated systems. Faulkner and Petersen[7] showed that treatment of 2-methyl-1-penten-3-ol with phenyl chlorothionoformate in pyridine at -20 °C afforded a mixture of phenyl 2-methyl-2-pentenyl thiolcarbonates containing 96.5% (*E*)-olefin and 3.5% (*Z*)-olefin by rearrangement of the intermediate allylic thionocarbonate.[8]

Recently, we reported[9] that treatment of a diol monothionocarbonate (**1a**) with sodium bis(trimethylsilyl)amide [$(TMS)_2NNa$][9b] in tetrahydrofuran (THF) resulted in the formation of an 8-membered thionocarbonate (**2a**)[1] followed by spontaneous [3,3]sigmatropic ring expansion to give a 10-membered heterocyclic thiolcarbonate (**3a**)[9a] containing a (*Z*)-double bond in 78% yield (Scheme 1). This result is in contrast to the high (*E*)-selectivity of allylic thiolcarbonate by rearrangement of a linear allylic thionocarbonate

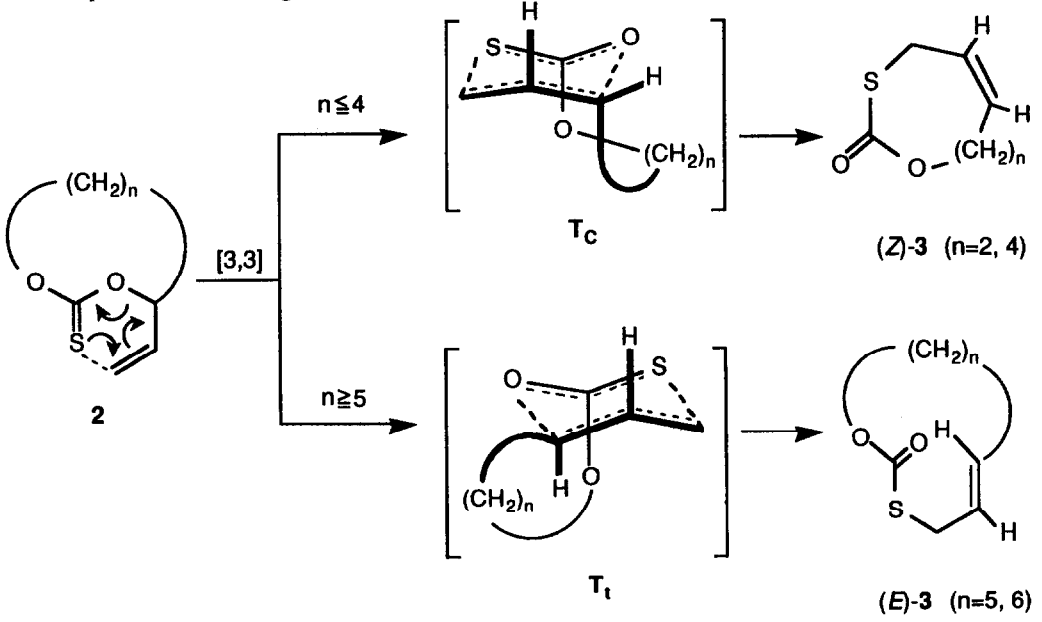
mentioned above. Although the intermediate (**2a**) has not been isolated, the easy production of 8-membered thionocarbonates,[1] which contain the alkyl groups instead of the ethenyl group of **2a**, confirmed this mechanism.



1a **2a** **3a** (78%)

Scheme 1

The relationship between ring size of cyclic thionocarbonates (**2**) and geometry of the created double bond in medium- and large-membered thiolcarbonates (**3**, n=2-6) has been clarified (Scheme 2).[9b] Importantly, the ring size of the cyclic thionocarbonate (**2**) determines the double bond geometry of the products (**3**). This study provides an interesting insight into factors influencing the transition state of the [3,3]sigmatropic rearrangement. The formation of the (*Z*)-olefins indicated that [3,3]sigmatropic ring expansion proceeded exclusively *via* the transition state ($\mathbf{T_c}$) tethered in a *cis* relationship when the cyclic thionocarbonates (**2**) are 8-membered or smaller ($n \leqq 4$). On the other hand, a relatively strain-free transition state ($\mathbf{T_t}$) tethered in a *trans* relationship was adopted when the ring size was 9-membered or larger. This study indicated that [3,3]sigmatropic



Scheme 2

rearrangement of 8-membered thionocarbonate proceeded most favorably in the synthesis of medium- and large-membered thiolcarbonates. Our continued interest in this area prompted us to clarify the relationship between the substituent pattern in the allylic system of substrate **1** and product geometry. We report herein that

the highly stereoselective construction of (*Z*)- or (*E*)-double bonds in 10-membered thiolcarbonates is achieved by controlling chairlike-boatlike transition states in the [3,3]sigmatropic rearrangement of 8-membered thionocarbonates.

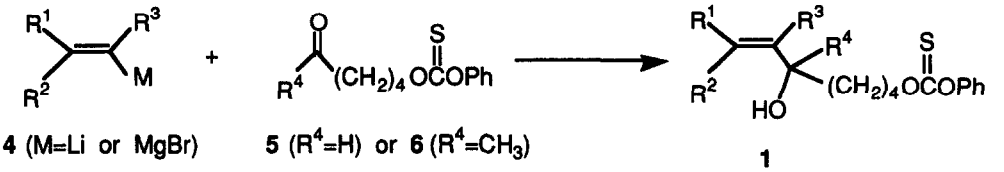
Synthesis of Diol Monothionocarbonates (1)

The diol monothionocarbonates (**1b-j**) used in the present study were prepared by two different routes as summarized in Tables 1 and 2. The mono- and disubstituted alkenyllithiums (**4**, M=Li) employed in the Table 1 were prepared by lithium-iodine exchange[10] from the corresponding alkenyl iodides.[11a),11b] Grignard reagents (**4**, M=MgBr) were generated *in situ* by treatment of magnesium metal with commercially available alkenyl bromides. *O*-4-Formylbutyl *O*-phenyl thionocarbonate (**5**) was prepared according to our previous report.[9b] *O*-5-Oxo-hexyl *O*-phenyl thionocarbonate (**6**) was synthesized by treatment of 6-hydroxy-2-hexanone (**8**)[12a] with phenyl chlorothionoformate (PCTF). Thus, (*E*)-1-hexenyllithium [(*E*)-**4b**][10] prepared from (*E*)-1-iodo-1-hexene[11a] was treated with aldehyde (**5**) in diethyl ether at -78 °C to give the diol monothionocarbonate [(*E*)-**1b**] (61%) (Table 1, run 1), which was purified by flash column chromatography. Similarly, diol monothionocarbonates [(*Z*)-**1b** and **1j**, (*E*)-**1c**, **1d**, and **1j**] having a mono- or disubstituted alkene were prepared. 2-Propenylmagnesium bromide (**4i**) was used for the formation of **1i** (Table 1, run 5). Reactions of 5-hydroxypentanal (**7**)[12b] or a ketone (**8**) with alkenylmagnesium bromides (**4b, e - g,** and **h**) in the Table 2 afforded diols (**9**), which were subsequently converted to diol monothionocarbonates (**1b, e - h**) by the slow addition of PCTF in the presence of pyridine and 4-dimethylaminopyridine (4-DMAP). *O*-[(*Z*)-5-Hydroxy-6-octenyl] *O*-phenyl thionocarbonate [(*Z*)-**1e**] was isolated from a 1:1 mixture of diol monothionocarbonates [(*E*)- and (*Z*)-**1e**] by flash chromatography. The MS and ^{1}H-NMR spectral data of the diol monothionocarbonates (**1**) are summarized in Table 5 (see Experimental).

Results and Discussion

Study was made to determine whether the introduction of an alkyl group into the allylic system of the substrate **1** influences the geometry of the created double bond in 10-membered thiolcarbonates (**3**). When a dry THF solution of $(TMS)_2NNa$ (1.1 eq) was rapidly added to a THF solution of diol monothionocarbonate [(*E*)-**1b**] having a n-butyl group at the R^1 position, the reaction went to completion immediately. After the usual workup a (*Z*)-10-membered thiolcarbonate [(*Z*)-**3b**] was isolated by flash chromatography in 88% yield (Scheme 3, eq-1). The structure of (*Z*)-**3b** was examined by the ^{1}H-NMR spectrum. The protons at C_{10} in (*Z*)-**3b** were separately observed at δ 3.76 (1H, ddd, *J*=11.8, 6.5, 4.2 Hz) and δ 4.95 (1H, dt, *J*=11.8, 3.5 Hz), suggesting that this 10-membered ring is conformationally fixed at room temperature.[13a] However, the geometry of the double bond in the product could not be determined at this stage since the vinyl proton signals of (*Z*)-**3b** were superimposed at δ 5.20-5.40 (2H, m). Thus, (*Z*)-**3b** was converted to a (*Z*)-allylic thiolcarbamate [(*Z*)-**11b**] (Table 4, run 2) in 83% yield by alkaline hydrolysis followed by treatment of the resulting allylic thiol [(*Z*)-**10b**] with dimethylcarbamoyl chloride in the presence of triethylamine and 4-DMAP, as shown in Table 4. Examination of (*Z*)-**11b** by the ^{1}H-NMR spectrum [δ 5.28 (t, *J*=11.0 Hz), 5.43 (ddd, *J*=11.0, 8.2, 7.1 Hz)] indicated the product to possibly be the (*Z*)-isomer. The complete isomeric purity of (*Z*)-**3b** was confirmed by vapor phase chromatography (VPC) analysis using a 1.5% silicon OV-17 column, as shown in Scheme 3.

Table 1. Synthesis of Diol Monothionocarbonates (**1b-d, i, and j**)

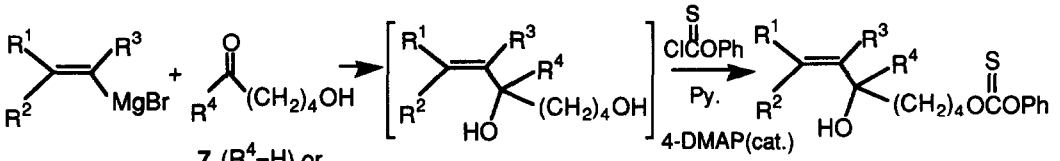


4 (M=Li or MgBr) **5** (R^4=H) or **6** (R^4=CH_3) **1**

Runs	4	M	5 or 6	R^1	R^2	R^3	R^4	1	Yields (%)[a]
1	(*E*)-**4b**	Li	**5**	$CH_3(CH_2)_3$-	H	H	H	(*E*)-**1b**	61
2	(*Z*)-**4b**	Li	**5**	H	$CH_3(CH_2)_3$-	H	H	(*Z*)-**1b**	61[b]
3	(*E*)-**4c**	Li	**5**	$CH_3(CH_2)_2$-	H	H	H	(*E*)-**1c**	53[c]
4	(*E*)-**4d**	Li	**5**	Ph	H	H	H	(*E*)-**1d**	68[c]
5	**4i**	MgBr	**6**	H	H	CH_3	CH_3	**1i**	87
6	(*E*)-**4j**	Li	**6**	$CH_3(CH_2)_3$-	H	H	CH_3	(*E*)-**1j**	37[d]
7	(*Z*)-**4j**	Li	**6**	H	$CH_3(CH_2)_3$-	H	CH_3	(*Z*)-**1j**	64[e]

a) Isolated yield. b) **5** (18%) was recovered. c) Reference 13). d) **5** (32%) was recovered. e) **6** (16%) was recovered.

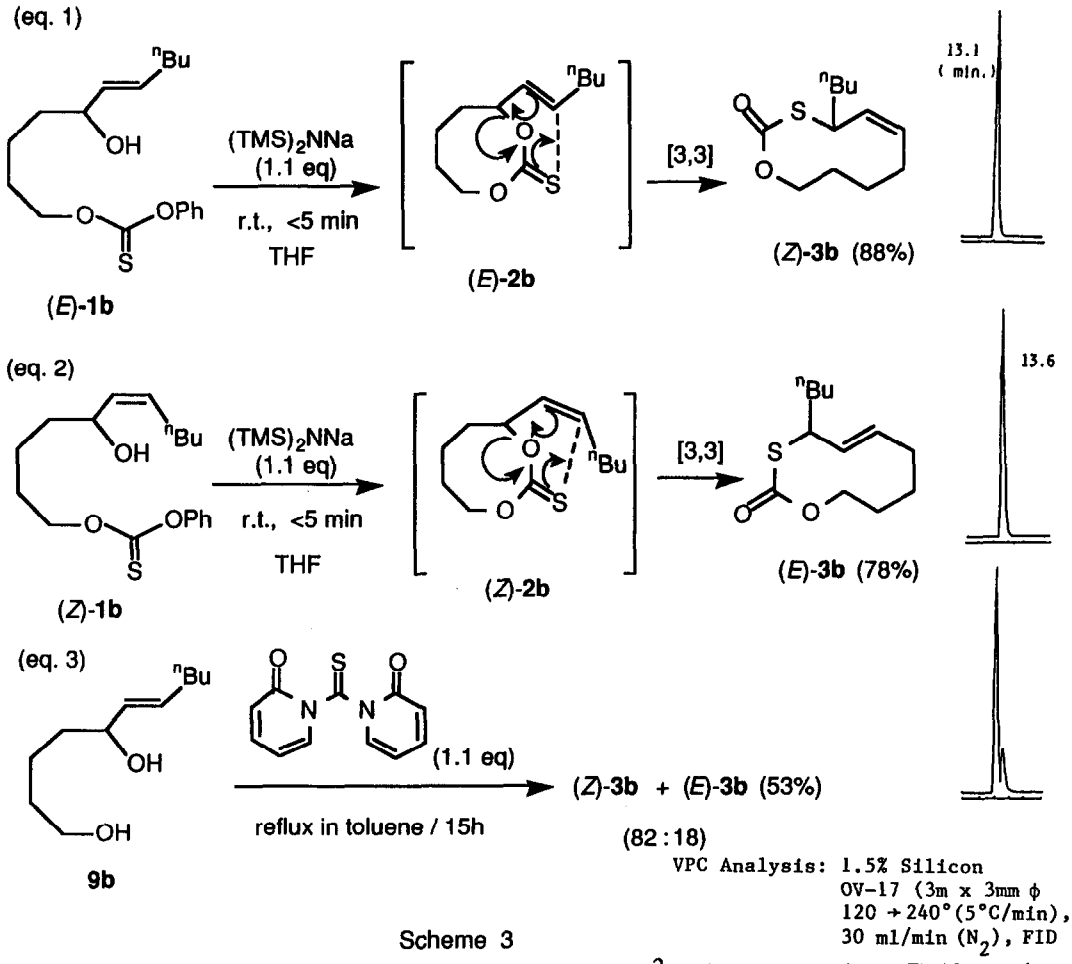
Table 2. Synthesis of Diol Monothionocarbonates (**1b, e - g,** and **h**)



4 **7** (R^4=H) or **8** (R^4=CH_3) **9** 4-DMAP(cat.) **1**

Runs	4	R^1	R^2	R^3	R^4	7 or 8	1	Yield (%)[a]
1	(*E*)-**4b**	$CH_3(CH_2)_3$-	H	H	H	**7**	(*E*)-**1b**	36
2	(*E*)-**4e**	CH_3	H	H	H	**7**	(*E*)-**1e**	49
3[b]	(*E*)-**4e**	CH_3	H	H	H	**7**	(*E*)-**1e**	36[d]
	(*Z*)-**4e**	H	CH_3	H	H	**7**	(*Z*)-**1e**[c]	
4	**4f**	H	H	CH_3	H	**7**	**1f**	67
5	**4g**	H	H	H	CH_3	**8**	**1g**	63
6	**4h**	CH_3	CH_3	H	H	**7**	**1h**	40

a) Isolated yields. b) A 1:1 mixture of (*E*)-and (*Z*)-**4e** was employed. c) (*Z*)-**1e** was isolated by a flash chromatography (see Experimental). d) A 1:1 mixture of (*E*)- and (*Z*)-**1e**.

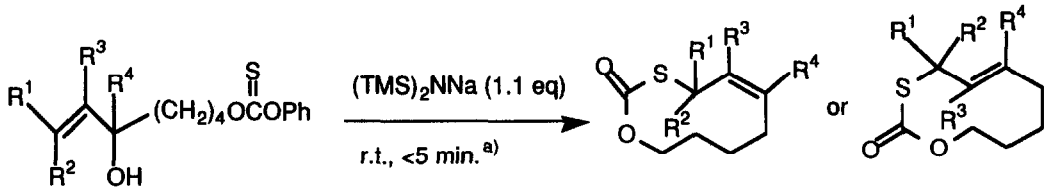


Scheme 3

The same treatment of (*Z*)-**1b** having a n-butyl group at the R^2 position provided an (*E*)-10-membered thiolcarbonate [(*E*)-**3b**] in 78% yield (Scheme 3, eq. 2). The presence of the (*E*)-double bond in the product was easily determined by inspection of the ^{1}H-NMR spectrum [δ 5.48 (ddd, *J*=15.3, 11.8, 3.5 Hz), 5.13 (ddd, *J*=15.3, 10.0, 1.8 Hz)]. VPC analysis and the ^{1}H-NMR spectrum showed (*E*)-**3b** to have 100% isomeric purity. An alternative approach[9b] using 1,1'-thiocarbonyldi-2(*H*)-pyridone (TCDP)[14] as the thiocarbonyl source was used for the synthesis of (*Z*)-**3b**. Heating of (*E*)-6-undecene-1,5-diol (**9b**) with TCDP (1.1 eq) in toluene under reflux for 15 h afforded an 82:12 mixture of (*Z*)- and (*E*)-**3b** in 53% yield (Scheme 3, eq 3). This indicates that the former method should be used to obtain the geometric integrity of a created double bond in the 10-membered thiolcarbonates (**3**).

We examined various substrates each having a substituent at the R^1-R^4 position. The results are summarized in Table 3. Substrates [(*E*)- and (*Z*)-**1e**] having a methyl group instead of a n-butyl group at R^1 or R^2 position afforded isomeric pairs of (*Z*)-**3e** and (*E*)-**3e** in 58% and 60% yields, respectively (Table 3, runs 6 and 7). It is thus evident that the respective olefin geometry in the starting materials is converted to the opposite geometry with complete isomeric purity. A n-propyl and a phenyl group at the R^1 position in each

Table 3. Synthesis of 10-Membered Thiolcarbonates (3) Containing (*Z*)- or (*E*)-Double Bond

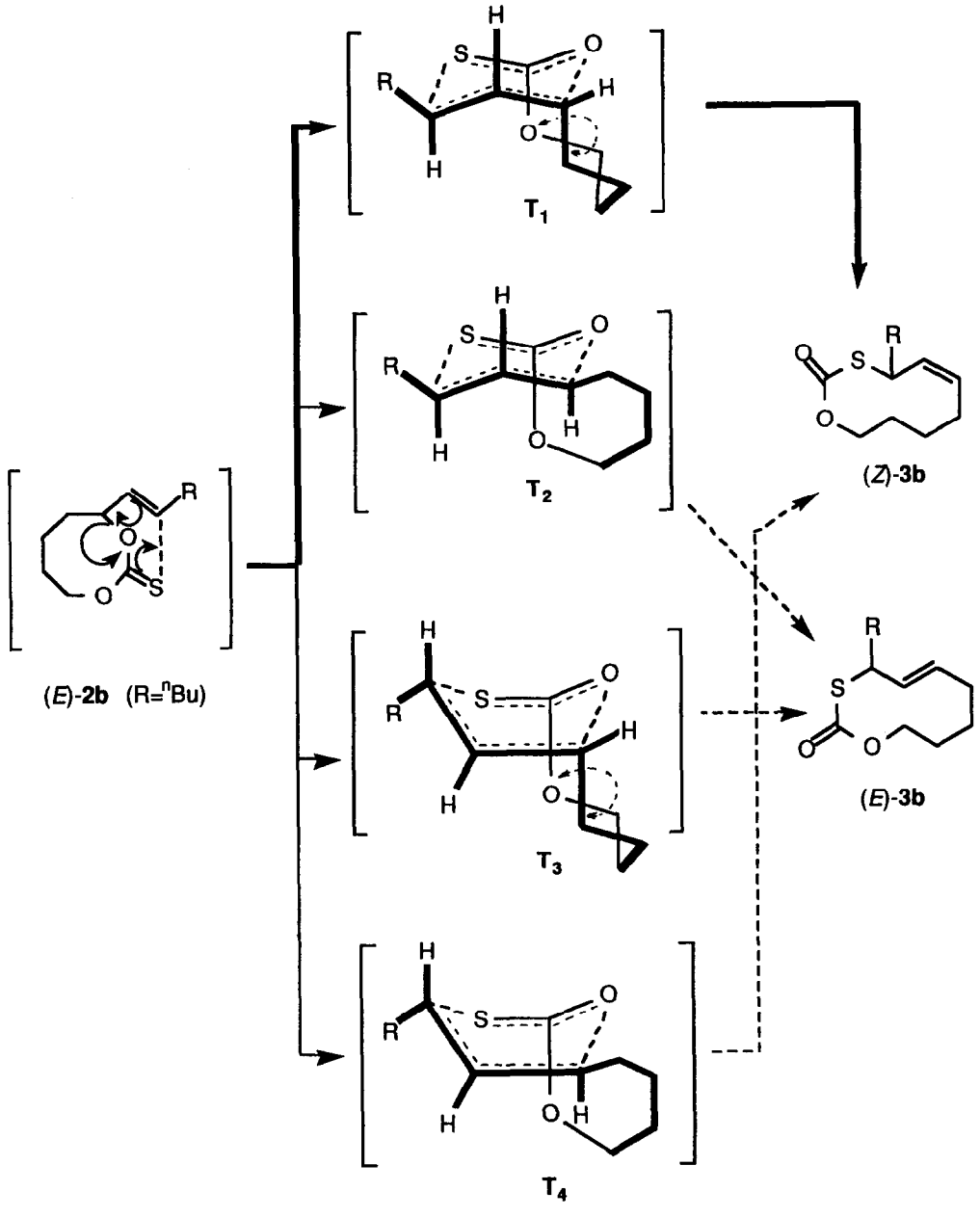


1 (*Z*)-3 (*E*)-3

Runs	1	R^1	R^2	R^3	R^4	T.S.[b]	Products[e]	Yields (%)[g]
1	**1a**	H	H	H	H	C[c]	(*Z*)-**3a**	78[h] (85)[i]
2	(*E*)-**1b**	$CH_3(CH_2)_3$-	H	H	H	C	(*Z*)-**3b**	88
3	(*Z*)-**1b**	H	$CH_3(CH_2)_3$-	H	H	B[d]	(*E*)-**3b**	78
4	(*E*)-**1c**	$CH_3(CH_2)_2$-	H	H	H	C	(*Z*)-**3c**	73[j]
5	(*E*)-**1d**	Ph	H	H	H	C	(*Z*)-**3d**	50[j]
6	(*E*)-**1e**	CH_3	H	H	H	C	(*Z*)-**3e**[f]	58
7	(*Z*)-**1e**	H	CH_3	H	H	B	(*E*)-**3e**[f]	60
8	**1f**	H	H	CH_3	H	C	(*Z*)-**3f**	74
9	**1g**	H	H	H	CH_3	C	(*Z*)-**3g**	43 (76)[k]
10	**1h**	CH_3	CH_3	H	H	B	(*E*)-**3h**	65
11	**1i**	H	H	CH_3	CH_3	C	(*Z*)-**3i**	18 (77)[i]
12	(*E*)-**1j**	$CH_3(CH_2)_3$-	H	H	CH_3	C	(*Z*)-**3j**	77
13	(*Z*)-**1j**	H	$CH_3(CH_2)_3$-	H	CH_3	C & B	(*Z*)-**3j**[l] (*E*)-**3j**	49[m]

a) Unless otherwise stated, the reactions were carried out according to general procedure. b) T.S. : Transition State. c) C: Chairlike Transition State. d) B: Boatlike Transition State. e) Unless otherwise stated, complete isomeric purity was determined by ^{1}H-NMR and VPC analysis. f) Isomeric purity was determined after conversion to the corresponding allylic thiolcarbamate (**11**). g) Isolated yield of purified product. h) See reference 9b). i) $(TMS)_2NLi$ (1.0 eq) was used. j) See reference 13b). k) $(TMS)_2NK$ (1.0 eq) was used under 10^{-1}M condition. l) A 52:48 mixture of (*Z*)- and (*E*)-**3j**. m) (*Z*)-**1j** (29%) was recovered.

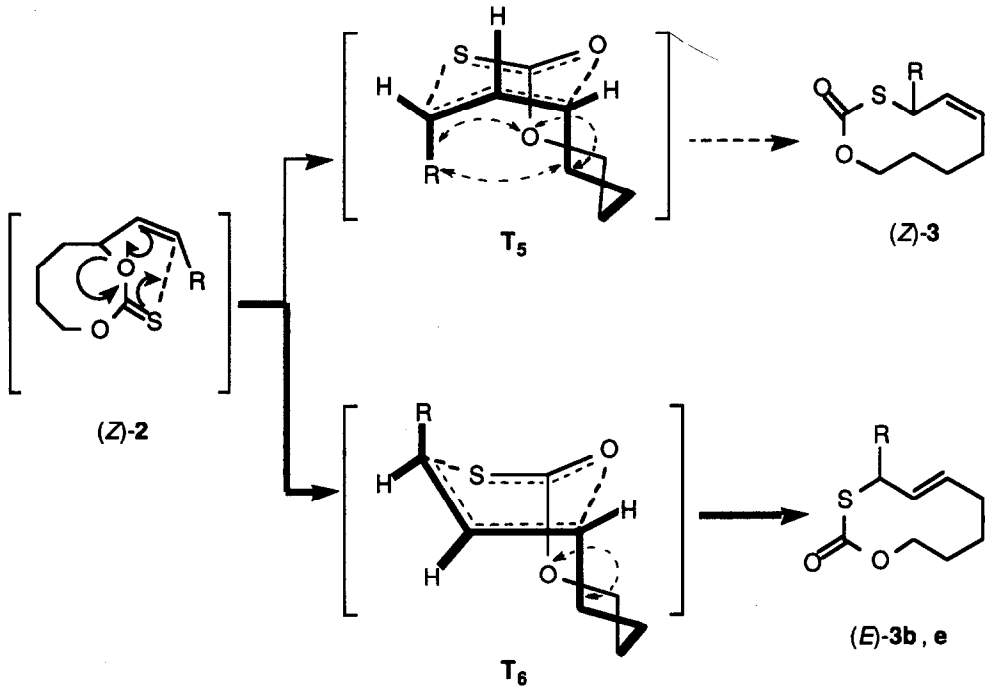
substrate (**1c** and **1d**) did not hinder the production of (*Z*)-**3c** and (*Z*)-**3d** in 73 and 50% yields, respectively (Table 3, *runs* 4 and 5).[13b] In *runs* 8 (R^3=CH_3) and 9 (R^4=CH_3), the reaction proceeds in the same manner to give only (*Z*)-isomers (**3f** and **3g**). Substrates, in which the R^1, R^3 or R^4 position is occupied by a substituent, thus afford only (*Z*)-**3**, whereas substrates having a substituent at the R^2 position, exclusively (*E*)-**3**.



Scheme 4

The formation of a (*Z*)-double bond in the 10-membered thiolcarbonate[(*Z*)-**3b**] can be discussed in the light of Scheme 4. In principle, the [3,3]sigmatropic rearrangement of the 8-membered thionocarbonate [(*E*)-**2b**] can provide four conformations as transition states, that is, chair- and boatlike transition states (T_1 and T_3) with the diaxially bridging chain and transition states (T_2 and T_4) bearing the chain tethered in a *trans* relationship. However, transition structures such as T_2 and T_4 would be ruled out because of severe strain incurred in the four-carbon tether during proper alignment of the thionocarbonyl group and double bond for the

[3,3]sigmatropic ring expansion. These conformations occur only when cyclic thionocarbonates are 9-membered or larger, as indicated in our previous paper.[9b] Examination of models of the possible transition states indicated that $\mathbf{T_1}$ and $\mathbf{T_3}$, although disposing an additional 1,3-diaxial interaction, are considerably less strained than $\mathbf{T_2}$ and $\mathbf{T_4}$. The (*Z*) selectivity of (*Z*)-**3b** can be explained by the chairlike transition state ($\mathbf{T_1}$), since the boatlike transition state ($\mathbf{T_3}$) leads to the opposite geometry. The formation of a (*Z*)-double bond in (*Z*)-**3c**, **3d**, and **3e** (Table 3, runs 4, 5, and 6) can be rationalized by the transition state ($\mathbf{T_1}$). With (*Z*)-**3f** and **3g** (R^3=CH_3 or R^4=CH_3), the geometry may be explained on the basis of the transition state ($\mathbf{T_1}$) (Table 3, runs 8 and 9). The formation of (*E*)-**3** (Table 3, runs 3 and 7), in which the R^2 position is occupied by a substituent (R^2=n-butyl or CH_3) may be accounted for by the conformational preference of a boatlike transition state ($\mathbf{T_6}$) over a chairlike transition state ($\mathbf{T_5}$) incurred a severe pseudo-1,3-diaxial interactions leading to the (*Z*)-**3** (Scheme 5).

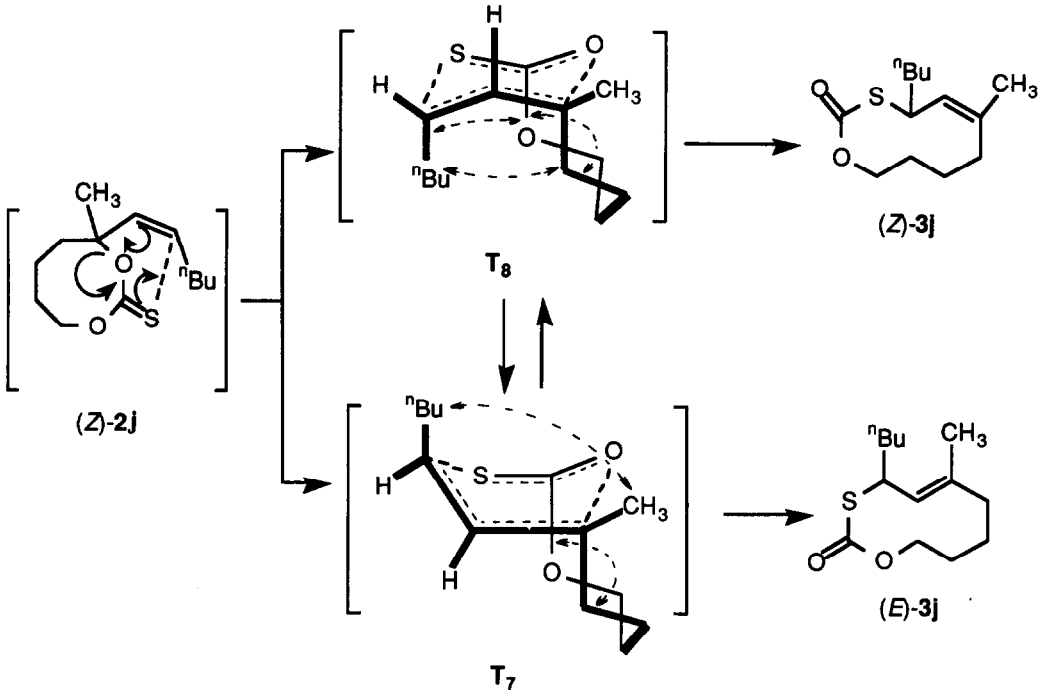


Scheme 5

We recently reported[15] computational evaluation of the proposed transition states ($\mathbf{T_1}$ and $\mathbf{T_6}$) using a combination of MM and MO-SCAN calculations. The calculated data were compatible with the observed results.[16]

We examined four additional substrates having two alkyl groups in the allylic systems to assess the scope and generality of this method. Substrate **1h** in which the R^1 and R^2 positions are occupied by methyl groups afforded only (*E*)-**3h** through the boatlike transition state, as anticipated (Table 3, run 10). Treatment of **1i** having two methyl groups at R^3 and R^4 positions with $(TMS)_2NNa$ gave a crystalline (*Z*)-**3i** though in low yield (Table 3, run 11). It is interesting to note that use of $(TMS)_2NLi$ as the base remarkably improved the

yield of the product from 18% to 77%. In this manner, we often observed that selection of the base provided better yields of **3** (Table 3, runs 1 and 9). The methylene protons of **3i** in the ^{1}H-NMR spectrum was observed as very broaded signals (CH_2 x 3: δ 2.34-5.43), suggesting that 10-membered thiolcarbonate in solution is conformationally dynamic at room temperature. The structure of (*Z*)-**3i** was confirmed by conversions of **3i** into a (*Z*)-allylic thiolcarbamate (**11i**) (Table 4, run 9) or a tetrasubstituted olefin (**12i**) (Scheme 7). The substrate (*E*)-**1j** having n-butyl and methyl groups at R^1 and R^4 positions afforded (*Z*)-**3j** in 77% yield as a result of the T_1-type transition state. However, in case of (*Z*)-**1j** (R^2=n-butyl, R^4=CH_3), the reaction gave a 52:48 mixture of (*Z*)-and (*E*)-**3j** in 49% yield with recovery of (*Z*)-**1j** (29%) (Table 3, run 13). This marked lack of the stereoselectivity may be explained as follows. The formation of the (*Z*)-**3j** may be accounted as due to the transition state (T_8) having severe pseudo-1,3-diaxial interactions in the chairlike transition state. On the other hand, the boatlike transition state (T_7) leading to the expected (*E*)-**3j** would incur additional $A^{(1,3)}$-type[17] interaction between n-butyl and methyl groups at R^2 and R^4 positions, as illustrated in Scheme 6. Consequently, since T_7 was energetically approximated to T_8, the reaction should give rise to (*Z*)-**3j** and (*E*)-**3j** in a ratio of approximately 1:1.



Scheme 6

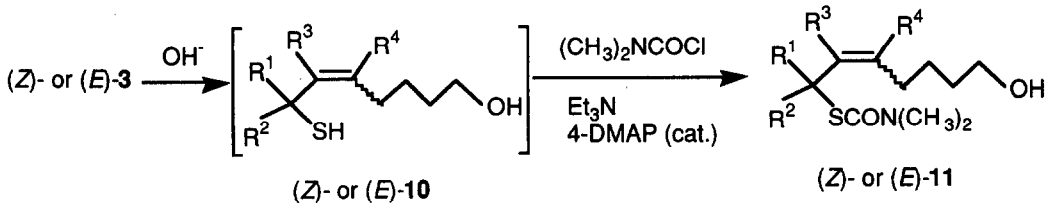
In conclusion, the geometry of the product (**3**) appears highly dependent on the substituent pattern in the allylic system of the substrates (**1**). The reaction can provide a (*Z*)- or (*E*)-double bond with geometric integrity in 10-membered thiolcarbonates. Importantly, the highly stereoselective synthesis of (*Z*)- or (*E*)-double bonds in 10-membered thiolcarbonates (**3**) was successfully conducted by controlling the chairlike-boatlike transition states in the [3,3]sigmatropic rearrangement of 8-membered thionocarbonates (**2**). This may help clarify how

transition state of the [3,3]sigmatropic rearrangement is controlled. The rearrangements of the intermediates (**2**) are exceptionally fast and attain completion immediately at room temperature as opposed to the elevated temperature often required for sigmatropic rearrangements.[3] Thus, the remarkable ease of these reactions is noteworthy.

Conversion of the 10-Membered Thiolcarbonates [(*Z*)- or (*E*)-3] into Allylic Thiolcarbamates [(*Z*)- or (*E*)-11] or Substituted Olefins (12)

The controlled formation of carbon-carbon bonds is often a critical step in organic synthesis. Organosulfur carbanions derived from allylic sulfides have proven extremely useful in this process.[6a),18] (*E*)-Allylic sulfides are synthesized by a variety of methods involving [3,3]sigmatropic rearrangement.[19] The present method[20] for (*Z*)-allylic sulfides still relies on Lindlar hydrogenation of the corresponding acetylenes.[20a,b] In a previous paper,[9] we showed that hydrolysis of the cyclic thiolcarbonates (**3a**) containing a (*Z*)-double bond with sodium hydroxide in aqueous methanol at room temperature easily afforded a (*Z*)-allylic thiol (**10a**) having a versatile alcohol function at the terminal position with liberation of carbon dioxide. The reaction of **10a** with dimethylcarbamoyl chloride led to a (*Z*)-allylic thiolcarbamate (**11a**) (Table 4, run 1), which under-

Table 4. Conversion of Cyclic Thionocarbonates (**3**) into (*Z*)- or (*E*)-Allylic Thiolcarbamates (**11**)

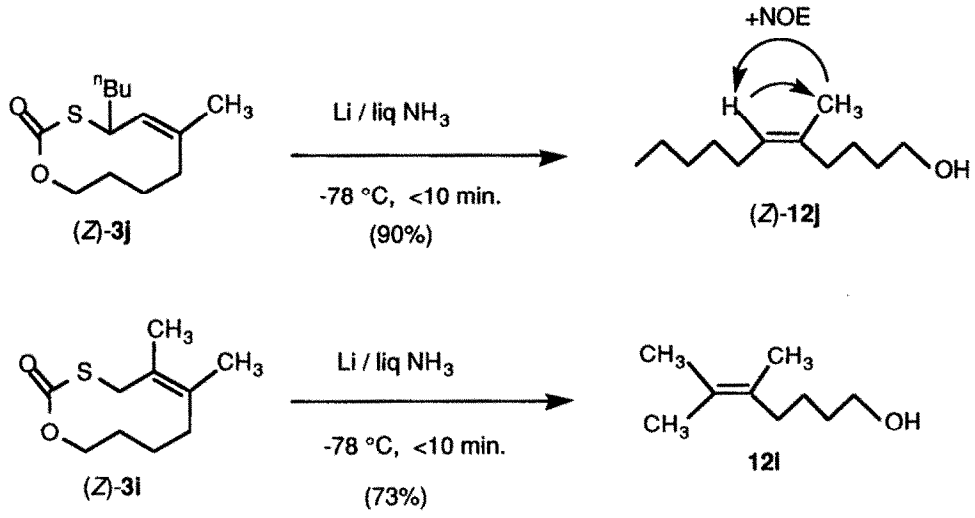


(*Z*)- or (*E*)-**10** (*Z*)- or (*E*)-**11**

Runs	Substrates	R^1	R^2	R^3	R^4	Products	Yields (%)[a]
1	(*Z*)-**3a**	H	H	H	H	(*Z*)-**11a**	92[b]
2	(*Z*)-**3b**	$CH_3(CH_2)_3$-	H	H	H	(*Z*)-**11b**	83
3	(*E*)-**3b**	H	$CH_3(CH_2)_3$-	H	H	(*E*)-**11b**	84
4	(*Z*)-**3e**	CH_3	H	H	H	(*Z*)-**11e**	58
5	(*E*)-**3e**	H	CH_3	H	H	(*E*)-**11e**	60
6	(*Z*)-**3f**	H	H	CH_3	H	(*Z*)-**11f**	60
7	(*Z*)-**3g**	H	H	H	CH_3	(*Z*)-**11g**	80
8	(*E*)-**3h**	CH_3	CH_3	H	H	(*E*)-**11h**	86
9	(*Z*)-**3i**	H	H	CH_3	CH_3	(*E*)-**11i**	64

a) Isolated yields. b) See reference 9).

went α-alkylation with complete retention of the double bond position and stereochemistry.[9] Alkaline hydrolysis of the 10-membered thiolcarbamates [(*Z*)- or (*E*)-**3**] obtained in this study easily afforded the corresponding allylic thiols (**10**) which was subsequently led to allylic thiolcarbamates [(*Z*)- or (*E*)-**11**] in good yields, as summarized in Table 4. The complete retention of the double bond in **11** was confirmed by the ^{1}H-NMR spectrum and VPC analysis. The conversions of cyclic thiolcarbonates (**3**) containing a (*Z*)- or (*E*)-double bond into **10** and **11** may provide a versatile and flexible approach for (*Z*)- or (*E*)-allylic sulfides. Treatment of (*Z*)-10-membered thiolcarbonate (**3j**) with lithium metal in liquid ammonia at -78 °C gave rise to liberation of SCO in **3j** and provided a mixture of (Z)-trisubstituted olefin (**12j**) with a versatile alcohol at the terminal position and an inseparable isomeric impurity in a ratio of 95 : 5 (95% yield) (Scheme 7). The (*Z*) geometry of **12j** was determined by a positive ^{1}H-nuclear Overhauser effect, as shown in Scheme 7. The SCO moiety in (*Z*)-**3i** was reductively removed by using lithium in liquid ammonia to give only a tetrasubstituted olefin (**12i**) in 73% yield. A complete retension of the stereochemistry was observed by the ^{1}H-NMR spectrum or VPC analysis.



Scheme 7

The reductive desulfurization of (Z)-10-membered thiolcarbonates has stimulated interest in the stereoselective synthesis of naturally occuring (Z)-alkenol sex pheromones.[21] We recently succeeded in a unique and stereoselective synthesis[22] of yellow scale pheromone, (±)-(*E*)-6-isopropyl-3,9-dimethyl-5,8-decadienyl acetate, by using the present method. This synthesis demonstrated the usefulness of the present method in organic synthesis. Further synthetic applications of cyclic thionocarbonates containing (*Z*)- or (*E*)-double bond are being investigated at our laboratories.

Experimental

General. A melting point of **3i** was determined on a Yanagimoto micromelting point apparatus and was uncorrected. The IR spectra were recorded on a Shimadzu IR-435, and MS on a Hitachi M-80 spectrometers.

^{1}H- and ^{13}C-NMR spectra were taken with tetramethylsilane as an internal standard on a Varian Gemini-200 spectrometer in $CDCl_3$. VPC 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. x 3 m). Capillary VPC analyses were carried out using a FS-WCOT OV-1701 column (0.25 mm i.d. x 25 m) and electron impact mass spectrometry was employed as detector. For column chromatography, SiO_2 (Merck 9385) was used. All reactions were carried out under a nitrogen stream unless otherwise noted.

***O*-5-Oxohexyl *O*-phenyl thionocarbonate (6)** A solution of phenyl chlorothionoformate[23] (0.7 ml, 4.94 mmol) in acetonitrile (10 ml) was added slowly over 40 min to a solution of 6-hydroxy-2-hexanone (**8**)[12a] (478 mg, 4.12 mmol) in acetonitrile (30 ml) in the presence of pyridine (391 mg, 4.94 mmol) and 4-DMAP (50 mg, 0.41 mmol) at 0 °C 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, 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 **6** (920 mg, 89%) as an oil. IR (neat) : 1705 cm^{-1}. ^{1}H-NMR : 1.61-1.93 (4H, br), 2.14 (3H, s), 2.50 (2H, t, *J*=5.0 Hz), 4.50 (2H, t, *J*=5.0 Hz), 7.0-7.47 (5H, m). MS *m/z*: 252 (M^+). HR-MS *m/z*: calcd for $C_{13}H_{16}O_3S$ 252.0819, Found: 252.0817.

***O*-[(*E*)-5-Hydroxy-6-undecenyl] *O*-phenyl thionocarbonate [(*E*)-1b]** Method A (General Procedure): A 1.7 M pentane solution of tert-butyllithium[23] (1.2 ml, 2.0 mmol) was added with stirring to (*E*)-1-iodo-1-hexene[11a] (212 mg, 1.0 mmol) in anhydrous ether (3 ml) at -70 °C. The mixture was stirred at the same temperatue for 30 min. *O*-4-Formylbutyl *O*-phenyl thionocarbonate (**5**) (120 mg, 0.5 mmol) in ether (6 ml) was subsequently added slowly at -70 °C to the ether solution of (*E*)-1-hexenyllithium thus prepared. The mixture was stirred for 30 min, allowed to warm to -20 °C, and further stirred for 1 h. The reaction mixture was quenched with saturated ammonium chloride solution (1 ml) and extracted with ether (50 ml x 2). 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 10% EtOAc-hexane for elution to give (*E*)-**1b** (99 mg, 61%). MS and ^{1}H-NMR spectral data are summarized in Table 5.

***O*-[(*Z*)-5-Hydroxy-6-undecenyl] *O*-phenyl thionocarbonate [(*Z*)-1b]** This compound was synthesized by the reaction of aldehyde (**5**) (760 mg, 3.2 mmol) with (*Z*)-1-hexenyllithium which was prepared from (*Z*)-1-iodo-1-hexene[11b] (611 mg, 2.9 mmol) according to the method A.

***O*-(5,6-Dimethyl-5-hydroxy-6-heptenyl) *O*-phenyl thionocarbonate (1i)** A solution of 2-bromo-2-propene[23] (678 mg, 5.6 mmol) in THF (7 ml) was added dropwise to a suspension of magnesium (136 mg, 5.6 mmol) in THF (3 ml) with efficiently stirring at room temperature. After magnesium had been consumed, a solution of **6** (941 mg, 3.7 mmol) in THF (6 ml) was added dropwise to the solution of generated Grignard reagent at room temperature. The mixture was stirred for 30 min, then cooled in an ice bath, and quenched with saturated ammonium chloride solution (1 ml). The THF was evaporated off under reduced pressure to give a residue, which 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 residual oil was purified by column chromatography using 20% EtOAc-hexane for elution to give **1i** (975 mg, 87%) as an oil.

***O*-[(*E*)-5-Hydroxy-5-methyl-6-undecenyl] *O*-phenyl thionocarbonate [(*E*)-1j]** This compound was synthesized by the reaction of **6** (756 mg, 3.0 mmol)with (*E*)-hexenyllithium derived from (*E*)-1-iodo-1-hexene (693 mg, 3.3 mmol) according to the method A.

***O*-[(*Z*)-5-Hydroxy-5-methyl-6-undecenyl] *O*-phenyl thionocarbonate [(*Z*)-1j]** This compound was synthesized by the reaction of **6** (504 mg, 2.0 mmol) with (*Z*)-hexenyllithium derived from (*Z*)-1-iodo-1-hexene (840 mg, 4.0 mmol) according to the method A.

***O*-[(*E*)-5-Hydroxy-6-octenyl] *O*-phenyl thionocarbonate [(*E*)-1e]** Method B (General Procedure): A solution of (*E*)-1-bromo-1-propene[24] (4.356 g, 36 mmol) in THF (10 ml) was added dropwise to a suspension of magnesium (875 mg, 36 mmol) in THF (8 ml) at room temperature with efficiently stirring. After the magnesium had been consumed, a solution of 5-hydroxypentanal (7)[12b] (1.224 g, 12 mmol) in THF (10 ml) was added dropwise to the resulting Grignard reagent. The mixture was stirred at room temperature for 1.5 h and then hydrolyzed with saturated ammonium chloride solution (30 ml). The THF was evaporated off under the reduced pressure to give a residue, which was extracted with EtOAc-hexane (1:1). The extract was washed with brine, dried over anhydrous Na_2SO_4 and then comdensed under reduced pressure to give crude (*E*)-6-octene-1,5-diol (**9e**) (1.53 g). A solution of phenyl chlorothionoformate (1.6 ml, 12 mmol) in acetonitrile (10 ml) was added dropwise over 13 h to a solution of (*E*)-**9e** in acetonitrile (65 ml) in the presence of pyridine (912 mg, 12 mmol) and 4-DMAP (128 mg, 1 mmol) at 0 °C by a syringe pump technique. The acetonitrile was evaporated off under reduced pressure to give an oily residue, which was dissolved in EtOAc-hexane (1:1). The organic layer was washed with H_2O, brine, and dried over anhydrous Na_2SO_4 and then condensed under reduced pressure. The residue was purified by column chromatography using 20% EtOAc-hexane to give (*E*)-**1e** (1.627 g, 49%) as an oil.

***O*-[(*Z*)-5-Hydroxy-6-octenyl] *O*-phenyl thionocarbonate [(*Z*)-1e]** A 1:1 mixture of diol monothionocarbonates [(*E*)- and (*Z*)-**1e**] was synthesized in 36% yield according to the method B. The mixture was purified by flash column chromatography using a 5% EtOAc-hexane for elution to give pure (*Z*)-**1e**.

***O*-(5-Hydroxy-6-methyl-6-heptenyl) *O*-phenyl thionocarbonate (1f)** This compound was synthesized by the reaction of **7** (1.1 g, 11 mmol) with 2-bromopropene[23] (4.1 g, 34 mmol) according to the method B.

***O*-(5-Hydroxy-5-methyl-6-heptenyl) *O*-phenyl thionocarbonate (1g)** This compound was synthesized by the reaction of **8**[12a] (4.9 g, 43 mmol) and vinylmagnesium bromide[23] (128 ml of 1.0 M solution in THF, 128 mmol) according to the method B.

***O*-(5-Hydroxy-7-methyl-6-octenyl) *O*-phenyl thionocarbonate (1h)** This compound was synthesized by the reaction of **7** (734 mg, 7.2 mmol) and 1-bromo-2-methylpropene (2.9 g, 22 mmol) according to the method B.

General Procedure for the Preparation of 10-Membered Thiolcarbonates (3) : (*Z*)-4-Butyl-7,8,9,10-tetrahydro-4*H*-1,3-oxathiecin-2-one [(*Z*)-3b] A 1.0 M THF solution of $(TMS)_2NNa$[23] (0.0 8 ml) was added to a dry THF (8 ml, 10^{-2} M) solution of (*E*)-**1b** (24 mg, 0.075 mmol) was added rapidly at room temperature. The reaction was quenched by the addition of H_2O within 5 min and the solvent was condensed under reduced pressure to give a residue which was extracted with EtOAc-hexane (1:1). The extract was

Table 5. MS and ^{1}H-NMR Spectral Data for the Diol Monothionocarbonates (**1**)[a)]

No	Formula	MS (*m/z*) Calcd (Found)	^{1}H-NMR ($CDCl_3$) δ
(*E*)-**1b**	$C_{18}H_{26}O_3S$	305.1574 (M^+-OH) (305.1591)	0.90 (3H, t, *J*=6.5 Hz), 1.18-1.68 (8H, br), 1.85 (2H, quint, *J*=7.0 Hz), 2.02 (2H, q, *J*=6.5 Hz), 4.05 (1H, br), 4.50 (2H, t, *J*=6.0 Hz), 5.44 (1H, dd, *J*=15.7, 7.4 Hz), 5.62 (1H, dt, *J*=15.7, 6.4 Hz), 7.01-7.47 (5H, m)
(*Z*)-**1b**	$C_{18}H_{26}O_3S$	305.1574 (M^+-OH) (305.1597)	0.91 (3H, t, *J*=6.5 Hz), 1.19-1.74 (8H, br), 1.84 (2H, quint, *J*=7.0 Hz), 2.08 (2H, br), 4.43 (1H, br), 4.51 (3H, t, *J*=6.0 Hz), 5.35 (1H, dd, *J*=11.1, 8.9 Hz), 5.49 (1H, dt, *J*=11.1, 7.1 Hz), 7.01-7.46 (5H, m)
1i	$C_{16}H_{22}O_3S$	294.1288 (M^+) (294.1286)	1.14-1.89 (6H, br), 1.30 (3H, s), 1.73 (3H, s), 4.49 (2H, t, *J*=6.6 Hz), 4.83 (1H, s), 4.98 (1H, s), 7.01-7.45 (5H, m)
(*E*)-**1j**	$C_{19}H_{28}O_3S$	319.1730 (M^+-OH) (319.1736)	0.87 (3H, t, *J*=6.5 Hz), 1.19-1.61 (4H, br), 1.26 (3H, s), 1.80 (2H, quint, *J*=7.0 Hz), 2.02 (2H, q, *J*=5.7 Hz), 4.50 (2H, t, *J*=6.6 Hz), 5.48 (1H, d, *J*=15.4 Hz), 5.61 (1H, dt, *J*=15.4 Hz), 7.04-7.45 (5H, m)
(*Z*)-**1j**	$C_{19}H_{28}O_3S$	319.1730 (M^+-OH) (319.1741)	0.89 (3H, t, *J*=6.5 Hz), 1.33 (3H, s), 1.36 (4H, br), 1.43-1.69 (4H, br), 1.81 (2H, quint, *J*=6.9 Hz), 2.30 (2H, br), 4.51 (2H, t, *J*=6.5 Hz), 5.26-5.45 (2H, m), 7.03-7.47 (5H, m)
(*E*)-**1e**	$C_{15}H_{20}O_3S$	263.1105 (M^+-OH) (263.1103)	1.31-1.62 (4H, br), 1.68 (3H, d, *J*=6.0 Hz), 1.84 (2H, quint, *J*=6.5 Hz), 4.03 (1H, br s), 4.50 (2H, t, *J*=6.5 Hz), 5.46 (1H, dd, *J*=15.5, 6.0 Hz), 5.67 (1H, dq, *J*=15.5, 6.0 Hz), 7.02-7.45 (5H, m)
(*Z*)-**1e**	$C_{15}H_{20}O_3S$	263.1105 (M^+-OH) (263.1104)	1.30-1.92 (6H, br), 1.68 (3H, d, *J*=6.9 Hz), 4.45 (1H, br), 4.50 (2H, t, *J*=6.9 Hz), 5.38 (1H, dd, *J*=11.4, 8.7 Hz), 5.57 (1H, dq, *J*=11.4, 6.9 Hz), 6.97-7.47 (5H, m)
1f	$C_{15}H_{20}O_3S$	281.1210 (M^++1) (281.1223)	1.36-1.68 (4H, br), 1.71 (3H, s), 1.75-1.94 (2H, quint, *J*=7.5 Hz), 4.07 (1H, t, *J*=5.0 Hz), 4.50 (2H, t, *J*=6.0 Hz), 4.83 (1H, s), 4.92 (1H, s), 7.03-7.45 (5H, m)
1g	$C_{15}H_{20}O_3S$	280.1132 (M^+) (280.1146)	1.28 (3H, s), 1.35-1.65 (6H, br), 1.80 (2H, quint, *J*=6.5 Hz, 4.50 (2H, t, *J*=6.5 Hz), 5.05 (1H, d, *J*=10.5 Hz), 5.20 (1H, d, *J*=17.0 Hz), 5.90 (1H, dd, *J*=17.0, 10.5 Hz), 7.02-7.47 (5H, m)
1h	$C_{16}H_{22}O_3S$	294.1288 (M^+) (294.1286)	1.34-1.65 (6H, m), 1.69 (3H, s), 1.71 (3H, s), 1.83 (2H, quint, *J*=6.0 Hz), 4.35 (1H, br), 4.51 (2H, t, *J*=6.0 Hz), 5.16 (1H, br d, *J*=8.5 Hz), 7.03-7.46 (5H, m)

a) These are oily materials.

washed with brine, dried over anhydrous Na_2SO_4, and then condensed under reduced pressure. The residual oil was purified by column chromatography using a 3% EtOAc-hexane for elution to give (*Z*)-**3b** (15 mg, 88%) as an oil. The spectral data are shown in Table 6.

Reaction of (*Z*)-1j with $(TMS)_2NNa$ A 1.0 M solution of $(TMS)_2NNa$ (1.1 ml, 1.1 mmol) in THF was added rapidly to a solution of (*Z*)-**1j** (339 mg, 1.01 mmol) in THF (100 ml) at room temperature. The ordinary work-up gave an inseparable mixture (52:48) of (*Z*)-**3j** and (*E*)-**3j** (120 mg, 49%) with recovery of (*Z*)-**1j** (75 mg, 22%). The spectral data of this mixture were as follows: IR (neat): 1690 cm^{-1}. ^{1}H-NMR : 0.85 (3H, br t), 1.20-1.65 (9H, br), 1.63 (3H, s), 1.70-2.0 (2H, br), 2.23 [0.5H, dt, *J*=12.5, 3.5 Hz for (*E*)-**3j**], 2.68-2.87 [0.5 H,

Table 6. MS and ^{1}H-NMR Spectral Data for 10-Membered Thiolcarbonates (3)[a]

No	Formula	MS (*m/z*) Calcd (Found)	^{1}H-NMR ($CDCl_3$) δ
(*Z*)-**3b**	$C_{12}H_{20}O_2S$	228.1183 (M^+) (228.1185)	0.89 (3H, t, *J*=7.5 Hz), 1.17-1.82 (10H, br), 2.05 (1H, br d, *J*=11.0 Hz), 2.62 (1H, br q, *J*=11.0 Hz), 3.76 (1H, ddd, *J*= 11.8, 6.5, 4.2 Hz), 4.26 (1H, q, *J*=10.0 Hz), 4.95 (1H, dt, *J*=11.8, 3.5 Hz), 5.20-5.40 (2H, m)
(*E*)-**3b**	$C_{12}H_{20}O_2S$	228.1183 (M^+) (228.1192)	0.89 (3H, t, *J*=7.5 Hz), 1.18-1.60 (8H, br), 1.70-2.02 (3H, br), 2.22-2.38 (1H, br), 3.59 (1H, td, *J*=11.8, 2.0 Hz), 3.87 (1H, dt, *J*=10.0, 7.6 Hz), 5.01 (1H, dd, *J*=11.8, 5.9 Hz), 5.13 (1H, ddd, *J*=15.3, 10.0, 1.8 Hz), 5.48 (1H, ddd, *J*= 15.3, 11.8, 3.5 Hz)
(*Z*)-**3e**	$C_9H_{14}O_2S$	186.0714 (M^+) (186.0717)	1.22 (3H, d, *J*=7.5 Hz), 1.48-1.84 (4H, br), 2.04 (1H, br d, *J*=13.0 Hz), 2.62 (1H, br qd, *J*=13.0, 3.7 Hz), 3.74 (1H, dt, *J*=11.3, 5.3 Hz), 4.39 (1H, dq, *J*=10.4, 6.8 Hz), 4.95 (1H, dt, *J*=11.3, 3.8 Hz), 5.21 (1H, td, *J*=10.4, 3.7 Hz), 5.36 (1H, td, *J*=10.4, 2.5 Hz)
(*E*)-**3e**	$C_9H_{14}O_2S$	186.0714 (M^+) (186.0715)	1.27 (3H, t, *J*=7.5 Hz), 1.31-2.12 (5H, br), 2.30 (1H, br d, *J*=17.5 Hz), 3.60 (1H, t, *J*=10.0), 4.01 (1H, dq, *J*=9.8, 7.5 Hz), 5.03 (1H, t, *J*=5.5 Hz), 5.17 (1H, dd, *J*=14.5, 9.5 Hz), 5.50 (1H, ddd, *J*=14.5, 12.0, 4.0 Hz)
(*Z*)-**3f**	$C_9H_{14}O_2S$	186.0714 (M^+) (186.0716)	1.45-1.75 (4H, br), 1.80 (3H, s), 2.30 (2H, br s), 3.40 (2H, br s), 4.35 (2H, br s), 5.14 (1H, t, *J*=8.0 Hz)
(*Z*)-**3g**	$C_9H_{14}O_2S$	186.0714 (M^+) (186.0716)	1.37-1.84 (4H, br), 1.66 (3H, s), 2.36 (2H, br s), 3.38 (2H, br s), 4.38 (2H, br s), 5.36 (1H, t, *J*=9.0 Hz)
(*E*)-**3h**	$C_{10}H_{16}O_2S$	200.0869 (M^+) (200.0871)	1.16-2.06 (5H, br), 1.34 (3H, s), 1.65 (3H, s), 2.36 (1H, br d, *J*=11.9 Hz), 3.61 (1H, t, *J*=10.2 Hz), 5.0 (1H, dd, *J*=10.8 5.4 Hz), 5.42 (1H, d, *J*=15.6 Hz), 5.53 (1H, dd, *J*=15.6, 3.2 Hz).
(*Z*)-**3i**[b]	$C_{10}H_{16}O_2S$	200.0869(M^+) (200.0868)	1.48 (2H, br s), 1.62 (3H, s), 1.77 (3H, s), 1.80 (2H, br s), 2.34-5.43 (6H, br)
(*Z*)-**3j**	$C_{13}H_{22}O_2S$	242.1340 (M^+) (242.1339)	0.85 (3H, t, *J*=7.0 Hz), 1.15-1.69 (10H, br), 1.62 (3H, s), 1.76-1.97 (1H, br), 2.63-2.93 (1H, m), 3.71 (1H, td, *J*= 11.9, 9.8 Hz), 4.21 (1H, ddd, *J*=10.6, 8.1, 6.4 Hz), 5.0 (1H, dt, *J*=11.9, 4.9 Hz), 5.13 (1H, d, *J*=10.6 Hz)

a) These are oily materials except for (*Z*)-**3i**. b) Recrystallization from MeOH gave colorless needles, mp 67-68 °C. *Anal.* Calcd : C, 59.97; H, 8.05. Found: C, 59.59; N, 8.01.

m for (*Z*)-**3j**], 3.44 [0.5H, t, *J*=11.8 Hz for (*E*)-**3j**], 3.71 [0.5H, td, *J*=11.9, 9.8 Hz for (*Z*)-**3j**, 4.10-4.28 (1H, m), 5.01 (1.5H, br d), 5.13 [0.5H, d, *J*=10.6 Hz, (*Z*)-**3j**]. ^{13}C-NMR [values in parentheses are the signals for pure (*E*)-**3j**]: (14.0), 16.7, (22.4), (22.5), (25.2), (26.6), 27.5, 29.3, (29.6), (30.0), (33.2), 33.3, 41.0, (45.5), 46.8, (68.4), 69.4, 126.5, (129.4), (135.8), 139.8, (170.4), 171.0. HR-MS *m/z*: Calcd for $C_{13}H_{22}O_2S$ 242.1340 Found: 242.1341 (M^+). Capillary VPC (programmed at 80-210 °C, 5 °C/min): t_R=23.7 min for (*Z*)-**3j** (52%) and 24.3 min for (*E*)-**3j** (48%).

Reaction of (*E*)-6-Undecene-1,5-diol (9b) with TCDP TCDP[23] (47 mg, 0.2 mmol) was added to a solution of **9b** (34 mg, 0.18 mmol) in toluene (20 ml), and the mixture was refluxed for 15 h. The solvent was evaporated off under reduced pressure to give an oily residue, which was dissolved in EtOAc-hexane (1:1). The extract was washed with brine, dried over anhydrous Na_2SO_4, and then condensed under reduced pressure. The

residual oil was purified by column chromatography to give an oily mixture of (*Z*)-**3b** and (*E*)-**3b** (82:18) (22 mg, 53%). VPC analysis (programmed at 120-240 °C, 5 °C/min): t_R=13.1 min for (*Z*)-**3b** (82%) and 13.6 min for (*E*)-**3b** (18%).

General Procedure for the Conversion of 10-Membered Thiolcarbonates (3) into (*Z*)- or (*E*)-Allylic Thiolcarbamates (11): (*Z*)-Dimethyl S-(1-n-Butyl-7-hydroxy-2-heptenyl)carbamate [(*Z*)-11b] An aqueous 2N NaOH solution (1 ml) was added to (*Z*)-**3b** (10 mg, 0.04 mmol) in MeOH (1 ml) at 0 °C, and the mixture was stirred for 15 min at room temperature. The MeOH was evaporated off under reduced pressure and the residue was neutralized with 5% HCl. Extraction with CH_2Cl_2 (50 ml x 2) by a salting-out technique gave almost pure allylic thiol [(*Z*)-**10b**] as an oil in almost quantitative yield. To avoid the formation of undesirable bis-allylic sulfide in air, (*Z*)-**10b** was subsequently converted into (*Z*)-**11b**. A mixture of (*Z*)-**10b**, dimethylcarbamoyl chloride (6 mg, 0.05 mmol), triethylamine (5 mg, 0.05 mmol) and 4-DMAP (1 mg, 0.01 mmol) in THF (1 ml) was stirred for 84 h at room temperature. The solvent was evaporated off under reduced pressure and the 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 condensed *in vacuo*. The residue was purified by column chromatography using 30% EtOAc-hexane for elution to give (*Z*)-**11b** (10 mg, 83%). The spectral data are shown in Table 7.

Table 7. MS and ^{1}H-NMR Spectral Data for Allylic Thiolcarbamates (**11**)[a]

No	Formula	MS (*m/z*) (M^+) Calcd (Found)	^{1}H-NMR ($CDCl_3$) δ
(*Z*)-**11b**	$C_{14}H_{27}NO_2S$	273.1760 (273.1759)	0.87 (3H, t, *J*=6.0 Hz), 1.10-1.80 (10H, br), 2.15 (2H, q, *J*= 7.3 Hz), 2.94 (6H, s), 3.63 (2H, t, *J*=5.7 Hz), 4.30 (1H, ddd, *J*=10.2, 8.4, 6.1 Hz), 5.28 (1H, t, *J*=11.0 Hz), 5.43 (1H, dt, *J*=11.0, 7.5 Hz)
(*E*)-**11b**	$C_{14}H_{27}NO_2S$	273.1760 (273.1759)	0.86 (3H, t, *J*=6.0 Hz), 1.0-1.82 (10H, br), 2.03 (2H, q, *J*= 6.0 Hz), 3.00 (6H, s), 3.61 (2H, t, *J*=6.5 Hz), 4.00 (1H, q, J=7.0 Hz), 5.39 (1H, dd, *J*=15.2, 8.4 Hz), 5.64 (1H, dt, *J*= 15.2, 7.0 Hz)
(*Z*)-**11e**	$C_{11}H_{21}NO_2S$	231.1292 (231.1292)	1.23-1.76 (4H, br), 1.36 (3H, d, *J*=7.5 Hz), 1.87-2.41 (2H, br), 2.93 (6H, s), 3.64 (2H, br), 4.41 (1H, quint, *J*=7.5 Hz), 5.26-5.50 (2H, m)
(*E*)-**11e**	$C_{11}H_{21}NO_2S$	231.1292 (231.1292)	1.40 (3H, d, *J*=7.0 Hz), 1.20-1.70 (5H, m), 2.02 (2H, q, *J*= 6.0 Hz), 2.94 (6H, s), 3.10 (2H, t, *J*=6.0 Hz), 4.08 (1H, quint, *J*=7.5 Hz), 5.50 (1H, dd, *J*=15.7, 6.8 Hz), 5.63 (1H, dt, *J*=15.7, 5.6 Hz)
(*Z*)-**11f**	$C_{11}H_{21}NO_2S$	231.1292 (231.1301)	1.30-1.70 (4H, br), 1.73 (3H, s), 2.10 (2H, q, *J*=7.5 Hz), 2.98 (6H, s), 3.61 (4H, m), 5.28 (1H, t, *J*=6.0 Hz)
(*Z*)-**11g**	$C_{11}H_{21}NO_2S$	231.1292 (231.1293)	1.35-1.73 (4H, br), 1.70 (3H, s), 2.11 (2H, t, *J*=6.0 Hz), 2.95 (6H, s), 3.53 (2H, d, *J*=7.5 Hz), 3.65 (2H, t, *J*=5.0 Hz), 5.25 (1H, t, *J*=7.5 Hz)
(*E*)-**11h**	$C_{12}H_{23}NO_2S$	245.1448 (245.1448)	1.32-1.62 (4H, br), 1.54 (6H, s), 2.04 (2H, q, *J*=6.0 Hz), 2.91 (6H, s), 3.58 (2H, t, *J*=6.0 Hz), 5.52 (1H, dt, *J*=15.0, 6.0 Hz), 5.78 (1H, *J*=15.0 Hz)
(*E*)-**11i**	$C_{12}H_{23}NO_2S$	245.1448 (245.1448)	1.35-1.78 (4H, br), 1.64 (3H, s), 1.68 (3H, s), 2.11 (2H, t, *J*= 6.0 Hz), 2.98 (6H, s), 3.65 (4H, m)

a) There are oily materials.

(Z)-5-Methyl-5-undecen-1-ol [(Z)-12j] Lithium wire (15 mg, 2.1 mmol) as small pieces was added to a distilled liquid ammonia (5 ml) at -78 °C. To a resulting blue solution was added a solution of (Z)-**3j** (52 mg, 0.2 mmol) in THF (2 ml) slowly. Within 10 min the reaction was quenched by the addition of ammonium chloride (1 g), and the volatiles were carefully evaporated off. The residue was extracted with ether (50 ml x 2) and the combined organic layers were washed with H_2O and brine, dried over anhydrous Na_2SO_4 and then evaporated *in vacuo*. The oily residue was chromatographied using a 20% EtOAc-hexane for elution to give a 95 : 5 mixture (38 mg, 95%) of **12j** and an impurity as an oil. IR ($CHCl_3$): 3320 cm^{-1}. ^{1}H-NMR: 0.85 (3H, t, *J*=6.6 Hz), 1.20-1.60 (10H, br), 1.64 (3H, s), 1.93 (2H, q, *J*=6.6 Hz), 2.01 (2H, t, *J*=7.4 Hz), 3.62 (2H, *J*=6.2 Hz), 5.11 (1H, t, *J*=7.0 Hz). ^{13}C-NMR (values in parentheses are the signals for the impurity): 14.0, 22.6, 23.2, 24.1, 27.8, 29.8, 31.4, 31.6, 32.6, 62.9, 125.8 (128.6), 134.7 (136.6). HR-MS *m/z*: Calcd for $C_{12}H_{24}O$ 184.1826, Found 184.1829 (M^+). VPC analysis (programmed at 140-270 °C, 10 °C/min): t_R=5.7 min (5%), 6.1 min (95%).

5,6-Dimethyl-5-hepten-1-ol (12i) Treatment of (Z)-**3i** (50 mg, 0.25 mmol) with lithium in liquid ammonia at -78 °C gave **12i** (36 mg, 73%) as an oil according to the above procedure. IR (neat): 3300 cm^{-1}. ^{1}H-NMR: 1.30-1.70 (4H, br m,), 1.60 (9H, s), 2.02 (2H, t, *J*=7.0 Hz), 3.60 (2H, t, *J*=7.0 Hz). ^{13}C-NMR: 18.4, 20.3, 20.7, 24.5, 32.9, 34.3, 63.3, 124.6, 128.0. HR-MS *m/z*: Calcd for $C_9H_{18}O$ 142.1357, Found 142.1359 (M^+). VPC analysis (programmed at 100-270 °C, 8 °C/min): t_R=6.1 min.

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