chlorosilane, and 3 drops of 5% aqueous $H_2PtCl_6·6H_2O$ was stirred at reflux for 24 h. Excess $(CH_3)_2SiHCl$ was removed by evaporation at reduced pressure and the residue treated with 0.3 mol of ethereal methylmagnesium iodide solution and then heated at reflux 48 h. Hydrolysis (saturated NH_4Cl solution), extraction with petroleum ether of the aqueous layer, drying (Na_2SO_4), and concentration of the combined organic layers gave an oil which was fractionated to afford 20.4 g (80%) of silane product: bp 81–82 °C (0.05 mm); NMR ($CDCl_3$) δ 7.1–7.5 (10 H, m), 4.0–4.3 (1 H, m), 2.4 (2 H, d), 0.17 (9 H, s). Anal. Calcd for $C_{16}H_{22}Si$: C, 80.25; H, 8.72. Found: C, 80.30; H, 8.99. Crystallization of the distillation residue from MeOH afforded 2.5 g (14%) of 1-methyl-1,3,3-triphenylindane, mp 141.5–142.5 °C (lit.[13] mp 143.5 °C).

Diethyl(2,2-diphenylethyl)methylsilane. Treatment of the crude hydrosilylation residue prepared as above (0.1-mol scale) with 0.3 mol of ethereal ethylmagnesium bromide and a similar workup afforded 12.7 g (45%) of silane product as a heavy oil. Anal. Calcd for $C_{18}H_{26}Si$: C, 80.77; H, 9.26. Found: C, 80.73; H, 9.25. IR and NMR spectra are in good accord with the assigned structure. Workup of the distillation residue as above gave 3.5 g (20%) of 1-methyl-1,3,3-triphenylindane.

1,1-Dimethylsilacycloheptane. The general procedure of Nametkin[14] was used. Since the Lewis acid-catalyzed rearrangement of 1-(chloromethyl)-1-chlorosilacyclohexane is violently exothermic and in some runs exploded, the following modification was employed. Behind an efficient shield, 13 g (0.08 mol) of 1-(chloromethyl)-1-methylsilacyclohexane[14] was treated with a small spatulaful of $AlCl_3$ (~10 mg). The mixture was heated with stirring to 70 °C. A vigorous reaction ensued which moderated within a few minutes. Direct distillation of the reaction mixture afforded 9.7 g (75%) of 1-chloro-1-methylsilacycloheptane, bp 92–94 °C (20 mm).

Triphenylcarbenium Tetrafluoroborate (TPMTFB). As commercial material gave erratic results, the dry salt, prepared by the Dauben procedure[15] was stored in a desiccator over $CaSO_4$ and used within 1 week, preferably sooner.

General Procedure for Oxidation with TPMTFB. A flame-dried, 100-mL, three-necked flask, equipped with a condenser, gas inlet, and serum cap, was swept with a strong stream of dry nitrogen and charged with 0.005 mol of silane in 50 mL of dichloromethane (freshly distilled from CaH_2) and ~2 g (0.006 mole) of TPMTFB in dichloromethane. The mixture was stirred at 22 ± 0.4 °C, and samples were periodically withdrawn by syringe for GLC analysis. A 0.006 × 11 m column of 15% SF-96 silicone oil on 60/80-mesh Chromosorb PAW was used for all analyses. During the reaction course, the mixture gradually turned from orange to black. Boron trifluoride was detected fuming from the gas exit and was analyzed for as previously.[6]

For acyclic silanes, trimethylfluorosilane was detected by GLC or better by condensation of vapors from a nitrogen purge of the reaction mixture: bp 15 °C; NMR ($CDCl_3$) δ 0.07 (d, $J = 7.5$ Hz). For cyclic silanes, alkenylfluorodimethylsilanes were characterized by GLC and NMR or in the case of reaction 7 by fractional distillation (20-cm, helix-packed column) of the reaction mixture and by NMR. Reactions carried out in 1,2-dichloroethane solvent showed no substantial differences with respect to rate or product distribution.

In preparative runs, the reaction mixture was washed with saturated sodium bicarbonate solution, dried (Na_2SO_4), and concentrated to one-third of the original volume. Solids were removed by filtration, and the product was collected from the filtrate by preparative GLC. (5-Hexenyl)trimethylsilane[16] (reaction 6) and (5-hexenyl)dimethylfluorosilane (reaction 10) were characterized by comparison with authentic samples. Sublimation (60 °C, 0.075 mm) of the solids afforded pure triphenylmethane.

Kinetic Measurements. The disappearance of silane substrate was determined by GLC, using an appropriate C_7 to C_{12} hydrocarbon, for which a response factor curve had been prepared, as internal standard. The laboratory temperature, determined by a recording thermograph, was 22 ± 0.4 °C. Second-order rate constants were calculated from the integrated form of the second-order rate equation by assuming $[TPMTFB] = [TPMTFB]_0 - ([silane]_0 - [silane])$.

(5-Hexenyl)dimethylfluorosilane. A mixture of 8.25 g (0.1 mol) of 1,5-hexadiene, 9.4 g (0.8 mol) of dichloromethylsilane, and 2 drops of 5% aqueous H_2PtCl_6 solution was stirred 16 h and then treated with 18 g (0.9 mol) of silver fluoroborate in 50 mL of anhydrous acetone. After being stirred for 45 min, the mixture was filtered and the filtrate fractionally distilled to afford 10.7 g (62%) of fluorosilane: bp 68–71 °C (20 mm); NMR ($CDCl_3$) δ 5.68 (1 H, m), 4.84 (2 H, m), 1.94 (2 H, m), 1.34 (4 H, m), 0.56 (2 H, m), 0.07 (6 H, d, $J = 8$ Hz).

Registry No. $(CH_3CH_2)_4Si$, 631-36-7; $CH_3CH_2CH_2CH_2Si(CH_3)_3$, 1000-49-3; $PhCH_2CH_2SiMe_3$, 772-64-5; $Ph_2CHCH_2SiMe_3$, 75961-63-6; $Ph_2CHCH_2SiMeEt_2$, 75961-64-7; $Me_3Si(CH_2)_6SiMe_3$, 13083-96-0; $\overline{(CH_2)_3Si}(CH_3)_2$, 2295-12-7; $\overline{(CH_2)_4Si}(CH_3)_2$, 1072-54-4; $\overline{(CH_2)_5Si}(CH_3)_2$, 4040-74-8; $\overline{(CH_2)_6Si}(CH_3)_2$, 15896-02-3; 1,1-diphenylethene, 530-48-3; dimethylchlorosilane, 1066-35-9; 1-methyl-1,3,3-triphenylindane, 19303-32-3; 1-(chloromethyl)-1-methylsilacyclohexane, 15303-37-4; TPMTFB, 341-02-6; (5-hexenyl)dimethylfluorosilane, 75961-65-8; 1,5-hexadiene, 592-42-7.

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(13) H. Wieland and E. Dorrer, *Chem. Ber.*, **63**, 404 (1930).

(14) N. S. Nametkin, V. W. Vdorin, K. S. Puschevaja, and A. N. Egorochkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2530 (1967).

(15) H. J. Dauben, L. R. Homien, and K. M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).

(16) F. V. Mironov and N. A. Pogonkina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 182 (1955).

Regiospecific Synthesis of Allylic Dimethylmethoxysilanes

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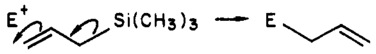
Photochemically generated dimethylsilylene reacts regiospecifically with allylic methyl ethers to yield allylic dimethylmethoxysilanes. Reaction of allylic methyl ethers with dimethyldichlorosilane and sodium metal likewise gives allylic dimethylmethoxysilanes in preparatively useful yields. Regiospecificity, however, is not always observed in this latter reaction. Such allylic dimethylmethoxysilanes can be converted to allylic trimethylsilanes easily by reaction with methyllithium.

Allylic trimethylsilanes have been shown to be versatile intermediates in organic synthesis.[1] They react regiospecifically with a wide range of electrophilic reagents to give substitution with allylic rearrangement in the sense shown (eq 1).[2–14] In addition, allylic trimethylsilanes can



(1)

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[1] For a recent review of the synthetic utility of allylic trimethylsilanes, see: Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761–786.

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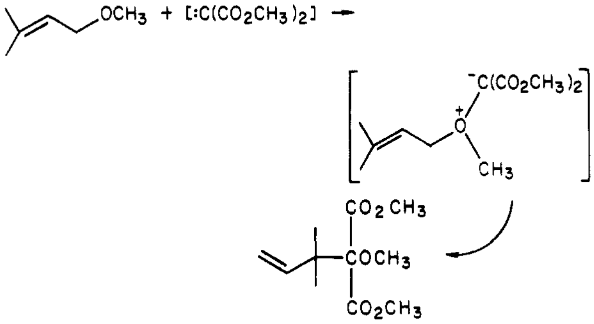
be metalated to yield α-(trimethylsilyl)allylic carbanions. The regioselectivity of reactions of these ambident anions with aldehydes and ketones can be controlled to yield products of either α[15] or γ attack.[16-20] This accounts for the considerable current interest in the regiospecific preparation of allylic trimethylsilanes.[21-24]

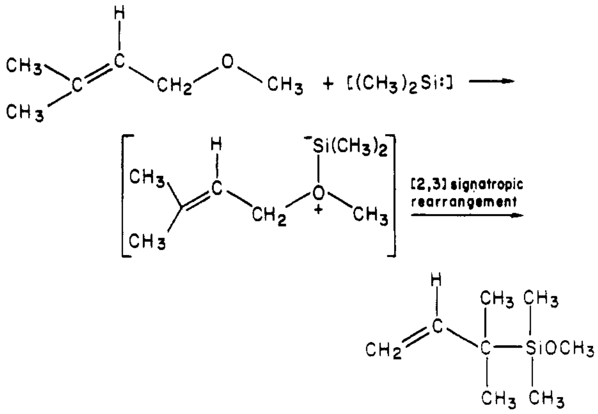
We report herein a novel insertion reaction of dimethylsilylene into the allylic carbon–oxygen single bonds of allylic methyl ethers to yield allylic dimethylmethoxysilanes.[25] Allylic dimethylmethoxysilanes react essentially quantitatively with methyllithium to yield allylic trimethylsilanes. For example, dimethylsilylene generated by photolysis of dodecamethylcyclohexasilane[26] in the presence of allyl methyl ether at 5 °C gives allyldimethylmethoxysilane (20%). The yields reported are based on the generation of 2 mol of dimethylsilylene from each mole of dodecamethylcyclohexasilane[26] and depend on the concentration of allylic methyl ether. It should be noted that in control experiments no reaction of dimethylsilylene with unstrained aliphatic ethers such as tetrahydrofuran or diethyl ether was observed.

The fact that bis(methoxycarbonyl)carbene[27,28] and carbethoxycarbene,[29] generated respectively by photolysis of dimethyl diazomalonate and ethyl diazoacetate, react predominantly with allylic ethers via initial electrophilic attack of these carbenes on a lone pair of electrons of the ether oxygen to form zwitterionic intermediates which undergo [2,3] sigmatropic rearrangements to produce insertion products led us to consider a similar mechanism (eq 2) for the insertion reaction of dimethylsilylene into allylic methyl ethers.



(2)

To test this mechanistic proposal, we have generated dimethylsilylene in the presence of α-methylallyl methyl ether. As predicted, the products isolated were a mixture of *cis*- and *trans*-(γ-methylallyl)dimethylmethoxysilanes. Similarly, dimethylsilylene reacts with *trans*-γ-methylallyl methyl ether to yield (α-methylallyl)dimethylmethoxysilane, with γ,γ-dimethylallyl methyl ether to give (α,α-dimethylallyl)dimethylmethoxysilane, and finally with α,α-dimethylallyl methyl ether to produce (γ,γ-dimethylallyl)dimethylmethoxysilane. These results are consistent with a reaction which occurs by initial coordination of dimethylsilylene to the oxygen of the allylic methyl ether to form a zwitterionic intermediate which undergoes a [2,3] sigmatropic rearrangement to yield the allylic dimethylmethoxysilane products observed (eq 3). Our results do not provide support for a mechanism in which the zwitterionic intermediate fragments to a radical pair, as recently proposed.[30]



(3)

This constitutes a new regiospecific carbon–silicon bond-forming reaction. As expected, such allylic dimethylmethoxysilanes can be converted into the corresponding allylic trimethylsilanes by reaction with methyllithium in virtually quantitative yield with neither rearrangement nor isomerization (eq 4). We have utilized this reaction to characterize our dimethylsilylene insertion products.[31]

While the reaction of dimethylsilylene generated by photolysis of dodecamethylcyclohexasilane with allylic methyl ethers is mechanistically interesting, photochemistry is seldom competitive with other methods for large-scale synthetic reactions. Allyl methyl ether, α,α-dimethylallyl methyl ether, and α-methylallyl methyl ether react regiospecifically with dimethyldichlorosilane and

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(2) Calas, R.; Dunogues, J.; Pillot, J. P.; Biran, C.; Pisciotti, F.; Arreguy, B. *J. Organomet. Chem.* **1975**, *85*, 149–158.

(3) Deleris, G.; Dunogues, J.; Calas, R. *J. Organomet. Chem.* **1975**, *94*, 43–50.

(4) Hosomi, A.; Sakurai, H. *Tetrahedron Lett.* **1976**, 1295–1298.

(5) Carter, M. J.; Fleming, I. *J. Chem. Soc., Chem. Commun.* **1976**, 679–680.

(6) Deleris, G.; Dunogues, J.; Calas, R. *Tetrahedron Lett.* **1976**, 2449–2450.

(7) Hosomi, A.; Sakurai, H. *Tetrahedron Lett.* **1978**, 2589–2592.

(8) Itoh, A.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1979**, 1783–1786.

(9) Wilson, S. R.; Phillips, L. R.; Natalie, K. J., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 3340–3344.

(10) Ojima, I.; Miyazawa, Y.; Kumagai, M. *J. Chem. Soc., Chem. Commun.* **1976**, 927–928.

(11) Au-Yeung, G. W.; Fleming, I. *J. Chem. Soc., Chem. Commun.* **1977**, 79–80.

(12) Hosomi, A.; Saito, M.; Sakurai, H. *Tetrahedron Lett.* **1979**, 429–432.

(13) Yanami, T.; Miyashita, M.; Yoshikoshi, A. *J. Org. Chem.* **1980**, *45*, 607–612.

(14) Kelly, L. F.; Narula, A. S.; Birch, A. J. *Tetrahedron Lett.* **1980**, 871–874.

(15) Lau, P. W. K.; Chan, T. H. *Tetrahedron Lett.* **1978**, 2383–2386.

(16) Ayalon-Chass, D.; Ehlinger, E.; Magnus, P. *J. Chem. Soc., Chem. Commun.* **1977**, 772–773.

(17) Ehlinger, E.; Magnus, P. *Tetrahedron Lett.* **1979**, 11–14.

(18) Corriu, R. J. P.; Masse, J. *J. Organomet. Chem.* **1973**, *57*, C5–C8.

(19) Corriu, R. J. P.; Masse, J.; Samate, D. *J. Organomet. Chem.* **1975**, *93*, 71–80.

(20) Corriu, R. J. P.; Lanneau, G. F.; Leclercq, D.; Samate, D. *J. Organomet. Chem.* **1978**, *144*, 155–164.

(21) Seyferth, D.; Worstorn, K. F.; Lim, T. F. O.; Sepelak, D. J. *J. Organomet. Chem.* **1979**, *181*, 293–304.

(22) Fleming, I.; Paterson, I. *Synthesis* **1979**, 446–448.

(23) Yatagai, H.; Yamamoto, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1980**, *102*, 4548–4550.

(24) Coughlin, D. J.; Saloman, R. G. *J. Org. Chem.* **1979**, *44*, 3784–3790.

(25) For a recent review of silylene chemistry, see: Gaspar, P.P. In "Reactive Intermediates"; Jones, M., Jr., Moss, R. A., Eds.; Wiley-Interscience: New York, 1978; Vol. I, pp 229–277.

(26) Ishikawa, M.; Kumada, M. *J. Organomet. Chem.* **1972**, *42*, 325–332.

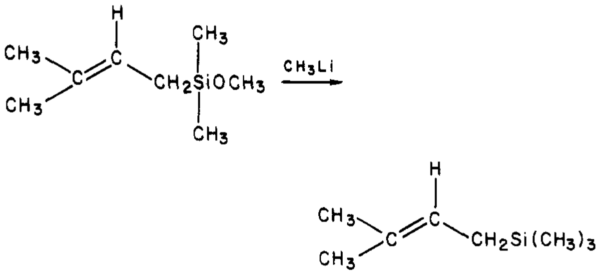
(27) Ando, W.; Kondo, S.; Nakayama, K.; Ichibori, K.; Kohoda, H.; Yamato, H.; Imai, I.; Nakaido, S.; Migita, T. *J. Am. Chem. Soc.* **1972**, *94*, 3870–3876.

(28) Ando, W.; Imai, I.; Migita, T. *J. Org. Chem.* **1972**, *37*, 3596–3600.

(29) Ando, W.; Yagihara, T.; Kondo, S.; Nakayama, K.; Yamato, H.; Nakaido, S.; Migita, T. *J. Org. Chem.* **1971**, *36*, 1732–1736.

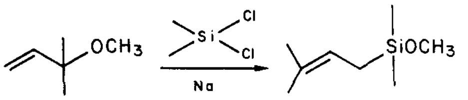
(30) Tortorelli, V. J.; Jones, M., Jr. *J. Chem. Soc., Chem. Commun.* **1980**, 785–786.

(31) Eaborn, C. "Organosilicon Compounds"; Butterworths: London, 1960; pp 13–33.



(4)

sodium or lithium dispersion to yield the same products as previously obtained in photochemical reactions of these allylic methyl ethers with dimethylsilylene (eq 5). While



(5)

these results may be interpreted in terms of generation of dimethylsilylene from the reaction of dimethyldichlorosilane with alkali metals in solution, the fact that *trans*-γ-methylallyl methyl ether reacts with dimethyldichlorosilane and sodium metal to yield predominantly *cis*- and *trans*-(γ-methylallyl)dimethylmethoxysilanes rather than (α-methylallyl)dimethylmethoxysilane as is observed with photochemically generated dimethylsilylene suggests that alternative mechanisms such as electron transfer to the substrate must be considered.[32-36] We are actively investigating the mechanism of this reaction.

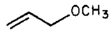
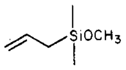
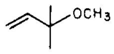
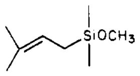
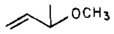
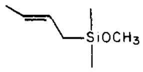
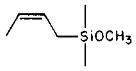
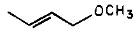
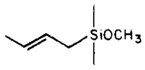
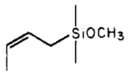
Experimental Section

IR spectra were determined as CCl_4 or CS_2 solutions on a Perkin-Elmer 281 spectrometer. ^1H NMR spectra were recorded on a Varian XL-100 spectrometer operating in the FT mode with 1% solutions in benzene-d_6 with an internal standard of benzene. Electron-impact mass spectra were determined on a Du Pont 21-492 mass spectrometer operating at an ionizing voltage of 70 eV. Samples of all compounds for spectral analysis were purified by preparative vapor-phase chromatography on a Hewlett-Packard F&M 700 using a 26 ft × $^1/_4$ in. 20% SE-30 on Chromosorb W 60/80-mesh column. GLC analysis of reactions were performed in a temperature-programming mode starting at 70 °C, with the oven temperature increasing at a rate of 0.5 °C/min. Yields of products were determined by GLC with bis(trimethylsilyl)acetylene (Silar) as a standard. Yields are based on 2 mol of dimethylsilylene/mol of dodecamethylcyclohexasilane. All reactions were run under an inert atmosphere of nitrogen. Elemental analysis was performed by Galbraith Laboratories, Inc.

Many of the starting materials and products are known compounds. They had physical and spectral properties in complete agreement with literature values. In those cases where spectral data have not been previously reported, we have included these data.

Preparation of Allylic Methyl Ethers. Allyl methyl ether [bp 40–41 °C (lit.[37] bp 42.5–43 °C)], α-methylallyl methyl ether [bp 54–56 °C (lit.[38] bp 53–55 °C)], *trans*-γ-methylallyl methyl ether [bp 78–80 °C (lit.[39] bp 79 °C)], α,α-dimethylallyl methyl ether [bp 79–80 °C (lit.[40] bp 79.8–80.2 °C)], and γ,γ-dimethylallyl methyl ether [bp 102–104 °C (lit.[40] bp 104.6–105.2 °C)] were prepared as follows.

Table I. Reaction of Dimethyldichlorosilane, Sodium and Allylic Methyl Ethers

allylic methyl ether	product	yield, %
		60
		50
		30
		30
		30
		30

In a dry, 250-mL, three-necked, round-bottomed flask equipped with a reflux condenser, a pressure-equalizing addition funnel, and a Teflon-covered magnetic stirring bar were placed sodium hydride (2.4 g, 0.1 mol) and 100 mL of xylene. Allylic alcohol (0.1 mol) was placed in the addition funnel and added dropwise to the stirred solution. After the addition was complete, the solution was heated to reflux for 1 h. Dimethyl sulfate (6.9 g, 55 mmol) in 50 mL of xylene was placed in the addition funnel and added to the solution. It was refluxed overnight. The xylene solution was cooled, washed with water, and dried over anhydrous sodium sulfate. The allylic methyl ether was distilled from the xylene solution through a 25-cm Vigreux column. Samples of the allylic methyl ethers used in photochemical experiments were further purified by preparative GLC.

Reaction of Allylic Methyl Ethers with Photochemically Generated Dimethylsilylene. Dodecamethylcyclohexasilane[41,42] (52.5 mg, 0.15 mmol) and the allylic methyl ether (1.5 mmol) were dissolved in dry spectroquality cyclohexane. The solution (total volume 1 mL) was placed in a 5-mm quartz NMR tube. The solution was photolyzed with a 450-W, medium-pressure Hanovia Hg lamp housed in a water-cooled quartz well for 90 min at 5 °C in an ice–water bath.

Allyldimethylmethoxysilane was obtained (20%) from the reaction of allyl methyl ether as above: NMR δ 5.55–6.05 (br m, 1 H), 4.85–5.15 (br m, 2 H), 3.32 (s, 3 H), 1.60 (d, 2 H, J = 8 Hz), 0.13 (s, 6 H); IR (CCl_4) 1635 (C═C), 1100 cm^{-1} (SiOC); mass spectrum, m/e (relative intensity) 130 (2.2, parent; calcd for $C_6H_{14}OSi$ 130.081, found 130.080), 115 (15.9, P − 15), 89 (100, P − 41), 75 (27). Anal. Calcd for $C_6H_{14}SiO$: C, 55.32; H, 10.83. Found: C, 55.10; H, 10.72.

(α-Methylallyl)dimethylmethoxysilane was obtained (8%) from the reaction of *trans*-γ-methylallyl methyl ether as above. The yield increased to 35% when γ-methylallyl methyl ether was used as the solvent: NMR δ 5.96 (ddd, 1 H, J = 16, 10, and 7 Hz), 4.99 (dd, 1 H, J = 16 and 1 Hz), 4.96 (dd, 1 H, J = 10 and 1 Hz), 3.34 (s, 3 H), 1.76 (dq, 1 H, J = 7 and 7 Hz), 1.20 (d, 3 H, J = 7.0 Hz), 0.13 (s, 6 H); IR (CCl_4) 1626 (C═C), 1082 cm^{-1} (SiOC). Anal. Calcd for $C_7H_{16}SiO$: C, 58.27; H, 11.18. Found: C, 58.08; H, 11.17.

(α,α-Dimethylallyl)dimethylmethoxysilane was obtained (6%) from the reaction of γ,γ-dimethylallyl methyl ether as above: NMR δ 6.05 (dd, J = 17 and 9 Hz), 5.05 (dd, 1 H, J = 9 and 1.5 Hz), 4.95 (dd, 1 H, J = 17 and 1.5 Hz), 3.35 (s, 3 H), 1.17 (s, 6 H), 0.11 (s, 6 H); IR (CCl_4) 1630 (C═C), 1085 cm^{-1} (SiOC).

(γ,γ-Dimethylallyl)dimethylmethoxysilane was obtained (14%) from the reaction of α,α-dimethylallyl methyl ether as

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(32) Skell, P. S.; Goldstein, E. J. *J. Am. Chem. Soc.* **1964**, *86*, 1442–1443.

(33) Weyenberg, D. R.; Toporcer, L. H.; Nelson, L. E. *J. Org. Chem.* **1968**, *33*, 1975–1982.

(34) Volpin, M. E.; Koreshkov, Y. D.; Dulova, V. G.; Kursanov, D. N. *Tetrahedron* **1962**, *18*, 107–122.

(35) Atwell, W. H.; Weyenberg, D. R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 469–477.

(36) Frye, C. L.; Salinger, R. M.; Patin, T. J. *J. Am. Chem. Soc.* **1966**, *88*, 2343–2344.

(37) Irvine, J. C.; McDonald, J. L. A.; Soutar, C. W. *J. Chem. Soc.* **1915**, 337–351.

(38) Wiberg, K. *J. Am. Chem. Soc.* **1952**, *74*, 3891–3892.

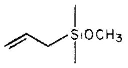
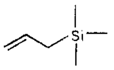
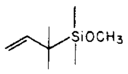
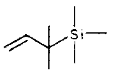
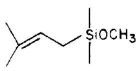
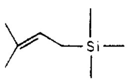
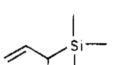
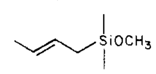
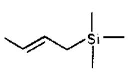
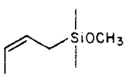
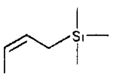
(39) Waters, R. C.; Vander Werf, C. A. *J. Am. Chem. Soc.* **1954**, *76*, 709–713.

(40) Winstein, S.; Goodman, L. *J. Am. Chem. Soc.* **1954**, *76*, 4373–4378.

(41) West, R. *Ann. N.Y. Acad. Sci.* **1974**, *239*, 262–277.

(42) Laguerre, M.; Dunogues, J.; Calas, R. *J. Chem. Soc., Chem. Commun.* **1978**, 272.

Table II. Reaction of Methyllithium with Allylic Dimethylmethoxysilanes

allylic methyl ether	product	yield, %
		85
		90
		90
		90
		90
		90

above: NMR δ 5.11 (t, 1 H, $J = 8$ Hz), 3.44 (s, 3 H), 1.69 (br s, 3 H), 1.58 (br s, 3 H), 1.50 (d, 2 H, $J = 8$ Hz), 0.11 (s, 6 H); IR (CCl_4) 1600 (C=C), 1080 cm^{-1} (SiOC). Anal. Calcd for $C_8H_{18}SiO$: C, 60.69; H, 11.46. Found: C, 60.59; H, 11.37.

***trans*-(γ-Methylallyl)dimethylmethoxysilane (6%) and *cis*-(γ-methylallyl)dimethylmethoxysilane (9%)** were obtained from the reaction of α-methylallyl methyl ether as above.

***cis*-(γ-Methylallyl)dimethylmethoxysilane**: NMR δ 5.27–5.60 (m, 2 H), 3.35 (s, 3 H), 1.52–1.78 (m, 5 H), 0.157 (s, 6 H); IR (CS_2) 1250 and 840 ($SiCH_3$), 1090 (SiOC), 1656 and 720 cm^{-1} (C=C). Anal. Calcd for $C_7H_{16}SiO$: C, 58.27; H, 11.18. Found: C, 58.06; H, 11.30.

***trans*-(γ-Methylallyl)dimethylmethoxysilane**: NMR δ 5.40–5.65 (m, 2 H), 3.35 (s, 3 H), 1.54–1.70 (m, 5 H), 0.156 (s, 6 H); IR (CS_2) 1250 and 840 ($SiCH_3$), 1085 (SiOC), 1630 and 960 cm^{-1} (C=C). Anal. Calcd for $C_7H_{16}SiO$: C, 58.27; H, 11.18. Found: C, 58.06; H, 11.30.

Reaction of Allylic Methyl Ethers with Dimethyldichlorosilane and Sodium Metal. In a dry 250-mL, three-necked, round-bottomed flask equipped with a reflux condenser, a pressure-equalizing addition funnel, and a Teflon-covered magnetic stirring bar were placed 100 mmol of allylic methyl ether, 100 mL of toluene, and sodium metal (4.6 g, 0.2 mol). Freshly distilled dimethyldichlorosilane (12.9 g, 0.1 mol) was placed in the addition funnel and was added dropwise over 1 h into the rapidly stirred, refluxing solution. The solution was refluxed overnight, cooled, and filtered to remove salts. The toluene solution was washed with 20 mL of water and dried over anhydrous sodium sulfate. Toluene was removed by fractional distillation. The high-boiling residues were analyzed by GLC (see Table I).

Reaction of Allylic Dimethylmethoxysilanes with Methyllithium. Allylic dimethylmethoxysilane (0.5 mmol) was placed in a 10-mL, round-bottomed flask equipped with a Teflon-covered magnetic stirring bar and sealed with a rubber septum. The flask was cooled to between −20 and −40 °C in an acetone/dry ice slush bath. Methyllithium (1.5 mmol; Alrich, 1.6 M solution in ether) was added to the flask via a syringe. The reaction was stirred while the temperature was maintained between −20 and −40 °C for 4 h. The reaction was quenched by addition of water. The aqueous layer was extracted with ether, and the combined organic layers were dried over anhydrous sodium sulfate. The ether solvent was removed by evaporation under reduced pressure. The residue was analyzed by GLC (see Table II for results).

(γ,γ-Dimethylallyl)trimethylsilane[7] was obtained (90%) from the reaction of (γ,γ-dimethylallyl)dimethylmethoxysilane with methyllithium as above: NMR δ 5.11 (t, 1 H, $J = 8$ Hz), 1.69 (br s, 3 H), 1.56 (br s, 3 H), 1.37 (d, 2 H, $J = 8$ Hz), −0.02 (s, 9 H); IR (CCl_4) 1260 and 860 cm^{-1} (CH_3Si); mass spectrum, m/e (relative intensity) 142 (6.7, parent; calcd for $C_8H_{18}Si$ 142.118, found 142.119), 127 (2.8, P − 15), 73 (100).

(α,α-Dimethylallyl)trimethylsilane[7] was obtained (90%) from the reaction of (α,α-dimethylallyl)dimethylmethoxysilane with methyllithium as above: NMR δ 5.93 (dd, 1 H, $J = 17$ and 11 Hz), 5.06 (dd, 1 H, $J = 17$ and 1 Hz), 4.92 (dd, 1 H, $J = 11$ and 1 Hz), 1.16 (s, 6 H), 0.08 (s, 9 H); IR (CCl_4) 1245 and 840 cm^{-1} (CH_3Si); mass spectrum, m/e (relative intensity) 142 (22.4, parent; calcd for $C_8H_{18}Si$ 142.118, found 142.118), 73 (100) (calcd for C_3H_9Si 73.047, found 73.047).

(α-Methylallyl)trimethylsilane[43] was obtained (90%) from the reaction of (α-methylallyl)dimethylmethoxysilane with methyllithium as above: NMR δ 5.91 (ddd, 1 H, $J = 18$, 9 and 7 Hz), 4.98 (d, 1 H, $J = 9$ Hz), 4.92 (d, 1 H, $J = 18$ Hz), 1.57 (dq, 1 H, $J = 7$ and 7 Hz), 1.12 (d, 3 H, $J = 7$ Hz), 0.035 (s, 9 H); IR (CCl_4) 1625 (C=C), 1250 and 830 cm^{-1} (CH_3Si).

Allyltrimethylsilane was obtained (85%) from the reaction of allyldimethylmethoxysilane with methyllithium as above.

***trans*-(γ-Methylallyl)trimethylsilane**[44] was obtained from the reaction of *trans*-(γ-methylallyl)dimethylmethoxysilane with methyllithium as above. It had spectral properties (NMR and IR) in complete agreement with those reported by Kwart.[44]

***cis*-(γ-Methylallyl)trimethylsilane** was obtained from the reaction of *cis*-(γ-methylallyl)dimethylmethoxysilane with methyllithium as above. It had spectral properties in complete agreement with those reported by Kwart.[44]

Acknowledgment. This work has been supported by the Air Force Office of Scientific Research Grant No. 80-0006.

Registry No. Allyl methyl ether, 627-40-7; α-methylallyl methyl ether, 17351-24-5; *trans*-γ-methylallyl methyl ether, 10034-14-7; α,α-dimethylallyl methyl ether, 40426-44-6; γ,γ-dimethylallyl methyl ether, 22093-99-8; dodecamethylcyclohexasilane, 4098-30-0; allyldimethylmethoxysilane, 30535-30-9; (α-methylallyl)dimethylmethoxysilane, 75732-19-3; (α,α-dimethylallyl)dimethylmethoxysilane, 75732-20-6; (γ,γ-dimethylallyl)dimethylmethoxysilane, 75732-21-7; *trans*-(γ-methylallyl)dimethylmethoxysilane, 75732-22-8; *cis*-(γ-methylallyl)dimethylmethoxysilane, 75732-23-9; dimethyldichlorosilane, 75-78-5; (γ,γ-dimethylallyl)trimethylsilane, 18293-99-7; methyllithium, 917-54-4; (α,α-dimethylallyl)trimethylsilane, 67707-64-6; (α-methylallyl)trimethylsilane, 34584-84-4; allyltrimethylsilane, 762-72-1; *trans*-(γ-methylallyl)trimethylsilane, 17486-12-3; *cis*-(γ-methylallyl)trimethylsilane, 17486-13-4.

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(43) Hosomi, A.; Shirahata, A.; Sakurai, H. *Tetrahedron Lett.* **1978**, 3043–3046.

(44) Slutsky, J.; Kwart, H. *J. Am. Chem. Soc.* **1973**, *95*, 8678–8685.