NEW METHOD FOR GENERATION OF THIOCARBONYL YLIDES FROM BIS(TRIMETHYLSILYLMETHYL) SULFOXIDES AND THEIR APPLICATION TO CYCLOADDITIONS

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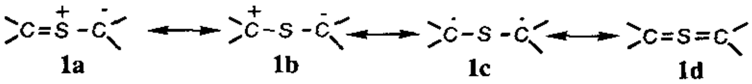
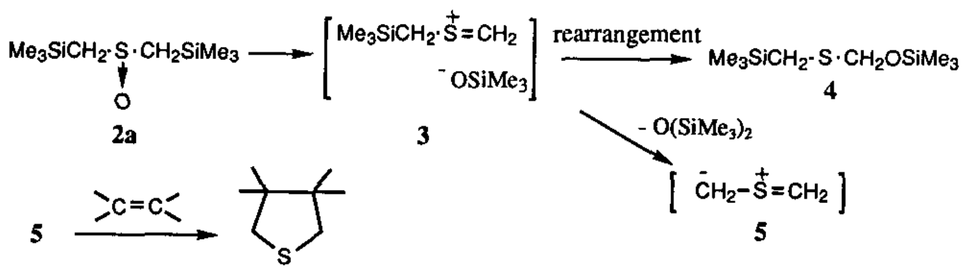
Abstract— Thiocarbonyl ylides were generated by heating of bis(trimethylsilylmethyl) sulfoxides. Cycloadditions of the ylides in the presence of dipolarophiles proceeded smoothly to give di- or tetrahydrothiophenes.

A thiocarbonyl ylide is conveniently represented by the structure (**1a**), which includes 1,3-dipolar structure (**1b**) as a resonance form, and it is a useful reactive intermediate for synthesis of heterocycles containing a sulfur atom.[1]



Representative method for generation of thiocarbonyl ylides was reported by Kellogg[2] and Huisgen.[3] They prepared the ylides by thermal decomposition of thiadiazolidines which were prepared from thioketones and diazoalkanes. Recently we reported a facile generation of silylthioaldehyde *S*-methylide by thermal desilylbromide of bromo(trimethylsilyl)methyl trimethylsilylmethyl sulfide and its derivatives.[4] After further investigation in order to overcome some limitations for this method, we have found a new method for generation of thiocarbonyl ylide from bis(trimethylsilylmethyl) sulfoxides and their 1,3-dipolar cycloadditions leading to di- or tetrahydrothiophenes. In this paper, details of these new methods are described.[5]

Our strategy for the generation of thiocarbonyl ylide involves the release of disiloxane from bis(trimethylsilylmethyl) sufoxide (**2a**) through a pathway related to the sila-Pummerer rearrangement (Scheme 1).[6]



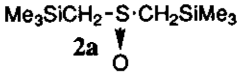
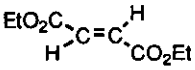
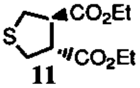
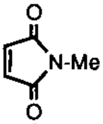
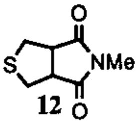
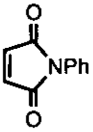
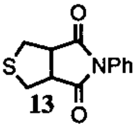
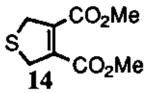
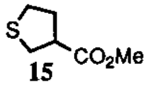
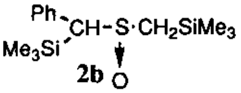
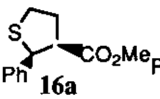
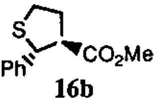
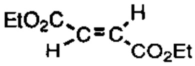
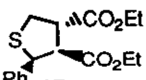
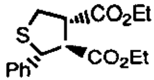
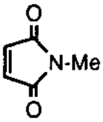
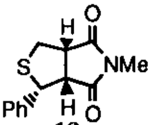
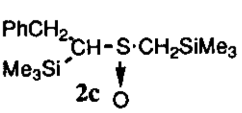
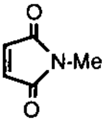
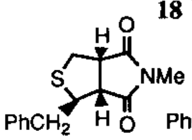
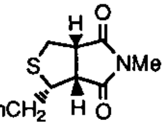
Scheme 1

The *S*-oxide (**2a**) was prepared by oxidation of readily available bis(trimethylsilylmethyl) sulfide with *m*-chloroperbenzoic acid (MCPBA). Treatment of **2a** with a dipolarophile at 100°C in HMPA gave the 1,3-dipolar cycloadduct (**6**). Formation of the rearrangement product (**4**) was observed by heating **2** without solvent.

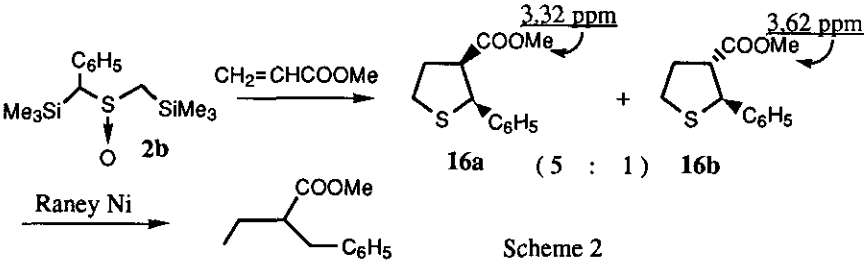
We examined the cycloaddition reactions of **2a** with several conjugated dipolarophiles under the conditions described above and the results are shown in Table 1. Entries 1-5 show that the reactions proceeded smoothly to give the corresponding cycloadducts in good yields. The structures of the products were elucidated by their analytical and spectral data (Tables 3 and 4). It is noteworthy that formation and cycloaddition of thioformaldehyde *S*-methylide (**5**), which is a basic thiocarbonyl ylide without any substituent, were realized for the first time by this convenient method.

Aromatic and aliphatic thioaldehyde *S*-methylides were also generated from the corresponding sulfoxides. The results are summarized in Entries 6-9 of Table 1. In these cases, the regio- and stereoselectivities of these 1,3-dipolar cycloaddition have become of interest. In some cases a mixture of two stereoisomers was obtained (Entries 6, 7 and 8). However, the possible regioisomer in Entry 6 and the steroisomer in Entry 8 were not detected. Structure elucidation of these isomers was as follows. The product in Entry 6 was shown to be a 5 : 1 mixture of 2,3-*cis* (**16a**) and 2,3-*trans* (**16b**) isomer. Desulfurization of the two isomers with Raney Ni afforded the same product, methyl 2-benzylbutylate, while methyl 4-phenyl-2-methylbutylate derived from a possible regioisomer was not observed (Scheme 2). The singlet of ester methyl protons in ^{1}H nmr spectrum of **16a** appeared at 3.32 ppm and that of **16b** did at 3.62 ppm, which suggested to be 2,3-*cis* and 2,3-*trans* isomer, respectively.[7]

Table 1. 1,3-Dipolar Cycloaddition of Thioaldehyde *S*-Methylides

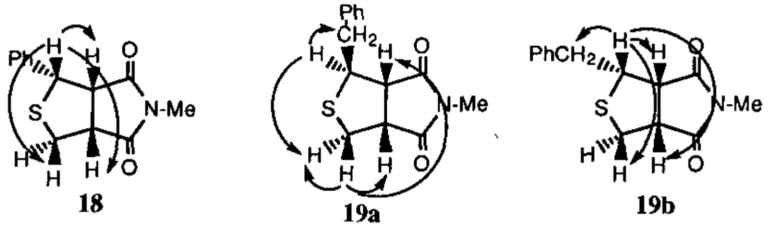
Entry	Sulfoxide	Dipolarophile	Product	Yield(%)[a]
1	 $\mathrm{Me_3SiCH_2\text{-}\underset{\downarrow\atop O}{S}\cdot CH_2SiMe_3}$ **2a**		 **11**	80
2	**2a**		 **12**	81
3	**2a**		 **13**	70
4	**2a**	$MeO_2C-C\equiv C-CO_2Me$	 **14**	61
5	**2a**	$H_2C{=}CHCO_2Me$	 **15**	55
6	 $\mathrm{Ph(Me_3Si)CH\text{-}\underset{\downarrow\atop O}{S}\cdot CH_2SiMe_3}$ **2b**	$H_2C{=}CHCO_2Me$	 **16a**  **16b**	45[b]
7	**2b**		 **17a**  **17b**	50[b]
8	**2b**		 **18**	65[c]
9	 $\mathrm{PhCH_2(Me_3Si)CH\text{-}\underset{\downarrow\atop O}{S}\cdot CH_2SiMe_3}$ **2c**		 **19a**  **19b**	65[b]

a) Isolated yields. b) **16a** : **16b** = 5 : 1, **17a** : **17b** = 1 : 1, **19a** : **19b** = 5 : 1 (determined by gas chromatography). c) The 2,3-*trans* isomer was not detected.



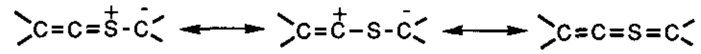
Scheme 2

Gas chromatogram of the reaction product in Entry 7 showed a 1:1 mixture of **17a** and **17b**, which was shown also by the nmr spectrum. The cycloadducts (**18**) and (**19b**) were determined as 2,3-*cis* isomer and **19a** was 2,3-*trans* isomer on the basis of the result of difference NOE experiments (500 MHz) shown in Scheme 3. It seems somewhat strange that the reaction of **2b** with *N*-methylmaleimide (Entry 8) gave only 2,3-*cis* isomer (**18**) although it has a sterically hindered phenyl group. Such stereoselectivity may be explained by secondary orbital interaction between the dipolarophile and the phenyl group of the dipole in frontier molecular orbital theory (FMO theory).[8]



Scheme 3. NOEs in the difference NOE spectra

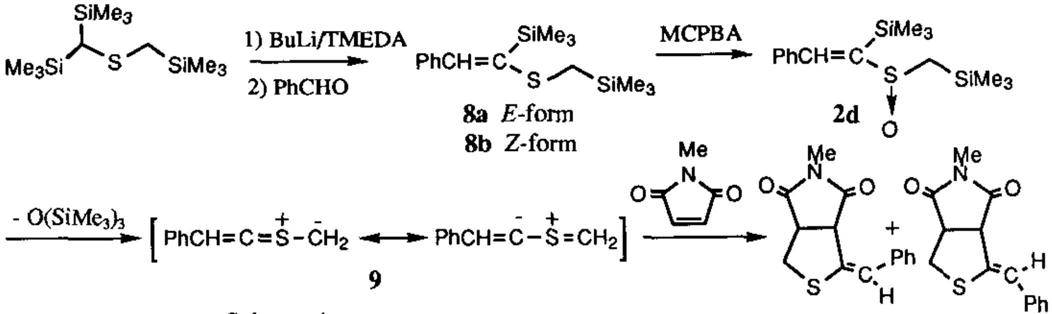
This finding prompted us to research a new class of thiocarbonyl ylide, thioketene *S*-methylide, the resonance structures of which include a 1,3-dipole species (**7b**) and an interesting heterocumulene skeleton (**7c**) containing a tetravalent sulfur.



$$>C{=}C{=}\overset{+}{S}{-}\overset{-}{C}< \;\longleftrightarrow\; >C{=}\overset{+}{C}{-}S{-}\overset{-}{C}< \;\longleftrightarrow\; >C{=}C{=}S{=}C<$$

7a **7b** **7c**

Treatment of bis(trimethylsilyl)methyl (trimethylsilyl)methyl sulfide with butyllithium and benzaldehyde gave α-(trimethylsilyl)stylyl (trimethylsilyl)methyl sulfide (**8**) (Scheme 4). Geometrical isomers (**8a** and **8b**) were separable by careful columun chromatography. Sulfoxide (**2d**) was prepared by oxidation of **8a** and **8b** with MCPBA, respectively. The reaction of **2d** derived from **8a** with *N*-methylmaleimide in HMPA at 100°C afforded a 1 : 1 mixture of two geometrical isomers (**20a** and **20b**). The sulfoxide (**2d**) derived from **8b** gave also the same mixture of **20a** and **20b** in the same ratio.



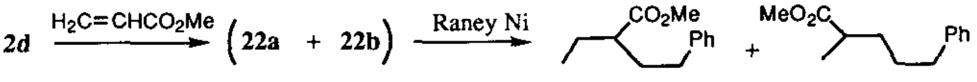
Scheme 4

20a (1 : 1) **20b**

Structures of the products were determined on the basis of analytical and spectral data (Tables 3 and 4). ^{13}C Nmr spectra of **20a** and **20b** showed the characteristic signals in support of tetrahydrothiophene ring system: **20a**; 34.3 (t), 47.8(d), 50.1(d), 135.8(s), **20b**; 35.0(t), 46.6(d), 55.2(d), 136.4(s). In ^{1}H nmr spectrum of **20a**, the methine proton at the 3-position resonates at the lower field (4.35 ppm) than that of **20b** (4.06 ppm) by the shielding effect of near benzene ring, and a proton of the benzene ring resonates at the lower field than the others by the deshielding effect of near carbonyl group, which was not observed in the spectrum of **20b**.

These facts suggested that both reactions proceed *via* the same intermediate, phenylthioketene *S*-methylide (**9**). Therefore, we carried out the 1,3-dipolar cycloaddition of thioketene *S*-methylides with some dipolarophiles without attention to the presence of isomers in the starting materials, and the results are summarized in Table 2.

In addition that these reactions produced a mixture of *E* and *Z*-isomer (entries 10-14), the cyloaddition with an unsymmetrical dipolarophile such as methyl aclylate gave a mixture of regioisomers (**22a** and **22b**) (Entry 12). For the confirmation of the presence of regioisomers, the mixture of **22a** and **22b** was reduced with Raney Ni to yield methyl 2-ethyl-4-phenylbutylate (**10a**) and its isomer (**10b**) (Scheme 5).

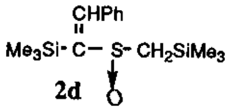
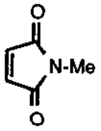
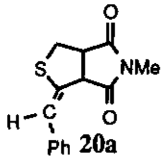
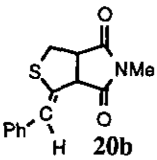
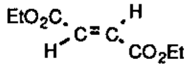
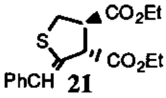
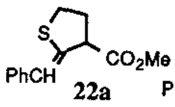
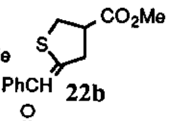
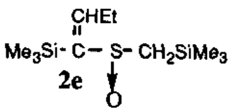
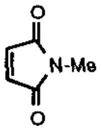
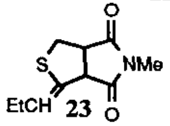
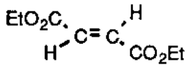
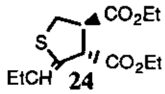
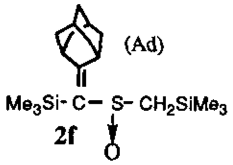
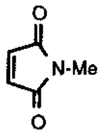
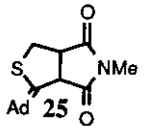
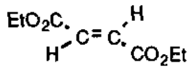
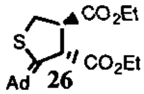


10a **10b**

Scheme 5

New method for generation of thiocarbonyl ylides by thermolysis of bis(silylmethyl) sulfoxides has some

Table 2. 1,3-Dipolar Cycloaddition of Thioketene *S*-Methylide

Entry	Sulfoxide	Dipolarophile	Product	Yield(%)[a]
10	 $Me_3Si-C(=CHPh)-S(\rightarrow O)-CH_2SiMe_3$ **2d**		 **20a**  **20b**	78[b]
11	**2d**		 **21**	60
12	**2d**	$H_2C=CHCO_2Me$	 **22a**  **22b**	45[b]
13	 $Me_3Si-C(=CHEt)-S(\rightarrow O)-CH_2SiMe_3$ **2e**		 **23**	36
14	**2e**		 **24**	50
15	 $Me_3Si-C(=Ad)-S(\rightarrow O)-CH_2SiMe_3$ **2f**		 **25**	65
16	**2f**		 **26**	50

a) Yields in Entries 10-14 are those of a mixture of *E* and *Z*-isomer.
b) **20a** : **20b** = 1 : 1, **22a** : **22b** = 1 : 2 (determined by gas chromatography).

charcteristics comparing the other methods: 1) Starting materials are easily available. 2) Various thioaldehyde *S*-methylides were produced as well as thioformaldehyde *S*-methylide under relatively mild conditions. 3) Generation of thioketene *S*-methylides was realized. Because thioketenes are well known to be very unstable,[5] it seems difficult that such ylides are prepared by the other methods using thioketenes as a starting materials.

The present method employing organosilicon compounds may promise a new development in the chemistry of thiocarbonyl ylides.

Table 3. Analytical Data for Di- or Tetrahydrothiophenes

Compound No.	mp °C or bp °C	Ir max[a)]	Formula	Analysis (%) Calcd. (Found) C	H	N
11	150-151	1740	$C_{10}H_{16}O_4S$	51.70	6.94	
	(15)			(51.42	6.94)	
12	90-91	1775	$C_7H_9NO_2S$	49.11	5.30	8.11
	(EtOH)	1690		(48.96	5.18	8.16)
13	152-153	1780	$C_{12}H_{11}NO_2S$	61.78	4.75	6.00
	(EtOH)	1715		(61.57	4.71	5.91)
14	95-97	1725	$C_8H_{10}O_4S$	47.52	4.94	
	(0.5)			(47.17	4.94)	
15	90-91	1740	$C_7H_{12}O_2S$	52.47	7.55	
	(5)			(52.03	7.49)	
16a	oil[c)]	1725	$C_{12}H_{14}O_2S$	65.13	6.38	
				(65.10	6.21)	
17	148-150[b)]	1745	$C_{16}H_{20}O_4S$	62.32	6.54	
	(6)			(61.98	6.54)	
18	166-167	1775	$C_{13}H_{13}NO_2S$	63.14	5.30	5.66
	(EtOH)			(63.05	5.31	5.60)
19a	84-85	1775	$C_{14}H_{15}NO_2S$	64.34	5.79	5.36
	(EtOH)	1705		(64.18	5.84	5.30)
19b	72-73	1775	$C_{14}H_{15}NO_2S$	64.34	5.31	5.60
	(EtOH)	1705		(64.41	5.80	5.42)
20a	126-127	1775	$C_{14}H_{13}NO_2S$	64.84	5.05	5.40
	(EtOH)	1770		(64.54	5.26	5.17)
20b	118-120	1775	$C_{14}H_{13}NO_2S$	64.84	5.05	5.40
	(EtOH)	1770		(64.59	5.08	5.29)
21	oil[b),c)]	1730	$C_{17}H_{20}O_4S$	63.73	6.29	
				(63.48	6.26)	
22	oil[b),c)]	1740	$C_{13}H_{14}O_2S$	66.64	6.02	
				(67.02	6.17)	
23	solid[b),c)]	1779	$C_{10}H_{13}NO_2S$	56.88	6.16	
		1700		(56.50	6.24)	
24	oil[b),c)]	1735	$C_{11}H_{20}O_4S$	57.33	7.40	
				(57.16	7.40)	
25	158-159	1775	$C_{17}H_{21}NO_2S$	67.29	6.98	4.62
	(EtOH)	1700		(67.35	6.97	4.69)
26	103-104	1740	$C_{20}H_{28}O_4S$	65.90	7.74	
	(EtOH)			(65.96	7.90)	

a) KBr or neat. b) A mixtre of 2,3-*cis* and *trans* isomer or *E*- and *Z*-isomer. c) Purified by ptlc.

Table 4. Nmr Spectral Data[a)] for Di- or Tetrahydrothiophenes

Comp. No.	^{1}H Nmr δ ($CDCl_3$)	^{13}C Nmr δ ($CDCl_3$)
11	1.26 (6H, t, J=7.1 Hz, 2xCH_3), 3.07-3.22 (4H, m, CH_2SCH_2), 3.33-3.56(2H, m, CHCH), 4.17 (4H, q, J=7.1 Hz, 2xOCH_2)	14.9, 33.3, 51.1, 61.2, 171.8
12	2.78-3.54 (6H, m, $CH_2CHCHCH_2$), 3.00 (3H, S, NCH_3)	25.3, 36.0, 48.6, 177.9
13	2.88-3.72 (6H, m, $CHCH_2SCH_2CH$), 7.15-7.57 (5H, m, C_6H_5)	36.5, 48.5, 126.4, 128.7, 129.1 132.5, 177.6
14	3.80 (6H, s, 2xOCH_3), 4.05 (4H, s, CH_2SCH_2)	39.4, 52.4, 138.5, 164.5
15	1.27 (3H, t, J=7.1 Hz, CH_3), 2.10-2.35 (2H, m, $SCH_2C\underline{H}_2CH$), 2.83-3.14 (5H, m, CH_2SCH_2CH), 4.16 (2H, q, J=7.1 Hz, OCH_2)	14.2, 30.7, 33.4, 33.9, 48.3, 60.8 169.4
16a	2.05-3.75 (5H, m, SCH_2CH_2CH), 3.32 (3H, s, OCH_3), 4.80 (1H, d, J=7.8 Hz, SCHPh), 7.12-7.80 (5H, m, C_6H_5)	31.0, 51.2, 52.8, 54.6, 127.5, 127.9 128.6, 140.5, 171.0
16b	2.14-3.76 (5H, m, SCH_2CH_2CH), 3.62 (1H, m, OCH_3) 4.22 (1H, d, J=5.6 Hz, SCHPh), 7.15-7.81 (5H, m, C_6H_5)	30.4, 51.9, 54.3, 56.9, 127.5, 127.7 128.5, 140.6, 172.9
17a & b	0.92 (t, J=7.1 Hz), 1.04 (t, J=7.1 Hz), 1.22 (t, J=7.1 Hz), 1.24 (t, J=7.1 Hz), (6H, 2xCH_3), 2.91-3.60 (4H, m, SCH_2CHCH), 3.75 (q, J=7.1 Hz), 4.03(q, J=7.1 Hz), 4.16 (q, J=7.1 Hz), 4.17 (q, J=7.1 Hz), (4H, 2xOCH_2), 4.59-4.97 (1H, m, $SC\underline{H}Ph$), 7.15-7.53 (5H, m, C_6H_5)	13.8, 14.1, 33.3, 33.4, 48.7, 51.7, 52.1, 54.7, 56.8, 59.2, 60.6, 60.9 61.1, 61.2, 127.7, 128.0, 128.1, 128.5, 128.7, 138.9, 140.3, 169.5 171.3, 171.8
18	2.96 (3H, s, NCH_3), 3.15-3.25 (1H, m, $SCHC\underline{H}$), 3.45-3.60 (3H, m, SCH_2CH), 4.67-4.77 (1H, m, $SC\underline{H}Ph$), 7.30 (5H, s, C_6H_5)	25.1, 34.4, 50.2, 52.2, 56.7, 128.3 134.7, 174.6, 177.8
19a	2.92 (2H, d, J=7.2 Hz, CH_2Ph), 2.96 (3H, s, NCH_3), 3.12-3.56 (4H, m, SCH_2CHCH), 4.92 (1H, td, J=1.0, 7.2 Hz, SCH), 7.28 (5H, s, C_6H_5)	25.3, 33.9, 41.6, 48.6, 52.7, 53.7, 127.0, 128.6, 129.2, 138.1, 177.6, 178.0
19b	2.70-2.97 (2H, m, CH_2Ph), 3.04 (3H, s, NCH_3), 3.20-3.76 (5H, m, $CHCHSCH_2CH$), 7.25 (5H, s, C_6H_5)	25.1, 34.7, 35.8, 49.1, 49.7, 55.0 126.7, 128.5, 128.6, 139.8, 178.0
20a	3.07 (3H, s, NCH_3), 3.11-3.63 (3H, m, SCH_2CH), 4.35 (1H, d, J=6.8 Hz, =CCH), 6.95 (1H, s, PhCH=), 7.14-7.50, 7.70-7.79 (5H, m, C_6H_5)	25.7, 34.4, 47.8, 50.1, 128.0, 128.1, 128.6, 129.7,134.9, 135.8, 175.8, 177.7
20b	3.03 (3H, s, NCH_3), 3.09-3.73 (3H, m, SCH_2CH), 4.06 (1H, dd, J=1.3, 7.6 Hz, =CCH), 6.95 (1H, d, J=1.3Hz, =CH), 7.14-7.48 (5H, m, C_6H_5)	25.6, 35.0, 46.6, 55.2, 124.7, 128.5, 134.3, 136.4, 175.4, 175.4, 177.3
21[b)]	1.23, 1.29, 1.31, 1.34 (6H, t, J=7.1Hz,CH_3), 2.74-3.79 (3H,m, SCH_2CH), 3.96-4.39 (1H, m, =CCH), 4.16, 4.18, 4.20, 4.24 (4H, q, J =7.1 Hz, 2xOCH_2), 6.61 (d,J=1.5Hz), 6.63 (d, J=1.3 Hz), (1H, =CH),7.03-7.50 (5H, m, C_6H_5)	14.1, 14.2, 34.8, 48.8, 48.9, 56.9, 61.5, 61.6, 120.6, 120.7, 126.5, 126.7, 128.1, 128.2, 128.3, 136.8, 136.9, 137.0, 170.4, 170.7, 170.9

22$^{b)}$	1.92-4.30 (5H, m, ring protons), 3.65, 3.66, 3.68 (3H, s, OCH_3), 6.30-6.62 (1H, m, =CH), 7.01-7.54 (5H, m, C_6H_5)	31.7, 33.9, 34.0, 36.4, 36.8, 42.5 45.2, 47.9, 52.1, 54.9, 118.1, 118.5, 120.2, 124.6, 124.7, 126.0, 126.3, 127.7, 128.0, 128.2, 137.1, 137.2, 139.6, 172.3, 172.6
23$^{b)}$	1.02, 1.05 (3H, t, J =7.5 Hz, CH_3), 1.74-4.29 (6H, m, SCH_2CHCH, $C\underline{H}_2CH_3$), 3.00 (3H, s, NCH_3), 5.60-5.96 (1H, m, =CH-)	13.4, 13.8, 25.5, 25.6, 33.6, 33.8, 35.8, 42.2, 42.3, 48.0, 48.4, 127.7, 130.8, 133.3, 175.8, 175.9, 176.5, 177.5
24$^{b)}$	0.90, 0.92, 0.98 (3H, t, J = 7.5 Hz, $CHCH_2C\underline{H}_3$), 1.26, 1.29 (6H, t, J =7.1 Hz, $OCH_2C\underline{H}_3$), 1.53-2.48 (2H, m, $CHC\underline{H}_2CH_3$), 3.02-4.39 (4H, m, SCH_2CH-CH), 4.17, 4.18, 4.22, 4.23 (4H, q, J =7.1 Hz, OCH_2) 5.38-5.57 (1H, m, =CH)	11.0, 13.3, 14.0, 14.1, 23.8, 24.8, 30.4, 32.9, 50.2, 50.3, 51.1, 54.3, 61.0, 61.3, 61.4, 122.3, 124.9, 134.3, 135.3, 170.9, 171.2, 171.3, 172.3
25	1.63-2.09, 2.64-2.84, 3.20-3.39 (14H, m, Adamantyl protons), 3.00 (3H, s, NCH_3), 3.06-3.73 (3H, m, SCH_2CH), 4.10 (1H, d, J =7.6 Hz, =CCH)	25.4, 28.0, 28.1, 33.6, 35.8, 37.0, 38.4, 38.8, 38.9, 48.4, 49.3, 119.1. 146.4, 175.7, 178.1
26	1.26 (6H, t, J =7.1 Hz, $2xCH_3$), 1.54-2.14, 2.45-2.63, 2.84-3.04 (14H, m, adamantyl protons), 3.29-3.66 (3H, m, SCH_2CH), 4.15, 4.17 (4H, q, j =7.1 Hz, $2xOCH_2$), 4.32 (1H, d, J =1.5 Hz, =CCH)	14.2, 28.0, 28.1, 32.7, 36.1, 36.9, 38.2, 38.3, 38.9, 49.8, 50.4, 61.2, 120.8, 140.3, 171.5, 171.6

a) 90 MHz. b) A mixture of *E*- and *Z*-isomer.

EXPERIMENTAL SECTION

All melting and boiling points were uncorrected. ^1H and ^{13}C nmr spectra were measured with a JEOL JNM FX-90Q or a JEOL JMN-GSX-500 instrument using tetramethylsilane as an internal standard. Following abbreviations were used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Infrared (ir) spectra were taken with a JASCO IR-810 spectrophotometer. Preparative thin layer chromatography (ptlc) was performed on precoated Kieselgel 60 F_{254} plates.

Bis(trimethylsilylmethyl) Sulfides: The synthetic procedure of saturated sulfides were described in previous paper.[4c] Unsaturated bis(trimethylsilylmethyl) sulfides were synthesized as follows: A hexane solution of butyllithium (12 mmol) was added dropwise to a stirred solution of bis(trimethylsilyl)methyl trimethylsilylmethyl sulfide (2.8 g 10 mmol) and tetramethylethylenediamine (1g) in THF (15 ml) at -10 ℃ and the whole was stirred for an additional hour. To the solution a solution of carbonyl compound (benzaldehyde, propionaldehyde or 2-adamantanone) (10 mmol) in THF (10 ml) was added dropwise at -10℃. The mixture was stirred for an additional hour, poured into ice-water, and then extracted with benzene. The benzene solution was dried over $MgSO_4$ and concentrated to give an oil which was subjected to column chromatography (hexane or AcOEt-hexane = 1 : 9).

(*E*)-α-(Trimethylsilyl)stylyl Trimethylsilylmethyl Sulfide (**8a**): Yield 42%, bp 150 ℃ (bath temp.) (4 mmHg), ms (m/z): 292 (M^+), ^{1}H nmr δ ($CDCl_3$): 0.09 (9H, s, $CH_2Si(C\underline{H}_3)_3$), 0.26 (9H, s, $=CHSi(C\underline{H}_3)_3$), 1.89 (2H, s, SCH_2), 6.90 (1H, s, =CH), 7.16-7.54, 7.64-7.78 (5H, m, C_6H_5). (*Z*)-α-(Trimethylsilyl)stylyl Trimethylsilylmethyl Sulfide (**8b**): Yield 37 %, bp 150 ℃ (bath temp.) (4 mmHg), ms (m/z): 292 (M^+), ^{1}H nmr δ ($CDCl_3$): 0.05 (9H, s, $CH_2Si(C\underline{H}_3)_3$), 0.17 (9H, s, $=CHSi(C\underline{H}_3)_3$), 1.93 (2H, s, SCH_2), 6.91 (1H, s, =CH), 7.17-7.47 (5H, m, C_6H_5). The structures of two isomers (**8a** and **8b**) were determined on the basis that A signal due to a trimethylsilyl group adjacent to double bond of **8a** shifts to the lower field than that of **8b**, owing to the deshielding effect of phenyl group.

(*E* and *Z*)-1-(Trimethylsilyl)butenyl Trimethylsilymethyl Sulfide: Yield 71%, bp 107-109℃ (20 mmHg), ms (m/z): 246 (M^+), ^{1}H nmr δ ($CDCl_3$): 0.08, 0.10, 0.13, 0.16 (9H, s, $Si(CH_3)_3$), 1.02, 1.00 (3H, t, J = 7.3 Hz, CH_3), 1.92, 1.93 (2H, s, SCH_2), 2.23, 2.38 (2H, dq, J =7.3, 7.8 Hz, $C\underline{H}_2CH_3$), 5.7, 6.0 (1H, t, J = 7.8 Hz, =CH).

(2-Adamantylidene)(trimethylsily)methyl Trimethylsilylmethyl Sulfide: Yield 84 %, colorless oil, ms (m/z): 338 (M^+), ^{1}H nmr δ ($CDCl_3$): 0.09 (9H, s, $Si(CH_3)_3$), 0.21 (9H, s, $Si(CH_3)_3$), 1.71-1.80, 1.85-1.95 (14H, m, adamantyl protons) 1.75 (2H, s, SCH_2).

A Typical Procedure for Syntheses of Bis(trimethylsilylmethyl) Sulfoxides, Bis(trimethylsilylmethyl) Sulfoxide (2a): MCPBA (2.1 g, 12 mmol) was added in portions to a stirred solution of bis(trimethylsilylmethyl) sulfide (1.9 g, 10 mmol) in dichloromethane (15 ml) at -40℃. After the mixture had been stirred for 3 h, the precipitates were removed by filtration and washed with cold dichloromethane. The combined solution was carefully washed with cold saturated aqueous sodium hydrogen carbonate and cold brine, and then dried over $MgSO_4$ for 10 min. The dichloromethane was removed *in vacuo* to give a colorless oil which is pure enough to be used in the subsequent reaction without further purification. **2a:** ^{1}H nmr δ ($CDCl_3$); 0.22 (18H, s, $2xSi(CH_3)_3$), 2.14 (2H, d, J =13.4 Hz, $2xCH\underline{H}_A$), 2.45 (2H, d, J =13.7 Hz, $2xCH\underline{H}_B$), ^{13}C nmr δ ($CDCl_3$); -0.8, 47.7, ir max (neat); 1028 cm^{-1} (SO).

Because the bis(silylmethyl) *S*-oxides are also subjected to sila-Pummerer rearrangement with increasing temperature or acidity, the operations and storage for a long time have to be performed carefully. Sometimes, it is convenient for confirmation of the product that a new absorption band at near 1030 cm^{-1} due to *S*-oxide is observed on comparison of the ir spectrum with that of the starting sulfide.

General Procedure for 1,3-Cycloaddition of 1a-f to Dipolarophiles: A solution of **1a-f** (3 mmol) and a dipolarophile (2 mmol) in HMPA (2 ml) was stirred in an oil bath (100°C) for 10-20 min. The cooled reaction mixture was subjected to column chromatography on silica gel with ethyl acetate-benzene (1 : 9) or THF-hexane (1 : 9) to give the cycloadduct. Yields and analytical and nmr spectral data of the products are listed in Tables 1-4.

In Entry 6, the product was subjected to ptlc (THF-hexane = 1 : 20) to afford **16a** (2,3-*cis*) and **16b** (2,3-*trans*). The product was also desulfurized by Raney Ni: A mixture of the product (200 mg) and Raney Ni (2 g as the alloy)(used after treatment with hydrogen) in EtOH (2 ml) was stirred at room temperature for 1 h. After removal of catalyst, concentration of the solution gave an oil (150 mg), gas chromatogrum of which showed only one peak. Methyl 2-benzylbutylate: ^{1}H nmr δ ($CDCl_3$): 0.91 (3H, t, J =7.1 Hz, $CH_2C\underline{H}_3$), 1.42-1.80 (2H, m, $CHC\underline{H}_2CH_3$), 2.39-3.20 (3H, m, $CHCH_2Ph$), 3.60 (3H, s, OCH_3), 7.02-7.40 (5H, m, C_6H_5).

In Entry 12, the product isolated (100 mg) was reducted with Raney Ni in the same manner as described above to give methyl 2-ethyl-4-phenylbutylate (**10a**) and methyl 5-phenyl-2-methylvalerate (**10b**), quantitatively. Each compound was separated by ptlc (AcOEt-hexane = 1 : 9). **10a**, ms (m/z): 206 (M^+), ^{1}H nmr δ ($CDCl_3$): 0.88 (3H, t, *J* =7.3 Hz, $CH_2C\underline{H}_3$), 1.37-2.75 (7H, m, $CH_2CHCH_2CH_2$), 3.67 (3H, s, OCH_3), 6.96-7.66 (5H, m, C_6H_5). **10b**, ms (m/z): 206 (M^+), ^{1}H nmr δ ($CDCl_3$): 1.13 (3H, d, *J* =7.1 Hz, $CHC\underline{H}_3$), 1.37-2.88 (7H, m, $CHCH_2CH_2CH_2$), 3.65 (3H, s, OCH_3), 7.08-7.41 (5H, m, C_6H_5).

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