

# A HIGHLY STEREOSELECTIVE SYNTHESIS OF (Z)-1-PHENYLTHIO-1-TRIALKYL-SILYLALKENES FROM 1-METHOXY-1-PHENYLTHIO-1-TRIALKYLSILYLALKANES

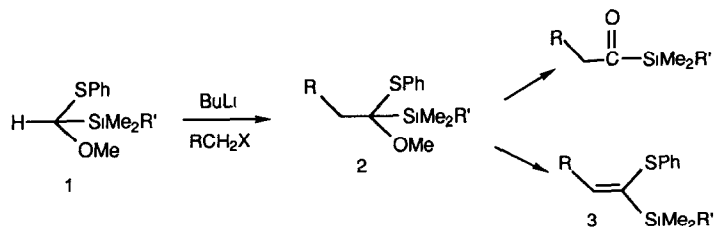
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**Abstract;** A new method for the highly stereoselective synthesis of (Z)-1-phenylthio-1-trialkylsilylalkenes **3** by the elimination of methanol from 1-methoxy-1-phenylthio-1-trialkylsilylalkane **2** in organic solvents is described.

## Introduction

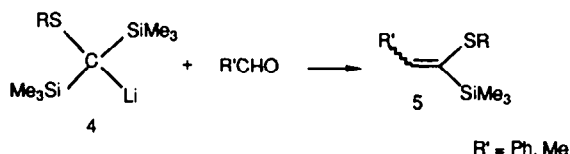
Recently we have introduced methoxy(phenylthio)trialkylsilylmethane **1** as useful one carbon homologation reagents.<sup>1</sup> These polyfunctionalized reagents have several synthetic applications. The compounds **1** undergo facile alkylation to give 1-methoxy-1-phenylthio-1-trialkylsilylalkanes **2**. As one synthetic application of **2**, we found that the oxidation of **2** gives acyl silanes in high yields. In our continuing works on synthetic applications of the compounds **2**, we found an interesting elimination reaction, namely the compounds **2** undergo unexpectedly facile elimination reaction of a methanol unit in a solution to afford 1-phenylthio-1-trialkylsilylalkenes **3** in good yields. The reaction is stereoselective and the Z isomer was formed with high selectivity. In this paper, we wish to report the stereoselective formation of (Z)-1-phenylthio-1-trialkylsilylalkenes **3**. Also preliminary studies on the synthetic applications of these polyfunctionalized alkenes **3** are presented.



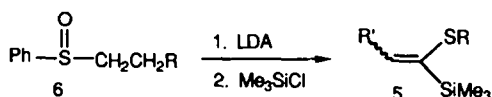
1-Phenylthio-1-trialkylsilylalkenes **3** can be regarded as derivatives of vinylsilanes, which have increasing synthetic applications.<sup>2</sup> Thus it seems

\*Dedicated on the occasion of the 65th birthday of Professor W. D. Ollis.

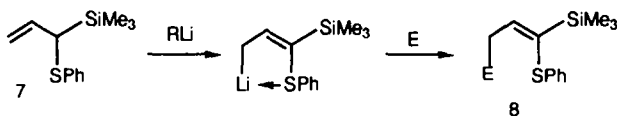
likely that the compounds **3** should have potential synthetic applications. But so far few applications have been reported. As one example, a synthetic utility of **3** was demonstrated in an elegant synthetic work on maytansinoids, in which this system **3** was chosen as a precursor of the corresponding sulfone derivative, and shown to be a very useful template to achieve a highly diastereoselective heteroconjugate addition.<sup>3</sup> Also this system was used for the construction of a steroid side chain.<sup>4</sup> As for the synthetic methods for these interesting polyfunctionalized compounds **3**, so far few synthetic methods are known. Grobel and Seebach prepared the compounds **5** by the Peterson olefination of bis(trimethylsilyl)-alkylthiomethyl lithium **4** with aldehydes. However, the reaction was not stereoselective, and **5** was a mixture of the **X** and **Z** isomers.<sup>5</sup>



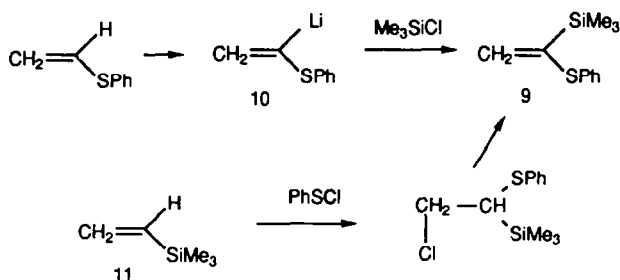
Miller and Hassig introduced a facile synthetic method for **5** by the treatment of the sulfoxide derivatives **6** with three equivalents of lithium diisopropylamide (LDA) in THF in the presence of six equivalents of trimethylsilyl chloride in a single step.<sup>6</sup> This is a simple method, but again the reaction is not stereoselective. Thus so far, to the best of our knowledge, there is no stereoselective synthetic method for **3**.



Kyler and Watt showed that 1-phenylthio-1-trimethylsilyl-2-propene (**7**) undergoes  $\gamma$ -lithiation, and the reaction of aldehydes takes place at  $\gamma$ -position, generating (**Z**)-1-phenylthio-1-trimethylsilylalkenes **8** *in situ*, and they applied the reaction to the construction of a steroid side chain.<sup>4</sup>



The simplest compound of this series of the compounds **3** is 1-phenylthio-1-trimethylsilyl-2-propene (**9**), which was prepared by Magnus and coworkers either by the reaction of  $\alpha$ -lithiovinyl phenyl sulfide (**10**) with trimethylsilyl chloride,<sup>7</sup> or the addition of arylsulfenyl chloride to vinyltrimethylsilane (**11**), followed by elimination of hydrogen chloride.<sup>8</sup>



## Results and Discussion




We have prepared easily a number of the compounds of the type **2** by alkylation of the lithiated **1** with corresponding alkyl halides.<sup>1</sup> Their elimination reaction was performed in several non-polar solvents such as xylene, toluene, benzene, and THF at temperatures from a room temperature to their boiling temperatures. Results of the elimination reactions of several derivatives of **2** under various conditions are shown in the Table.

For smooth elimination reaction, somewhat elevated temperatures are required. At a room temperature under argon atmosphere, no elimination took place. However, we found that the presence of oxygen very much favors the elimination reaction, and the elimination proceeded slowly at a room temperature under oxygen atmosphere. Further acceleration was observed by the addition of triethylborane, and the olefins **3** were obtained in high yields at the room temperature in about 20 hours. (Runs 6, 9, 11, 12) The reaction proceeded rapidly in all above-shown solvents at their boiling temperatures under oxygen atmosphere in the presence of triethylborane. Thus the elimination reaction was carried out efficiently in the presence of triethylborane under the oxygen atmosphere as shown in the Table. The use of THF at its boiling temperature is the most convenient.

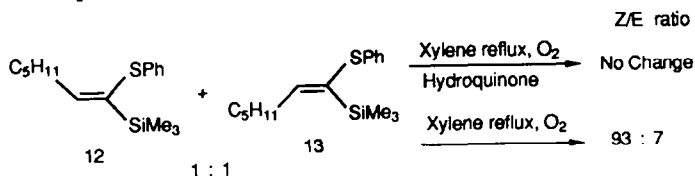
In addition to the facile elimination, another interesting point is that the **Z** isomers **3** were obtained with high stereoselectivity, which is difficult to achieve by other means. It is reasonable to assume that a mixture of the **E** and **Z** olefins is formed at first by the elimination. The preferential formation of the **Z**-isomers can be understood by the subsequent rapid isomerization of the **E** forms to the **Z** isomers. The reactivity of 1-phenylthio-1-trialkylsilylethane (**2**, R = H) is somewhat exceptional and dependent on the bulkiness of the silyl group. The elimination reaction of t-butyldimethylsilyl and dimethylphenylsilyl derivatives proceeded in boiling dichloromethane. (Runs 1 and 3) But no reaction took place with 1-trimethylsilyl-1-phenylthioethane under the same conditions. (Run 2) In order to gain an insight into a mechanism of the isomerization, the following reactions were carried out. A mixture of (**Z**) and (**E**)-1-phenylthio-1-trimethylsilylheptene (**12** and **13**) (ca. 1 : 1) was prepared by the known method,<sup>5</sup> and heated in boiling xylene with

Table Conversion of 1-Methoxy-1-phenylthio-1-trialkylsilylalkanes to (Z)-1-Phenylthio-1-trialkylsilylalkenes under Oxygen Atmosphere

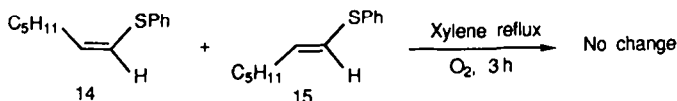


Run	R	R'	Solvents	Temp.	Time hr	Et <sub>3</sub> B equiv	Yield %	Z/E
1	H	t-Bu	CH <sub>2</sub> Cl <sub>2</sub>	Reflux	0.5	none	85	
2	H	Me	"	"	10	"	0	
3	H	Ph	"	"	"	"	82	
4	H	Me	Toluene	"	0.5	"	90	
5	C <sub>5</sub> H <sub>11</sub>	t-Bu	"	"	6	"	74	96/4
6	"	"	Benzene	R. T.	24	1.2	62	98/2
7	"	"	THF	Reflux	3	0.5	72	97/3
8	"	Me	Toluene	"	6	none	84	94/6
9	"	"	Benzene	R. T.	24	1.2	38	97/3
10	"	"	THF	Reflux	5	0.5	77	95/5
11	"	"	"	R. T.	22	"	80	95/5
12	"	Ph	Xylene	"	24	1.2	49	96/4
13	"	"	THF	Reflux	3	0.5	75	94/6
14	Ph	Me	"	"	"	"	72	92/8
15	t-BuSiO(CH <sub>2</sub> ) <sub>3</sub> - Ph <sub>2</sub>	Me	"	"	"	"	89	94/6
16	t-BuSiO(CH <sub>2</sub> ) <sub>10</sub> - Me <sub>2</sub>	"	"	"	"	"	78	95/5
17		"	"	"	"	"	95	95/5
18	t-BuSiO(CH <sub>2</sub> ) <sub>10</sub> - Me <sub>2</sub>	t-Bu	"	"	"	"	89	97/3
19		"	"	"	"	"	84	92/8
20	 -O(CH <sub>2</sub> ) <sub>3</sub> -	Me	"	"	"	"	84	93/7

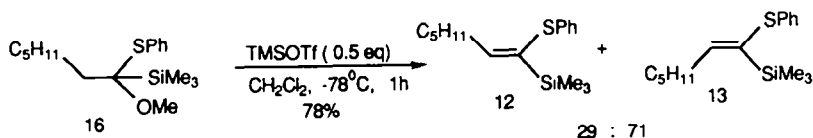
hydroquinone, and we observed no change of the **Z/E** ratio at all. On the other hand, the ratio changed to 93:7, when the mixture was heated in xylene under oxygen atmosphere in the absence of hydroquinone.



As mentioned above, the elimination was facilitated with oxygen and accelerated by the addition of triethylborane. It is known that an ethyl radical is generated from triethylborane and oxygen.<sup>9</sup> In addition, the reaction was completely suppressed by the addition of hydroquinone. These results show that both the elimination and isomerization processes should involve radical intermediates. The intermediate radical can be stabilized by the presence of sulfur and silicon atoms. For the isomerization, the presence of both sulfur and silicon functionalities is essential. In fact, no isomerization was observed at all when a mixture of the vinyl sulfides **14** and **15** was heated in refluxing xylene even under oxygen atmosphere.



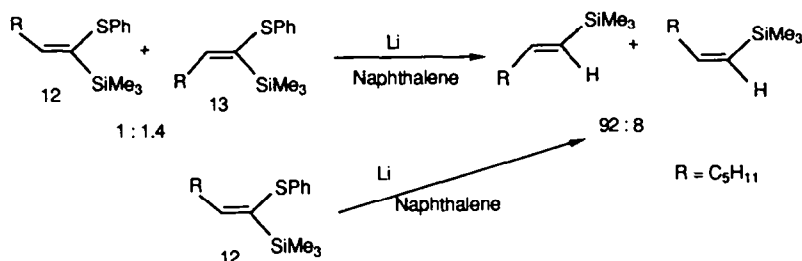
With respect to the elimination step, however, a cationic mechanism is also operating depending on the reaction conditions. Although it is difficult to explain, we observed that no elimination took place by the addition of triethylamine in boiling xylene even under oxygen atmosphere. In addition, a mixture of the **Z** and **E** isomers **12** and **13** was obtained when **16** was treated with trimethylsilyl trifluoromethanesulfonate (TMSOTf, 0.5 equiv) at -78°C in dichloromethane in one hour. In this acid-promoted elimination, the ratio of **Z/E** observed was 29/71. Namely the **E** isomer was a major product. Thus the isomerization of the **E** to **Z** is not possible under these conditions.



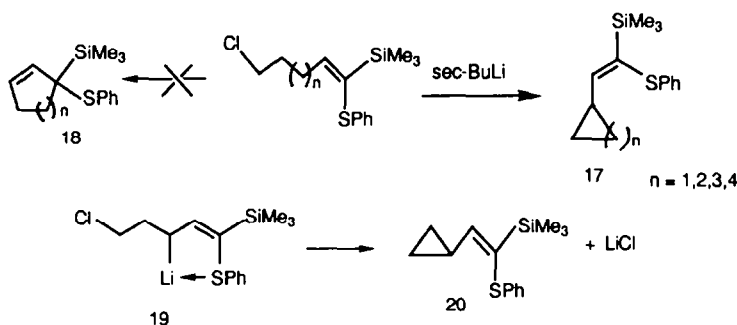
### Synthetic Applications.

Since we have found the facile synthetic method for **3**, we studied their synthetic applications. As one application, we carried out the synthesis of vinylsilanes from **3** by removal of the phenylthio group with lithium.

Elimination of the phenylthio group from a mixture of the (**Z**) and (**E**)-1-phenylthio-1-trimethylsilylheptenes (**12** and **13**) proceeded smoothly with lithium naphthalene to give 1-trimethylsilylheptene. The **E**/**Z** ratio of the vinylsilane obtained by this way was 92:8. Also we confirmed that the pure **12** was converted to the **E** and **Z** vinylsilanes in the same ratio. Therefore, this is a convenient synthetic method for **E**-vinylsilanes.



As another synthetic application, we have prepared several derivatives of **3**, which have a chlorine at the end of the alkyl chain and tried their cyclization reactions. These compounds were treated with *sec*-butyllithium in THF containing HMPA at -82°C and the mixture was warmed to -40°C. Smooth cyclization took place to give the three- to six-membered rings **17** bearing 2-phenylthio-2-trimethylsilylvinyl group. These cyclizations to give **17** are particularly interesting. Kyler and Watt reported that their compound **7** reacts with alkyl lithium to generate carbanions at two sites, namely α and γ carbons. They confirmed that the reaction of aldehydes took place at γ carbon, and alkylation at α carbon.<sup>4</sup> On the other hand, we found that the intramolecular alkylation took place at the γ carbon exclusively, contrary to their results. No cyclic olefins **18**, formed by the reaction at α, was detected. In addition, only one isomer was obtained. This is reasonable because the cyclization should proceed via the intermediate **19** to give the **Z** isomer **20** exclusively.



## Experimental Part.

**General.** NMR (400 MHz) spectra were taken in CDCl<sub>3</sub> as a solvent. Chemical shifts are given in  $\delta$  units relative to tetramethylsilane as an internal standard. HRMS spectra were taken with JEOL-JMS-DX 303 HF.

### 1. Elimination Reaction of 3 (Run 20).

The 5-tetrahydropyranyloxy-pentyl derivative (382 mg, 1 mmol) was dissolved in THF in a round-bottomed flask equipped with a reflux condenser, and triethylborane (0.5 ml, 0.5 mmol) was added. A rubber balloon filled with oxygen was placed on the top of the reflux condenser. The mixture was refluxed for 3 h. To the reaction mixture, hexane was added and the solution was washed with water. The organic layer was dried (MgSO<sub>4</sub>) and evaporated to give a crude oily product (340 mg), which was purified by silica gel column chromatography to give 1-phenylthio-1-trimethylsilyl-5-(2-tetrahydropyranyloxy)-1-pentene (295 mg, 84%) as an oil.

### 2. Assignment of the E and Z Structures.

This was done based on the NMR data given by Seebach<sup>5</sup>. In addition, the **E** and **Z** structures were confirmed by the following method. A mixture of the **Z** and **E** isomers was prepared by the method of Grobel and Seebach, and the pure **Z** and **E** forms were isolated by column chromatography. They were oxidized with m-chloroperbenzoic acid to the corresponding sulfoxides. Their NMR spectra were measured in CCl<sub>4</sub>. Then they were remeasured three times after the addition of a shift reagent (Eu(fod)<sub>3</sub>) at different concentrations. The **E** isomer showed no change in the spectrum, but the **Z** isomer showed large shift of the olefinic proton to a low field. Thus the **Z/E** ratios of all 1-phenylthio-1-trialkylsilylalkenes obtained in this experiment were determined by GLC using a capillary column ULBON HR-101 (0.2 mm X 25 m). <sup>1</sup>H NMR and high resolution mass spectra (HRMS) of all 1-phenylthio-1-trialkylsilylalkenes are shown below.

1-t-Butyldimethylsilyl-1-phenylthioethylene (run 1).

NMR,  $\delta$  0.18 (s, 6H, SiCH<sub>3</sub>), 0.98 (s, 9H, SiCMe<sub>3</sub>), 5.17 (s, 1H, CH=C), 5.41 (s, 1H, C=CH), 7.31-7.46 (m, 5H, aromatic protons),  
HRMS for C<sub>14</sub>H<sub>22</sub>SSi, calcd 250.1212, found 250.1223.

1-Dimethylphenylsilyl-1-phenylthioethylene (run 3).

NMR,  $\delta$  0.47 (s, 6H, SiCH<sub>3</sub>), 5.31 (s, 1H, CH=C), 5.50 (s, 1H, C=CH), 7.30-7.60 (m, 10H, aromatic protons).  
HRMS for C<sub>16</sub>H<sub>18</sub>SSi, calcd 270.0898, found 270.0887.

1-Phenylthio-1-trimethylsilylethylene (run 4).

NMR,  $\delta$  0.19 (s, 9H, SiCH<sub>3</sub>), 5.24 (s, 1H, CH=C), 5.49 (s, 1H, C=CH), 7.30-7.45 (m, 5H, aromatic protons).  
HRMS for C<sub>11</sub>H<sub>16</sub>SSi, calcd 208.0742, found 208.0705.

1-*t*-Butyldimethylsilyl-1-phenylthioheptene(run 5).

NMR,  $\delta$  0.03(s, 6H, SiCH<sub>3</sub>), 0.88(t, 3H, J=7.0 Hz, CH<sub>3</sub>), 0.92(s, 9H, SiCMe<sub>3</sub>), 1.27-1.45(m, 6H, CH<sub>2</sub>), 2.40(dt, 2H, J=7.33, 6.60 Hz, CH<sub>2</sub>C=C), 6.68(t, 1H, J=6.60 Hz, CH=C), 7.06-7.26(m, 5H, aromatic protons).

HRMS for C<sub>19</sub>H<sub>32</sub>SSi, calcd 320.1994, found 320.2023.

## 1-Phenylthio-1-trimethylsilylheptene(run 8).

NMR,  $\delta$  0.03(s, 9H, SiCH<sub>3</sub>), 0.87(t, 3H, J=7.3 Hz, CH<sub>3</sub>), 1.28-1.43(m, 6H, CH<sub>2</sub>), 2.38(dt, 2H, J=8.0, 6.96 Hz, CH<sub>2</sub>C=C), 6.59(t, 1H, J=6.96 Hz, CH=C), 7.06-7.23(m, 5H, aromatic protons).

HRMS for C<sub>16</sub>H<sub>26</sub>SSi, calcd 278.1525, found 278.1436.

## 1-Dimethylphenylsilyl-1-phenylthioheptene(run 12).

NMR,  $\delta$  0.28(s, 6H, SiCH<sub>3</sub>), 0.85(t, 3H, J=7.0 Hz, CH<sub>3</sub>), 1.23-1.39(m, 6H, CH<sub>2</sub>), 2.37(dt, 2H, J=7.70, 6.96 Hz, CH<sub>2</sub>C=C), 6.56(t, J=6.96 Hz, CH=C), 7.03-7.50(m, 10H, aromatic protons).

HRMS for C<sub>21</sub>H<sub>28</sub>SSi, calcd 340.1681, found 340.1683.

## 1-Phenylthio-1-trimethylsilyl-2-phenylethylene(run 14).

NMR,  $\delta$  0.09(s, 9H, SiCH<sub>3</sub>), 7.05-7.66(m, 11H, CH=C, aromatic protons).

HRMS for C<sub>17</sub>H<sub>20</sub>OSSi, calcd 284.1055, found 284.1089.

1-Phenylthio-1-trimethylsilyl-5-(*t*-butyldiphenylsiloxy)pentene(run 15).

NMR,  $\delta$  0.02(s, 9H, SiCH<sub>3</sub>), 1.03(s, 9H, SiCMe<sub>3</sub>), 1.68(m, 2H, CH<sub>2</sub>), 2.48(dt, J=7.69, 6.60 Hz), 3.64(t, 2H, J=6.59 Hz, OCH<sub>2</sub>), 6.57(t, 1H, J=6.60 Hz, CH=C), 7.05-7.65(m, 15H, aromatic protons).

HRMS for C<sub>30</sub>H<sub>40</sub>OSSi<sub>2</sub>, calcd 504.2338, found 504.2180.

1-Phenylthio-1-trimethylsilyl-12-(*t*-butyldimethylsilyloxy)dodecene(run 16).

NMR  $\delta$  0.03(s, 9H, SiCH<sub>3</sub>), 0.05(s, 6H, SiCH<sub>3</sub>), 0.90(s, 9H, SiCMe<sub>3</sub>), 1.20-1.55(m, 16H, CH<sub>2</sub>), 2.39(dt, 2H, J=7.60, 7.0 Hz, CH<sub>2</sub>C=C), 3.60(t, 2H, J=6.96 Hz, OCH<sub>2</sub>), 6.59(t, 1H, J=6.90 Hz, CH=C), 7.05-7.36(m, 5H, phenyl).

HRMS for C<sub>27</sub>H<sub>50</sub>OSSi<sub>2</sub>, calcd 478.3121, found 478.3058.

## 1-Phenylthio-1-trimethylsilyl-3-(1,3-dioxolan-2-yl)propene(run 17).

NMR,  $\delta$  0.02(s, 9H, SiCH<sub>3</sub>), 2.76(dt, 2H, J=6.59, 4.76 Hz, CH<sub>2</sub>C=C), 3.79-3.93(m, 4H, OCH<sub>2</sub>), 4.93(t, 1H, J=4.76 Hz, OCH), 6.69(t, 1H, J=6.59 Hz, CH=C), 7.05-7.30(m, 5H, aromatic protons).

HRMS for C<sub>15</sub>H<sub>22</sub>O<sub>2</sub>SSi, calcd 294.1110, found 294.1054.

1-*t*-Butyldimethylsilyl-1-phenylthio-12-(*t*-butyldimethylsiloxy)dodecene(run 18).

NMR,  $\delta$  0.02(s, 6H, SiCH<sub>3</sub>), 0.06(s, 6H, SiCH<sub>3</sub>), 0.91(s, 9H, SiCMe<sub>3</sub>), 0.92(s, 9H, SiCMe<sub>3</sub>), 1.05-1.55(m, 16H, CH<sub>2</sub>), 2.38(dt, 2H, J=7.32, 7.0 Hz, CH<sub>2</sub>C=C), 3.60(t, 2H, J=6.64 Hz, OCH<sub>2</sub>), 6.67(t, 1H, J=7.0 Hz, CH=C), 7.05-7.38(m, 5H, aromatic protons).

HRMS for C<sub>30</sub>H<sub>56</sub>OSSi<sub>2</sub>, calcd 520.3591, found 520.3554.

1-*t*-Butyldimethylsilyl-1-phenylthio-3-(1,3-dioxolan-2-yl)propene(run 19).



NMR,  $\delta$  0.02(s, 6H, SiMe), 0.90(s, 9H, SiCMe<sub>3</sub>), 2.79(dd, 2H, J=6.59, 4.40 Hz, CH<sub>2</sub>C=C), 3.79-3.97(m, 4H, OCH<sub>2</sub>), 4.96(t, 1H, J=4.40 Hz, OCH), 6.71(t, 1H, J=6.59 Hz, CH=C), 7.05-7.35(m, 5H, aromatic protons).

HRMS for C<sub>18</sub>H<sub>28</sub>O<sub>2</sub>SSi, calcd 336.1579, found 336.1563.

1-Phenylthio-1-trimethylsilyl-5-(2-tetrahydropyranyloxy)pentene (run 20).

NMR,  $\delta$  0.03(s, 9H, SiCH<sub>3</sub>), 1.45-1.85(m, 8H, CH<sub>2</sub>), 2.42-2.55(m, 2H, CH<sub>2</sub>C=C), 3.30-3.85(m, 4H, OCH<sub>2</sub>), 4.55(t, 1H, J=2.93 Hz, OCHO), 6.61(t, 1H, J=6.96 Hz, CH=C), 7.05-7.30(m, 5H, aromatic protons).

HRMS for C<sub>14</sub>H<sub>22</sub>OSSi(M<sup>+</sup>-84(dihydropyran)), calcd 266.1161, found 266.1116.

### 3. Preparation of the Vinylsilanes.

Li(21 mg, 3 mmol) and naphthalene(102 mg, 0.8 mmol) were mixed under argon atmosphere in THF(2 ml) and the mixture was stirred at 0°C for 2 h. Then 1-phenylthio-1-trimethylsilyl-12-(t-butyldimethylsiloxy)dodecene(100 mg, 0.21 mmol) in THF(1 ml) was added, and the mixture was stirred for 1 h. Ether(20 ml) and water(3 drops) were added and the mixture was washed with water. The organic layer was dried(MgSO<sub>4</sub>) and concentrated under vacuum to give a crude semi-solid. The crude product was purified by column chromatography to remove naphthalene and dihydronaphthalene, and 1-trimethylsilyl-12-(t-butyldimethylsiloxy)dodecene was obtained as an oil (70 mg, 90%). Similarly results were obtained with other compounds. The NMR and HRMS spectra of the vinylsilanes obtained are shown below.

1-Trimethylsilyl-12-(t-butyldimethylsiloxy)dodecene.

NMR,  $\delta$  0.03(s, 9H, SiCH<sub>3</sub>), 0.04(s, 6H, SiCH<sub>3</sub>), 0.89(s, 9H, SiCMe<sub>3</sub>), 1.20-1.52(m, 16H, CH<sub>2</sub>), 2.08(dt, 2H, J=7.33, 6.96 Hz, CH<sub>2</sub>C=C), 3.60(t, 2H, J=6.59 Hz, OCH<sub>2</sub>), 5.61(d, 1H, J=18.3 Hz, CH=C), 6.02(dt, 1H, J=18.3, 6.23 Hz, C=CH).

HRMS for C<sub>21</sub>H<sub>46</sub>OSi<sub>2</sub>, calcd 370.3087, found 370.3182.

1-t-Butyldimethylsilyl-12-(t-butyldimethylsiloxy)dodecene.

NMR,  $\delta$  0(s, 6H, SiCH<sub>3</sub>), 0.05(s, 6H, SiCH<sub>3</sub>), 0.86(s, 9H, SiCMe<sub>3</sub>), 0.90(s, 9H, SiCMe<sub>3</sub>), 1.27-1.53(m, 16H, CH<sub>2</sub>), 2.11(dt, 2H, J=6.59, 6.23 Hz, CH<sub>2</sub>C=C), 3.60(t, 2H, J=6.60 Hz, OCH<sub>2</sub>), 5.60(d, 1H, J=18.7 Hz, CH=C), 6.03(dt, 1H, J=18.7, 6.23 Hz, C=CH).

HRMS for C<sub>20</sub>H<sub>43</sub>OSi<sub>2</sub>(M<sup>+</sup>-57(t-butyl)), calcd 355.2852, found 355.2867

1-Trimethylsilyl-5-(2-tetrahydropyranyloxy)pentene.

NMR,  $\delta$  0.03(s, 9H, SiCH<sub>3</sub>), 1.45-1.90(m, 8H, CH<sub>2</sub>), 2.16-2.22(m, 2H, CH<sub>2</sub>C=C), 3.30-3.92(m, 4H, OCH<sub>2</sub>), 4.57-4.58(m, 1H, OCHO), 5.64(d, 1H, J=18.3 Hz, CH=C), 6.03(dt, 1H, J=18.3, 6.23 Hz, C=CH).

### 4. Cyclization Reactions.

To a THF(5 ml) solution of 1-phenylthio-1-trimethyl-5-chloropentene(142 mg, 0.5 mmol) was added sec-BuLi(0.6 mmol) dropwise at -82°C, and the mixture

was stirred at this temperature for 30 min. Then HMPA(0.6 mmol) was added. The mixture was slowly warmed to  $-40^{\circ}\text{C}$ , and stirred at this temperature for 1 h. Then the reaction was quenched by the addition of water and the mixture was extracted with hexane. The hexane solution was dried( $\text{MgSO}_4$ ) and evaporated. The residue was purified by silica gel column chromatography to give 1-phenylthio-1-trimethylsilyl-2-cyclopropylethylene, 102 mg(82%). Under similar conditions, 2-phenylthio-2-trimethylsilylvinyl-substituted cyclobutane(53%), cyclopentane(65%), and cyclohexane(54%) were obtained. Their NMR and HRMS spectra are shown below.

1-Phenylthio-1-trimethylsilyl-2-cyclopropylethylene.

NMR  $\delta$  0.03(s, 9H,  $\text{SiCH}_3$ ), 0.40-1.00(m, 4H,  $\text{CH}_2$ ), 1.95-2.50(m, 1H, CH), 5.85(d, 1H,  $J=9.2$  Hz,  $\text{CH}=\text{C}$ ), 7.00-7.40(m, 5H, aromatic protons).  
HRMS for  $\text{C}_{14}\text{H}_{20}\text{SSi}$ , calcd 248.1055, found 248.1054.

1-Phenylthio-1-trimethylsilyl-2-cyclobutylethylene.

NMR,  $\delta$  0.02(s, 9H,  $\text{SiCH}_3$ ), 1.52-2.25(m, 6H,  $\text{CH}_2$ ), 3.40-3.90(m, 1H, CH), 6.50(d, 1H,  $J=8.2$  Hz,  $\text{CH}=\text{C}$ ), 7.00-7.30(m, 5H, aromatic protons).  
HRMS for  $\text{C}_{15}\text{H}_{22}\text{SSi}$ , calcd 262.1212, found 262.1183.

1-Phenylthio-1-trimethylsilyl-2-cyclopentylethylene.

NMR  $\delta$  0.03(s, 9H,  $\text{SiCH}_3$ ), 1.10-2.10(m, 8H,  $\text{CH}_2$ ), 2.95-3.60(m, 1H, CH), 6.45(d, 1H,  $J=9.0$  Hz,  $\text{CH}=\text{C}$ ), 7.00-7.40(m, 5H, aromatic protons).  
HRMS for  $\text{C}_{16}\text{H}_{24}\text{SSi}$ , calcd 276.1368, found 276.1367.

1-Phenylthio-1-trimethylsilyl-2-cyclohexylethylene.

NMR,  $\delta$  0.02(s, 9H,  $\text{SiCH}_3$ ), 1.00-1.90(m, 10H,  $\text{CH}_2$ ), 2.60-3.20(m, 1H, CH), 6.37(d, 1H,  $J=9.0$  Hz,  $\text{CH}=\text{C}$ ), 7.00-7.35(m, 5H, aromatic protons).  
HRMS for  $\text{C}_{17}\text{H}_{26}\text{SSi}$ , calcd 290.1524, found 290.1522.

## References and Notes

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