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A CONVENIENT SYNTHESIS OF 1,2-DIMETHYLTETRAMETHOXYDISILANE

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Summary

Photolysis of methyldimethoxysilane in the gas phase yields 1,2-dimethyltetramethoxydisilane. The mass spectrum of 1,2-dimethyltetramethoxydisilane is discussed.

Results and discussion

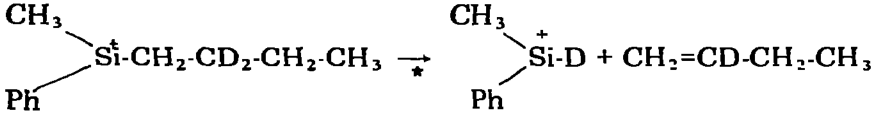
1,2-Dimethyltetramethoxydisilane is a most useful compound since it has been shown to undergo an α-elimination reaction at 200° to yield trimethoxymethylsilane and methoxymethylsilylene [1-5]. However, despite recent interest in functionalized silylenes [6, 7] no convenient laboratory synthesis of this efficient silylene precursor has been reported.

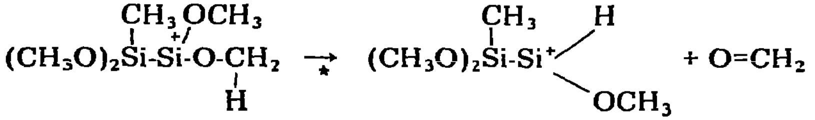
Preparation of this compound has been based on the reaction of 1,2-dimethyltetrachlorodisilane with methanol [8, 9]. However, 1,2-dimethyltetrachlorodisilane itself is not readily available, being only a by-product of the direct synthesis of methylchlorosilanes from the reaction of methyl chloride with copper silicon [9, 10]. A laboratory synthesis has been reported which is based on the electrophilic cleavage of carbon—silicon bonds of hexamethyldisilane [10, 11]. Thus hexamethyldisilane reacts with a mixture of acetyl chloride and aluminum chloride to yield acetone and 1,2-dimethyltetrachlorosilane [12]. While this procedure will work given patience, it has not been described in full experimental detail.

We should like to report a convenient laboratory synthesis of 1,2-dimethyltetramethoxydisilane starting from readily available, inexpensive reagents. Reaction of methyldichlorosilane with trimethyl orthoformate yields dimethoxymethylsilane [13, 14]. Photolysis of methyldimethoxysilane in the gas phase using 2537 Å light in the presence of a trace of mercury yields hydrogen and 1,2-dimethyltetramethoxydisilane. This reaction is related to the mercury-sensitized photolysis of methylsilanes reported almost ten years ago [15,16]. It is quite efficient, since 25 g of dimethoxymethylsilane is converted to 20.5 g of 1,2-dimethyltetramethoxydisilane after eight hours of photolysis in a Rayonet type reactor. However, the rate of this photochemical reaction is quite dependent on the purity of the methyldimethoxysilane. Even small amounts of methyl formate appreciably inhibit the reaction.

$$(CH_3O)_2CH_3Si{-}H \xrightarrow[Hg]{h\nu} (CH_3O)_2CH_3Si{-}SiCH_3(OCH_3)_2 + H_2$$

The mass spectrum of 1,2-dimethyltetramethoxydisilane is quite interesting. The parent ion at m/e 210 undergoes simple fragmentation in all of the three possible ways: loss of a methyl group yields the $P - CH_3$ ion at m/e 195; loss of a methoxy group yields the m/e 179 ion, while cleavage of the Si—Si bond yields the methyldimethoxysiliconium ion at m/e 105. The intensities of these ions vary inversely with the strength of the Si—X bond being broken. Thus the Si—Si bond is weakest, while the m/e 105 ion is relatively the most intense. However, this correlation may be due to other factors. Two series of ions are formed by further fragmentation of the $P - CH_3$ and the $P - OCH_3$ ions. These daughter ions are formed by loss of formadehyde. This process is probably related to the specific transfer of a β hydrogen from carbon to the silyl center of the methylphenylbutyl-2,2-d_2-siliconium ion with loss of butene-d_1 reported by Kinstle [16]. The mass spectral fragmentation pattern of 1,2-dimethyltetramethoxydisilane is outlined in Scheme 1 (see Table 1 for supporting data).





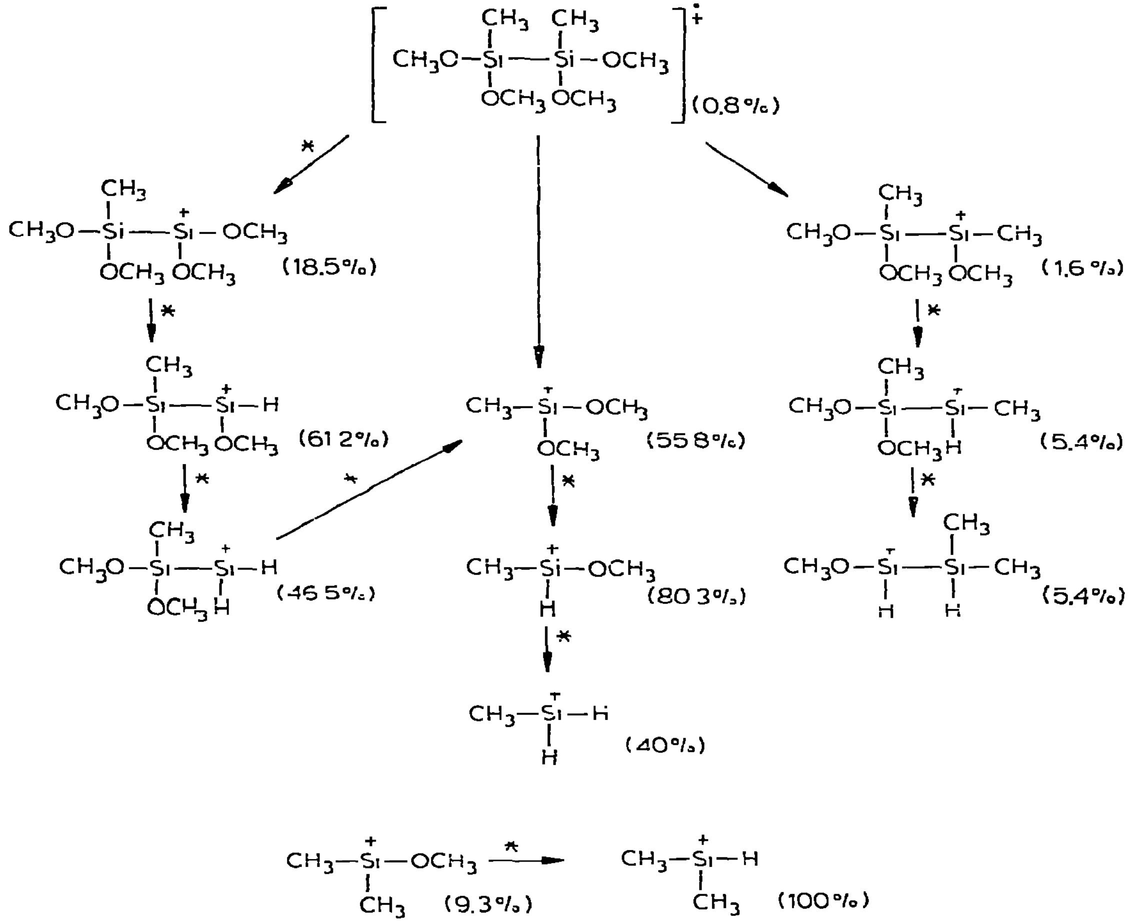
Experimental

Infrared spectra were obtained on a Perkin—Elmer 337 spectrometer and were calibrated against known bands in a polystyrene film. NMR spectra were recorded on a Varian HA-100 spectrometer with methylene chloride (δ 5.28 ppm) as internal standard. Mass spectra were obtained on a Hitachi—Perkin—Elmer RMU-6E spectrometer. Conditions used: source temperature 150°; liquid inlet 60°; ionizing voltage 70eV; filament emission 70 μA; target current 50 μA. Vapor phase chromatography was carried out on a Hewlett Packard F & M 700.

Methyldimethoxysilane

In a dry 3-neck 1 l flask equipped with a reflux condenser, an addition funnel, and a magnetic stirring bar was placed 232 g (2.2 mol) of trimethyl orthoformate. Methyldichlorosilane 115 g (1 mol) was placed in the addition funnel and was added dropwise to the reaction flask. After the addition was

SCHEME 1. MASS SPECTRAL FRAGMENTATION PATTERN OF 1,2-DIMETHYLTETRAMETHOXYDISILANE



complete, the solution was stirred overnight at room temperature, then fractionally distilled through a vacuum jacketed 25 cm spiral wire column. The following fractions were collected: methyl formate b.p. 34°, 100 g (1.8 mol); methyldimethoxysilane b.p. 61° [14], 70 g (0.61 mol) 61% yield; and trimethyl orthoformate b.p. 98-100°, 15 g (0.13 mol). The spectral properties of methyldimethoxysilane were in agreement with literature values [14].
IR: Si—H 2250 and 2210, Si—CH_3 1265, Si—OCH_3 1090 cm^{-1}. NMR: δ 0.04 (d, 3H, J 2 Hz), 3.38 (s, 6H), 4.39 (q, 1H, J 2 Hz).

1,2-Dimethyltetramethoxydisilane

In a dry 500 ml cylindrical (O.D. 5 cm, length 45 cm) quartz flask connected to a reflux condenser was placed 25 g (0.23 mol) methyldimethoxysilane, a drop of mercury, and a few boiling chips. The flask was placed at the center of a circular array of sixteen 12" G.E. Germicidal lamps (2537 Å). The bottom of the flask was heated using a heating mantle. The refluxing vapor was photolyz-

TABLE 1

MASS SPECTRA OF TETRAMETHOXYDIMETHYLDISILANE AT 70eV

m/e	Rel. int. (%)	*m/e*	Rel. int. (%)
41	0.8	105	55.8
42	1.9	106	4.9
43	18.5	107	2.4
44	1.4	119	5.4
45	40.0	120	0.8
46	2.7	121	3.0
47	3.8	133	3.0
58	3.8	135	46.5
59	100.0	136	6.3
60	11.1	137	3.8
61	13.6	149	5.4
62	1.1	150	0.8
73	0.8	151	1.1
74	6.3	165	61.2
75	80.3	166	9.3
76	5.7	167	5.2
77	3.8	179	1.6
87	0.8	181	0.8
89	9.3	195	18.5
90	4.4	196	3.0
91	6.8	197	1.6
103	4.9	210	0.8
104	1.4		

ed for eight hours under an inert atmosphere of purified nitrogen. The pot temperature was kept below 150°. At the end of this time, the solution was decanted from the mercury. It weighed 20.5 (81% yield). Analysis by GLC on a 1/4" X 18" 20% SE-30 on Chromosorb P column at 100° indicated that the solution was at least 95% pure 1,2-dimethyltetramethoxydisilane. The spectral properties of 1,2-dimethyltetramethoxydisilane were in agreement with literature values [8]. IR: Si—OCH_3 1090, Si—CH_3 1248 cm^{-1}. NMR: δ 0.15 (s, 6H), 3.46, (s, 12H).

Acknowledgement

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