

INSERTION OF DIMETHYLSILYLENE INTO O—H AND N—H SINGLE BONDS

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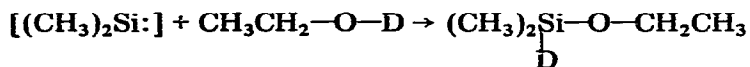
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Summary

Dimethylsilylene, generated by photolysis of dodecamethylcyclohexasilane, inserts efficiently into O—H single bonds of alcohols to yield alkoxydimethylsilanes. Use of ethanol-O-*d*₁ yields ethoxydimethylsilane-Si-*d*₁. Dimethylsilylene also inserts into O—H single bonds of water or D₂O to yield respectively tetramethyldisiloxane or tetramethyldisiloxane-Si₂-*d*₂. Dimethylsilylene also inserts into N—H bonds of primary and secondary amines to yield aminodimethylsilanes. This reaction provides an efficient route to difunctional silanes.

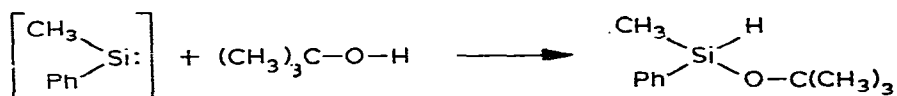
Insertion reactions of dimethylsilylene into silicon—hydrogen single bonds [1,2], and into silicon—oxygen single bonds of alkoxysilanes [3,4] and strained cyclic siloxanes [5,6] have been previously reported. We should like to report insertion reactions of dimethylsilylene into both O—H and N—H single bonds which provide efficient methods to generate difunctional organosilanes.

Dimethylsilylene generated by photolysis of dodecamethylcyclohexasilane [4] in a solution of ether and ethanol yields ethoxydimethylsilane (87%) [7]. Yields are reported based on the generation of two dimethylsilylenes for each dodecamethylcyclohexasilane which is the limiting reagent. Similar reaction of dimethylsilylene with ethanol-O-*d*₁ yields ethoxydimethylsilane-Si-*d*₁ (84%). We believe this procedure, which does not involve reduction with lithium aluminum deuteride, may provide the most efficient and economical route to functional deuterium labelled silanes.



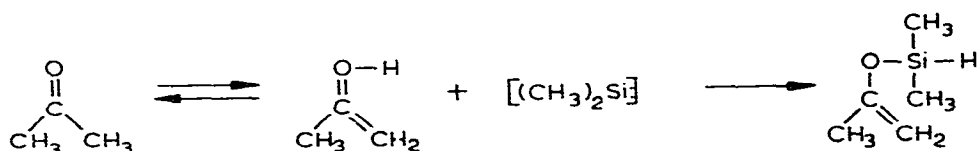
Similar reactions of dimethylsilylene with methanol and t-butanol yield methoxydimethylsilane (89%) [8] and t-butoxydimethylsilane (85%) [9] respectively. Likewise, methylphenylsilylene generated by photolysis of octamethyl-2,3-diphenyltetrasilane [10,11] in a solution of ether and t-butanol

yields *t*-butoxymethylphenylsilane (77%).



It should be noted that dimethoxysilylene has been reported to insert into the O—H bond of methanol to yield trimethoxysilane although no experimental details have been reported [12]. On the other hand, the reaction of difluorosilylene with methanol did not yield the expected adduct, methoxydifluorosilane, although it was proposed as an intermediate involved in the formation of dimethoxydifluorosilane, a minor product of this reaction [13].

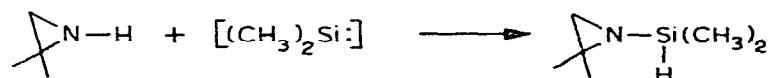
The observation that dimethylsilylene reacts with enolizable ketones to yield dimethylsilyl enol ethers may result from efficient trapping of the enol tautomer by insertion of dimethylsilylene into the O—H single bond [14].



Dimethylsilylene also inserts into the O—H single bonds of water to yield tetramethyldisiloxane (85%). The reaction is carried out by photolysis of a solution of dodecamethylcyclohexasilane in ether saturated with water. The efficiency of this reaction makes it imperative that anhydrous conditions be rigorously maintained if reaction of dimethylsilylene with other substrates are to be successful. If water is replaced by D₂O, tetramethyldisiloxane-Si₂-d₂ is produced (82%). Analogous reaction of difluorosilylene with water to yield tetrafluorodisiloxane has been previously observed [15].



Likewise, dimethylsilylene inserts into N—H single bonds of secondary amines, such as diethylamine and 2,2-dimethylaziridine [16] to yield respectively *N,N*-diethylaminodimethylsilane (81%) [17] and 2,2-dimethylaziridinodimethylsilane (85%). No insertion of the dimethylsilylene into the strained carbon–nitrogen single bonds of 2,2-dimethylaziridine was observed.



The insertion of dimethylsilylene into one of the primary N—H single bonds of *t*-butylamine yields *N*-*t*-butylaminodimethylsilane (86%) [18].

On the other hand, photolysis (2537 Å) of an ether solution of dodecamethylcyclohexasilane and *n*-propanethiol did not yield any *n*-propylthiodimethylsilane, the expected product of insertion of dimethylsilylene into the S—H single bond of *n*-propanethiol.

Experimental

IR spectra were determined as CCl_4 solutions on a Perkin-Elmer 281 spectrometer. NMR spectra were recorded on a Varian XL-100 spectrometer using 5% solutions in CDCl_3 with an internal standard of chloroform. Mass spectra were determined on a duPont 21-492 at an ionizing voltage of 70 eV. UV spectra were run on a Beckman Acta M spectrometer. Samples of all compounds for spectra analysis were purified by preparative vapor phase chromatography on a Hewlett Packard F & M 700. Yields of products were determined by GLPC with cyclooctane added as an internal standard. Yields are based on two moles of dimethylsilylene per mole of dodecamethylcyclohexasilane.

All of the starting materials and most of the products are known compounds. They have 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.

Ether and tetrahydrofuran were purified by distillation from a solution of sodium benzophenone ketyl immediately prior to use.

Diethylamine and *t*-butylamine were distilled from potassium hydroxide pellets immediately prior to use.

2,2-Dimethylaziridine was prepared from 2-amino-2-methyl-1-propanol by the method of Meyers [16].

Absolute ethanol was used without further purification. Methanol and ethanol-*O-d*, [19] were refluxed over calcium oxide and were distilled immediately prior to use. *t*-Butanol was refluxed over calcium hydride and was distilled immediately prior to use. Deuterium oxide (D_2O) (Merck, Sharp and Dohme of Canada) was used without further purification.

Dodecamethylcyclohexasilane was prepared by the reaction of dimethyldichlorosilane and excess lithium metal in tetrahydrofuran [19,20].

Octamethyl-2,3-diphenyltetrasilane was prepared by the reaction of trimethylchlorosilane and methylphenyldichlorosilane with lithium metal in tetrahydrofuran [11].

Photolysis of dodecamethylcyclohexasilane in 2,2-dimethylaziridine

The following is a typical procedure. A solution of dodecamethylcyclohexasilane (105 mg, 0.3 mmol) in 2,2-dimethylaziridine (1.42 g, 20 mmol) was placed in a quartz NMR tube. The solution was deoxygenated by bubbling purified nitrogen through it for 10 min prior to irradiation with a 450 W medium pressure Hanovia Hg lamp for 90 min at 5°C in an ice/water bath. GLPC analysis of the resulting colorless solution on a $1/4" \times 7'$ 20% SE-30 on Chromosorb W 60/80 mesh column indicated 85% yield of 2,2-dimethylaziridinodimethylsilane. It had the following spectral properties. IR: $\nu(\text{Si-H})$, 2060 cm^{-1} . NMR δ (ppm): 4.27 (sept, 1 H, J 3 Hz), 1.65 (s, 2 H), 1.24 (s, 6 H), 0.19 (d, 6 H, J 3 Hz). Mass spectrum: Parent (m/e) = 129 (54%), found: 129.097; $\text{C}_6\text{H}_{15}\text{NSi}$ calcd. 129.097; $P-1(m/e)$ = 128 (78%), $P-15(m/e)$ = 114 (100%).

Photolysis of dodecamethylcyclohexasilane in diethylamine

The reaction was carried out as above to yield *N,N*-diethylaminodimethylsilane [17] (81%). It had the following spectral properties. IR: $\nu(\text{Si-H})$, 2120

cm^{-1} . NMR, δ (ppm): 4.27 (sept., 1 H, J 3 Hz), 2.79 (q, 4 H, J 7 Hz), 0.97 (t, 6 H, J 7 Hz), 0.095 (d, 6 H, J 3 Hz). Mass spectrum: Parent(m/e) = 131 (20%), $P - 1(m/e)$ = 130 (8%), $P - 15(m/e)$ = 116 (100%).

*Photolysis of dodecamethylcyclohexasilane in *t*-butylamine*

The reaction was carried out as above to yield *N*-*t*-butylaminodimethylsilane [18] (86%). It had the following spectral properties. IR: $\nu(\text{N-H})$, 3395 cm^{-1} , $\nu(\text{Si-H})$, 2110 cm^{-1} . NMR, δ (ppm): 4.49 (d sept., 1 H, J 2.75 and 3 Hz), 1.11 (s, 9 H), 0.097 (d, 6 H, J 3 Hz). Mass spectrum: Parent(m/e) = 131 (21%), $P - 15(m/e)$ = 116 (100%).

Photolysis of dodecamethylcyclohexasilane with water.

Dodecamethylcyclohexasilane (70 mg, 0.2 mmol) was dissolved in ether (1.18 g, 16 mmol) saturated with water in a quartz NMR tube. This solution was photolyzed as above and the resulting colorless solution was analyzed by GLPC on a $1/4" \times 12'$ 20% SE-30 on Chromosorb W 60/80 mesh column. 1,1,2,2-Tetramethyldisiloxane (85%) was isolated. It was identified by comparison of its IR and NMR spectral properties and GLPC retention time with those of an authentic sample (Petrach Systems). IR: $\nu(\text{Si-H})$ 2120 cm^{-1} , $\nu(\text{Si-O})$ 1055 cm^{-1} . NMR δ (ppm): 4.66 (sept., 2 H, J 2.8 Hz), 0.17 (d, 6 H, J 2.8 Hz). Mass spectrum: Parent — 1(m/e) = 133 (72%), $P - 15(m/e)$ = 119 (100%).

Photolysis of dodecamethylcyclohexasilane with D_2O

The reaction was carried out as above. 1,1,2,2-Tetramethyldisiloxane- $\text{Si}_2\text{-}d_2$ was obtained in 82% yield. It had the following spectral properties. IR: $\nu(\text{Si-D})$ 1550 cm^{-1} , $\nu(\text{Si-O})$ 1055 cm^{-1} . NMR, δ (ppm): 0.17 (s). Mass spectrum: Parent — 2(m/e) = 134 (52%), $P - 15(m/e)$ = 121 (100%).

Photolysis of dodecamethylcyclohexasilane with ethanol

A mixture of dodecamethylcyclohexasilane (70 mg, 0.2 mmol) and ethanol (230 mg, 5 mmol) was dissolved in ether (1.11 g, 15 mmol) in a quartz NMR tube. This solution was photolyzed as above. Analysis of the resulting colorless solution by GLPC on a $1/4" \times 12'$ 20% SE-30 on Chromosorb W 60/80 mesh column showed the formation of ethoxydimethylsilane (87%) [7]. It had the following spectral properties. IR: $\nu(\text{Si-H})$ 2110 cm^{-1} , $\nu(\text{Si-O})$ and $\nu(\text{C-O})$ $1080, 1110\text{ cm}^{-1}$. NMR, δ (ppm): 4.59 (sept., 1 H, J 2.8 Hz), 3.68 (q, 2 H, J 7 Hz), 1.19 (t, 3 H, J 7 Hz), 0.19 (d, 6 H, J 2.8 Hz). Mass spectrum: Parent- (m/e) = 104 (44%), $P - 1(m/e)$ = 103 (100%), $P - 15(m/e)$ = 89 (72%), $P - 29(m/e)$ = 75 (81%).

Photolysis of dodecamethylcyclohexasilane with ethanol- $O\text{-}d_1$

The reaction was carried out as above. Ethoxydimethylsilane- $\text{Si-}d_1$ was obtained in 84% yield. It had the following spectral properties. IR: $\nu(\text{Si-D})$ 1535 cm^{-1} , $\nu(\text{Si-O})$ and $\nu(\text{C-O})$ $1080, 1110\text{ cm}^{-1}$. NMR, δ (ppm): 3.68 (q, 2 H, J 7 Hz), 1.19 (t, 3 H, J 7 Hz), 0.19 (s, 6 H). Mass spectrum: Parent(m/e) = 105 (3.3%), $P - 2(m/e)$ = 103 (54%), $P - 15(m/e)$ = 90 (100%).

*Photolysis of dodecamethylcyclohexasilane with *t*-butanol*

The reaction was carried out as above. *t*-Butoxydimethylsilane [9] was

obtained in 85% yield. It had the following spectral properties. IR: $\nu(\text{Si-H})$ 2110 cm^{-1} , $\nu(\text{Si-O})$ and $\nu(\text{C-O})$ 1020 and 1045 cm^{-1} . NMR, δ (ppm): 4.72 (sept., 1 H, J 2.8 Hz), 1.26 (s, 9 H), 0.16 (d, 6 H, J 2.8 Hz). Mass spectrum: Parent — 1(m/e) = 131 (0.2%), P — 15(m/e) = 117 (58%), P — 57(m/e) = 75 (100%).

Photolysis of dodecamethylcyclohexasilane with methanol

The reaction was carried out as above except that THF was used in the place of ether as solvent. Methoxydimethylsilane [7] was obtained in 89% yield. It had the following spectral properties. IR: $\nu(\text{Si-H})$ 2120 cm^{-1} , $\nu(\text{Si-O})$ and $\nu(\text{C-O})$ broad 1095 cm^{-1} . NMR, δ (ppm): 4.57 (sept., 1 H, J 2.8 Hz), 3.45 (s, 3 H), 0.19 (d, 5 H, J 2.8 Hz).

*Photolysis of octamethyl-2,3-diphenyltetrasilane with *t*-butanol*

A mixture of octamethyl-2,3-diphenyltetrasilane (42.5 mg, 0.11 mmol) and *t*-butanol (122 mg, 1.65 mmol) was dissolved in ether (1.11 g, 15 mmol) in a quartz NMR tube. This solution was photolyzed as above. GLPC analysis of the resulting pale yellow solution on a $1/4'' \times 12'$ 20% SE-30 on Chromosorb W 60/80 mesh column indicated a 77% yield of *t*-butoxymethylphenylsilane. It had the following spectral properties: IR: $\nu(\text{Si-H})$ 2130 cm^{-1} , $\nu(\text{Si-O})$ and $\nu(\text{C-O})$ 1020 and 1040 cm^{-1} . UV (cyclohexane), λ_{max} ($\text{\AA}$) (ϵ): 2470(sh) (397), 2530 (490), 2590 (600), 2640 (588), 2700 (441), 2750(sh) (206). NMR, δ (ppm): 7.62–7.45 (m, 2 H), 7.39–7.25 (m, 3 H), 5.12 (q, 1 H, J 2.8 Hz), 1.28 (s, 9 H), 0.40 (d, 3 H, J 2.8 Hz). Mass spectrum: Parent(m/e) = 194 (16.5%), found: 194.115; $\text{C}_{11}\text{H}_{18}\text{OSi}$ calcd.: 194.113; P — 15(m/e) = 179 (75%); P — 57(m/e) = 137 (100%).

Acknowledgements

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