

Reaction of [Arylthio(chloro)methyl]trimethylsilanes with Arenes and Alk-1-enes in the Presence of Lewis Acid: Syntheses of [Aryl(arylthio)methyl]- and (1-Arylthioalk-3-enyl)-trimethylsilanes

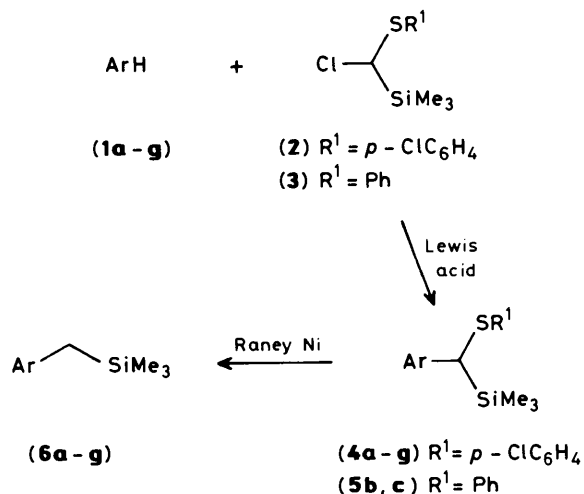
Hiroyuki Ishibashi,* Hiroshi Nakatani, Yoshizumi Umei, Wako Yamamoto, and Masazumi Ikeda
Kyoto Pharmaceutical University, Misasagi, Yamashina, Kyoto 607, Japan

Treatment of equimolar amounts of the [arylthio(chloro)methyl]trimethylsilanes (**2**) or (**3**) and electron-rich arenes with an equimolar amount of Lewis acid (SnCl_4 or TiCl_4) gave the Friedel-Crafts reaction products, [aryl(arylthio)methyl]trimethylsilanes (**4**) or (**5**), in high yields. Similar treatment of the chlorides (**2**) or (**3**) with alk-1-enes gave ene type products, [1-arylthioalk-3-enyl]trimethylsilanes (**12**) or (**13**), in moderate yields. Some chemical transformations of these products are also described.

Arylthio(trimethylsilyl)methyl groups are versatile functional groups in organic synthesis.¹ With an interest in the synthetic use of α -chloro sulphides,² we have now investigated the Lewis acid-promoted reactions of the [arylthio(chloro)methyl]trimethylsilanes (**2**) and (**3**) with arenes³ and alkenes in the hope of developing a new method for the direct introduction of arylthio(trimethylsilyl)methyl groups into the latter. Here we describe the syntheses and some reactions of [aryl(arylthio)methyl]- and (1-arylthioalk-3-enyl)-trimethylsilanes.

The chlorides (**2**) and (**3**)^{1c,f} were prepared by the reaction of [(4-chlorophenylthio)methyl]trimethylsilane and (phenylthio)methyltrimethylsilane with *N*-chlorosuccinimide, respectively.

Reaction with Arenes: Synthesis of [Aryl(arylthio)methyl]-trimethylsilanes.—In general, a solution of equimolar amounts of the chloride (**2**) and the arene (**1**) in methylene dichloride was treated with an equimolar amount of Lewis acid such as stannic



Scheme 1.

Table. Reactions of the arene (**1a**–**f**) with the chloride (**2**) or (**3**).^a

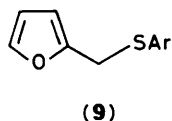
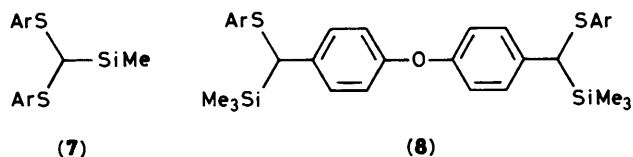
Entry	ArH	Chloride	Lewis acid	Reaction temp. (°C)	Product	
					No.	Yield (%)
1	(1a)	(2)	SnCl_4	–20	(4a)	47
2 ^b	(1a)	(2)	SnCl_4	–20	(4a)	95
3 ^b	(1a)	(2)	TiCl_4	–20	(4a)	70
4	(1b)	(2)	SnCl_4	–20	(4b)	71
5	(1b)	(2)	TiCl_4	–20	(4b)	90
6 ^c	(1b)	(2)	TiCl_4	–20	(4b)	40
7	(1b)	(2)	TiCl_4	0	(4b)	65
8	(1b)	(2)	ZnCl_2	Room temp.	(4b)	78
9	(1b)	(3)	TiCl_4	–20	(5b)	82
10	(1c)	(2)	SnCl_4	–20	(4c)	98
11	(1c)	(2)	SnCl_4	0	(4c)	84
12	(1c)	(2)	TiCl_4	–20	(4c)	55
13	(1c)	(3)	SnCl_4	0	(5c)	79
14	(1d)	(2)	SnCl_4	–20	(4d)	91
15	(1e)	(2)	SnCl_4	–20	(4e)	44
16	(1e)	(2)	TiCl_4	–20	(4e)	72
17	(1f)	(2)	SnCl_4	–20	(4f)	87
					(8)	Trace
18 ^d	(1f)	(2)	SnCl_4	–20	(4f)	Trace
					(8)	35

^a Molar ratio of ArH (**1**):chloride (**2**) or (**3**):Lewis acid = 1:1:1, unless otherwise stated. ^b (**1a**):(**2**):Lewis acid = 1:2:1. ^c (**1b**):(**2**): TiCl_4 = 1:1:1/2. ^d (**1f**):(**2**): SnCl_4 = 1:3:4.5.

chloride (SnCl_4) or titanium tetrachloride (TiCl_4) at –20 °C for 30 min. Work-up gave the [aryl(4-chlorophenylthio)methyl]trimethylsilanes (**4**) in high yields (see Table). The structures of the products (**4**) were established by elemental analyses, spectroscopic evidence, and desulphurization to (arylmethyl)trimethylsilanes (**6**) (*vide infra*).

The electron-rich benzene derivatives such as anisole (**1b**) and dimethoxybenzenes reacted smoothly with the chloride (**2**) (entry 5, 10, 14, and 16), while benzene or chlorobenzene gave no satisfactory result even after the reaction was carried out under refluxing conditions using the arene itself as solvent: the only isolated product was [bis(4-chlorophenylthio)methyl]trimethylsilane (**7**). In the case of toluene (**1a**), the product (**4a**) was obtained in 47% yield (entry 1), but use of 2 molar equivalents of the chloride (**2**) increased the yield of the product to 95% (based on toluene (entry 2)).

These reactions afforded no other positional isomers (checked by g.l.c. and n.m.r.). This is probably because of steric bulkiness of the introduced 4-chlorophenylthio(trimethylsilyl)-



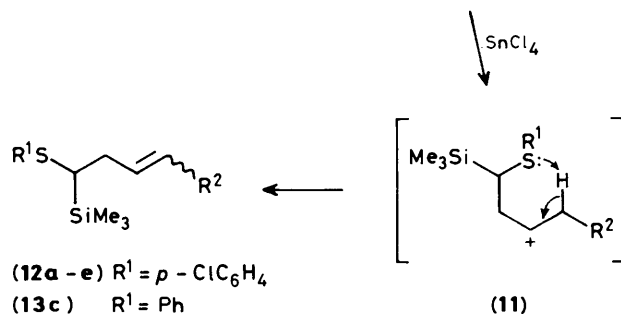
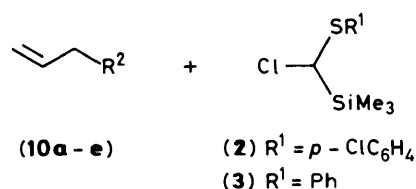
methyl group. Further, they gave no polyalkylated products. This may be attributed to the deactivation of the benzene ring caused by co-ordination of Lewis acid to the sulphur atom of the arylthio group in the products (4). In fact, 1 mole equivalent of Lewis acid was required to complete this reaction (compare the reactions between entry 5 and 6). The choice of the Lewis acid for these Friedel-Crafts reactions depends upon the nature of the arenes used (see Table). The chloride (3) can also be used for this reaction, but the yields of the products (5) were slightly lower than that with the chloride (2) (compare the reactions between entry 5 and 9).

When diphenyl ether (1f) was subjected to the reaction with an equimolar amount of the chloride (2), the mono-substituted product (4f) was obtained in 87% yield, along with a trace amount of the di-substituted product (8) (entry 17). Use of 3 equivalents of the chloride (2) in this reaction yielded (8) as a major product, though the yield was low (entry 18). The reaction of the chloride (2) with naphthalene (1g) gave an inseparable mixture of the β -substituted isomer (4g) and the dithioacetal (7). The mixture was then treated with Raney nickel in boiling ethanol to give (2-naphthylmethyl)trimethylsilane (6g) in 48% yield (based on naphthalene), whose structure was confirmed by transforming it to 2-methylnaphthalene with fluoride anion. Exclusive formation of the β -substituted isomer (4g) may also be explained by the steric reason.

Interestingly, the reaction of furan with (2) in the presence of zinc chloride (ZnCl₂)* gave directly the desilylated product (9) in 65% yield. The reason for this abnormal reaction is not clear. Even if the reaction of anisole (1b) with (2) was carried out in the presence of ZnCl₂, the normal Friedel-Crafts product (4b) was obtained (entry 8).

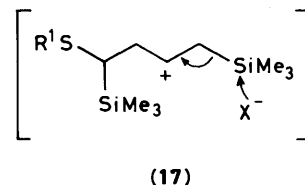
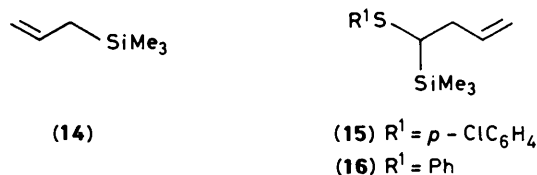
As exemplified above in the formation of (6g) from (4g), desulphurization of the compounds (4a–f) with Raney nickel gave the corresponding (arylmethyl)trimethylsilanes (6a–f) in high yields (70–98%). (Arylmethyl)trimethylsilanes (6) are important building blocks in organic synthesis.⁴ Thus, the present method provides an alternative simple route to this class of compounds.

Reaction with Alkenes: Synthesis of (1-Arylthioalk-3-enyl)-trimethylsilanes.—The reactions of the chloride (2) with the terminal alkenes (10a–e) in the presence of SnCl₄ were found to give the [1-(4-chlorophenylthio)alk-3-enyl]trimethylsilanes (12a–e) in good yields,[†] whose structures were confirmed by their spectroscopic evidence and chemical transformations (*vide*



(10) (11) (12) (13)

- a ; R² = Et
b ; R² = Bu
c ; R² = C₅H₁₁
d ; R² = C₇H₁₅
e ; R² = -(CH₂)₇CO₂Me



Scheme 2.

infra). Similarly, the chloride (3) reacted with oct-1-ene (10e) to give the product (13c).

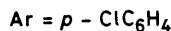
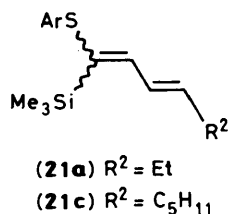
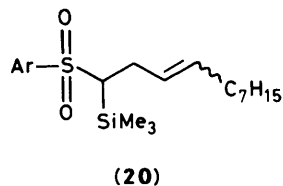
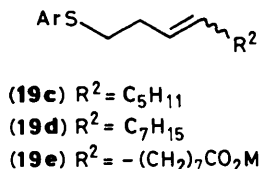
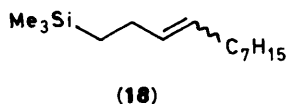
A possible mechanism for the formation of these ene type reaction products⁵ (12) and (13) would involve initial formation of carbenium ion intermediates such as (11) which could then lose a proton *via* a six-membered transition state.

The chlorides (2) and (3) reacted also with allyltrimethylsilane (14) to give the (1-arylthiobut-3-enyl)trimethylsilanes (15) and (16) in 80 and 53% yields, respectively. In these cases, the carbenium ion intermediate such as (17) loses a trimethylsilyl group to give the product (15) or (16).

The products obtained herein could be converted into various unsaturated compounds bearing sulphur and/or silicon atoms. For example, sequential treatment of the product (12d) with lithium naphthalenide in tetrahydrofuran and aqueous ammonium chloride gave the alk-3-enyltrimethylsilane (18) in 98% yield. G.l.c. analysis of this product showed it to be a mixture of *E* and *Z* isomers in a ratio of 88:12, which led us to assume the *E*:*Z* ratios of the ene products (12a–e) to be ca. 88:12. Desilylation of the compounds (12c) with tetrabutyl-

* Use of SnCl₄ or TiCl₄ as a Lewis acid for this reaction gave a mixture of many products.

† When TiCl₄ was used in these reactions, considerable amounts of by-products were formed.



ammonium fluoride in acetonitrile gave the non-3-enyl sulphide (19c) in 80% yield.

Similarly, compounds (12d) and (12e) afforded the corresponding sulphides (19d) and (19e) in 96 and 90% yields, respectively. The sulphides (19c–e) thus obtained were identical with the products prepared by reactions of 4-chlorophenyl trifluoroacetoxymethyl sulphide with the alkenes (10c–d) in trifluoroacetic acid.^{5c} Oxidation of the compound (12d) with 2 molar equivalents of *m*-chloroperbenzoic acid gave the sulphone (20) in 52% yield. Finally, chlorination of compound (12a) with *N*-chlorosuccinimide at room temperature followed by treatment of the resulting chloride with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) afforded the diene (21a) (55%)* together with its stereoisomers. Similar treatment of compound (12c) gave the diene (21c) in 52% yield.

Experimental

M.p.s were determined on a Yanagimoto micro melting point apparatus and uncorrected. ¹H N.m.r. spectra were obtained on JEOL JNM-PMX 60 (60 MHz) or Varian XL-300 (300 MHz) spectrometers with tetramethylsilane as internal standard in CDCl₃. Exact mass determinations were obtained on a Hitachi M-80 instrument at 20 eV. Column chromatography was performed on silica gel 60 PF₂₅₄ for p.l.c. (Merck) under pressure.

[(4-Chlorophenylthio)methyl]trimethylsilane.—4-Chlorothiophenol (17.7 g, 0.12 mol) and (chloromethyl)trimethylsilane (15.0 g, 0.12 mol) were successively added to a solution of NaOH (4.9 g, 0.12 mol) in water (50 ml) and ethanol (20 ml) and the mixture was heated under reflux for 4 h. Ethanol used as a co-solvent was evaporated off and the remainder was poured into water (200 ml) and then extracted with chloroform. The organic layer was dried (MgSO₄) and evaporated, and the residual oil was distilled *in vacuo* to give [(4-chlorophenylthio)methyl]trimethylsilane (26.3 g, 95%), b.p. 118 °C at 6 mmHg (Found: C, 51.5; H, 6.5. C₁₀H₁₅ClSSi requires C, 52.0; H, 6.55%); δ_H (60 MHz) 0.16 (9 H, s), 2.13 (2 H, s), and 7.17 (4 H, s).

(Phenylthiomethyl)trimethylsilane.—By the same procedure as described for the preparation of [(4-chlorophenylthio)-

methyl]trimethylsilane, thiophenol (13.5 g, 0.12 mol) was allowed to react with (chloromethyl)trimethylsilane (15.0 g, 0.12 mol) to give (phenylthiomethyl)trimethylsilane (22.4 g, 95%), b.p. 114 °C at 10 mmHg (lit.,⁶ 158.5 °C at 67 mmHg); δ_H (60 MHz) 0.17 (9 H, s), 2.17 (2 H, s), and 7.0–7.3 (5 H, m).

[Chloro(4-chlorophenylthio)methyl]trimethylsilane (2).—*N*-Chlorosuccinimide (9.5 g, 71 mmol) was added to a stirred solution of [(4-chlorophenylthio)methyl]trimethylsilane (16.4 g, 71 mmol) in carbon tetrachloride (50 ml) in small portions at 0 °C and stirring was continued at room temperature for 15 h. The precipitated succinimide was filtered off and the filtrate evaporated to leave a residual oil which was distilled *in vacuo* to give the chloride (2) (17.0 g, 90%), b.p. 132–133 °C at 4 mmHg (Found: M⁺, 263.9967. C₁₀H₁₄Cl₂SSi requires M, 263.9962); δ_H (60 MHz) 0.27 (9 H, s), 4.80 (1 H, s), and 7.20 and 7.38 (each 2 H, AB q, J 9.0 Hz).

[Chloro(phenylthio)methyl]trimethylsilane (3).—By the same procedure as that described for the preparation of the chloride (2), (phenylthiomethyl)trimethylsilane (13.7 g, 70 mmol) was chlorinated with *N*-chlorosuccinimide (9.4 g, 70 mmol) to give the chloride (3)^{1f} (13.4 g, 83%), b.p. 112–114 °C at 3 mmHg (Found: M⁺, 230.0354. Calc. for C₁₀H₁₅ClSSi: M, 230.0351); δ_H (60 MHz) 0.26 (9 H, s), 4.92 (1 H, s), and 7.15–7.65 (5 H, m).

[Aryl(4-chlorophenylthio)methyl]trimethylsilanes (4a–f): General Procedure.—To a solution of the arene (1a–f) (2 mmol) and the chloride (2) (530 mg, 2 mmol) in methylene dichloride (5 ml) was added Lewis acid (2 mmol) at –20 °C and the mixture was stirred at the temperature indicated in the Table for 30 min. The reaction was quenched with water (10 ml) and the organic layer was separated. The aqueous layer was further extracted with methylene dichloride and the combined organic layers were dried (MgSO₄) and evaporated and the residue chromatographed on silica gel (hexane). The following compounds, whose yields are given in the Table, were thus obtained.

[4-Chlorophenylthio(4-methylphenyl)methyl]trimethylsilane (4a), an oil (Found: M⁺, 320.0832. C₁₇H₂₁ClSSi requires M, 320.0821); δ_H (60 MHz) 0.08 (9 H, s), 2.23 (3 H, s), 3.64 (1 H, s), and 6.98 (8 H, br s).

[4-Chlorophenylthio(4-methoxyphenyl)methyl]trimethylsilane (4b), an oil (Found: C, 60.8; H, 6.35. C₁₇H₂₁OCISSi requires C, 60.6; H, 6.3%); δ_H (60 MHz) 0.12 (9 H, s), 3.71 (3 H + 1 H, s), 6.66 (2 H, d, J 9 Hz), 6.96 (4 H, s), and 7.07 (2 H, d, J 9 Hz).

[4-Chlorophenylthio(3,4-dimethoxyphenyl)methyl]trimethylsilane (4c), m.p. 74.5–75.0 °C (Found: C, 58.8; H, 6.3. C₁₈H₂₃ClO₂SSi requires C, 58.9; H, 6.3%); δ_H (60 MHz) 0.12 (9 H, s), 3.62 (1 H, s), 3.80 (6 H, s), 6.6–6.9 (3 H, m), and 7.00 (4 H, s).

[4-Chlorophenylthio(3,4-methylenedioxyphenyl)methyl]trimethylsilane (4d), m.p. 65.5–66.0 °C (Found: C, 57.95; H, 5.5. C₁₇H₁₉ClO₂SSi requires C, 58.2; H, 5.5%); δ_H (60 MHz) 0.10 (9 H, s), 3.62 (1 H, s), 5.84 (2 H, s), 6.63 (2 H, br s), 6.80 (1 H, br s), and 7.04 (4 H, s).

[4-Chlorophenylthio(2,4-dimethoxyphenyl)methyl]trimethylsilane (4e), m.p. 77–78 °C (Found: C, 59.0; H, 6.2. C₁₈H₂₃ClO₂SSi requires C, 58.9; H, 6.3%); δ_H (60 MHz) 0.18 (9 H, s), 3.77 (3 H, s), 3.81 (3 H, s), 4.33 (1 H, s), 6.3–6.6 (2 H, m), 7.10 (4 H, s), and 7.40 (1 H, d, J 9 Hz).

[4-Chlorophenylthio(4-phenoxyphenyl)methyl]trimethylsilane (4f), m.p. 71.5–72.5 °C (Found: C, 66.2; H, 6.0. C₂₂H₂₃ClOSSi requires C, 66.2; H, 5.8%); δ_H (60 MHz) 0.10 (9 H, s), 3.64 (1 H, s), and 6.7–7.4 (13 H, s).

4,4'-Oxybis[phenyl(4-chlorophenylthio)methyl]trimethylsilane (8), an oil (Found: C, 61.2; H, 6.0. C₃₂H₃₆Cl₂OS₂Si₂

* ¹H N.m.r. spectrum of (21a) (see Experimental section) shows it to be a single stereoisomer, though the stereochemistry of the sulphur and silicon atoms is unknown.

requires C, 61.2; H, 5.8%; δ_{H} (60 MHz) 0.10 (18 H, s), 3.66 (2 H, s), 6.76 (4 H, br d, J 9 Hz), and 7.0–7.3 (12 H, m).

[4-Methoxyphenyl(phenylthio)methyl]trimethylsilane (**5b**).—By the same procedure as that described for the preparation of (**4a–f**), the chloride (**3**) (461 mg, 2 mmol) was allowed to react with anisole (216 mg, 2 mmol) at -20°C for 30 min in the presence of titanium tetrachloride (379 mg, 2 mmol) to give (**5b**) (496 mg, 82%) as an oil (Found: C, 67.5; H, 7.3. $\text{C}_{17}\text{H}_{22}\text{OSSi}$ requires C, 67.5; H, 7.35%; δ_{H} (60 MHz) 0.10 (9 H, s), 3.68 (1 H, s), 3.74 (3 H, s), 6.76 (2 H, d, J 9 Hz), and 7.0–7.3 (7 H, m).

[3,4-Dimethoxyphenyl(phenylthio)methyl]trimethylsilane (**5c**).—By the same procedure as that described for the preparation of (**4a–f**), the chloride (**3**) (461 mg, 2 mmol) was allowed to react with 1,2-dimethoxybenzene (276 mg, 2 mmol) in the presence of stannic chloride (520 mg, 2 mmol) to give (**5c**) (525 mg, 79%) as an oil (Found: C, 65.0; H, 7.3. $\text{C}_{18}\text{H}_{24}\text{O}_2\text{SSi}$ requires C, 65.0; H, 7.3%; δ_{H} (60 MHz) 0.11 (9 H, s), 3.69 (1 H, s), 3.82 (6 H, s), 6.72 (2 H, br s), 6.85 (1 H, br s), and 7.0–7.3 (5 H, m).

[Bis(4-chlorophenylthio)methyl]trimethylsilane (**7**).—Stannic chloride (208 mg, 0.8 mmol) was added to a solution of the chloride (**2**) (212 mg, 0.8 mmol) in methylene dichloride (5 ml) and the mixture was stirred at room temperature for 1 h. The reaction mixture was poured into water (10 ml) and extracted with methylene dichloride. The extract was dried (MgSO_4), evaporated, and the residue chromatographed on silica gel (hexane–benzene, 4:1) to give the dithioacetal (**7**) (60 mg, 20%), m.p. 81–82 $^{\circ}\text{C}$ (Found: C, 51.5; H, 4.9. $\text{C}_{16}\text{H}_{18}\text{Cl}_2\text{S}_2\text{Si}$ requires C, 51.5; H, 4.9%; δ_{H} (60 MHz) 0.20 (9 H, s), 3.83 (1 H, s), and 7.13 (8 H, s).

Reaction of Naphthalene with Compound (**2**).—By the same procedure as that described for the preparation of (**4a–f**), the chloride (**2**) (530 mg, 2 mmol) was allowed to react with naphthalene (260 mg, 2 mmol) at -20°C for 30 min in the presence of stannic chloride (521 mg, 2 mmol) to give a mixture of the products (**4g**) and (**7**). This crude mixture was then heated under reflux in ethanol (10 ml) containing Raney nickel (*ca.* 3 g) for 10 h. The Raney nickel was filtered off and the filtrate concentrated under reduced pressure to leave a residue which was chromatographed on silica gel (hexane) to give the silane (**6g**) [204 mg, 48% (based on naphthalene)], m.p. 60.0–60.5 $^{\circ}\text{C}$ (Found: C, 77.3; H, 8.45. $\text{C}_{14}\text{H}_{18}\text{Si}\cdot 1/4\text{H}_2\text{O}$ requires C, 76.8; H, 8.5%; δ_{H} (60 MHz) 0.04 (9 H, s), 2.24 (2 H, s), and 6.9–7.9 (7 H, m). This compound was further characterized by transforming it into 2-methylnaphthalene as follows. A mixture of the product (**6g**) (100 mg, 0.47 mmol) and tetrabutylammonium fluoride (244 mg, 0.94 mmol) in acetonitrile (5 ml) was stirred at room temperature for 1 h and then evaporated. Diethyl ether (5 ml) and hexane (5 ml) were added to the residue and the inorganic materials were filtered off. The filtrate was concentrated under reduced pressure and the residue was chromatographed on silica gel (hexane) to give 2-methylnaphthalene (55 mg, 82%), whose physical data are in accord with those of an authentic sample (Aldrich Chem. Co.).

2-[(4-Chlorophenylthio)methyl]furan (**9**).—By the same procedure as that described for the preparation of (**4a–f**), the chloride (**2**) (530 mg, 2 mmol) was allowed to react with furan (140 mg, 2 mmol) at room temperature for 1 h in the presence of zinc chloride (300 mg, 2.2 mmol) to give compound (**9**) (390 mg, 65%) as an oil (Found: C, 58.5; H, 4.1. $\text{C}_{11}\text{H}_9\text{ClOS}$ requires C, 58.8; H, 4.0%; δ_{H} (60 MHz) 4.03 (2 H, s), 6.03 (1 H, d, J 3 Hz), 6.22 (1 H, dd, J 3 and 2 Hz), 7.20 (4 H, s), and 7.30 (1 H, d, J 2 Hz).

(Arylmethyl)trimethylsilanes (**6a–f**): General Procedure.—A solution of compound (**4a–f**) (2 mmol) in ethanol (10 ml) containing Raney nickel (*ca.* 3 g) was heated under reflux for 3 h. The Raney nickel was filtered off, the filtrate evaporated, and the residue chromatographed on silica gel (hexane). The following compounds were thus prepared.

[(4-Methylphenyl)methyl]trimethylsilane (**6a**)⁷ (83%), an oil; δ_{H} (60 MHz) 0.00 (9 H, s), 2.05 (2 H, s), 2.30 (3 H, s), and 6.80, 6.96 (each 2 H, AB q, J 9 Hz).

[(4-Methoxyphenyl)methyl]trimethylsilane (**6b**)^{4a} (88%), an oil; δ_{H} (60 MHz) 0.00 (9 H, s), 2.01 (2 H, s), 3.73 (3 H, s), and 6.73, 6.90 (each 2 H, AB q, J 9 Hz).

[(3,4-Dimethoxyphenyl)methyl]trimethylsilane (**6c**)^{4c} (98%), and oil (Found: C, 64.0; H, 9.1. Calc. for $\text{C}_{12}\text{H}_{20}\text{O}_2\text{Si}$: C, 64.2; H, 9.0%; δ_{H} (60 MHz) 0.00 (9 H, s), 2.03 (2 H, s), 3.84 (6 H, s), 6.4–6.6 (2 H, m), and 6.70 (1 H, d, J 9 Hz).

[(3,4-Methylenedioxyphenyl)methyl]trimethylsilane (**6d**)^{4d} (70%), an oil; δ_{H} (60 MHz) 0.00 (9 H, s), 2.00 (2 H, s), 5.85 (2 H, s), 6.3–6.5 (2 H, m), and 6.63 (1 H, d, J 9 Hz).

[(2,4-Dimethoxyphenyl)methyl]trimethylsilane (**6e**) (88%), an oil (Found: M^+ , 224.1230. $\text{C}_{12}\text{H}_{20}\text{O}_2\text{Si}$ requires M , 224.1231); δ_{H} (60 MHz) -0.06 (9 H, s), 1.99 (2 H, s), 3.76 (6 H, br s), 6.2–6.5 (2 H, m), and 6.80 (1 H, br d, J 9 Hz).

[(4-Phenoxyphenyl)methyl]trimethylsilane (**6f**) (88%), an oil (Found: C, 75.4; H, 7.85. $\text{C}_{16}\text{H}_{20}\text{OSi}$ requires C, 74.95; H, 7.9%; δ_{H} (60 MHz) 0.00 (9 H, s), 2.03 (2 H, s), and 6.70–7.45 (9 H, m).

[1-(4-Chlorophenylthio)alk-3-enyl]trimethylsilanes (**12a–e**): General Procedure.—Stannic chloride (2.29 g, 8.8 mmol) was added to a solution of the chloride (**2**) (2.12 g, 8 mmol) and the alkene (**10a–e**) (8 mmol) in methylene dichloride (20 ml) at -78°C and the mixture was stirred at -20°C for 30 min. The reaction was quenched with water (10 ml) and the organic layer was separated. The aqueous layer was further extracted with methylene dichloride and the combined organic layers were dried (MgSO_4), evaporated, and the residue chromatographed on silica gel (hexane). The following compounds were thus obtained.

[1-(4-Chlorophenylthio)hex-3-enyl]trimethylsilane (**12a**) (88%), an oil (Found: M^+ , 298.0957. $\text{C}_{15}\text{H}_{23}\text{ClSi}$ requires M , 298.0977); δ_{H} (300 MHz) 0.14 (9 H, s), 0.92 (3 H, t, J 7.7 Hz), 1.90–2.02 (2 H, m), 2.25–2.48 (2 H, m), 2.50 (1 H, t, J 6.2 Hz), 5.35–5.52 (2 H, m), 7.22 (2 H, d, J 8.9 Hz), and 7.27 (2 H, d, J 8.9 Hz).

[1-(4-Chlorophenylthio)oct-3-enyl]trimethylsilane (**12b**) (71%), an oil (Found: C, 62.4; H, 8.4. $\text{C}_{17}\text{H}_{27}\text{ClSi}$ requires C, 62.4; H, 8.3%; δ_{H} (60 MHz) 0.13 (9 H, s), 0.6–1.6 (7 H, m), 1.7–2.2 (2 H, m), 2.3–2.6 (3 H, m), 5.25–5.50 (2 H, m), and 7.20 (4 H, s).

[1-(4-Chlorophenylthio)non-3-enyl]trimethylsilane (**12c**) (74%), an oil (Found: C, 63.5; H, 8.6. $\text{C}_{18}\text{H}_{29}\text{ClSi}$ requires C, 63.40; H, 8.6%; δ_{H} (60 MHz) 0.13 (9 H, s), 0.6–1.6 (9 H, m), 1.7–2.2 (2 H, m), 2.3–2.6 (3 H, m), 5.25–5.50 (2 H, m), and 7.20 (4 H, s).

[1-(4-Chlorophenylthio)undec-3-enyl]trimethylsilane (**12d**) (80%), an oil (Found: C, 65.3; H, 9.2. $\text{C}_{20}\text{H}_{33}\text{ClSi}$ requires C, 65.1; H, 9.0%; δ_{H} (60 MHz) 0.13 (9 H, s), 0.6–1.6 (13 H, m), 1.7–2.2 (2 H, m), 2.3–2.6 (3 H, m), 5.25–5.50 (2 H, m), and 7.30 (4 H, s).

Methyl 12-(4-Chlorophenylthio)-12-trimethylsilyldodec-9-enoate (**12e**) (76%), an oil (Found: M^+ , 426.1798. $\text{C}_{22}\text{H}_{35}\text{ClO}_2\text{Si}$ requires M , 426.1813); δ_{H} (60 MHz) 0.13 (9 H, s), 1.10–2.10 (12 H, m), 2.30 (2 H, t, J 7 Hz), 2.3–2.6 (3 H, m), 3.63 (3 H, s), 5.25–5.50 (2 H, m), and 7.20 (4 H, s).

(1-Phenylthionon-3-enyl)trimethylsilane (**13c**).—By the same procedure as that described for the preparation of (**12a–e**), the chloride (**3**) (461 mg, 2 mmol) was allowed to react with oct-1-

ene (**10c**) (224 mg, 2 mmol) in the presence of stannic chloride (573 mg, 2.2 mmol) to give (**13c**) (416 mg, 68%) as an oil (Found: M^+ , 306.1839. $C_{18}H_{30}SSi$ requires M , 306.1836); δ_H (60 MHz) 0.13 (9 H, s), 0.6—1.6 (9 H, m), 1.7—2.1 (2 H, m), 2.3—2.6 (3 H, m), 5.25—5.50 (2 H, m), and 6.8—7.5 (5 H, m).

[1-(4-Chlorophenylthio)but-3-enyl]trimethylsilane (**15**).—By the same procedure as that described for the preparation of (**12a—e**), the chloride (**2**) (530 mg, 2 mmol) was allowed to react with allylsilane (**14**) (230 mg, 2 mmol) in the presence of stannic chloride (570 mg, 2.2 mmol) to give (**15**) (430 mg, 80%) as an oil (Found: C, 57.45; H, 7.1. $C_{13}H_{19}ClSSi$ requires C, 57.6; H, 7.1%); δ_H (60 MHz) 0.13 (9 H, s), 2.15—2.60 (3 H, m), 4.75—5.20 (2 H, m), 5.45—6.25 (1 H, m), and 7.20 (4 H, s).

(1-Phenylthiobut-3-enyl)trimethylsilane (**16**).—By the same procedure as that described for the preparation of (**12a—e**), the chloride (**3**) (461 mg, 2 mmol) was allowed to react with allylsilane (230 mg, 2 mmol) in the presence of stannic chloride (570 mg, 2.2 mmol) to give (**16**)^{1b} (250 mg, 53%) as an oil; δ_H (60 MHz) 0.13 (9 H, s), 2.2—2.7 (3 H, m), 4.75—5.20 (2 H, m), 5.45—6.25 (1 H, m), and 7.0—7.5 (5 H, m).

(Undec-3-enyl)trimethylsilane (**18**).—Lithium metal (91.6 mg, 13.2 mmol) and naphthalene (564 mg, 4.4 mmol) were successively added to tetrahydrofuran (15 ml) at room temperature and the mixture was stirred at the same temperature for 1 h. The resulting dark green mixture was cooled to -78°C and a solution of compound (**12d**) (738 mg, 2 mmol) in tetrahydrofuran (5 ml) was added. The mixture was stirred at the same temperature for 3 h after which it was quenched with saturated aqueous ammonium chloride (10 ml) and extracted with ethyl ether. The organic layer was washed successively with 2M-NaOH solution and brine and then dried ($MgSO_4$). The solvent was evaporated off and the residue was chromatographed on silica gel (hexane) to give (**18**) (443 mg, 98%) as an oil (Found: M^+ , 226.2113. $C_{14}H_{20}Si$ requires M , 226.2114); δ_H (60 MHz) 0.00 (9 H, s), 0.30—1.05 (5 H, m), 1.1—1.5 (10 H, m), 1.8—2.3 (4 H, m), and 5.25—5.50 (2 H, m).

1-Alk-3-enylthio-4-chlorobenzenes (**19c—e**): *General Procedure*.—To a solution of compound (**12c—e**) (1 mmol) in acetonitrile (5 ml) was added a solution of tetrabutylammonium fluoride (288 mg, 1.1 mmol) in acetonitrile (5 ml) and the mixture was stirred at room temperature for 1 h. It was then evaporated and diethyl ether (1 ml) and hexane (1 ml) were added to the residue. Inorganic materials were filtered off and the filtrate was concentrated under reduced pressure to leave a residue which was chromatographed on silica gel (hexane). The following compounds were thus prepared.

4-Chloro-1-undec-3-enylthiobenzene (**19d**)^{5c} (96%), an oil; (300 MHz) 0.88 (3 H, t, J 6.9 Hz), 1.2—1.4 (6 H, m), 1.97 (2 H, q, J 6.8 Hz), 2.26—2.40 (2 H, m), 2.90 (2 H, br t, J 7.5 Hz), 5.33—5.54 (2 H, m), and 7.24 (4 H, s).

4-Chloro-1-undec-3-enylthiobenzene (**19d**)^{5c} (96%), an oil; δ_H (60 MHz) 0.7—1.6 (13 H, m), 1.7—2.5 (4 H, m), 2.90 (2 H, br t, J 7.5 Hz), 5.30—5.55 (2 H, m), and 7.23 (4 H, s).

Methyl 12-(4-chlorophenylthio)dodec-3-enoate (**19e**)^{5c} (96%), an oil; δ_H (300 MHz) 1.29 (10 H, br s), 1.61 (2 H, q, J 7.3 Hz), 1.95 (2 H, q, J 6.4 Hz), 2.30 (2 H, t, J 7.3 Hz), 2.26—2.40 (2 H, m), 2.91 (2 H, br t, J 7.5 Hz), 5.41 (dt, J 15.2 and 5.5 Hz, 1 olefinic H of *E* isomer), 5.47 (dt, J 15.2 and 5.5 Hz, 1 olefinic H of *E* isomer), 5.33—5.48 (m, olefinic H of *Z* isomer), and 7.24 (4 H, s).

[1-(4-Chlorophenylsulphonyl)undec-3-enyl]trimethylsilane (**20**).—To a solution of compound (**12d**) (360 mg, 0.98 mmol) in methylene dichloride (10 ml) was added *m*-chloroperbenzoic acid (85%) (406 mg, 2 mmol) and the mixture was stirred

at room temperature for 15 h. The reaction mixture was washed successively with saturated aqueous $NaHCO_3$ and brine and then dried ($MgSO_4$). The solvent was evaporated off and the residue was chromatographed on silica gel (hexane-AcOEt, 9:1) to give the *sulphone* (**20**) (205 mg, 52%) as an oil (Found: C, 59.8; H, 8.5. $C_{20}H_{33}ClO_2SSi$ requires C, 60.0; H, 8.3%); δ_H (60 MHz) 0.32 (9 H, s), 0.75—2.00 (15 H, m), 2.2—2.5 (2 H, m), 2.66 (1 H, br t, J 7 Hz), 4.7—5.5 (2 H, m), and 7.74 and 7.80 (each 2 H, AB q, J 9 Hz).

[1-(4-Chlorophenylthio)alka-1,3-dienyl]trimethylsilane (**21a,c**): *General Procedure*.—*N*-Chlorosuccinimide (134 mg, 1 mmol) was added to a solution of compound (**12a,c**) (1 mmol) in carbon tetrachloride (5 ml) at 0°C and the mixture was stirred at room temperature for 15 h. The precipitated succinimide was filtered off, 1,8-diazabicyclo[5.4.0]undec-7-ene (167 mg, 1.1 mmol) was added to the filtrate, and the mixture was heated at 50°C for 3 h. The precipitated salts were filtered off and the filtrate was evaporated to provide a residue which was chromatographed on silica gel (hexane). The following compounds were thus obtained.

[1-(4-Chlorophenylthio)hexa-1,3-dienyl]trimethylsilane (**21a**) (55%), an oil (Found: M^+ , 296.0813. $C_{15}H_{22}ClSSi$ requires M , 296.0820); δ_H (300 MHz) 0.05 (9 H, s), 1.00 (3 H, t, J 7.6 Hz), 2.15 (2 H, quint., J 7.9 Hz), 6.07 (1 H, dt, t 15.1 and 6.7 Hz), 6.72 (1 H, ddt, J 15.1, 10.3, and 1.5 Hz), 7.02 (1 H, d, J 10.3 Hz), 7.11 (2 H, d, J 8.4 Hz), and 7.18 (2 H, d, J 8.4 Hz).

[1-(4-Chlorophenylthio)nona-1,3-dienyl]trimethylsilane (**21c**) (52%), an oil (Found: M^+ , 338.1290. $C_{18}H_{27}ClSSi$ requires M , 338.1290); δ_H (60 MHz) 0.05 (9 H, s), 0.7—1.5 (6 H, m), 1.8—2.4 (2 H, m), 6.00 (1 H, dt, J 15 and 7 Hz), 6.70 (1 H, br dd, J 15 and 10 Hz), 7.03 (1 H, d, J 10 Hz), and 7.10 (4 H, s).

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