model predicts more than two bending modes in the 400–500-cm^{-1} region, which also points to the C_{3v} structure. However, the use of lack of observation of bands in structure assignments is risky, and while the C_{3v} structure is preferred for this complex, the spectra are insufficient to definitively rule a C_{2v} interaction.

$SiCl_4{\cdot}NH_3$

An adduct between $SiCl_4$ and NH_3 is not known; to date only distinct reactions have been reported.[14,15] However, under matrix-isolation conditions stabilization of an adduct would appear feasible. Moreover, $SiCl_4$ adducts are known with stronger bases such as trimethylamine.[16,30] When $SiCl_4$ was codeposited with NH_3 in argon matrices, product bands were observed when relatively high concentrations were employed. Even so, these product bands were quite weak, indicating immediately that product formation does not occur nearly as readily with $SiCl_4$ as with SiF_4. Three of these bands, at 412, 504, and 544 cm^{-1}, showed no deuterium shift, within the bandwidth of the bands, and are in the Si–Cl stretching region. Hence, these bands are assigned to Si–Cl stretching motions in the product species. The upper band, at 1289 cm^{-1}, did show a large deuterium shift inasmuch as this band disappeared when ND_3 was employed, although a deuterium counterpart was not observed. A strong deuterium shift would put this band in the 970-cm^{-1} region, which is obscured by residual NH_3. This band is probably the symmetric deformation mode of the NH_3 group in the product adduct, analogous to the 1253-cm^{-1} band in the SiF_4 experiments.

A possible alternative product would be $Si(NH_2)Cl_3$, formed through reaction and elimination of HCl. However, no HCl was detected in the final spectrum. Also, the aminochlorosilane would be expected to have three essentially equivalent chlorines, and only two distinct Si–Cl stretching modes would be anticipated, one singly and one doubly degenerate. Instead, three such modes were observed, as would be anticipated for either a C_{3v} or C_{2v} adduct. Hence, the product species is very likely the 1:1 adduct, although the dehydrochlorination product cannot be completely ruled out.

Acid/Base Chemistry

The extreme ease of formation of the 1:1 adduct between SiF_4 and NH_3 and the relative difficulty of formation of the adduct between $SiCl_4$ and NH_3 suggest either that $SiCl_4$ is a considerably weaker Lewis acid than SiF_4 or that a larger barrier to complex formation is present. There is no particular reason to anticipate a larger barrier for $SiCl_4$; indeed one might have expected a larger barrier for SiF_4 on the basis of reorganizational energies. Rather, these results seem to indicate that $SiCl_4$ is a weaker Lewis acid than SiF_4; this is consistent with the chloride compound being weaker than the fluoride compound for a number of second-row compounds, including PX_3 and PX_5.[31,32]

It is also interesting to note that no Lewis acid/base adducts have been reported between SiF_4 and oxygen-containing bases. In the present study, SiF_4 was codeposited with $(CH_3)_2O$ in several experiments, and no product was detected. Dimethyl ether is a somewhat weaker base than NH_3,[33] and hence there appears to be some minimum acidity/basicity difference needed to effect adduct formation under these conditions; BF_3, which is a stronger Lewis acid[35] than SiF_4, will form a 1:1 adduct with $(CH_3)_2O$.[34] In addition, the codeposition of Ar/SiF_4 samples with Ar/PH_3 samples at dilutions of 1/250 + 1/250 gave little, if any, product.[36] PH_3 has a proton affinity[33] nearly exactly that of $(CH_3)_2O$, supporting the notion of a minimum basicity necessary for complex formation under these conditions.

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Registry No. $SiF_4{\cdot}NH_3$, 71562-57-7; $SiCl_4{\cdot}NH_3$, 77924-85-7; SiF_4, 7783-61-1; $SiCl_4$, 10026-04-7; deuterium, 7782-39-0; ^{15}N, 14390-96-6.

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Reaction of Dimethylsilylene with Allylic Methyl Sulfides

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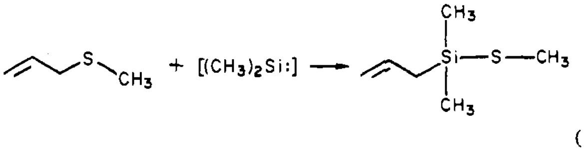
Photochemically generated dimethylsilylene reacts regiospecifically with allylic methyl sulfides to yield allylic dimethyl(methylthio)silanes.

We should like to report a novel insertion reaction of dimethylsilylene into allylic carbon–sulfur single bonds of allylic methyl sulfides.[1] For example, dimethylsilylene generated by photolysis of dodecamethylcyclohexasilane[2] in the presence of allyl methyl sulfide in cyclohexane solvent yields allyldimethyl(methylthio)silane (36%). It should be noted that in control experiments no reaction of dimethylsilylene with dialkyl sulfides such as diethyl sulfide was observed (eq 1).



(1)

The fact that dichlorocarbene and carbethoxycarbene both react with allylic methyl sulfides via initial electrophilic attack of the carbene on a lone pair of electrons of the sulfur to yield a zwitterionic intermediate which reacts further via a 2,3-

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(1) 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. 1, pp 229-277.

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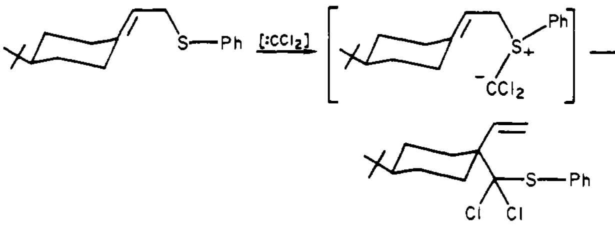
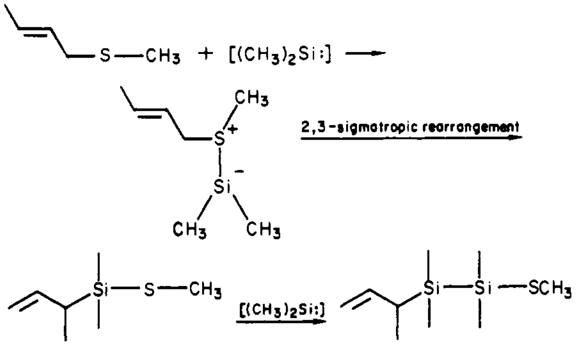
sigmatropic rearrangement to yield the product[3-6] led us to consider a similar mechanism for the reaction of dimethylsilylene with allylic methyl sulfides (see eq 2).

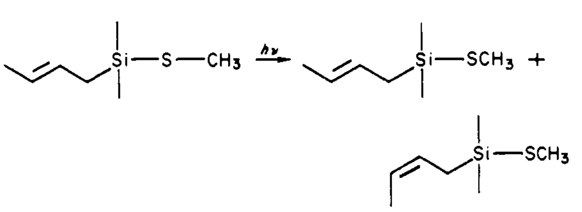


(2)

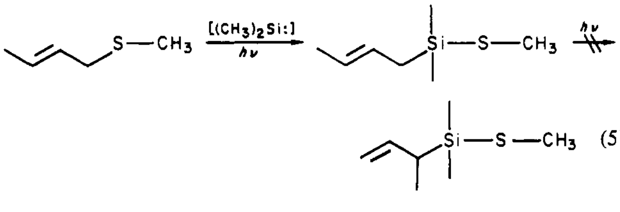
To test this mechanistic proposal, we have generated dimethylsilylene in the presence of *trans*-γ-methylallyl methyl sulfide. As predicted, (α-methylallyl)dimethyl(methylthio)silane was isolated (18%). In addition, 1-(α-methylallyl)-1,1,2,2-tetramethyl-2-(methylthio)disilane was found (25%). We believe this latter product arises by insertion of a second dimethylsilylene into the silicon–sulfur single bond of (α-methylallyl)dimethyl(methylthio)silane[7] (eq 3). Photolysis of *trans*-(γ-methylallyl)dimethyl(methylthio)silane results in isomerization to a mixture of *cis*- and *trans*-(γ-methylallyl)dimethyl(methylthio)silanes (eq 4). No (α-methylallyl)dimethyl(methylthio)silane is found in this reaction. This observation permits elimination of an alternative mechanism in which dimethylsilylene inserts directly into the allylic carbon–sulfur bond of γ-methylallyl methyl sulfide to yield (γ-methylallyl)dimethyl(methylthio)silane which then undergoes rapid photoisomerization to the (α-methylallyl)dimethyl(methylthio)silane observed (eq 5).



(3)



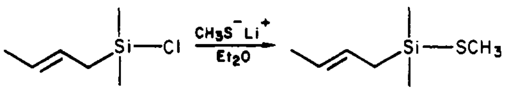
(4)



(5)

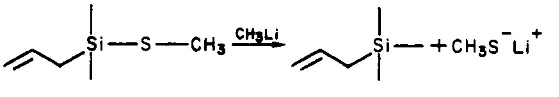
It was not possible to study the reaction of dimethylsilylene with α-methylallyl methyl sulfide due to known photoisomerization of α-methylallyl methyl sulfide to γ-methylallyl methyl sulfide.[8] Control experiments demonstrated that this is not a problem with γ-methylallyl methyl sulfide.

We have independently prepared allyldimethyl(methylthio)silane, (α-methylallyl)dimethyl(methylthio)silane, and *cis*- and *trans*-(γ-methylallyl)dimethyl(methylthio)silanes by reaction of the appropriate allylic dimethylchlorosilane with lithium methyl sulfide (eq 6). Their spectra were consistent with expectation and were in agreement with previous structural assignments.



(6)

As expected, allyldimethyl(methylthio)silane reacts with methyllithium to yield allyltrimethylsilane[9] (eq 7).



(7)

It should be noted that the reaction of dimethylsilylene with allylic methyl sulfides constitutes a new regiospecific carbon–silicon bond forming reaction. The scope and generality of this reaction is under active investigation.

Experimental Section

Silyl sulfides are extremely sensitive to hydrolysis due to both the weakness of the starting Si–S bond and the strength of the product Si–O bond. For this reason, IR spectra were run neat on KBr disks on a Perkin-Elmer 281 spectrometer. ^{1}H NMR spectra were recorded on a Varian XL-100 spectrometer operating in the FT mode with use of sealed capillaries of neat samples. Chloroform-d_1 was used for the lock signal with an internal standard of chloroform. Electron-impact mass spectra were determined on a Hewlett-Packard 5985 GC-MS system operating at an ionizing voltage of 70 eV. A 5 ft × $^1/_4$ in. 3% OV-1 on Chromosorb W 60–80 mesh column was used in the GC. UV spectra were run in dry spectroquality cyclohexane on a Beckman Acta M spectrometer. Starting materials and samples of all compounds for spectral analysis were purified by preparative vapor-phase chromatography on a Hewlett-Packard F&M 700 using a 31 ft × $^1/_4$ in. 20% SE-30 on Chromosorb W 60–80 mesh in high-nickel stainless-steel column. The injection ports of the vapor-phase chromatograph were glass lined. Extensive decomposition is observed when GLC analysis is carried out with copper columns. Yields of products were determined by GLC with decane and cyclododecane as standards. Yields are based on 1 mol of dimethylsilylene/mol of dodecamethylcyclohexasilane consumed which was found to be equal to the decamethylcyclopentasilane produced. Photolysis were run to low conversion to eliminate secondary photolysis of products. All reactions were run under an inert atmosphere of nitrogen. The starting materials are known compounds. Elemental analysis was performed by the Cal Tech Microanalytical Lab, Pasadena, CA.

Allyl Methyl Sulfide. Allyl methyl sulfide was prepared by the reaction of sodium methyl sulfide in dry methanol with allyl bromide. It was purified by fractional distillation through a 30-cm column packed with glass beads; bp 92.5 °C (lit. bp 90–93 °C).[10]

α-Methylallyl Methyl Sulfide and *trans*-γ-Methylallyl Methyl Sulfide. A mixture of α-methylallyl methyl sulfide and *trans*-γ-methylallyl methyl sulfide was prepared by the reaction of a mixture[11] of 3-bromo-1-butene (20%) and 1-bromo-2-butene (80%) with sodium methyl sulfide in methanol. The mixture of the sulfides was separated by preparative GLC. The first fraction (15%) was α-methylallyl methyl sulfide. H NMR: δ 1.30 (d, 3 H, $J = 7$ Hz), 1.96 (s, 3 H), 3.16 [d of q (quintet), 1 H, $J = 7$ Hz)], 4.93 (d, 1 H, $J = 18$ Hz), 4.98 (d, 1 H, $J = 10$ Hz), 5.63 (d of d of d, 1 H, $J = 18$, 10, and

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7 Hz). The second fraction (85%) was *trans*-γ-methylallyl methyl sulfide. H NMR: 1.64 (d, 3 H, J = 4 Hz), 1.96 (s, 3 H), 2.99 (d, 2 H, J = 6 Hz), 5.4 (br m, 2 H). NMR spectra were in agreement with literature values.[8]

Reaction of Dimethylsilylene with Allyl Methyl Sulfide. A solution of dodecamethylcyclohexasilane[12] (35 mg, 0.10 mmol) and allyl methyl sulfide (103 mg, 1.17 mmol) in dry cyclohexane (700 mg, 8.33 mmol) was placed in a 5-mm quartz NMR tube sealed with a rubber septum. The tube was irradiated in a quartz water jacket placed at the center of a circular array of 16 12-in. low-pressure mercury lamps (G. E. Germicidal, (2537 Å) for 2 h. GLC analysis of the photolyzed solution showed the formation of allyldimethyl(methylthio)silane in 36% yield. This product has the following spectral properties: NMR δ 0.30 (s, 6 H), 1.74 (d, 2 H, J = 8 Hz), 1.99 (s, 3 H), 4.88 (d, 1 H, J = 10 Hz), 4.90 (d, 1 H, J = 16 Hz), 5.8 (d of d of t, 1 H, J = 16, 10, and 8 Hz); UV λ_{max} 225 nm (ε 623); mass spectrum parent m/e 146.2 (15.5%), P − 15 131.2 (2.3%), P − 41 105.0 (100%). Anal. Calcd for $C_6H_{14}SiS$: C, 49.24; H, 9.66. Found: C, 49.15; H, 9.60.

Allyldimethylchlorosilane. A flame-dried three-neck round-bottom flask (500 mL) was fitted with a mechanical overhead stirrer, a reflux condenser, and a pressure equalizing addition funnel. Dry ethyl ether (200 mL), freshly distilled dimethyldichlorosilane (32.25 g, 0.25 mol), and magnesium metal (6 g, 0.25 mol) were placed in the flask. Dry, distilled allyl bromide (30.25 g, 0.25 mol) was added at such a rate that reflux was maintained. The mixture was refluxed for 2 h. All volatile material was then removed under high vacuum and condensed at −78 °C. Fractional distillation of the condensate through a 30-cm column packed with glass beads gave allyldimethylchlorosilane; 75% yield, bp 110–112 °C (lit. bp 111–113 °C).[13]

Independent Preparation of Allyldimethyl(methylthio)silane. Allyldimethyl(methylthio)silane was prepared by the reaction of allyldimethylchlorosilane (16.81 g, 0.12 mol) with lithium methyl sulfide (6.75 g, 0.12 mol) in dry ethyl ether (50 mL). Its spectral properties are identical with those of allyldimethyl(methylthio)silane prepared by the reaction of dimethylsilylene with allyl methyl sulfide.

Reaction of Dimethylsilylene with *trans*-γ-Methylallyl Methyl Sulfide. A solution of dodecamethylcyclohexasilane (38 mg, 0.10 mmol) and *trans*-γ-methylallyl methyl sulfide (102 mg, 1.0 mmol) in cyclohexane (685 mg, 8.15 mmol) was photolyzed as above. GLC analysis of the photolysis mixture showed the formation of (α-methylallyl)dimethyl(methylthio)silane (I) in 18% yield and 1-(α-methylallyl)-1,1,2,2-tetramethyl-2-(methylthio)disilane (II) in 25% yield.

The monosilane product (I) has the following spectral properties: NMR δ 0.24 (s, 6 H), 1.14 (d, 3 H, J = 8 Hz), 1.80 (q, 1 H, J = 8 Hz), 1.98 (s, 3 H), 4.87 (d, 1 H, J = 18 Hz), 4.91 (d, 1 H, J = 6 Hz), 6.88 (d of d of d, 1 H, J = 18, 8, and 6 Hz); IR 990 and 910 cm^{-1} (C=C); UV λ_{max} 225 nm (ε 660); mass spectrum parent m/e 160.1 (10.7%), P − 15 145.2 (32.8%), P − SCH_3 113.2 (84.1%), P − C_4H_7 105.2 (100%). Anal. Calcd for $C_7H_{16}SiS$: C, 52.47; H, 9.99 Found: C, 52.53; H, 9.97. The disilane product (II) has the following NMR spectrum: δ 0.07 (s, 6 H), 0.34 (s, 6 H), 1.1 (d, 3 H, J = 8 Hz), 1.21 [d of q (quintet), 1 H, J = 4 Hz], 1.96 (s, 3 H), 4.79 (d, 1 H, J = 18 Hz), 4.83 (d, 1 H, J = 10 Hz), 5.80 (d of d of d, J = 18, 10, and 8 Hz); UV λ_{max} 243 nm (ε 93). Anal. calcd for $C_9H_{22}Si_2S$: C, 49.51; H, 10.07. Found: C, 50.43; H, 10.06.

(α-Methylallyl)- and (γ-Methylallyl)dimethylchlorosilane. A three-neck round-bottom flask (500 mL) was fitted with an overhead stirrer, a reflux condenser, and a pressure-equalizing additional funnel. It was flame-dried. Magnesium turnings (6.0 g, 0.25 mol), 200 mL of anhydrous ethyl ether, and freshly distilled dimethyldichlorosilane (32.25 g, 0.25 mol) were placed in the flask. Redistilled-γ-methylallyl bromide (33.75 g, 0.25 mol) in dry ether (50 mL) was added slowly through the addition funnel to the vigorously stirred mixture. The reaction mixture was refluxed for 2 h. The mixture was filtered under nitrogen, and the filtrate was fractionally distilled through a 30-cm column packed with glass beads to yield a mixture of (α-methylallyl)- and (γ-methylallyl)dimethylchlorosilane; 36% yield, bp 133–135 °C (lit. bp 134 °C).[14]

Preparation of (γ-Methylallyl)dimethyl(methylthio)silane. A 300-mL three-neck round-bottom flask was fitted with an overhead mechanical stirrer, a pressure-equalizing additional funnel, and a dry ice/actone cold finger condenser. The whole apparatus was flame-dried, and 88 mL of a 1.6 M solution of butyllithium (9.0 g, 0.14 mol) in cyclohexane was syringed into the flask cooled to 0 °C. Dry cyclohexane (50 mL) was added. Methanethiol (6.72 g, 0.14 mol) was slowly added to the stirred mixture over a period of 30 min. Immediate reaction with butyllithium occurred. A white precipitate of lithium methyl sulfide formed. After completion of the addition, the reaction mixture was allowed to warm to room temperature. A mixture of (α-methylallyl)- and (γ-methylallyl)dimethylchlorosilane 20.8 g, 0.14 mol) in dry cyclohexane (30 mL) was slowly added. The reaction mixture was refluxed gently for 2 h. Fractional distillation followed by GC analysis showed three peaks corresponding to the *cis*- and *trans*-(γ-methylallyl)dimethyl(methylthio)silane and (α-methylallyl)dimethyl(methylthio)silane. The latter had spectral properties identical with (α-methylallyl)dimethyl(methylthio)silane prepared by reaction of dimethylsilylene with *trans*-γ-methylallyl methyl sulfide.

Photolysis of α-methylallyl methyl sulfide resulted in photoisomerization of the substrate to γ-methylallyl methyl sulfide. Such photoisomerization of α-methylallyl methyl sulfide has been previously reported.[8]

***trans*-(γ-Methylallyl)dimethyl(methylthio)silane**: NMR δ 0.26 (s, 6 H), 1.62 (d, 5 H, J = 4 Hz), 1.96 (s, 3 H), 5.36 (br m, 2 H); IR 960 cm^{-1} (C=C); mass spectrum parent m/e 160.2 (14.5%), P − C_4H_7 105 (100%). Anal. Calcd for $C_7H_{16}SiS$: C, 52.47; H, 9.99. Found: C, 52.53, H, 9.97.

***cis*-(γ-Methylallyl)dimethyl(methylthnio)silane**: NMR δ 0.28 (s, 6 H), 1.57 (d, 3 H, J = 4 Hz), 1.72 (d, 2 H, J = 6 Hz), 1.98 (s, 3 H), 5.42 (br m, 2 H); IR 675 cm^{-1} (C=C); mass spectrum parent m/e 160.2 (12.2%), P − 15 145 (1%), P − C_4H_7 105 (100%). Anal. Calcd for $C_7H_{15}SiS$: C, 52.47, H, 9.99. Found: C, 52.53; H, 9.97.

Photolysis of *trans*-(γ-Methylallyl)dimethyl(methylthio)silane. A solution of *trans*-(γ-methylallyl)dimethyl(methylthio)silane (14.8 mg, 925 × 10^{-2} mmol) in dry cyclohexane (99 mg, 1.18 mmol) was placed in a 5-mm quartz NMR tube sealed with a rubber septum. The tube was photolyzed in a quartz water jacket placed at the center of a circular array of 16 12-in. low-pressure mercury lamps (2537 Å) for 2 h. GLC chromatography showed that the starting material has isomerized to a mixture of *cis*-(γ-methylallyl)dimethyl(methylthio)silane (29%) and *trans*-(γ-methylallyl)dimethyl(methylthio)silane (71%).

Reaction of Allyldimethyl(methylthio)silane with Methyllithium. Dodecamethylcyclohexasilane (35.7 mg, 0.10 mmol), allyl methyl sulfide (103 mg, 0.29 mmol), and dry cyclohexane (680 mg, 8.09 mmol) were placed in a 5-mm quartz NMR tube. After photolysis of the mixture for 2 h, a solution of methyllithium in ether (18 mL) was introduced into the NMR tube. GLC analysis showed the formation of allyltrimethylsilane whose spectral properties were identical with an authentic sample.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research (Grant No. AFOSR 80-0006).

Registry No. I, 77846-34-5; II, 77846-35-6; allyldimethyl(methylthio)silane, 77846-36-7; (α-methylallyl)dimethylchlorosilane, 77846-37-8; (γ-methylallyl)dimethylchlorosilane, 29310-15-4; *cis*-(γ-methylallyl)dimethyl(methylthio)silane, 77846-38-9; *trans*-(γ-methylallyl)dimethyl(methylthio)silane, 77846-39-0; allyldimethylchlorosilane, 4028-23-3; α-methylallyl methyl sulfide, 4088-56-6; *trans*-γ-methylallyl methyl sulfide, 4088-54-4; dimethyldichlorosilane, 75-78-5; dodecamethylcyclohexasilane, 4098-30-0; allyl methyl sulfide, 10152-76-8; allyl bromide, 106-95-6; lithium methyl sulfide, 35638-70-1; γ-methylallyl bromide, 4784-77-4; methanethiol, 74-93-1; methyllithium, 917-54-4; allyltrimethylsilane, 762-72-1.

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