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INSERTION REACTIONS OF DIMETHYLSILYLENE INTO SILICON—SULFUR AND SULFUR—SULFUR SINGLE BONDS

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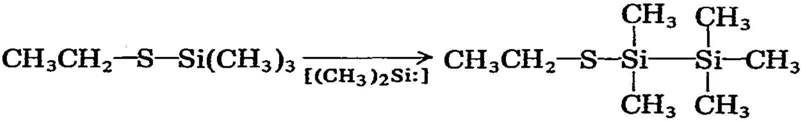
Summary

Dimethylsilylene inserts into silicon—sulfur single bonds of alkyl trimethylsilyl sulfides $R—S—Si(CH_3)_3$ and into silicon—sulfur single bonds of hexamethyldisilthiane $(CH_3)_3Si—S—Si(CH_3)_3$ to yield alkyl pentamethyldisilyl sulfides and pentamethyldisilyl trimethylsilyl sulfide, respectively. Dimethylsilylene also inserts into sulfur—sulfur single bonds of dialkyl disulfides to yield bis(alkylmercapto)dimethylsilanes.

While a number of reactions of dimethylsilylene with oxygen containing substrates are known [1—15] virtually no work has been reported on reactions of dimethylsilylene with sulfur containing substrates [16]. We should like to report our results on the reactions of dimethylsilylene with three types of sulfur-containing functional groups.

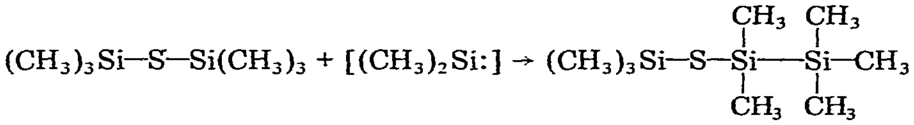
We find that dimethylsilylene, generated by photolysis of dodecamethylcyclohexasilane [17], will insert into Si—S single bonds of methyl trimethylsilyl sulfide and ethyl trimethylsilyl sulfide to yield respectively methyl pentamethyldisilyl sulfide and ethyl pentamethyldisilyl sulfide. This reactions is analogous to the well known insertion reaction of dimethylsilylene into Si—O single bonds of alkoxysilanes to yield alkoxydisilanes [1—4].



$$CH_3CH_2—S—Si(CH_3)_3 \xrightarrow[{[(CH_3)_2Si:]}]{} CH_3CH_2—S—\underset{CH_3}{\overset{CH_3}{Si}}—\underset{CH_3}{\overset{CH_3}{Si}}—CH_3$$

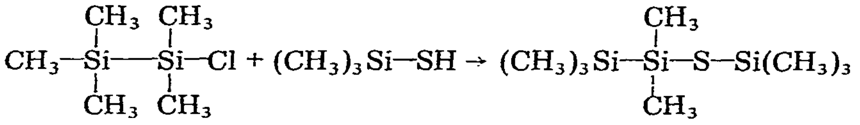
While the insertion of dimethylsilylene into Si—O single bonds of alkoxysilanes is a general reaction, the insertion of dimethylsilylene into Si—O—Si single bonds of siloxanes is limited to angle-strained siloxanes [5,6]. We have previously reported that dimethylsilylene will insert into the angle strained

Si—S single bond of tetramethyldisilthiane to yield 1,2,4-trisila-3,5-dithiacyclopentane [16]. Recently, we have observed that dimethylsilylene will insert into the unstrained Si—S single bond of hexamethyldisilthiane to yield pentamethyldisilyl trimethylsilyl sulfide. Thus the insertion of dimethylsilylene into Si—S bonds of disilthianes is more general than the analogous insertion to dimethylsilylene into Si—O single bonds of siloxanes [6].



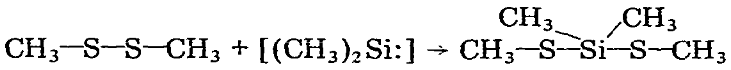
$$(CH_3)_3Si{-}S{-}Si(CH_3)_3 + [(CH_3)_2Si:] \rightarrow (CH_3)_3Si{-}S{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}CH_3$$

We have also prepared pentamethyldisilyl trimethylsilyl sulfide by reaction of pentamethylchlorodisilane with trimethylsilanethiol in the presence of pyridine.

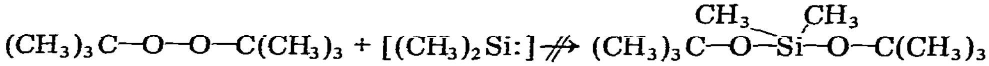


$$CH_3{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}Cl + (CH_3)_3Si{-}SH \rightarrow (CH_3)_3Si{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}S{-}Si(CH_3)_3$$

Finally, we would like to report the insertion of dimethylsilylene into the S—S single bonds of dialkyl disulfides. Specifically dimethylsilylene reacts with dimethyl disulfide and diethyl disulfide to yield respectively bis(methylmercapto)dimethylsilane and bis(ethylmercapto)dimethylsilane. For comparison, dimethylsilylene does not insert into the O—O single bond of di-t-butyl peroxide [18]. An analogous insertion reaction of dimethylstannalylenes into the S—S single bond of disulfides has been observed [19].



$$CH_3{-}S{-}S{-}CH_3 + [(CH_3)_2Si:] \rightarrow CH_3{-}S{-}\overset{CH_3\ \ CH_3}{Si}{-}S{-}CH_3$$



$$(CH_3)_3C{-}O{-}O{-}C(CH_3)_3 + [(CH_3)_2Si:] \not\rightarrow (CH_3)_3C{-}O{-}\overset{CH_3\ \ CH_3}{Si}{-}O{-}C(CH_3)_3$$

The observation that the reactions of dimethylsilylene with sulfur containing functionalities are more facile than with comparable oxygen functionalities is surprising since the Si—S single bond energy (70 kcal/mol) is much lower than the Si—O single bond energy (108 kcal/mol) [20,21]. This unexpected reactivity pattern may be a reflection of the "soft" electrophilic character of dimethylsilylene [22].

Experimental

Silyl sulfides are extremely sensitive compounds 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 solution IR spectra are not reported since we have found no procedure which permits the rigorous removal of water from solution IR cells. ^1H NMR spectra were recorded on a Varian XL-100 spectrometer operating in the FT mode using sealed capillaries of neat samples. Chloroform-d_1 was used for the lock signal with an external standard of chloroform. Electron impact mass spectra were determined on a DuPont 21-492 or MS-9 mass spectrometer operating at an ionizing voltage of 70 eV. 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 E&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 n-decane and cyclooctane as standards. Yields are based on 1 mol of dimethylsilylene per mol of dodecamethylcyclohexasilane. Photolysis were run to low conversion to eliminate secondary photolysis of products. All reactions were run under an inert atmosphere of nitrogen. Many of the starting materials and products are known compounds. In these cases where spectral data have not been previously reported we have included this information. Unknown compounds have been prepared by alternative methods to verify their structures. Elemental analysis were performed by the Caltech Microanalytical Laboratory, Pasadena, Calif. (C) or by Galbraith Laboratories, Knoxville, Tenn. (T).

Dimethyl disulfide was obtained from Aldrich. It was redistilled prior to use b.p. 110°C (lit. [23] b.p. 110°C).

Diethyl disulfide was prepared by reaction of ethyl bromide with sodium disulfide in liquid ammonia [24]. It was purified by fractional distillation through a 15 cm Vigreux column b.p. 70°C/30 mmHg (lit. [24] 45°C/14 mmHg).

Methyl trimethylsilyl sulfide was prepared by reaction of methylthiomagnesium iodide with trimethylchlorosilane in ether. It was purified by fractional distillation through a 15 cm Vigreux column b.p. 110°C (lit. [25] b.p. 110—111°C).

Ethyl trimethylsilyl sulfide was prepared by reaction of the dry lead(II) salt of ethane thiol with trimethylchlorosilane [26]. It was purified by fractional distillation b.p. 130°C (lit. [26] b.p. 130°C).

Hexamethyldisilthiane was prepared by reaction of hydrogen sulfide, pyridine and trimethylchlorosilane [27]. It was purified by fractional distillation b.p. 162°C (lit. [17] b.p. 162°C).

Reaction of dimethylsilylene with methyl trimethylsilyl sulfide

A solution of dodecamethylcyclohexasilane [28,29] (33 mg, 9.5×10^{-2} mmol) and methyl trimethylsilyl sulfide (115 mg, 0.96 mmol) in spectroquality cyclohexane (750 mg, 8.9 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 sixteen-12 in G.E. Germicidal lamps (2537 Å) for 2 h. GLC analysis of the photolysis solution showed the formation of methyl pentamethyldisilyl sulfide (16%).

Methyl pentamethyldisilyl sulfide [30] had the following spectral properties: NMR: δ 1.76 (s, 3 H), 0.14 (s, 6 H), −0.04 (s, 9 H). Mass spectrum: parent m/e = 178 (3%) (found 178.069, $C_6H_{18}Si_2S$ calcd. 178.067), $P - 15$ 163 (50.0%), $P - 73$ 105 (12.2%), 73 (100%). UV: λ_{max} 243 nm, ϵ 1036.

Reaction of dimethylsilylene with ethyl trimethylsilyl sulfide

A solution of dodecamethylcyclohexasilane (32 mg, 9.2×10^{-2} mmol) and ethyl trimethylsilyl sulfide (160 mg, 1.2 mmol) in cyclohexane (700 mg, 8.3 mmol) was photolyzed as above. GLC analysis showed the formation of ethyl pentamethyldisilyl sulfide (38%).

Ethyl pentamethyldisilyl sulfide had the following properties. NMR: δ 2.5 (q, 2 H, J 8 Hz), 1.26 (t, 3 H, J 8 Hz), 0.3 (s, 6 H), 0.1 (s, 9 H). Mass spectrum: parent $m/e = 192$ (1.8%) (found 192.083, $C_7H_{20}Si_2S$ calcd. 192.082), $P -$ 15 177 (9%), $P -$ 29 163 (73%) (found 163.044, $C_5H_{15}Si_2S$ calcd. 163.043), 73 (100%). UV: λ_{max} 240 nm, ϵ 740. Found (C): C, 43.46; H, 10.33. $C_7H_{20}Si_2S$ calcd.: C, 43.72; H, 10.40%.

Ethyl pentamethyldisilyl sulfide

n-Butyllithium (31 ml, 1.6 *M* 0.05 mol) in cyclohexane was placed in a flame dried three-neck round bottom flask (300 ml) equipped with an overhead mechanical stirrer, a reflux condenser, and a pressure equalizing addition funnel. Dry cyclohexane (100 ml) was added. The reaction mixture was cooled to 0° C. Ethanethiol (3.10 g, 0.05 mol) in cyclohexane (10 ml) was added dropwise to the stirred solution. A white precipitate, lithium ethyl sulfide, formed immediately. After 0.5 h, pentamethylchlorodisilane [31] (8.33 g, 0.05 mol) in 20 ml of cyclohexane was added and the reaction mixture refluxed overnight. Lithium chloride was removed by filtration and the filtrate distilled under vacuum. The fraction boiling between 45—65° C/4.5 mmHg was analyzed by GLC. Ethyl pentamethyldisilyl sulfide was obtained in 37% yield. Its spectral properties were identical to those of the ethyl pentamethyldisilyl sulfide prepared by reaction of dimethylsilylene with ethyl trimethylsilyl sulfide above.

Reaction of dimethylsilylene with dimethyl disulfide

A solution of dodecamethylcyclohexasilane (33 mg, 9.5×10^{-2} mmol) and dimethyl disulfide (91.5 mg, 9.7×10^{-1} mmol) in cyclohexane (690 mg, 8.2 mmol) was photolyzed as above. GLC analysis showed the formation of bis(methylmercapto)dimethylsilane in 81% yield. Bis(methylmercapto)dimethylsilane [25]. NMR 2.63 (s, 6H), 0.51 (s, 6H). UV λ_{max} 224 nm, ϵ 17.23.

Reaction of dimethylsilylene with diethyl disulfide

A solution of dodecamethylcyclohexasilane (33 mg, 9.5×10^{-2} mmol) and diethyl disulfide (106 mg, 8.7×10^{-1} mmol) in cyclohexane (688 mg, 8.2 mmol) were photolyzed as above. GLC analysis showed the formation of bis(ethylmercapto)dimethylsilane in 97% yield.

Bis(ethylmercapto)dimethylsilane had the following spectral properties: NMR: 2.58 (q, 4 H, J 8 Hz), 1.28 (t, 6 H, J 8 Hz), 0.5 (s, 6 H). Mass spectrum parent $m/e = 180$ (54%) (found 180.048, $C_6H_{16}SiS_2$ calcd. 180.046) $P -$ 15 165 (36%), $P -$ 28 152 (29%), $P -$ 29 151 (15%), $P -$ 61 119 (100%), 91 (58%). UV: λ_{max} 223 nm, ϵ 3607. Found (C): C, 39.58; H, 8.75. $C_6H_{16}SiS_2$ calcd.: C, 39.96; H, 8.96%.

Bis(ethylmercapto)dimethylsilane

A flame dried three neck round bottom flask (300 ml) equipped with a pressure equalizing additional funnel, a reflux condenser, a rubber septum and a Teflon covered magnetic stirring bar was charged with ethanethiol (24 g, 0.40

mol), pyridine (63 g, 0.80 mol), and toluene (150 g, 1.63 mol). The solution was cooled to 0°C. To the vigorously stirred mixture was added freshly distilled dimethyldichlorosilane (26 g, 0.20 mol). The solution was stirred overnight at room temperature. Pyridinium hydrochloride was removed by filtration. The filtrate was fractionally distilled under nitrogen through a 30 cm column packed with glass beads to remove the starting materials and the solvent. GLC analysis of the residue gave bis(ethylmercapto)dimethylsilane (13.68 g, 0.07 mol, 38%) whose spectral properties were identical to those of the bis(ethylmercapto)dimethylsilane prepared by the reaction of dimethylsilylene with diethyl disulfide.

Reaction of dimethylsilylene with hexamethyldisilthiane

A solution of dodecamethylcyclohexasilane (33.6 mg, 9.65×10^{-2} mmol) and hexamethyldisilthiane (168.8 mg, 9.5×10^{-1} mmol) in cyclohexane (650 mg, 7.7 mmol) was photolyzed as above. GLC analysis showed the formation of pentamethyldisilyl trimethylsilyl sulfide (21%).

Pentamethyldisilyl trimethylsilyl sulfide had the following properties: NMR: δ 0.12 (s, 6 H), 0.08 (s, 9 H), −0.14 (s, 9 H). UV: λ_{max} 233 nm ϵ 2809. Mass spectrum: parent m/e 236 (25%) (found 239.091, $C_8H_{24}Si_3S$ calcd. 236.091), $P - 15$ 221 (20.5%), (found 221.067, $C_7H_{21}Si_3S$ calcd. 221.067), $P - 73$ 163 (74.7%) (found 163.044, $C_5H_{15}Si_2S$ calcd. 163.043), 73 (100%). Anal. $C_8H_{24}Si_3S$ calcd.: C, 40.39; H, 10.17. Found (T): C, 40.49; H, 10.25%.

Trimethylsilanethiol

A three neck round bottom flask (500 ml) was equipped with an overhead stirrer, a dry ice/acetone cold finger condenser, and a rubber septum. The whole apparatus was flame dried and flushed with nitrogen. Methyllithium (180 ml, 1.4 *M*, 0.25 mol) in ether and 150 ml of dry ether were placed in the flask. Hydrogen sulfide (8.5 g, 0.25 mol) was bubbled through the solution which was cooled to 0°C. Immediate deposition of a white precipitate, lithium hydrogen sulfide, occurred. The reaction mixture was warmed to room temperature. Trimethylchlorosilane (18 g, 0.165 mol) in ether (30 ml) was added slowly through the addition funnel to the vigorously stirred mixture. Volatile materials was removed under high vacuum and condensed at −178°C. The condensate was distilled through a 30 cm column packed with glass beads to yield trimethylsilanethiol in 35% yield, b.p. 78—82°C, lit. [32] b.p. 75—76°C).

Pentamethyldisilyl trimethylsilyl sulfide

A dry centrifuge tube was fitted with a rubber septum. Ether (1 ml), triethylamine (40.4 mg; 0.20 mmol), pentamethylchlorodisilane [31] (16.6 mg, 0.10 mmol) and trimethylsilanethiol (10.6 mg, 0.1 mmol) were syringed into the tube. The mixture was shaken for 5 min. A white precipitate deposited on the bottom of the tube. The mixture was centifuged and the upper liquid layer was analyzed by GLC. Pentamethyldisilyl trimethylsilyl-sulfide was obtained in 28% yield. Its spectral properties are identical to those of the pentamethyldisilyl trimethylsilyl sulfide prepared by the reaction of dimethylsilylene and hexamethyldisilthiane as above.

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