



	R ¹	R ²
2, 3, 4a	C ₆ H ₅	C ₆ H ₅
b	SCH ₃	SCH ₃
c	-S-(CH ₂) ₃ -S-	
d (E)	SC ₆ H ₅	SCH ₃
d (Z)	SCH ₃	SC ₆ H ₅
e	SC ₆ H ₅	SC ₆ H ₅
f	Si(CH ₃) ₃	C ₆ H ₅
2, 3g	COOCH ₃	C ₆ H ₅

Nucleophilic Addition of Lithiated Phenyl Trimethylsilylmethyl Sulfide to Activated Olefins. A Facile Synthesis of 2-(Functionally) Substituted Silylcyclopropanes

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The lithio derivative of phenyl trimethylsilylmethyl sulfide undergoes smooth addition to activated ethylene derivatives to afford trimethylsilylcyclopropanes, except for the addition to methyl 2-phenylpropenoate which leads to the formation of methyl 4-trimethylsilyl-2-phenyl-4-(phenylthio)butanoate.

Functionally substituted cyclopropanes are increasingly important as C₃ building blocks in synthetic organic chemistry¹. In line with the current interest in silicon-mediated reactions², trimethylsilyl-substituted derivatives are particularly promising and have found some use³. Cyclopropanes of the type **4** with a vicinal arrangement of a silyl group and another functionality provide a handle for further use in synthesis. We envisaged the tandem addition/cycloelimination approach as exploited for the synthesis of cyclopropanone phenylthioacetals⁴ or 1-trimethylsilylcyclopropyl sulfides⁵ to allow general access to our target molecules **4**.

On addition of the lithio derivative (**1**) of phenyl trimethylsilylmethyl sulfide⁶ to a broad range of activated olefins such as 1,1-diphenylethylene (**2a**), ketene dithioacetals (**2b-e**), or the vinylsilane **2f**, we observed smooth addition to afford silylcyclopropanes **4** in good yields.

The reaction of reagent **1** with ketene *S,S*-dimethyl acetal (**2b**) was monitored by quenching samples with water at regular intervals and recording ¹H-NMR spectra. This revealed that the addition takes place at 0°C (t_{1/2} = 1.75 h) to give cyclization product **4b** directly because protonated **3b** could not be detected. This experimental evidence does not preclude a pathway involving formation of **4** via a carbene from **1** and subsequent [2+1]-cycloaddition. However, starting from the unsaturated ester **2g**, only addition product **5** was isolated and no cyclopropane of type **4**. These observations together with previous experience with lithiated sulfides^{4,5,6} lead to the suggestion that anions **3** are intermediates and that formation of products **4** follows in a fast 1,3-cycloelimination step.

The present approach to silylcyclopropanes **4** has the advantages of giving a clean reaction course, allowing facile distillative work-up, and providing good yields (Table). We are presently investigating the application of **4** as reagents in three-carbon annulation reactions.

Ketene thioacetals **2b-e** were obtained using literature procedures⁷. Silane **2f**⁸ (81%) was prepared by analogy with β-trimethylsilylstyrene⁹, and ester **2g**¹⁰ (45%) from α-bromostyrene¹¹ via the corresponding acid (96%) by analogy with methyl 2-(trimethylsilyl)acrylate¹².

(Trimethylsilyl)cyclopropanes (**4**); General Procedure:

To a solution of phenyl trimethylsilylmethyl sulfide⁷ (4.91 g, 25 mmol) in tetrahydrofuran (50 ml), a 1.6 molar solution of butyllithium in hexane (15.63 ml, 25 mmol) is added at -78°C and the mixture is stirred for 30 min. The temperature is then allowed to rise to 20°C within 30 min and stirring is continued for 2 h. The pale yellow solution is again cooled to -78°C, the olefin **2** (25 mmol) is

Table. 2,2-Disubstituted 1-Trimethylsilylcyclopropanes **4** and Methyl 4-Trimethylsilyl-2-phenyl-4-phenylthiobutanoate **5** Prepared

Product	Yield ^a [%]	b. p. [°C]/torr	Molecular Formula ^b	MS <i>m/e</i> (M ⁺)	¹ H-NMR (CDCl ₃) δ [ppm]	¹³ C-NMR (CDCl ₃) δ [ppm]		
						Cyclopropane C-Atoms tert. sec. quart		
4a	75	105–110/0.006	C ₁₈ H ₂₂ Si (266.5)	266	0.05 [s, 9H, Si(CH ₃) ₃]; 0.94 (AMX, 1H, <i>J</i> _{AX} = 10.6 Hz, <i>J</i> _{MX} = 7.9 Hz); 1.54 (AMX, 1H, <i>J</i> _{AX} = 10.6 Hz, <i>J</i> _{AM} = 3.8 Hz); 1.73 (AMX, 1H, <i>J</i> _{MX} = 7.9 Hz, <i>J</i> _{AM} = 3.8 Hz); 7.26–7.89 (m, 10H _{arom})	17.62	15.32	35.69
4b	74	40/0.01	C ₈ H ₁₈ S ₂ Si (206.4)	206	0.02 [s, 9H, Si(CH ₃) ₃]; 0.36 (AMX, 1H, <i>J</i> _{AX} = 10.6 Hz, <i>J</i> _{MX} = 8.2 Hz); 0.92 (AMX, 1H, <i>J</i> _{MX} = 8.2 Hz, <i>J</i> _{AM} = 3.8 Hz); 1.28 (AMX, 1H, <i>J</i> _{AX} = 10.6 Hz, <i>J</i> _{AB} = 3.8 Hz); 2.10 (s, 3H, SCH ₃); 2.12 (s, 3H, SCH ₃)	21.71	22.83	38.48
4c	42	65–67/0.01	C ₉ H ₁₈ S ₂ Si (218.5)	218	0.01 [s, 9H, Si(CH ₃) ₃]; 0.39 (AMX, 1H, <i>J</i> _{AX} = 10.6 Hz, <i>J</i> _{MX} = 8.2 Hz); 1.05 (AMX, 1H, <i>J</i> _{MX} = 8.2 Hz, <i>J</i> _{AM} = 3.6 Hz); 1.33 (AMX, 1H, <i>J</i> _{AX} = 10.6 Hz, <i>J</i> _{AM} = 3.6 Hz); 1.91–2.18 (m, 2H, –CH ₂ –); 2.74–3.10 (m, 4H, –S–CH ₂ CH ₂ CH ₂ –S)	19.41	24.18	30.47
<i>E</i> - 4d ^d	30	85–86/0.1	C ₁₃ H ₂₀ S ₂ Si (268.5)	268	0.29 [s, 9H, Si(CH ₃) ₃]; 0.70 (AMX, 1H, <i>J</i> _{AX} = 10.6 Hz, <i>J</i> _{MX} = 8.4 Hz); 1.42 (AMX, 1H, <i>J</i> _{MX} = 8.4 Hz, <i>J</i> _{AM} = 4.0 Hz); 1.78 (AMX, 1H, <i>J</i> _{AX} = 10.6 Hz, <i>J</i> _{AM} = 4.0 Hz); 2.42 (s, 3H, SCH ₃); 7.25–7.67 (m, 5H _{arom})	21.88	24.16	37.62
<i>Z</i> - 4d ^d					0.26 [s, 9H, Si(CH ₃) ₃]; 0.85 (AMX, 1H, <i>J</i> _{AX} = 10.5 Hz, <i>J</i> _{MX} = 8.4 Hz); 1.22 (AMX, 1H, <i>J</i> _{MX} = 8.4 Hz, <i>J</i> _{AM} = 4.0 Hz); 1.68 (AMX, 1H, <i>J</i> _{AX} = 10.5 Hz, <i>J</i> _{AM} = 4.0 Hz); 2.38 (s, 3H, SCH ₃); 7.25–7.67 (m, 5H _{arom})	21.88	22.71	38.03
4e	78	135–140/0.0006	C ₁₈ H ₂₂ S ₂ Si (330.6)	330	0.13 [s, 9H, Si(CH ₃) ₃]; 0.77 (AMX, 1H, <i>J</i> _{AX} = 10.5 Hz, <i>J</i> _{MX} = 8.5 Hz); 1.33 (AMX, 1H, <i>J</i> _{MX} = 8.5 Hz, <i>J</i> _{AM} = 4.0 Hz); 1.77 (AMX, 1H, <i>J</i> _{AX} = 10.5 Hz, <i>J</i> _{AM} = 4.0 Hz); 7.2–7.8 (m, 10H _{arom})	22.54	24.20	37.78
4f	64	65/0.1	C ₁₅ H ₂₆ Si ₂ (262.6)	262	–0.17 [s, 9H, Si(CH ₃) ₃]; 0.02 [s, 9H, Si(CH ₃) ₃]; 0.09 (AMX, 1H, <i>J</i> _{AX} = 9.2 Hz, <i>J</i> _{MX} = 7.0 Hz); 0.98 (AMX, 1H, <i>J</i> _{MX} = 7.0 Hz, <i>J</i> _{AM} = 3.2 Hz); 1.11 (AMX, 1H, <i>J</i> _{AX} = 9.2 Hz, <i>J</i> _{AM} = 3.2 Hz); 7.12–7.43 (m, 5H _{arom})	8.95	12.18	20.84
5 ^e	61	168–172/0.2 (semi-solid)	C ₂₀ H ₂₆ O ₂ SSi (358.6)	358	0.12 [s, 9H, Si(CH ₃) ₃]; 0.23 [s, 9H, Si(CH ₃) ₃]; 1.84 (ddd, 1H, <i>J</i> = 4.0 Hz, <i>J</i> = 10.8 Hz, <i>J</i> = 14.2 Hz); 2.12 (dd, 1H, <i>J</i> = 3.1 Hz, <i>J</i> = 11.6 Hz); 2.30 (ddd, 1H, <i>J</i> = 4.4 Hz, 11.6 Hz, 14.4 Hz); 2.48 (ddd, 1H, <i>J</i> = 3.1 Hz, 10.6 Hz, 14.4 Hz); 2.59 (dd, 1H, <i>J</i> = 3.8 Hz, 10.8 Hz); 2.67 (ddd, 1H, <i>J</i> = 3.8 Hz, 10.4 Hz, 14.2 Hz); 3.46 (s, 3H, OCH ₃); 3.62 (s, 3H, OCH ₃); 4.10 (dd, 1H, <i>J</i> = 4.4 Hz, 10.6 Hz); 4.13 (dd, 1H, <i>J</i> = 4.0 Hz, 10.4 Hz); 7.00–7.78 (m, 10H _{arom})			

^a Yield of isolated pure product.^b Satisfactory microanalyses obtained: C ± 0.16, H ± 0.09, S ± 0.21. Exceptions: **4f** (C – 0.51), **4a** (H + 0.23).^c Distillation using a spinning-band column.^d Mixture of diastereomers (*E*:*Z* = 3:1).^e Mixture of diastereomers (1:1).

injected by syringe, and the temperature is allowed to rise to 20°C within 4–5 h with subsequent stirring at 20°C for 10 h. The mixture is then poured into water (150 ml) and the resultant mixture is extracted with petroleum ether (150 ml). The extract is washed with water (150 ml) and saturated sodium chloride solution (150 ml), and dried with sodium sulfate. The solvent is evaporated and products **4** or **5** are purified by distillation. In the case of product **4c**, a contaminant (phenyltrimethylsilylmethylsulfide) is removed by preparative TLC using a chromatotron (eluent petroleum ether).

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- ¹ de Meijere, A. *Angew. Chem.* **1979**, *91*, 867; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 809.
- de Meijere, A. *Chem. Unserer Zeit* **1982**, *13*, 1.
- ² Fleming, I. *Organic Silicon Chem.* in: *Comprehensive Organic Chemistry*, Barton, D. H. R., Ollis, W. D., eds., Vol. 3, Pergamon Press, Oxford, 1979, p. 539.
- Colvin, E. *Silicon in Organic Synthesis*, Butterworth, London, 1981.
- Weber, W. P. *Silicon Reactions for Organic Synthesis*, Springer-Verlag, Berlin · Heidelberg · New York, 1983.
- Reißig, H. U. *Chem. in unserer Zeit* **1984**, *2*, 46.
- ³ Paquette, L. A. *Isr. J. Chem.* **1981**, *21*, 128.
- Paquette, L. A., Yan, T.-H., Wells, G. J. *J. Org. Chem.* **1984**, *49*, 3604.
- Paquette, L. A., Yan, T.-H., Wells, G. J. *J. Org. Chem.* **1984**, *49*, 3610.
- Paquette, L. A., Wells, G. J., Wickham, G. *J. Org. Chem.* **1984**, *49*, 3618.
- Ahira, M., Grignon-Dubois, M., Dunoguès, J. *J. Organomet. Chem.* **1984**, *271*, 15; and references cited therein.
- ⁴ Cohen, T., Weisenfeld, R. B., Gapinski, R. E. *J. Org. Chem.* **1979**, *44*, 4744.
- ⁵ Cohen, T., Sherbine, J. P., Mendelson, S. A., Myers, M. *Tetrahedron Lett.* **1985**, *26*, 2965.
- ⁶ Gröbel, B. T., Seebach, D. *Chem. Ber.* **1977**, *110*, 852.
- Gilman, H., Webb, F. J. *J. Am. Chem. Soc.* **1940**, *62*, 987.
- Ager, D. J., Cookson, R. C. *Tetrahedron Lett.* **1980**, *21*, 1677.
- ⁷ Seebach, D., Kolb, M., Gröbel, B. T. *Chem. Ber.* **1973**, *106*, 2277.
- Jones, P. F., Lappert, M. F., Szary, A. C. *J. Chem. Soc. Perkin Trans. I* **1973**, 2272.
- Carey, F. A., Court, A. S. *J. Org. Chem.* **1972**, *37*, 1926.
- ⁸ Chan, T. H., Baldassarre, A., Massuda, D. *Synthesis* **1976**, 801.
- ⁹ Sommer, L. H., Bailey, D. L., Goldberg, G. M., Buck, C. E., Bye, T. S., Evans, F. J., Whitmore, F. G. *J. Am. Chem. Soc.* **1954**, *76*, 1613.
- ¹⁰ Schauble, J. H., Walter, G. J., Morin, J. G. *J. Org. Chem.* **1974**, *39*, 755.
- ¹¹ Newman, M. S., Dhawan, B., Hashem, M. M., Khanna, V. K., Springer, J. M. *J. Org. Chem.* **1976**, *41*, 3925.
- ¹² Ottolenghi, A., Fridkin, M., Zilkha, A. *Can. J. Chem.* **1963**, *41*, 2977.