Preparation of (*Z*)-Alk-2-ene-1,5-diols by the Titanocene(II)-Promoted Cyclization of Thioacetals Possessing a Terminal Carbon−Carbon Double Bond

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Keywords: Cyclizations / Metathesis / Olefins / Thioacetals / Titanium

Titanocene(II)-promoted ring-closing metathesis of the titanium carbene complexes prepared from [2,2-bis(phenylthio)ethyl](but-3-enyloxy)dimethylsilanes or dimethyl(prop-2-enyl)silyl ethers of 3,3-bis(phenythio)propanols gave seven-membered cyclic unsaturated silyl ethers. Oxidative cleavage of a silicon–carbon bond of the cyclic silyl ethers resulted in olefinic diols, with high *Z* stereoselectivity.

Introduction

Recently we disclosed a new method for the construction of cycloalkenes by a titanocene(II)-promoted reaction of diphenyl thioacetals possessing a C=C bond.[1] We assume that the reaction proceeds via the initial formation of a titanium carbene complex, by the desulfurization of thioacetal with the low-valent titanium species $Cp_2Ti[P(OEt)_3]_2$ (**1**). This methodology was successfully applied to the synthesis of various nitrogen[2] and oxygen[3] heterocycles. The success of these techniques inspired us to study further the application of titanium carbene chemistry to the synthesis of heterocyclic compounds. Ring-closing metathesis (RCM) of dienes, catalyzed by ruthenium or molybdenum catalysts, has been employed for the preparation of various cyclic compounds.[4] Several groups have reported the cyclization of silicon-linked dienes by this method.[5] It has also been reported that the combination of this reaction and the oxidative cleavage of a silicon-carbon bond constitute a useful synthetic route to benzyl ethers of unsaturated triols.[5a] The advantage over these reactions of our new strategy for the construction of cyclic compounds is that the starting materials are accessible by means of carbon-carbon bond formation using a variety of organosulfur building blocks. We were interested in the application of our methodology to the preparation of similar silicon-containing heterocyclic compounds **2**. Here we report the stereoselective preparation of olefinic 1,5-diols **3** by the cyclization of organosilicon compounds possessing a thioacetal moiety, and by oxidative cleavage of a silicon-carbon bond.[6] The two types of starting materials can be employed for the present preparation. The first approach includes the cyclization of [2,2-bis(phenylthio)ethyl](but-3-enyloxy)dimethylsilanes **4** (Route A). The second class of starting materials are allylsilyl ethers of 3,3-bis(phenythio)propanols **5** (Route B). For the preparation of trisubstituted olefins, these two types of cyclization are complementary to each other (Scheme 1).

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Results and Discussion

We began our synthesis of unsaturated diols **3** with the [2,2-bis(phenylthio)ethyl]silanes **4**. These in turn were prepared from the homoallyl alcohols **6**. The alcohols **6** were treated with chloro(chloromethyl)dimethylsilane in the presence of triethylamine and 4-dimethylaminopyridine (DMAP) to produce the silyl ethers **7**. After treatment of the silyl ethers **7** with sodium iodide, the resulting iodides **8** were subjected to alkylation with bis(phenylthio)methyllithium to produce thioacetals **4**, possessing terminal C=C bonds, in good overall yields (Scheme 2, Table 1).

The cyclization of **4a** was performed under various reaction conditions. It was found that the cyclic allylsilane **2a** was isolated in 70% yield when **4a** was treated with an excess quantity of titanocene(II) species **1**. Similarly, the RCM product **2c** was isolated in 80% yield on treatment of the acyclic silane **4c** (Scheme 3). Since it was found that some cyclic allylsilanes **2** partially decomposed during purification, the crude compounds **2** were subjected to oxidation once triethyl phosphite had been removed by silica gel column chromatography. The 1,5-diols **3** were obtained in good overall yields by oxidation of **2** using the method developed by Tamao and co-workers (H_2O_2/KF/$KHCO_3$) (Scheme 4). It was found that the use of a larger quantity of hydrogen peroxide (40 equiv.) and a longer reaction time (24 h) than those employed in the original procedure was indispensable for completion of these oxidations (Table 2).[7]

The yield of the oxidative cleavage of the silicon-carbon bond is largely dependent on the substituent α to oxygen. In the case of the phenyl group-substituted silyl ether **2a**, the oxidation proceeds quantitatively while the yield of the oxidation of **2c**, with an α phenethyl group, is estimated at 76% (see entries 1 and 3 in Table 2, and Scheme 3). The

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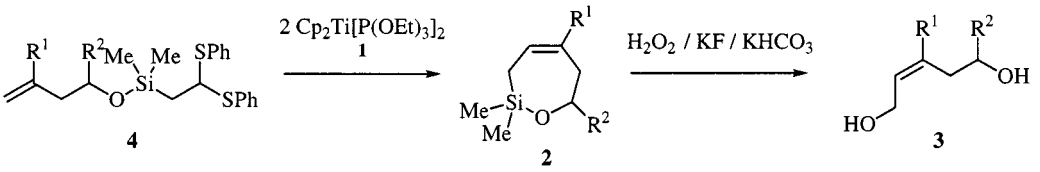
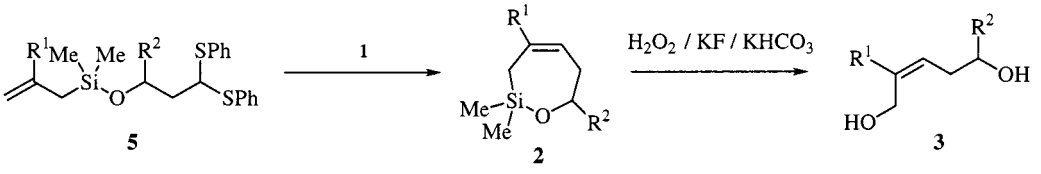
Route A



2, 3, 4	a	b	c	d	e	f
R^1	H	CH_3	H	CH_3	H	CH_3
R^2	Ph	Ph	$Ph(CH_2)_2$	$Ph(CH_2)_2$	$CH_3(CH_2)_8$	$CH_3(CH_2)_8$

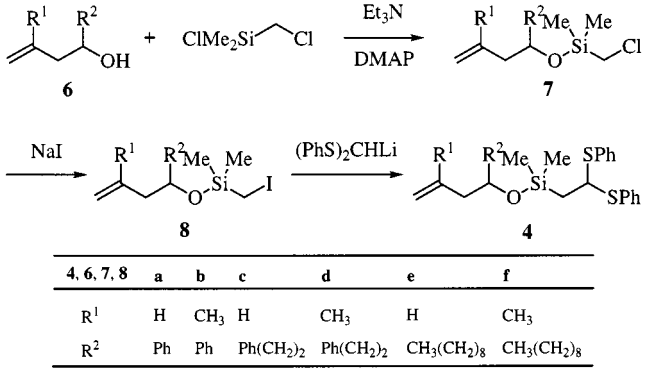
Route B



5	a	b	c	d	e
R^1	H	CH_3	H	CH_3	H
R^2	Ph	Ph	$Ph(CH_2)_2$	$Ph(CH_2)_2$	$CH_3(CH_2)_7$

2, 3	a	c	g	h	i
R^1	H	H	CH_3	CH_3	H
R^2	Ph	$Ph(CH_2)_2$	Ph	$Ph(CH_2)_2$	$CH_3(CH_2)_7$

Scheme 1



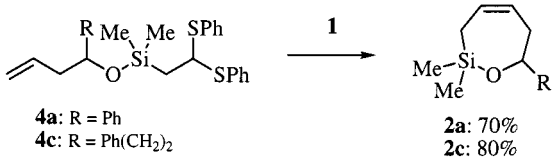
4, 6, 7, 8	a	b	c	d	e	f
R^1	H	CH_3	H	CH_3	H	CH_3
R^2	Ph	Ph	$Ph(CH_2)_2$	$Ph(CH_2)_2$	$CH_3(CH_2)_8$	$CH_3(CH_2)_8$

Scheme 2

Table 1. Preparation of [2,2-bis(phenylthio)ethyl] (but-3-enyloxy)dimethylsilanes **4**

Homoallyl alcohol **6**	R^1	R^2	**4**, Overall yield [%][a]
6a	H	Ph	**4a** (55)
6b	CH_3	Ph	**4b** (56)
6c	H	$Ph(CH_2)_2$	**4c** (79)
6d	CH_3	$Ph(CH_2)_2$	**4d** (78)
6e	H	$CH_3(CH_2)_8$	**4e** (70)
6f	CH_3	$CH_3(CH_2)_8$	**4f** (51)

[a] Based on the alcohol **6** used.



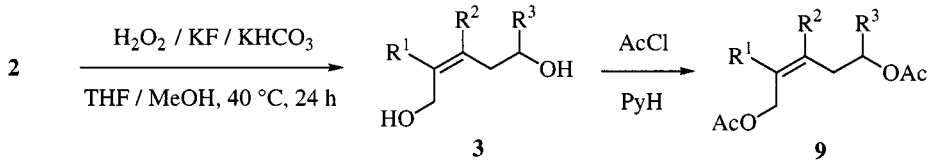
Scheme 3

^{13}C and ^1H NMR spectra of diols **3** indicate that they consist only of *Z* isomers. The diols **3** were further transformed into the diacetates **9** for microanalysis.

Additional starting materials **5** were synthesized by the condensation of allylchlorodimethylsilanes **10** with 3,3-bis(phenylthio)propanols **11** (Scheme 5, Table 3). 1-Phenyl-3,3-bis(phenylthio)-1-propanol **11a** was prepared by treatment of styrene oxide with bis(phenylthio)methyllithium.[3] Similarly, alcohols **11b** and **11c**, possessing thioacetal moieties, were synthesized using the corresponding epoxides.

The cyclization of **5e** was performed under the same reaction conditions as employed for the reaction of **4**, and the RCM product **2i** was isolated in 88% yield (Scheme 6). Similar treatment of the several allylsilanes **5** with titanocene(II) species **1**, followed by oxidative cleavage, produced the *Z* 1,5-diols **3** as sole products (Table 4). The trisubstituted olefin **3g**, which is the structural isomer of **3b**, could be synthesized using **5b** as a starting material. The overall yield from **5b** to **3g** was much better than that of the conversion of **4b**, though the reason for this is uncertain at present.

We next examined the preparation of 1,5-diol **3a** using a larger quantity of **5a**. The aforementioned cyclizations of **4** and **5** had been performed on a 0.5 mmol scale. Because water prevents the reduction of titanocene dichloride, thoroughly dried reagents should be used for the preparation of the low-valent titanium species **1**. In the cases of these small-scale experiments, all the solid reagents had been placed in a flask and dried by heating with stirring under reduced pressure. However, we found that magnesium turnings thus treated are too reactive for the preparation of the low-valent titanium reagent **1** when performed on a large scale. Therefore, we employed an improved procedure for

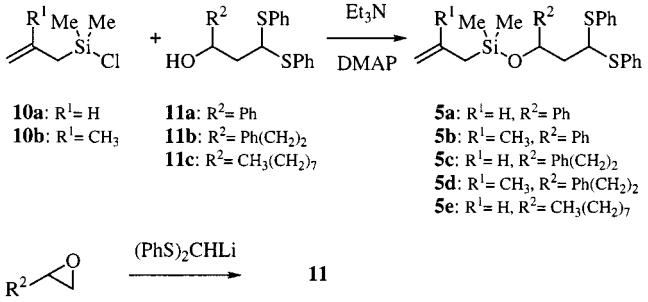


3, 9	a	b	c	d	e	f	g	h	i
R^1	H	H	H	H	H	H	CH_3	CH_3	H
R^2	H	CH_3	H	CH_3	H	CH_3	H	H	H
R^3	Ph	Ph	$Ph(CH_2)_2$	$Ph(CH_2)_2$	$CH_3(CH_2)_8$	$CH_3(CH_2)_8$	Ph	$Ph(CH_2)_2$	$CH_3(CH_2)_7$

Scheme 4

Table 2. Preparation of the olefinic 1,5-diols **3** from the silanes **4**

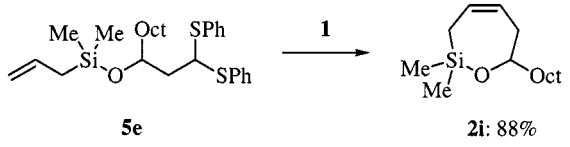
Entry	Silane **4**	1,5-Diol **3** [Overall yield from **4**/%]	Diacetate **9** [Yield/%]
1	**4a**	**3a** (68)	**9a** (91)
2	**4b**	**3b** (50)	**9b** (74)
3	**4c**	**3c** (61)	**9c** (86)
4	**4d**	**3d** (61)	**9d** (92)
5	**4e**	**3e** (51)	**9e** (97)
6	**4f**	**3f** (53)	**9f** (79)



Scheme 5

Table 3. Preparation of [3,3-bis(phenylthio)propoxy]dimethyl(prop-2-enyl)silanes **5**

Allylchloro-dimethylsilane **10** R^1	1,1-Bis(phenylthio)-3-alkanol **11** R^2	**5** [Yield/%]
10a: H	**11a**: Ph	**5a** (79)
10b: CH_3	**11a**	**5b** (85)
10a	**11b**: $Ph(CH_2)_2$	**5c** (89)
10b	**11b**	**5d** (78)
10a	**11c**: $CH_3(CH_2)_7$	**5e** (70)



Scheme 6

the preparative-scale reaction, introducing magnesium turnings into the reactor after the drying of the titanocene dichloride and 4Å molecular sieves.[8] Using the newly developed procedure, the 1,5-diol **3a** was obtained in comparable yield (65%) on a 5 mmol scale.

Table 4. Preparation of the olefinic 1,5-diols **3** from the silanes **5**

Entry	Silane **5**	1,5-Diol **3** [Overall yield from **5**/%]	Diacetate **9** [Yield/%]
1	**5a**	**3a** (71)	
2	**5b**	**3g** (80)	**9g** (73)
3	**5c**	**3c** (62)	
4	**5d**	**3h** (60)	**9h** (73)
5	**5e**	**3i** (61)	**9i** (77)

Conclusion

We have established a new method for the preparation of *Z* olefinic diols, using homoallyl alcohols or 3,3-bis(phenylthio)propanols. Since a diphenyl thioacetal functionality can easily be introduced into silicon compounds possessing a C=C bond, exploiting the sulfur-stabilized carbanion, it should be noted that this method is useful for the preparation of *Z* olefinic 1,5-diols possessing different substituents.

Experimental Section

General Remarks: ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra were measured in $CDCl_3$ on a Jeol ALPHA-500 instrument and are reported in parts per million from tetramethylsilane for ^{1}H and $CDCl_3$ for ^{13}C spectroscopy, unless otherwise noted. − IR spectra were recorded on a Jeol Diamond-20 FT-IR spectrometer; absorptions are reported in cm^{-1}. Elemental analyses were performed using a Perkin−Elmer 2400II. − Wakogel B-5F was used for preparative thin layer chromatography (PTLC) and Merck Si 60 was used for column chromatography. THF was distilled from sodium and benzophenone. Magnesium turnings were purchased from Nacalai Tesque Inc. (Kyoto, Japan).

Preparation of [2,2-Bis(phenylthio)ethyl](but-3-enyloxy)dimethylsilanes (4)

Preparation of [2,2-Bis(phenylthio)ethyl]dimethyl(3-methylbut-3-enyloxy)silane (4b): To a THF (2.5 mL) solution of 3-methyl-1-phenylbut-3-en-1-ol (**6b**) (0.811 g, 5 mmol), DMAP (0.305 g, 2.5 mmol), and triethylamine (1.74 mL, 12.5 mmol) at 0 °C under argon was added chloro(chloromethyl)dimethylsilane (0.79 mL, 6 mmol), dropwise over 10 min. After warming to room temperature, the reaction mixture was stirred overnight. The reaction was quenched by addition of a saturated aqueous $NaHCO_3$ solution (20 mL), and organic materials were extracted with ether (3 × 30 mL). The combined extracts were washed with brine (20 mL)

and dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel deactivated with 5% of H_2O; hexane/ AcOEt = 95:5) to give the silyl ether **7b**. Sodium iodide (1.50 g, 10 mmol) and **7b** were dissolved in acetone (5 mL) and the mixture was refluxed for 3 h. After evaporation of the solvent, the inorganic salts were dissolved in water (20 mL) and the organic materials were extracted with ether (3 × 30 mL). The combined extracts were washed with a saturated, aqueous Na_2SO_3 solution (20 mL), water (20 mL), and brine (20 mL). The ethereal solution was dried (Na_2SO_4) and concentrated under reduced pressure to afford the crude iodide **8b**. To a THF (9 mL) solution of bis(phenylthio)methane (0.976 g, 4.2 mmol) at 0 °C under argon was added a hexane solution of butyllithium (2.93 mL, 4.4 mmol). After stirring for 30 min, **8b** in THF (2 mL) was added, and the reaction mixture was stirred overnight. The reaction was quenched by addition of a saturated, aqueous NH_4Cl solution (20 mL), and organic materials were extracted with ether (3 × 30 mL). The combined extracts were dried (K_2CO_3) and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel deactivated with 5% of H_2O; hexane/AcOEt = 200:1) to give **4b** (1.30 g, 56%). **4b:** ^{1}H NMR (C_6D_6): δ = 0.10 (s, 3 H), 0.17 (s, 3 H), 1.51 (d, *J* = 7.6 Hz, 2 H), 1.63 (s, 3 H), 2.29 (dd, *J* = 13.4, 4.6 Hz, 1 H), 2.51 (ddd, *J* = 13.4, 8.2, 0.9 Hz, 1 H), 4.73−4.81 (m, 3 H), 4.84 (t, *J* = 7.6 Hz, 1 H), 6.94−7.24 (m, 11 H), 7.46−7.54 (m, 4 H). − ^{13}C NMR: δ = −0.3, −0.2, 23.0, 25.6, 49.1, 53.6, 74.3, 113.3, 125.9, 127.2, 127.40, 127.42, 128.1, 128.7, 132.39, 132.44, 134.5, 134.6, 142.2, 144.8. − IR (neat): $\tilde{\nu}$ = 3076, 2966, 1653, 1585, 1481, 1439, 1254, 1090, 1070, 839, 741, 700, 690 cm^{-1}. − $C_{27}H_{32}OS_2Si$: calcd. C 69.78, H 6.94; found C 69.94, H 6.97.

The following silanes **4** were obtained in a similar manner.

[2,2-Bis(phenylthio)ethyl]dimethyl(1-phenylbut-3-enyloxy)silane (4a): ^{1}H NMR (C_6D_6) : δ = 0.09 (s, 3 H), 0.15 (s, 3 H), 1.51 (d, *J* = 7.6 Hz, 2 H), 2.32−2.40 (m, 1 H), 2.45−2.54 (m, 1 H), 4.62 (dd, *J* = 7.3, 5.2 Hz, 1 H), 4.83 (t, *J* = 7.6 Hz, 1 H), 4.94−5.01 (m, 2 H), 5.77 (ddt, *J* = 16.8, 10.4, 7.3 Hz, 1 H), 6.94−7.22 (m, 11 H), 7.46−7.54 (m, 4 H). − ^{13}C NMR: δ = −0.2, 1.8, 25.6, 45.1, 53.7, 75.1, 117.1, 125.9, 127.2, 127.5, 128.2, 128.8, 132.5, 134.5, 135.0. − IR (neat) 3074, 2954, 1641, 1583, 1481, 1439, 1252, 1088, 1066, 837, 744, 700, 690 cm^{-1}. − $C_{26}H_{30}OS_2Si$: calcd. C 69.28, H 6.71; found C 69.60, H 6.79.

[2,2-Bis(phenylthio)ethyl]dimethyl(1-phenethylbut-3-enyloxy)silane (4c): ^{1}H NMR (C_6D_6): δ = 0.19 (s, 3 H), 0.20 (s, 3 H), 1.57 (d, *J* = 7.6 Hz, 2 H), 1.63−1.78 (m, 2 H), 2.15 (t, *J* = 6.4 Hz, 2 H), 2.45−2.54 (m, 1 H), 2.60−2.70 (m, 1 H), 3.60 (quint, *J* = 5.8 Hz, 1 H), 4.90 (t, *J* = 7.6 Hz, 1 H), 4.91−5.03 (m, 2 H), 5.70−5.80 (m, 1 H), 6.92−7.20 (m, 11 H), 7.50−7.60 (m, 4 H). − ^{13}C NMR: δ = 0.0, 0.1, 25.9, 31.9, 38.6, 41.9, 54.0, 71.9, 117.2, 125.7, 127.5, 127.6, 128.3, 128.8, 132.5, 132.6, 134.5, 134.8, 142.2. − IR (neat): $\tilde{\nu}$ = 3076, 2952, 1583, 1481, 1439, 1254, 1090, 1066, 839, 748, 690 cm^{-1}. − $C_{28}H_{34}OS_2Si$: calcd. C 70.24, H 7.16; found C 70.01, H 7.14.

[2,2-Bis(phenylthio)ethyl]dimethyl(3-methyl-1-phenethylbut-3-enyloxy)silane (4d): ^{1}H NMR (C_6D_6): δ = 0.21 (s, 3 H), 0.22 (s, 3 H), 1.55−1.65 (m, 5 H), 1.65−1.82 (m, 2 H), 2.11 (dd, *J* = 13.6, 6.3 Hz, 1 H), 2.19 (dd, *J* = 13.6, 6.3 Hz, 1 H), 2.50−2.60 (m, 1 H), 2.65−2.75 (m, 1 H), 3.74−3.83 (m, 1 H), 4.74 (s, 1 H), 4.78 (s, 1 H), 4.90 (t, *J* = 7.5 Hz, 1 H), 6.92−7.20 (m, 11 H), 7.52−7.60 (m, 4 H). − ^{13}C NMR: δ = −0.01, 0.03, 22.9, 25.9, 31.8, 38.6, 46.0, 54.0, 70.8, 113.2, 125.7, 127.5, 127.6, 128.30, 128.32, 128.8, 132.5, 132.6, 134.5, 134.6, 142.3, 142.4. − IR (neat): $\tilde{\nu}$ = 3074, 2949, 1647, 1583, 1481, 1439, 1252, 1090, 1066, 837, 748, 692 cm^{-1}. − $C_{29}H_{36}OS_2Si$: calcd. C 70.68, H 7.36; found C 70.19, H 7.28.

[2,2-Bis(phenylthio)ethyl]dimethyl(1-nonylbut-3-enyloxy)silane (4e): ^{1}H NMR (C_6D_6): δ = 0.23 (s, 3 H), 0.24 (s, 3 H), 0.92 (t, *J* = 6.9 Hz, 3 H), 1.20−1.53 (m, 16 H), 1.56−1.60 (m, 2 H), 2.15−2.21 (m, 2 H), 3.59−3.66 (m, 1 H), 4.86−4.94 (m, 1 H), 4.99−5.06 (m, 2 H), 5.75−5.88 (m, 1 H), 6.94−7.00 (m, 5 H), 7.01−7.08 (m, 2 H), 7.52−7.59 (m, 3 H). − ^{13}C NMR: δ = 0.0, 0.1, 14.1, 22.7, 25.5, 25.8, 29.3, 29.60, 29.63, 29.7, 31.9, 36.9, 41.9, 53.9, 72.5, 116.9, 127.48, 127.51, 128.8, 132.47, 132.54, 134.60, 134.63, 135.3. − IR (neat): $\tilde{\nu}$ = 3074, 2925, 1641, 1583, 1481, 1439, 1252, 1090, 1066, 835, 737, 690 cm^{-1}. − $C_{29}H_{44}OS_2Si$: calcd. C 69.54, H 8.86; found C 69.79, H 8.98.

[2,2-Bis(phenylthio)ethyl]dimethyl(3-methyl-1-nonylbut-3-enyloxy)-silane (4f): ^{1}H NMR (C_6D_6): δ = 0.25 (s, 3 H), 0.27 (s, 3 H), 0.91 (t, *J* = 7.0 Hz, 3 H), 1.22−1.38 (m, 13 H), 1.40−1.54 (m, 3 H), 1.60 (dd, *J* = 7.6, 1.5 Hz, 2 H), 1.65 (s, 3 H), 2.14 (dd, *J* = 13.3, 9.0 Hz, 1 H), 2.22 (dd, *J* = 13.3, 6.6 Hz, 1 H), 3.77−3.84 (m, 1 H), 4.80 (s, 1 H), 4.82 (s, 1 H), 4.92 (t, *J* = 7.5 Hz, 1 H), 6.94−7.10 (m, 6 H), 7.55−7.62 (m, 4 H). − ^{13}C NMR: δ = −0.03, 0.03, 14.1, 22.7, 23.0, 25.6, 25.9, 29.3, 29.60, 29.65, 29.7, 31.9, 37.1, 46.1, 53.9, 71.3, 112.9, 127.47, 127.51, 128.8, 128.9, 132.5, 132.6, 134.58, 134.64, 142.8. − IR (neat): $\tilde{\nu}$ = 3076, 2931, 1651, 1585, 1481, 1439, 1252, 1093, 1068, 837, 741, 690 cm^{-1}. − $C_{30}H_{46}OS_2Si$: calcd. C 69.98, H 9.01; found C 70.18, H 9.15.

Preparation of 1,1-Bis(phenylthio)-3-alkanols 11

Preparation of 1,1-Bis(phenylthio)-3-undecanol (11c): To a THF (20 mL) solution of bis(phenylthio)methane (2.32 g, 10 mmol), at 0 °C under argon, was added a hexane solution of butyllithium (7.3 mL, 11 mmol). After stirring for 30 min, 1,2-epoxydodecane (2.6 mL, 12 mmol) was added and the reaction mixture was stirred overnight. The reaction was quenched by addition of a saturated, aqueous NH_4Cl solution (40 mL) and the organic materials were extracted with ether (3 × 50 mL). The combined extracts were dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by column chromatography (hexane/AcOEt = 9:1) to afford **11c** (3.79 g, 98%). **11c:** ^{1}H NMR: δ = 0.88 (t, *J* = 7.0 Hz, 3 H), 1.19−1.48 (m, 14 H), 1.81 (br, 1 H), 1.89 (ddd, *J* = 14.7, 9.5, 2.8 Hz, 1 H), 1.99 (ddd, *J* = 14.7, 9.5, 4.6 Hz, 1 H), 3.98−4.07 (m, 1 H), 4.70 (dd, *J* = 9.5, 4.6 Hz, 1 H), 7.24−7.33 (m, 6 H), 7.43−7.51 (m, 4 H). − ^{13}C NMR: δ = 14.1, 22.6, 25.5, 29.2, 29.5, 31.8, 37.6, 43.1, 55.1, 69.4, 127.6, 127.8, 128.9, 132.5, 132.8, 133.6, 134.0. − IR (neat): $\tilde{\nu}$ = 3396, 3074, 2925, 2856, 1583, 1481, 1439, 1026, 737, 690 cm^{-1}. − $C_{23}H_{32}OS_2$: calcd. C 71.08, H 8.30; found C 71.16, H 8.72.

In a similar manner, 1-phenyl-5,5-bis(phenylthio)-3-pentanol (**11b**) was prepared from 1,2-epoxy-4-phenylbutane. **11b:** ^{1}H NMR: δ = 1.67−1.80 (m, 2 H), 1.82−1.97 (m, 2 H), 2.05 (ddd, *J* = 14.7, 9.5, 4.9 Hz, 1 H), 2.58−2.78 (m, 2 H), 4.06 (br, 1 H), 4.66 (dd, *J* = 9.5, 4.9 Hz, 1 H), 7.13−7.33 (m, 11 H), 7.41−7.48 (m, 4 H). − ^{13}C NMR: δ = 31.8, 39.1, 43.1, 55.2, 68.9, 125.9, 127.8, 127.9, 128.37, 128.43, 128.9, 132.6, 132.9, 133.4, 133.9, 141.7. − IR (neat): $\tilde{\nu}$ = 3435, 3062, 2947, 1604, 1583, 1481, 1441, 1090, 1026, 744, 702 cm^{-1}. − $C_{23}H_{24}OS_2$: calcd. C 72.59, H 6.36; found C 72.57, H 6.58.

Preparation of [3,3-Bis(phenylthio)propoxy]dimethyl(prop-2-enyl)-silanes 5

Preparation of Allyldimethyl[1-phenyl-3,3-bis(phenylthio)propoxy]-silane (5a): To a THF (3 mL) solution of **11a** (1.41 g, 4 mmol), DMAP (0.244 g, 2 mmol), and triethylamine (1.39 mL, 10 mmol), at 0 °C under argon, was added dropwise allylchlorodimethylsilane (**10a**) (0.61 mL, 4 mmol), over 10 min. After warming to room temperature, the reaction mixture was stirred overnight. The reaction

was quenched by addition of a saturated, aqueous $NaHCO_3$ solution (20 mL), and organic materials were extracted with ether (3 × 30 mL). The combined extracts were washed with water (20 mL) and brine (20 mL), dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel deactivated with 5% of H_2O; hexane/AcOEt = 200:1) to give **5a** (1.43 g, 79%). **5a**: ^{1}H NMR (C_6D_6): δ = 0.12 (s, 3 H), 0.17 (s, 3 H), 1.59−1.70 (m, 2 H), 2.33 (ddd, *J* = 14.4, 9.4, 4.3 Hz, 1 H), 2.70 (ddd, *J* = 14.4, 9.1, 5.1 Hz, 1 H), 4.95−5.02 (m, 3 H), 5.35 (dd, *J* = 9.1, 4.3 Hz, 1 H), 5.83 (ddt, *J* = 18.6, 10.5, 7.9 Hz, 1 H), 7.02−7.21 (m, 9 H), 7.26−7.33 (m, 2 H), 7.60−7.69 (m, 4 H) . − ^{13}C NMR: δ = −2.1, −1.9, 24.8, 46.2, 53.2, 72.5, 113.7, 126.0, 127.3, 127.6, 128.3, 128.85, 128.88, 131.7, 132.2, 133.6, 133.9, 134.3, 143.9. − IR (neat): $\tilde{\nu}$ = 3076, 2958, 1631, 1583, 1481, 1439, 1255, 1090, 1070, 700, 690 cm^{-1}. − $C_{26}H_{30}OS_2Si$: calcd. C 69.28, H 6.71; found C 69.64, H 6.74.

The following silanes **5** were obtained in a similar manner.

Dimethyl(2-methylprop-2-enyl)[1-phenyl-3,3-bis(phenylthio)-propoxy]silane (5b): ^{1}H NMR (C_6D_6): δ = −0.05 (s, 3 H), 0.07 (s, 3 H), 1.53 (d, *J* = 13.6 Hz, 1 H), 1.56 (d, *J* = 13.6 Hz, 1 H), 1.64 (s, 3 H), 2.18 (ddd, *J* = 14.3, 9.3, 4.3 Hz, 1 H), 2.56 (ddd, *J* = 14.3, 8.9, 5.2 Hz, 1 H), 4.58 (s, 1 H), 4.69 (s, 1 H), 4.83 (dd, *J* = 9.3, 5.2 Hz, 1 H), 5.20 (dd, *J* = 8.9, 4.3 Hz, 1 H), 6.87−7.06 (m, 9 H), 7.14−7.19 (m, 2 H), 7.45−7.54 (m, 4 H). − ^{13}C NMR: δ = −1.6, −1.3, 25.2, 28.7, 46.2, 53.2, 72.5, 109.0, 126.1, 127.3, 127.5, 128.3, 128.8, 128.9, 131.8, 132.2, 133.6, 134.3, 142.6, 143.9. − IR (neat): $\tilde{\nu}$ = 3074, 2960, 1637, 1583, 1481, 1439, 1254, 1090, 1070, 741, 702, 690 cm^{-1}. − $C_{27}H_{32}OS_2Si$: calcd. C 69.78, H 6.94; found C 69.63, H 7.08.

Allyldimethyl[1-phenethyl-3,3-bis(phenylthio)propoxy]silane (5c): ^{1}H NMR (C_6D_6): δ = 0.09 (s, 6 H), 1.58 (d, *J* = 7.9 Hz, 2 H), 1.65−1.73 (m, 2 H), 2.05 (ddd, *J* = 14.7, 9.7, 3.7 Hz, 1 H), 2.30 (ddd, *J* = 14.7, 8.9, 4.6 Hz, 1 H), 2.48 (t, *J* = 8.1 Hz, 2 H), 4.20−4.28 (m, 1 H), 4.85 (dd, *J* = 9.8, 4.6 Hz, 1 H), 4.88−4.97 (m, 2 H), 5.54−5.57 (m, 1 H), 6.90−7.20 (m, 11 H), 7.50−7.62 (m, 4 H). − ^{13}C NMR: δ = −1.7, −1.5, 25.1, 31.3, 39.1, 43.1, 53.7, 69.7, 113.9, 125.8, 127.3, 127.7, 128.3, 128.4, 128.87, 128.94, 131.7, 132.5, 133.4, 134.0, 134.6, 142.0. − IR (neat): $\tilde{\nu}$ = 3076, 2956, 1631, 1583, 1481, 1439, 1255, 1093, 839, 748, 690 cm^{-1}. − $C_{28}H_{34}OS_2Si$: calcd. C 70.24, H 7.16; found C 70.59, H 7.23.

Dimethyl(2-methylprop-2-enyl)[1-phenethyl-3,3-bis(phenylthio)-propoxy]silane (5d): ^{1}H NMR (C_6D_6): δ = 0.12 (s, 6 H), 1.48 (s, 2 H), 1.66−1.73 (m, 5 H), 2.05 (ddd, *J* = 14.3, 9.8, 3.7 Hz, 1 H), 2.30 (ddd, *J* = 14.7, 8.5, 4.6 Hz, 1 H), 2.47 (dt, *J* = 16.2, 7.2 Hz, 2 H), 4.20−4.26 (m, 1 H), 4.65 (d, *J* = 0.9 Hz, 1 H), 4.74 (d, *J* = 0.9 Hz, 1 H), 4.86 (dd, *J* = 9.9, 4.4 Hz, 1 H), 6.90−7.19 (m, 11 H), 7.50−7.62 (m, 4 H). − ^{13}C NMR: δ = −1.2, −1.0, 25.3, 29.0, 31.3, 39.1, 43.1, 53.7, 69.6, 109.1, 125.8, 127.3, 127.7, 128.3, 128.4, 128.85, 128.91, 131.8, 132.5, 133.4, 134.5, 142.0, 142.6. − IR (neat): $\tilde{\nu}$ = 3074, 2951, 1637, 1583, 1481, 1439, 1252, 1090, 843, 748, 690 cm^{-1}. − $C_{29}H_{36}OS_2Si$: calcd. C 70.68, H 7.36; found C 70.83, H 7.73.

Allyldimethyl[1-octyl-3,3-bis(phenylthio)propoxy]silane (5e): ^{1}H NMR (C_6D_6): δ = 0.19 (s, 6 H), 0.91 (d, *J* = 7.0 Hz, 3 H), 1.15−1.50 (m, 14 H), 1.63 (d, *J* = 7.9 Hz, 2 H), 2.06 (ddd, *J* = 14.7, 10.1, 3.6 Hz, 1 H), 2.29 (ddd, *J* = 14.7, 9.0, 4.4 Hz, 1 H), 4.22−4.28 (m, 1 H), 4.88−4.98 (m, 3 H), 5.82 (ddt, *J* = 16.8, 10.4, 7.9 Hz, 1 H), 6.90−7.08 (m, 6 H), 7.50−7.64 (m, 4 H). − ^{13}C NMR: δ = −1.7, −1.5, 14.1, 22.7, 25.0, 25.2, 29.2, 29.5, 29.7, 31.9, 37.5, 43.1, 53.5, 70.1, 113.7, 127.2, 127.6, 128.8, 128.9, 131.6, 132.5, 134.1. − IR (neat): $\tilde{\nu}$ = 3076, 2929, 1631, 1583, 1481, 1439, 1255, 1090, 1026, 837, 737, 690 cm^{-1}. − $C_{28}H_{42}OS_2Si$: calcd. C 69.08, H 8.69; found C 69.48, H 9.00.

Preparation of the Cyclic Allylsilanes 2

Preparation of 2,2-Dimethyl-7-phenyl-2,3,6,7-tetrahydro-1,2-oxasilepin (2a): Titanocene dichloride (498 mg, 2 mmol), magnesium turnings (54 mg, 2.2 mmol), and 4 Å molecular sieves (200 mg) were placed in a 100 mL flask. The mixture was stirred and warmed in a heating bath at 100 °C for 1 h under reduced pressure (2−3 Torr). After cooling, the reaction vessel was flushed with argon. THF (3.0 mL) and triethyl phosphite (0.69 mL, 4 mmol) were added successively, and the reaction mixture was stirred for 3 h at room temperature. A THF (13.7 mL) solution of **4a** (243 mg, 0.5 mmol) was added, and the reaction mixture was stirred for 4 h and then refluxed for 1 h. After cooling to room temperature, the reaction mixture was diluted with hexane (100 mL). The insoluble materials were filtered off through Celite and washed with hexane (50 mL). The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography (silica gel deactivated with 5% of H_2O; hexane/AcOEt = 100:1) to give **2a** (77 mg, 70%). **2a**: ^{1}H NMR (C_6D_6): δ = 0.15 (s, 3 H), 0.19 (s, 3 H), 1.34 (dd, *J* = 15.0, 7.8 Hz, 1 H), 1.72 (ddd, *J* = 15.0, 6.7, 1.8 Hz, 1 H), 2.25 (ddd, *J* = 15.6, 7.6, 1.8 Hz, 1 H), 2.58−2.68 (m, 1 H), 4.99 (dd, *J* = 9.8, 1.5 Hz, 1 H), 5.55−5.63 (m, 1 H), 5.78−5.87 (m, 1 H), 7.07−7.12 (m, 1 H), 7.18−7.23 (m, 2 H), 7.34−7.39 (m, 2 H) . − IR (neat): $\tilde{\nu}$ = 3024, 2958, 1637, 1452, 1252, 1070, 1026, 937, 839, 698 cm^{-1}. − $C_{13}H_{18}OSi$: calcd. C 71.51, H 8.31; found C 71.44, H 8.45.

In a similar manner, the cyclic allylsilanes **2c** and **2i** were obtained from **4c** and **5e**, respectively.

2,2-Dimethyl-7-phenethyl-2,3,6,7-tetrahydro-1,2-oxasilepin (2c): ^{1}H NMR (C_6D_6): δ = 0.14 (s, 3 H), 0.16 (s, 3 H), 1.36 (dd, *J* = 15.0, 7.6 Hz, 1 H), 1.52 (dddd, *J* = 13.4, 9.8, 7.0, 3.7 Hz, 1 H), 1.59 (dd, *J* = 15.0, 6.7 Hz, 1 H), 1.80 (dddd, *J* = 13.4, 9.5, 9.2, 4.9 Hz, 1 H), 1.96 (dd, *J* = 15.2, 7.3 Hz, 1 H), 2.27 (dt, *J* = 15.2, 7.8 Hz, 1 H), 2.61 (ddd, *J* = 13.7, 9.5, 7.0 Hz, 1 H), 2.77 (ddd, *J* = 13.7, 9.8, 4.9 Hz, 1 H), 3.78 (br t, *J* = 9.2 Hz, 1 H), 5.46−5.56 (m, 1 H), 5.79 (ddt, *J* = 10.7, 7.3, 1.5 Hz, 1 H), 7.05−7.10 (m, 1 H), 7.11−7.20 (m, 4 H). − ^{13}C NMR: δ = −1.6, −0.2, 18.3, 32.2, 37.0, 39.9, 72.0, 125.6, 126.4, 128.0, 128.3, 128.5, 142.4. − IR (neat): $\tilde{\nu}$ = 3026, 2956, 1631, 1496, 1456, 1252, 1097, 839, 698 cm^{-1}.

2,2-Dimethyl-7-octyl-2,3,6,7-tetrahydro-1,2-oxasilepin (2i): ^{1}H NMR (C_6D_6): δ = 0.16 (s, 3 H), 0.17 (s, 3 H), 0.93 (t, *J* = 7.0 Hz, 3 H), 1.20−1.64 (m, 16 H), 2.09 (ddd, *J* = 15.3, 7.3, 0.9 Hz, 1 H), 2.33 (dt, *J* = 15.3, 7.7 Hz, 1 H), 3.83−3.91 (m, 1 H), 5.56−5.64 (m, 1 H), 5.83 (ddt, *J* = 10.7, 7.2, 1.5 Hz, 1 H). − ^{13}C NMR: δ = −1.5, −0.3, 14.1, 18.2, 22.7, 26.0, 29.3, 29.56, 29.61, 31.9, 37.0, 38.3, 72.8, 126.6, 127.6. − IR (neat): $\tilde{\nu}$ = 3020, 2956, 1637, 1377, 1250, 1090, 839 cm^{-1}.

Preparation of the 1,5-Diols 3

Preparation of (*Z*)-3-Methyl-5-phenyl-2-pentene-1,5-diol (3b): After the RCM of **4b** (232 mg, 0.5 mmol) had been performed according to the procedure described above, the reaction mixture was diluted with hexane (100 mL). The insoluble materials were filtered off through Celite and washed with hexane (50 mL). After the filtrate had been concentrated under reduced pressure, triethyl phosphite and the polar by-products were quickly removed by column chromatography (silica gel deactivated with 5% of H_2O; hexane/AcOEt = 100:1). The crude cyclic ether thus obtained, together with potassium fluoride (145 mg, 2.5 mmol) and $KHCO_3$ (115 mg, 1.15 mmol), were dissolved in THF−MeOH (5 mL each). Hydro-

gen peroxide (30%, 2.3 mL) was added to the solution at 40 °C and the reaction mixture was stirred for 24 h. After cooling, the organic materials were extracted with AcOEt (3 × 30 mL), washed with brine (20 mL), and dried (Na_2SO_4). The combined extracts were concentrated under reduced pressure and the residue was purified by PTLC (hexane/AcOEt = 1:1) to give **3b** (48 mg, 50%). **3b**: ^{1}H NMR: δ = 1.82 (s, 3 H), 2.24 (dd, *J* = 13.4, 3.7 Hz, 1 H), 2.50−2.69 (br, 1 H), 2.74 (dd, *J* = 13.4, 9.5 Hz, 1 H), 2.96−3.19 (br, 1 H), 3.87 (dd, *J* = 11.9, 7.2 Hz, 1 H), 4.10 (dd, *J* = 11.9, 7.9 Hz, 1 H), 4.77 (dd, *J* = 9.5, 3.7 Hz, 1 H), 5.73 (t, *J* = 7.6 Hz, 1 H), 7.24−7.32 (m, 2 H), 7.32−7.40 (m, 3 H). − ^{13}C NMR: δ = 23.8, 42.2, 57.8, 71.1, 125.6, 127.1, 127.6, 128.5, 137.8, 144.5. − IR (neat): $\tilde{\nu}$ = 3352, 3062, 2916, 1664, 1452, 1053, 1028, 756, 700 cm^{-1}.

In a similar manner, the following 1,5-diols **3** were obtained from compounds **4** and compounds **5**.

(*Z*)-5-Phenyl-2-pentene-1,5-diol (3a): ^{1}H NMR: δ = 2.40−2.50 (m, 1 H), 2.54−2.64 (m, 1 H), 2.64−2.98 (br, 1 H), 3.06−3.28 (br, 1 H), 3.98 (dd, *J* = 12.4, 6.9 Hz, 1 H), 4.11 (dd, *J* = 12.4, 7.5 Hz, 1 H), 4.71 (dd, *J* = 7.9, 4.6 Hz, 1 H), 5.55−5.64 (m, 1 H), 5.78−5.88 (m, 1 H), 7.20−7.42 (m, 5 H). − ^{13}C NMR: δ = 37.0, 57.4, 72.8, 125.7, 127.5, 128.3, 128.9, 131.2, 143.8. − IR (neat): $\tilde{\nu}$ = 3354, 3028, 2925, 1658, 1456, 1030, 760, 702 cm^{-1}.

(*Z*)-7-Phenyl-2-heptene-1,5-diol (3c): ^{1}H NMR: δ = 1.75−1.85 (m, 2 H), 1.86−2.03 (br, 1H), 2.23−2.37 (m, 2 H), 2.48−2.73 (m, 2 H), 2.75−2.85 (m, 1 H), 3.61−3.72 (m, 1 H), 4.08 (dd, *J* = 12.4, 6.9 Hz, 1 H), 4.19 (dd, *J* = 12.4, 7.5 Hz, 1 H), 5.58−5.67 (m, 1 H), 5.82−5.91 (m, 1 H), 7.15−7.24 (m, 3 H), 7.24−7.35 (m, 2 H). − ^{13}C NMR: δ = 32.1, 35.2, 38.7, 57.6, 69.9, 125.9, 128.37, 128.41, 129.3, 131.4, 141.8. − IR (neat): $\tilde{\nu}$ = 3402, 3030, 2945, 1653, 1496, 1456, 1034, 748, 702 cm^{-1}.

(*Z*)-3-Methyl-7-phenyl-2-heptene-1,5-diol (3d): ^{1}H NMR: δ = 1.75 (s, 3 H), 1.76−1.88 (m, 2 H), 2.01 (dd, *J* = 13.4, 2.4 Hz, 1 H), 2.48 (dd, *J* = 13.4, 9.8 Hz, 1 H), 2.69 (ddd, *J* = 14.0, 9.8, 6.7 Hz, 1 H), 2.80 (ddd, *J* = 14.0, 9.8, 6.1 Hz, 1 H), 3.17−3.42 (br, 2 H), 3.65−3.74 (m, 1 H), 3.91 (dd, *J* = 11.8, 6.9 Hz, 1 H), 4.13 (dd, *J* = 11.8, 8.1 Hz, 1 H), 5.71 (t, *J* = 6.9 Hz, 1 H), 7.16−7.22 (m, 3 H), 7.24−7.31 (m, 2 H). − ^{13}C NMR: δ = 23.8, 32.1, 39.6, 39.8, 57.6, 67.8, 125.8, 126.5, 128.3, 128.4, 138.5, 141.9. − IR (neat): $\tilde{\nu}$ = 3336, 3030, 2945, 1668, 1496, 1456, 1053, 1030, 748, 700 cm^{-1}.

(*Z*)-2-Tetradecene-1,5-diol (3e): ^{1}H NMR: δ = 0.88 (t, *J* = 6.9 Hz, 3 H), 1.20−1.53 (m, 16 H), 1.95−2.75 (br, 2 H), 2.21−2.33 (m, 2 H), 3.58−3.69 (m, 1 H), 4.04−4.13 (m, 1 H), 4.15−4.23 (m, 1 H), 5.64 (dt, *J* = 9.5, 8.7 Hz, 1 H), 5.82−5.91 (m, 1 H). − ^{13}C NMR: δ = 14.1, 22.7, 25.8, 29.3, 29.5, 29.59, 29.60, 31.9, 35.0, 37.1, 57.6, 70.7, 129.6, 131.3. − IR (neat): $\tilde{\nu}$ = 3356, 3022, 2960, 2929, 2858, 1468, 1078, 1014 cm^{-1}.

(*Z*)-3-Methyl-2-tetradecene-1,5-diol (3f): ^{1}H NMR: δ = 0.88 (t, *J* = 6.6 Hz, 3 H), 1.20−1.57 (m, 16 H), 1.78 (s, 3 H), 1.99 (d, *J* = 13.4 Hz, 1 H), 2.44 (dd, *J* = 13.4, 10.1 Hz, 1 H), 2.66−3.26 (br, 2 H), 3.61−3.72 (m, 1 H), 3.86−3.97 (m, 1 H), 4.08−4.18 (m, 1 H), 5.72 (t, *J* = 7.5 Hz, 1 H). − ^{13}C NMR: δ = 14.1, 22.7, 23.8, 25.8, 29.3, 29.55, 29.60, 29.62, 31.9, 38.0, 39.8, 57.7, 68.6, 126.6, 138.6. − IR (neat): $\tilde{\nu}$ = 3348, 2925, 2856, 1666, 1454, 1090, 1003 cm^{-1}.

(*Z*)-2-Methyl-5-phenyl-2-pentene-1,5-diol (3g): ^{1}H NMR: δ = 1.80 (s, 3 H), 2.34−2.43 (m, 1 H), 2.54 (dt, *J* = 14.3, 8.6 Hz, 1 H), 3.44−3.93 (br, 2 H), 3.87 (d, *J* = 11.6 Hz, 1 H), 4.13 (d, *J* = 11.6 Hz, 1 H), 4.62−4.70 (m, 1 H), 5.25−5.34 (m, 1 H), 7.22−7.38 (m, 5 H). − ^{13}C NMR: δ = 22.3, 37.6, 61.0, 65.8, 73.0, 123.8, 125.7, 127.4, 128.3, 138.6, 144.2. − IR (neat): $\tilde{\nu}$ = 3338, 3066, 2925, 1456, 1055, 1028, 1005, 756, 702 cm^{-1}.

(*Z*)-2-Methyl-7-phenyl-2-heptene-1,5-diol (3h): ^{1}H NMR: δ = 1.74−1.81 (m, 2 H), 1.83 (s, 3 H), 2.17−2.31 (m, 2 H), 2.62−2.70 (m, 1 H), 2.74−2.82 (m, 1 H), 3.00−3.52 (br, 2 H), 3.57−3.65 (m, 1 H), 3.92 (d, *J* = 11.6 Hz, 1 H), 4.15 (d, *J* = 11.6 Hz, 1 H), 5.34 (t, *J* = 8.5 Hz, 1 H), 7.14−7.30 (m, 5 H). − ^{13}C NMR: δ = 22.4, 32.1, 35.4, 38.7, 60.9, 70.0, 124.1, 125.8, 128.3, 138.3, 141.9. − IR (neat): $\tilde{\nu}$ = 3406, 3030, 2945, 1641, 1604, 1496, 1454, 1055, 752, 702 cm^{-1}.

(*Z*)-2-Tridecene-1,5-diol (3i): ^{1}H NMR: δ = 0.88 (t, *J* = 6.9 Hz, 3 H), 1.20−1.54 (m, 14 H), 1.80−2.38 (br, 2 H), 2.23−2.34 (m, 2 H), 3.62−3.68 (m, 1 H), 4.11 (dd, *J* = 12.2, 6.9 Hz, 1 H), 4.20 (dd, *J* = 12.2, 7.3 Hz, 1 H), 5.62−5.71 (m, 1 H), 5.84−5.94 (m, 1 H). − ^{13}C NMR: δ = 14.1, 22.7, 25.7, 29.2, 29.5, 29.6, 31.8, 35.0, 37.1, 57.7, 70.7, 129.6, 131.4. − IR (neat): $\tilde{\nu}$ = 3334, 3018, 2981, 2856, 1657, 1468, 1082, 1014 cm−1.

Large-scale Preparation of 3a: A 1-L round-bottomed flask, equipped with a magnetic stirring bar, a thermometer, and a rubber septum, was charged with titanocene dichloride (3.74 g, 15 mmol) and finely powdered 4Å molecular sieves (0.75 g). The mixture was stirred and warmed in a heating bath at 100 °C for 1 h under reduced pressure (2 Torr). After cooling, the reaction vessel was flushed with argon, and magnesium turnings (0.40 g, 16.5 mmol) were added. THF (60 mL) and triethyl phosphite (5.1 mL, 30 mmol) were injected successively through the septum. During the addition of triethyl phosphite, the reaction mixture was cooled in a water bath to maintain the temperature below 30 °C. After stirring the reaction mixture for 3 h at room temperature, a THF (107 mL) solution of **5a** (2.25 g, 5 mmol) was added, and the reaction mixture was stirred for 4 h and then refluxed for 1 h. After being cooled to room temperature, the reaction mixture was diluted with hexane (300 mL). The insoluble materials were filtered off through Celite and washed with hexane (150 mL). The filtrate was concentrated under reduced pressure, and the residue was dissolved in hexane (300 mL). The insoluble materials were again filtered off through Celite and washed with hexane (150 mL). After removal of solvent, triethyl phosphite and the polar by-products were quickly removed by column chromatography (silica gel deactivated with 5% of H_2O; hexane/ AcOEt = 100:1). The obtained crude cyclic ether **2a**, together with potassium fluoride (1.45 g, 25 mmol) and $KHCO_3$ (1.15 g, 11.5 mmol), were dissolved in THF−MeOH (50 mL each). Hydrogen peroxide (30%, 23 mL) was added dropwise to the solution over 15 min at 40 °C, and the reaction mixture was stirred for 24 h. After cooling, the organic materials were extracted with AcOEt (3 × 50 mL), washed with brine (30 mL), and dried (Na_2SO_4). The extract was concentrated under reduced pressure and the residue was purified by PTLC (hexane/ AcOEt = 1:1) to give **3a** (0.576 g, 65%).

Acetylation of the 1,5-Diols 3

Acetylation of 3a: To a pyridine (4 mL) solution of **3a** (75 mg, 0.42 mmol) was added acetyl chloride (0.11 mL, 1.5 mmol) at 0 °C. After stirring for 1 h, the reaction was quenched by addition of water (10 mL). The organic materials were extracted with ether (3 × 20 mL) and washed successively with 1 M HCl (20 mL), 1 M NaOH (20 mL), water (20 mL), and brine (20 mL). The extract was dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by PTLC (hexane/ AcOEt = 4:1) to give (*Z*)-1,5-diacetoxy-5-phenyl-2-pentene (**9a**) (100 mg, 91%). **9a**: ^{1}H NMR: δ = 2.03 (s, 3 H), 2.07 (s, 3 H), 2.56−2.64 (m, 1 H), 2.70−2.78 (m, 1 H), 4.52 (d, *J* = 6.1 Hz, 2 H), 5.54−5.66 (m, 2 H), 5.78 (dd, *J* =

7.5, 6.3 Hz, 1 H), 7.26−7.37 (m, 5 H). − ^{13}C NMR: δ = 20.8, 21.1, 34.5, 60.0, 74.9, 126.4, 126.6, 128.0, 128.4, 129.0, 139.7, 170.1, 170.7. − IR (neat): $\tilde{\nu}$ = 3033, 2941, 1732, 1456, 1375, 1232, 1026, 964, 764, 702 cm^{-1}. − $C_{15}H_{18}O_4$: calcd. C 68.68, H 6.92; found C 68.77, H 7.12.

In a similar manner, the following 1,5-diacetates **9** were obtained by the acetylation of compounds **3**.

(*Z*)-1,5-Diacetoxy-3-methyl-5-phenyl-2-pentene (9b): ^{1}H NMR: δ = 1.78 (d, *J* = 1.2 Hz, 3 H), 2.03 (s, 3 H), 2.06 (s, 3 H), 2.43 (dd, *J* = 13.7, 5.8 Hz, 1 H), 2.81 (dd, *J* = 13.7, 8.5 Hz, 1 H), 4.44 (dd, *J* = 7.3, 0.6 Hz, 2 H), 5.44 (t, *J* = 7.3 Hz, 1 H), 5.86 (dd, *J* = 8.5, 5.8 Hz, 1 H), 7.27−7.37 (m, 5 H). − ^{13}C NMR: δ = 21.0, 21.2, 24.0, 39.4, 60.9, 74.0, 122.6, 126.3, 128.1, 128.5, 137.2, 140.0, 170.1, 170.9. − IR (neat): $\tilde{\nu}$ = 3035, 2976, 2943, 1734, 1456, 1385, 1234, 1026, 762, 702 cm^{-1}. − $C_{16}H_{20}O_4$: calcd. C 69.55, H 7.29; found C 69.86, H 7.37.

(*Z*)-1,5-Diacetoxy-7-phenyl-2-heptene (9c): ^{1}H NMR: δ = 1.80−1.96 (m, 2 H), 2.03 (s, 3 H), 2.04 (s, 3 H), 2.35−2.48 (m, 2 H), 2.60 (ddd, *J* = 13.7, 9.8, 6.4 Hz, 1 H), 2.67 (ddd, *J* = 13.7, 10.1, 5.8 Hz, 1 H), 4.55−4.66 (m, 2 H), 4.92−5.00 (m, 1 H), 5.58−5.70 (m, 2 H), 7.12−7.35 (m, 5 H). − ^{13}C NMR: δ = 20.9, 21.1, 31.8, 32.3, 35.4, 60.1, 72.8, 126.0, 126.3, 128.3, 128.4, 129.5, 141.3, 170.7, 170.9. − IR (neat): $\tilde{\nu}$ = 3028, 2952, 2864, 1739, 1456, 1373, 1234, 1028, 750, 702 cm^{-1}. − $C_{17}H_{22}O_4$: calcd. C 70.32, H 7.64; found C 70.55, H 7.80.

(*Z*)-1,5-Diacetoxy-3-methyl-7-phenyl-2-heptene (9d): ^{1}H NMR: δ = 1.77 (d, *J* = 0.9 Hz, 3 H), 1.80−1.94 (m, 2 H), 2.01 (s, 3 H), 2.02 (s, 3 H), 2.20 (dd, *J* = 13.7, 5.0 Hz, 1 H), 2.52 (dd, *J* = 13.7, 8.5 Hz, 1 H), 2.61 (ddd, *J* = 13.7, 9.8, 6.4 Hz, 1 H), 2.67 (ddd, *J* = 13.7, 9.8, 6.1 Hz, 1 H), 4.52 (dd, *J* = 11.9, 7.0 Hz, 1 H), 4.63 (dd, *J* = 11.9, 7.3 Hz, 1 H), 5.07 (septet, *J* = 4.6 Hz, 1 H), 5.45 (t, *J* = 7.0 Hz, 1 H), 7.14−7.21 (m, 3 H), 7.25−7.31 (m, 2 H). − ^{13}C NMR: δ = 20.9, 21.0, 23.9, 31.9, 36.0, 37.1, 60.9, 71.7, 122.1, 126.0, 128.3, 128.4, 138.0, 141.3, 170.5, 171.0. − IR (neat): $\tilde{\nu}$ = 3030, 2943, 2864, 1732, 1496, 1456, 1385, 1234, 1030, 957, 750, 702 cm^{-1}. − $C_{18}H_{24}O_4$: calcd. C 71.03, H 7.95: found C 71.15, H 8.08.

(*Z*)-1,5-Diacetoxy-2-tetradecene (9e): ^{1}H NMR: δ = 0.88 (t, *J* = 6.9 Hz, 3 H), 1.20−1.35 (m, 14 H), 1.48−1.60 (m, 2 H), 2.03 (s, 3H), 2.06 (s, 3 H), 2.31−2.42 (m, 2 H), 4.56−4.66 (m, 2 H), 4.86−4.94 (m, 1 H), 5.62 (dt, *J* = 10.7, 6.1 Hz, 1 H), 5.66 (dt, *J* = 10.7, 5.8 Hz, 1 H). − ^{13}C NMR: δ = 14.1, 21.0, 21.2, 22.7, 25.3, 29.3, 29.4, 29.5, 31.9, 32.3, 33.7, 57.5, 60.2, 73.3, 126.1, 129.8, 170.8, 170.9. − IR (neat): $\tilde{\nu}$ = 3029, 2929, 2858, 1743, 1468, 1375, 1238, 1026 cm^{-1}. − $C_{18}H_{32}O_4$: calcd. C 69.20, H 10.32; found C 69.50, H 10.20.

(*Z*)-1,5-Diacetoxy-3-methyl-2-tetradecene (9f): ^{1}H NMR: δ = 0.88 (t, *J* = 6.9 Hz, 3 H), 1.20−1.36 (m, 14 H), 1.46−1.58 (m, 2 H), 1.79 (d, *J* = 0.9 Hz, 3 H), 2.01 (s, 3 H), 2.05 (s, 3 H), 2.15 (dd, *J* = 13.7, 4.3 Hz, 1 H), 2.48 (dd, *J* = 13.7, 8.9 Hz, 1 H), 4.53 (dd, *J* = 12.2, 6.7 Hz, 1 H), 4.64 (dd, *J* = 12.2, 7.6 Hz, 1 H), 4.97−5.06 (m, 1 H), 5.44 (t, *J* = 6.7 Hz, 1 H). − ^{13}C NMR: δ = 14.1, 21.0, 22.7, 24.0, 25.5, 29.3, 29.4, 29.5, 31.9, 34.5, 37.2, 61.1, 72.1, 121.8, 138.4, 170.6, 171.0. − IR (neat): $\tilde{\nu}$ = 2929, 2858, 1743, 1466, 1379, 1236, 1022, 957 cm^{-1}. − $C_{19}H_{34}O_4$: calcd. C 69.90, H 10.50; found C 69.82, H 10.57.

(*Z*)-1,5-Diacetoxy-2-methyl-5-phenyl-2-pentene (9g): ^{1}H NMR: δ = 1.73 (d, *J* = 1.2 Hz, 3 H), 2.05 (s, 3 H), 2.07 (s, 3 H), 2.56 (ddd, *J* = 14.7, 7.3, 6.1 Hz, 1 H), 2.70 (ddt, *J* = 14.7, 7.6, 0.9 Hz, 1 H), 4.46 (d, *J* = 12.2 Hz, 1 H), 4.49 (d, *J* = 12.2 Hz, 1 H), 5.33 (t, *J* = 6.7 Hz, 1 H), 5.73 (dd, *J* = 7.3, 6.1 Hz, 1 H), 7.25−7.37 (m, 5 H). − ^{13}C NMR: δ = 20.9, 21.2, 21.5, 34.8, 62.9, 75.3, 124.7, 126.5, 128.0, 128.4, 133.2, 139.9, 170.2, 171.0. − IR (neat): $\tilde{\nu}$ = 3035, 2979, 2945, 1732, 1456, 1373, 1238, 1026, 760, 702 cm^{-1}. − $C_{16}H_{20}O_4$: calcd. C 69.55, H 7.29; found C 69.40, H 7.32.

(*Z*)-1,5-Diacetoxy-2-methyl-7-phenyl-2-heptene (9h): ^{1}H NMR: δ = 1.76 (d, *J* = 1.2 Hz, 3 H), 1.79−1.93 (m, 2 H), 2.03 (s, 3 H), 2.04 (s, 3 H), 2.30−2.44 (m, 2 H), 2.59 (ddd, *J* = 13.9, 9.7, 6.4 Hz, 1 H), 2.66 (ddd, *J* = 13.9, 10.4, 6.0 Hz, 1 H), 4.53, (d, *J* = 11.9 Hz, 1 H), 4.59 (d, *J* = 11.9 Hz, 1 H), 4.88−4.95 (m, 1 H), 5.37 (t, *J* = 7.5 Hz, 1 H), 7.14−7.21 (m, 3 H), 7.25−7.30 (m, 2 H). − ^{13}C NMR: δ = 20.9, 21.1, 21.6, 31.8, 32.5, 35.3, 62.9, 73.2, 125.0, 125.9, 128.3, 128.4, 132.9, 141.4, 170.7, 171.0. − IR (neat): $\tilde{\nu}$ = 3030, 2949, 1734, 1456, 1373, 1238, 1026, 958, 750, 702 cm^{-1}. − $C_{18}H_{24}O_4$: calcd. C 71.03, H 7.95; found C 71.11, H 8.27.

(*Z*)-1,5-Diacetoxy-2-tridecene (9i): ^{1}H NMR: δ = 0.88 (t, *J* = 6.9 Hz, 3 H), 1.20−1.36 (m, 12 H), 1.47−1.60 (m, 2 H), 2.03 (s, 3 H), 2.06 (s, 3 H), 2.31−2.43 (m, 2 H), 4.56−4.67 (m, 2 H), 4.87−4.94 (m, 1 H), 5.62 (dt, *J* = 10.8, 6.4 Hz, 1 H), 5.65 (dt, *J* = 10.8, 5.8 Hz, 1 H). − ^{13}C NMR: δ = 14.1, 21.0, 21.2, 22.6, 25.3, 29.2, 29.42, 29.44, 31.8, 32.3, 33.7, 60.2, 73.3, 126.1, 129.8, 170.8. − IR (neat): $\tilde{\nu}$ = 3028, 2929, 2856, 1741, 1460, 1373, 1236, 1022, 964 cm^{-1}. − $C_{17}H_{30}O_4$: calcd. C 68.42, H 10.13; found C 68.73, H 10.18.

Acknowledgments

This work was supported by Grants-in-Aid for Scientific Research from the Japanese Ministry of Education, Science, Sports, and Culture (No. 11119214 and 11440213).

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Received May 29, 2000
[O00270]