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INSERTION REACTION OF DIMETHYLSILYLENE INTO Si—H AND Si—OR BONDS

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Summary

Dimethylsilylene generated by photolysis of dodecamethylcyclohexasilane inserts sequentially into Si—H and Si—OR bonds of monosilanes to give high yields of the corresponding unsymmetrical di-, tri- and tetrasilanes.

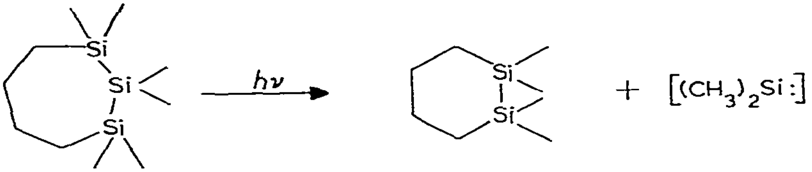
Relative reactivities of Si—H, Si_2—H, Si—OR, Si_2—OR and Si_3—OR bonds toward insertion of dimethylsilylene have been determined.

Insertion reactions of silylene intermediates into Si—H and Si—OR single bonds of monosilanes to yield the corresponding disilanes have been studied in considerable detail [1]. We should like to report that dimethylsilylene generated by photolysis of dodecamethylcyclohexasilane [2] will insert sequentially into Si—H and Si—OR single bonds of monosilanes to yield disilanes, which react further with additional dimethylsilylene to yield trisilanes and tetrasilanes. It should be noted that no pentasilanes or higher polysilanes were detected in the reaction mixture.

Pentasilanes and higher polysilanes are most probably not observed because they strongly absorb light in the vicinity of 2500 Å [3] undergoing photochemical extrusion of dimethylsilylene and formation of smaller polysilanes [4,5]. Linear pentasilanes absorb light more strongly in this region λ_{max} 2480—2500 Å (ϵ = 18000—22000) than the dimethylsilylene precursor dodecamethylcyclohexasilane λ_{max} 2300 (ϵ = 6000) and 2520 Å (ϵ = 1200) [6,7]. On the other hand, trisilanes and tetrasilanes absorb ultraviolet light at shorter wavelengths, they have maxima respectively at λ_{max} 2150—2220 Å (ϵ = 6000—9000) and 2350—2380 Å (ϵ = 12000—15000) [3].

While linear α,ω-dimethoxypermethylated polysilanes with up to five silicon atoms have been isolated from the pyrolysis of *sym*-dimethoxytetramethyldisilane, a reaction known to involve dimethylsilylene as an intermediate [8], trisilanes are the largest polysilanes previously reported in photochemical insertion reactions of silylenes into Si—H and Si—OR bonds. For example dimethylsilylene generated by photolysis of dodecamethylcyclohexasilane reacts with diethylmethylsilane to give both 1-*H*-2,2-diethyltrimethyldisilane and 1-*H*-3,3-diethylpentamethyltrisilane while reaction of dimethylsilylene with dimethoxydimethylsilane gave *sym*-dimethoxytetramethyldisilane and 1,3-dimethoxyhexamethyltrisilane [2,9]. No previous examples of the photochemical synthesis of tetrasilanes by insertion of dimethylsilylene have been reported.

It should be noted that, in general, previous work has reported the photolysis of polysilanes to yield silylene intermediates and smaller polysilanes, rather than utilizing silylenes to build up larger polysilanes as reported here. Thus photolysis of linear permethylated polysilanes $CH_3[(CH_3)_2Si]_nCH_3$ (n = 4 to 8) has been reported to involve the extrusion of dimethylsilylene and formation of octamethyltrisilane as the major polysilane product [4,5]. Likewise photolysis (2537 Å) of 1,2,3-trisilacycloheptane derivatives has been reported to yield 1,2-disilacyclohexanes by extrusion of the central silicon of the starting material as a silylene [10].



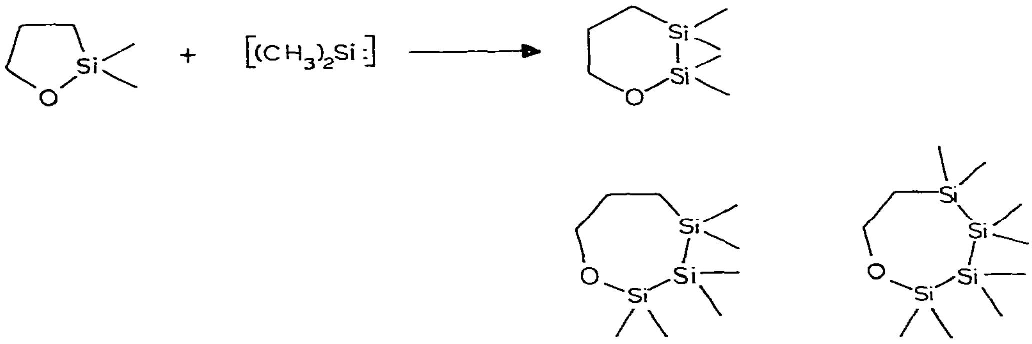
In addition, we will present relative reactivity data which establish that the Si—OR single bond of alkoxydi- and trisilane is considerably more reactive than the Si—OR single bond of alkoxysilanes toward dimethylsilylene in agreement with previous qualitative data [11]. Further we have found that Si—H and Si—OR bonds of monosilanes have approximately equal reactivity toward dimethylsilylene insertion while the Si—H of disilanes is only slightly more reactive than the Si—H bond of monosilanes toward dimethylsilylene.

Results

Reaction of dimethylsilylene generated by photolysis of dodecamethylcyclohexasilane with trimethylsilane (1 : 3 molar ratio of $[(CH_3)_2Si:]$ to Si—H) was found to yield pentamethyldisilane (28.5%), 1,1,1,2,2,3,3-heptamethyltrisilane (22%) and 1,1,1,2,2,3,3,4,4-nonamethyltetrasilane (11%). Yields are calculated on the basis of two dimethylsilylenes per molecule of dodecamethylcyclohexasilane [2]. In order to account for this unexpected distribution of products, we have explored the question of the relative reactivity of Si—H bonds of monosilanes compared to those of disilanes toward dimethylsilene insertion. Dimethylsilylene was generated in the presence of a large excess of equal concentrations of n-butyldimethylsilane and pentamethyldisilane. 1-n-Butyl-1,1,2,2-tetramethyldisilane and 1,1,1,2,2,3,3-heptamethyltrisilane were produced in a ratio of 1 : 1.5. On the assumption that there is not significant steric difference between a methyl and an n-butyl group as far as reactivity at the respective Si—H bonds, we must conclude that the Si—H bond of a disilane is more reactive than that of a monosilane.

A number of examples of insertion of dimethylsilylene into Si—OR single bonds of alkoxysilanes have been studied. For example, reaction of dimethylsilylene with ethoxytrimethylsilane (1 : 2 ratio of $[(CH_3)_2Si:]$ to Si—OR) was found to yield ethoxypentamethyldisilane (10%), 1-ethoxyheptamethyltrisilane (25%) and 1-ethoxynonamethyltetrasilane (32%). In the case of reaction of dimethylsilylene with an excess of trimethylsilane the yields of insertion products decreased in going from disilane to trisilane to tetrasilane. For ethoxytrimethylsilane, the yields of insertion products increased from di- to tri- to tetrasilane. This difference is partially the result of a higher ratio of dimethylsilylene to trapping reagent (ethoxytrimethylsilane). However, a more fundamental difference exists. Specifically, the Si—OR bond of a disilane or trisilane was found to be considerably more reactive than the Si—OR bond of a monosilane. This was determined by competition reactions in which dimethylsilylene was generated in the presence of a large excess of equal concentrations of methoxytrimethylsilane and ethoxypentamethyldisilane. Methoxypentamethyldisilane and 1-ethoxyheptamethyltrisilane were produced in a ratio of 1 : 7. Control experiments demonstrated that no exchange of alkoxy groups occurred under the reaction conditions. Likewise competition reactions of dimethylsilylene as above for ethoxytrimethylsilane and 1-ethoxyheptamethyltrisilane gave ethoxypentamethyldisilane and 1-ethoxynonamethyltetrasilane in a 1 : 6 ratio. Thus Si—OR single bonds of alkoxydi- and trisilanes have approximately equal reactivity toward dimethylsilylene insertion and are both between 6 to 7 times more reactive toward insertion of dimethylsilylene than the Si—OR single bond of alkoxysilanes. This equal reactivity of Si—OR single bonds of alkoxydi- and trisilane is consistent with previous work [11].

The insertion reactions of dimethylsilylene into Si—OR single bonds of two cyclic alkoxysilanes were examined. Thus dimethylsilylene inserts into the Si—OR single bond of 2,2-dimethyl-1-oxa-2-silacyclopentane (molar ratio of $[(CH_3)_2Si:]$ to Si—OR 1 : 1.1) to yield 2,2,3,3-tetramethyl-1-oxa-2,3-disilacyclohexane (22.5%), 2,2,3,3,4,4-hexamethyl-1-oxa-2,3,4-trisilacycloheptane (27.5%) and 2,2,3,3,4,4,5,5-octamethyl-1-oxa-2,3,4,5-tetrasilacyclooctane (34%).



Similar results have been obtained from the reaction of dimethylsilylene with 2,2,4,4-tetramethyl-1-oxa-2-silacyclopentane (2 : 1 molar ratio of $[(CH_3)_2Si:]$ to Si—OR). The following products were obtained: 2,2,3,3,5,5-hexamethyl-1-oxa-2,3-disilacyclohexane (29%), 2,2,3,3,4,4,6,6-octamethyl-1-oxa-2,3,4-trisilacycloheptane (27%) and finally 2,2,3,3,4,4,5,5,7,7-decamethyl-1-oxa-2,3,4,5-tetrasilacyclooctane (33%). The formation of cyclic alkoxytri- and tetrasilanes stands in contrast to the previous report of photolysis of 1,2,3-trisilacycloheptanes [10].

Finally, we have studied the insertion reactions of dimethylsilylene with methoxydimethylsilane (1 : 2 molar ratio). The following product were obtained: 1-methoxy-1,1,2,2-tetramethyldisilane (9%), 1-methoxy-1,1,2,2,3,3-hexamethyltrisilane (21.5%) and 1-methoxy-1,1,2,2,3,3,4,4-octamethyltetrasilane (41.5%). These products can be formed by insertion of dimethylsilylene into either the reactive Si—H or Si—OR single bonds. To determine the course of the reaction, competition reactions of dimethylsilylene for ethoxytrimethylsilane and n-butyldimethylsilane were carried out as above. 1-Ethoxypentamethyldisilane (22.2%), 1-ethoxyheptamethyltrisilane (11.1%) and 1-n-butyl-1,1,2,2-tetramethyldisilane (29.2%) were obtained. Combining the yields of Si—OR and Si_2—OR insertion products a 33.3% yield of 1-ethoxypentamethyldisilane was estimated compared to the 29.2% yield of 1-n-butyl-1,1,2,2-tetramethyldisilane. Thus an Si—OR bond of a monosilane is 1.14 times as reactive as Si—H bond. However, an Si—OR bond of a di- or trisilane is considerably more reactive. While these relative reactivity results are significant, considerable additional work needs to be done to determine all factors affecting such reactivity. We believe our results clearly demonstrate the synthetic potential of photochemical dimethylsilylene insertion reactions into Si—OR and Si—H bonds to form unsymmetrical tri- and tetrasilanes.

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% solution 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 of solutions made in spectroquality cyclohexane. Samples of all compounds for spectral analysis were purified by preparative gas liquid phase chromatography on a 12′ × 1/4″ 20% SE-30 on Chromosorb W 60/80 mesh column (A) at temperatures between 50—200°C on a Hewlett Packard F&M 700 equipped with a thermal conductivity detector. GLPC analysis of photolysis reactions was carried out under the same conditions used for preparative GLPC or on a 1/8″ × 12′ (B) or 1/8″ × 18′ (C) 20% SE-30 on Chromosorb W 60/80 mesh column at temperatures between 80—240°C on a Hewlett Packard 5710 A equipped with a flame ionization detector. Yields of products were determined by GLPC with cyclooctane or cyclohexane added as an internal standard. Yields are based on two moles of dimethylsilylene per mole of dodecamethylcyclohexasilane.

All of the starting materials and some of the 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.

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

Ethoxytrimethylsilane [12] was prepared by reaction of trimethylchlorosilane with sodium ethoxide in 80% yield. It was purified by prep GLPC.

Methoxydimethylsilane was prepared by the reaction of dimethylchlorosilane and trimethylorthoformate in 55% yield [13] and was purified by prep GLPC.

n-Butyldimethylsilane was prepared by reaction of dimethylchlorosilane with n-butyl lithium in ether [14].

2,2-Dimethyl-1-oxa-2-silacyclopentane was prepared by treatment of 3-chloropropyloxydimethylchlorosilane with sodium in boiling decalin, by the method of Knoth [15]. NMR: δ 3.82 (t, 2H, J 6 Hz), 1.85 (tt, 2H, J 7.5 and 6 Hz), 0.72 (t, 2H, J 7.5 Hz), 0.18 ppm (s, 6H). IR: Si—O and C—O broad 1050 and 1085 cm^{-1}. Mass spectrum: Parent $m/e = 116$ (13%), $P - 1$ $m/e = 115$ (1.7%), $P - 15$ $m/e = 101$ (100%), $P - 17$ $m/e = 99$ (16.9%), $P - 28$ $m/e = 88$ (22.4%).

2,2,4,4-Tetramethyl-1-oxa-2-silacyclopentane [16—18] was prepared by reaction of dimethylsilylene generated by photolysis of dodecamethylcyclohexasilane with 3,3-dimethyloxetane (Aldrich) in 90% yield. NMR: δ 3.49 (s, 2H), 1.03 (s, 6H), 0.66 (s, 2H), 0.21 ppm (s, 6H). IR: Si—O 1020 cm^{-1}. Mass spectrum: Parent $m/e = 144$ (14%), calcd. $C_7H_{16}OSi$ 144.097; found 144.099; $P - 15$ $m/e = 129$ (13%), $m/e = 99$ (33%), $m/e = 89$ (100%), $m/e = 88$ (54%).

Trimethylsilane was obtained from PCR and was used without further purification.

Pentamethyldisilane [19] was prepared by the reaction of dimethylchlorosilane and trimethylchlorosilane in the presence of excess sodium [20] in xylene and was purified by prep GLPC.

Ethoxypentamethyldisilane [21] was prepared by the reaction of pentamethyldisilane and tri-n-butylethoxytin [22] (prepared from sodium ethoxide and tri-n-butyltin chloride *) following the method of Pereyre [23]. It was purified by GLPC.

Dodecamethylcyclohexasilane was prepared by the reaction of dimethyldichlorosilane and excess lithium metal in tetrahydrofuran [6,24].

Reaction of dimethylsilylene with trimethylsilane

Trimethylsilane (245 mg, 3.3 mmol) was condensed into a solution of dodecamethylcyclohexasilane (174.3 mg, 0.5 mmol) in ether (1.04 g, 14 mmol) in a 5 mm quartz NMR tube at —78°C. This solution was photolyzed with a 450 W medium pressure Hanovia Hg Lamp ** for 1 h at 0.5°C in an ice/water bath to yield pentamethyldisilane [20] (28.5%), 1,1,1,2,2,3,3-heptamethyltrisilane [19] (22%), and 1,1,1,2,2,3,3,4,4-nonamethyltetrasilane [25] (11%). These compounds were identified by comparison of their IR, NMR and UV spectra with literature values.

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* Aldrich Chemical Company.

** The medium pressure Hg lamp used emits not only in the vicinity of 2500 Å but also at shorter wavelengths: 2652—2655 (relative energy 5.3). 2571 (6), 2637 (16.6), 2482 (8.6), 2400 (7.3), 2480 (8.6), 2360 (6.0), 2320 (8.0) and 2224 (14.0) [25]. These shorter wavelength emissions have not prevented the accumulation of significant concentrations of tri- and tetrasilanes, however.

Competition reactions of dimethylsilylene with n-butyldimethylsilane and pentamethyldisilane

A solution of dodecamethylcyclohexasilane (2 mg, 5.7 × 10^{-3} mmol), n-butyldimethylsilane (16.2 mg, 0.14 mmol) and pentamethyldisilane (18.5 mg, 0.14 mmol) in ether (89 mg, 1.2 mmol) was placed in a 5 mm quartz NMR tube. This solution was photolyzed as above at 0—5° C for 15 min. GLPC analysis (C) indicated the formation of 1-n-butyl-1,1,2,2-tetramethyldisilane and 1,1,1,2,2,3,3-heptamethyltrisilane [19] in a ratio of 1 : 1.5.

1-n-Butyl-1,1,2,2-tetramethyldisilane. NMR: δ 3.60 (sept. 1H, J 4.6 Hz), 1.21—1.43 (m, 4H), 0.869 (t, 3H, J 6.2 Hz), 0.506—0.676 (m, 2H), 0.103 (d, 6H, J 4.6 Hz), 0.045 ppm (s, 6H), IR: Si—H 2100 cm^{-1}. Mass spectrum: Parent m/e = 174 (18.7%), calcd. $C_8H_{22}Si_2$ 174.1220; found 174.1240; $P - 57$ m/e = 117 (23.8%), calcd. $C_4H_{13}Si_2$ 117.0556; found 117.0549; $P - 59$ m/e = 115 (88.5%), calcd. $C_6H_{15}Si$ 115.0943; found 115.0931; m/e = 73 (100%), calcd. C_3H_9Si 73.0474; found 73.0480.

Reaction of dimethylsilylene with ethoxytrimethylsilane

Dodecamethylcyclohexasilane (174.3 mg, 0.5 mmol) was dissolved in a mixture of ethoxytrimethylsilane (236.2 mg, 2.0 mmol) and ether (1.04 g, 14 mmol) in a 5 mm quartz NMR tube. This solution was photolyzed as above for 90 min. GLPC analysis (A) of the resulting colorless solution showed the formation of ethoxypentamethyldisilane [21] (10%), 1-ethoxyheptamethyltrisilane [27] (25.5%) and 1-ethoxynonamethyltetrasilane (32.5%).

Ethoxypentamethyldisilane [21]. NMR: δ 3.62 (q, 2H, J 6.95 Hz), 1.17 (t, 3H, J 6.95 Hz), 0.186 (s, 6H), 0.079 ppm (s, 9H). IR: Si—O and C—O 1065 and 1100 cm^{-1}.

1-Ethoxyheptamethyltrisilane [27]. NMR: δ 3.62 (q, 2H, J 7.0 Hz), 1.17 (t, 3H, J 7.0 Hz), 0.214 (s, 6H), 0.111 (s, 6H), 0.0831 ppm (s, 9H). IR: Si—O and C—O 1070 and 1100 cm^{-1}. Mass spectrum: Parent m/e = 234 (6.0%), $P - 1$ m/e = 233 (1.3%), $P - 15$ m/e = 219 (14.1%). $P - 29$ m/e = 205 (27.3%), $P - 45$ m/e = 189 (6.4%), m/e = 175 (20.0%), m/e = 147 (45.6%), m/e = 131 (33.0%), m/e = 117 (43.2%), m/e = 116 (100.0%), m/e = 103 (38.3%).

1-Ethoxynonamethyltetrasilane. NMR: δ 3.62 (q, 2H, J 6.97 Hz), 1.16 (t, 3H, J 6.97 Hz), 0.217 (s, 6H), 0.159 (s, 6H), 0.109 (s, 6H), 0.078 ppm (s, 9H). IR: Si—O and C—O 1072 and 1100 cm^{-1}. UV: λ_{max} 2350 Å (ϵ 11,820). Mass spectrum: $P - 15$ m/e = 277 (4.7%), calcd. $C_{10}H_{29}OSi_4$ 277.1296; found 277.1306; $P - 59$ m/e = 233 (4.1%), $P - 73$ m/e = 219 (100%), calcd. for $C_8H_{23}OSi_3$ 219.1057; found 219.1057; m/e = 73 (89%).

Competition reactions of dimethylsilylene with methoxytrimethylsilane and ethoxypentamethyldisilane

A solution of dodecamethylcyclohexasilane (2.5 mg, 7.2 × 10^{-3} mmol), methoxytrimethylsilane (13.5 mg, 0.13 mmol) and ethoxypentamethyldisilane (22.8 mg, 0.13 mmol) in ether (50 mg, 0.68 mmol) was placed in a 5 mm quartz NMR tube. This solution was photolyzed as above at 0—5° C for 25 min. GLPC analysis (B) of the resulting colorless solution showed the formation of methoxypentamethyldisilane [29] and 1-ethoxyheptamethyltrisilane [27] in a ratio of 1 : 7.

Methoxypentamethyldisilane [29]. NMR: δ 3.41 (s, 3H), 0.19 (s, 6H), 0.09 ppm (s, 9H). IR: Si—O and C—O 1060 and 1090 cm^{-1}.

Photolysis of methoxytrimethylsilane and ethoxypentamethyldisilane in ether

A solution of methoxytrimethylsilane (10.4 mg, 0.1 mmol) and ethoxypentamethyldisilane (17.6 mg, 0.1 mmol) in ether (40 mg, 0.54 mmol) was placed in a 5 mm quartz NMR tube. This solution was photolyzed as above at 0—5°C for 25 min. GLPC analysis (B) of the resulting colorless solution showed no change in the quantities of either methoxytrimethylsilane or ethoxypentamethyldisilane.

Competition reactions of dimethylsilylene with ethoxytrimethylsilane and 1-ethoxyheptamethyltrisilane

A solution of dodecamethylcyclohexasilane (2.5 mg, 7.2×10^{-3} mmol), ethoxytrimethylsilane (10.2 mg, 0.086 mmol) and 1-ethoxyheptamethyltrisilane (20.2 mg, 0.086 mmol) in ether (50 mg, 0.68 mmol) was placed in a 5 mm quartz NMR tube. This solution was photolyzed as above at 0—5°C for 20 min GLPC analysis (B) showed the formation of ethoxypentamethyldisilane [21] and 1-ethoxynonamethyltetrasilane in a ratio of 1 : 6.

Reaction of dimethylsilylene with 2,2-dimethyl-1-oxa-2-silacyclopentane

A solution of dodecamethylcyclohexasilane (200 mg, 0.57 mmol) and 2,2-dimethyl-1-oxa-2-silacyclopentane [16] (140 mg, 1.2 mmol) in ether (800 mg, 10.8 mmol) was prepared and photolyzed as above to yield 2,2,3,3-tetramethyl-1-oxa-2,3-disilacyclohexane (22.5%), 2,2,3,3,4,4-hexamethyl-1-oxa-2,3,4-trisilacycloheptane (27.5%) and 2,2,3,3,4,4,5,5-octamethyl-1-oxa-2,3,4,5-tetrasilacyclooctane (34%).

2,2,3,3-Tetramethyl-1-oxa-2,3-disilacyclohexane. NMR: δ 3.75 (dd, 2H, *J* 4.74 and 4.76 Hz), 1.64—1.83 (m, 2H), 0.829 (dd, 2H, *J* 6.7 and 6.0 Hz), 0.224 (s, 6H), 0.094 ppm (s, 6H). IR: Si—O and C—O broad 1050 and 1070 cm^{-1}. Mass spectrum: Parent $m/e = 174$ (2.7%), $P - 1$ $m/e = 173$ (1.9%), $P - 15$ $m/e = 159$ (74.9%), calcd. $C_6H_{15}OSi_2$ 159.066; found 159.067; $m/e = 133$ (67.8%), $m/e = 131$ (100%), $m/e = 117$ (34.1%), $m/e = 101$ (60.6%).

2,2,3,3,4,4-Hexamethyl-1-oxa-2,3,4-trisilacycloheptane. NMR: δ 3.65 (dd, 2H, *J* 5.2 and 5.0 Hz), 1.67—1.81 (m, 2H), 0.78 (dd, 2H, *J* 6.9 and 6.3 Hz), 0.220 (s, 6H), 0.128 (s, 6H), 0.070 ppm (s, 6H). IR: Si—O and C—O 1040 cm^{-1}. Mass spectrum: Parent $m/e = 232$ (5.9%), $P - 1$ $m/e = 231$ (5.5%), $P - 15$ $m/e = 217$ (11.7%), calcd. $C_8H_{21}OSi_3$ 217.090; found 217.090; $m/e = 175$ (21.9%), $m/e = 159$ (77.5%), $m/e = 133$ (46.5%), $m/e = 131$ (100%), $m/e = 117$ (59.3%), $m/e = 116$ (41%).

2,2,3,3,4,4,5,5-Octamethyl-1-oxa-2,3,4,5-tetrasilacyclooctane. NMR: δ 3.58 (t, 2H, *J* 5.5 Hz), 1.57—1.75 (m, 2H), 0.803 (dd, *J* 6.8 and 6.5 Hz), 0.223 (s, 6H), 0.133 (s, 6H), 0.119 (s, 6H), 0.043 ppm (s, 6H). IR: Si—O and C—O broad 1040 and 1090 cm^{-1}. UV: λ_{max} 2360 Å (ε 11710). Mass spectrum: Parent $m/e = 290$ (2.7%), calcd. $C_{11}H_{30}OSi_4$ 290.137; found 290.134; $P - 15$ $m/e = 275$ (10.9%), $m/e = 233$ (18.7%), $m/e = 205$ (7.8%), $m/e = 189$ (10.5%), $m/e = 175$ (18.0%), $m/e = 174$ (31.8%), $m/e = 159$ (9.8%), $m/e = 133$ (22.7%), $m/e = 131$ (20.0%), $m/e = 129$ (81.8%), $m/e = 117$ (29.6%), $m/e = 75$ (72.6%), $m/e = 73$ (100%).

Reactions of dimethylsilylene with 2,2,4,4-tetramethyl-1-oxa-2-silacyclopentane

Dodecamethylcyclohexasilane (348.5 mg, 1.0 mmol) was dissolved in 2,2,4,4-tetramethyl-1-oxa-2-silacyclopentane [17—19] (158 mg, 1.1 mmol) and ether in a 5 mm quartz NMR tube. The solution was photolyzed as above at 0—5° C for 60 min and the resulting colorless solution was analyzed by GLPC-A. 2,2,3,3,5,5-Hexamethyl-1-oxa-2,3-disilacyclohexane (29%), 2,2,3,3,4,4,6,6-octamethyl-1-oxa-2,3,4-trisilacycloheptane (27%) and 2,2,3,3,4,4,5,5,7,7-decamethyl-1-oxa-2,3,4,5-tetrasilacyclooctane (33%) were isolated.

2,2,3,3,5,5-Hexamethyl-1-oxa-2,3-disilacyclohexane. NMR: δ 3.41 (s, 2H), 0.92 (s, 6H), 0.76 (s, 2H), 0.23 (s, 6H), 0.08 ppm (s, 6H). IR: Si—O and C—O broad 1055 cm^{-1}. Mass spectrum: Parent $m/e = 202$ (2%), calcd. $C_9H_{22}OSi_2$ 202.121; found 202.121; $P - 1$ $m/e = 201$ (0.5%), $P - 15$ $m/e = 187$ (100%), $m/e = 171$ (7.4%), $m/e = 133$ (95%), $m/e = 131$ (99%), $m/e = 117$ (56%), $m/e = 73$ (50%).

2,2,3,3,4,4,6,6-Octamethyl-1-oxa-2,3,4-trisilacycloheptane. NMR: δ 3.33 (s, 2H), 0.90 (s, 6H), 0.76 (s, 2H), 0.23 (s, 6H), 0.13 (s, 6H), 0.085 ppm (s, 6H). IR: Si—O and C—O broad 1070 cm^{-1}. Mass spectrum: Parent $m/e = 260$ (12.1%), calcd. $C_{11}H_{28}OSi_3$ 260.145; found 260.145; $P - 15$ $m/e = 245$ (9.6%), $m/e = 189$ (38.1%), $m/e = 187$ (19.4%), $m/e = 175$ (33.1%), $m/e = 159$ (34.8%), $m/e = 147$ (16.1%), $m/e = 133$ (27.9%), $m/e = 131$ (30.9%), $m/e = 117$ (40.5%), $m/e = 116$ (40.7%), $m/e = 89$ (19.8%), $m/e = 73$ (100%).

2,2,3,3,4,4,5,5,7,7-Decamethyl-1-oxa-2,3,4,5-tetrasilacyclooctane. NMR: δ 3.23 (s, 2H), 0.88 (s, 6H), 0.83 (s, 2H), 0.21 (s, 6H), 0.14 (s, 6H), 0.11 (s, 6H), 0.039 ppm (s, 6H). IR: Si—O and C—O broad 1080 cm^{-1}. UV: λ_{max} 2340 Å (ϵ 7450). Mass spectrum: Parent $m/e = 318$ (5.6%), calcd. $C_{13}H_{34}OSi_4$ 318.168; found 318.169; $P - 15$ $m/e = 303$ (5.4%), $m/e = 233$ (26.2%), $m/e = 189$ (14.8%), $m/e = 174$ (55.7%), $m/e = 159$ (11.4%), $m/e = 133$ (11.3%), $m/e = 131$ (18.1%), $m/e = 117$ (31.1%), $m/e = 89$ (13.1%), $m/e = 73$ (100%).

Reaction of dimethylsilylene with methoxydimethylsilane

A solution of dodecamethylcyclohexasilane (174.3 mg, 0.5 mmol) and methoxydimethylsilane [13,27] (180 mg, 2.0 mmol) in ether (1.04 g, 14 mmol) was prepared in a 5 mm quartz NMR tube and photolyzed as above. 1-Methoxy-1,1,2,2-tetramethyldisilane (9%), 1-methoxy-1,1,2,2,3,3-hexamethyltrisilane (21.5%) and 1-methoxy-1,1,2,2,3,3,4,4-octamethyltetrasilane (41.5%) were isolated by GLPC.

1-Methoxy-1,1,2,2-tetramethyldisilane. NMR: δ 3.63 (sept, 1H, J 4.6 Hz), 3.42 (s, 3H), 0.234 (s, 6H), 0.159 ppm (d, 6H, J 4.6 Hz). IR: Si—H 2100, Si—O and C—O broad 1075 cm^{-1}. Mass spectrum: Parent $m/e = 148$ (4.4%), $P - 1$ $m/e = 147$ (30.8%), calcd. $C_5H_{15}OSi_2$ 147.066; found 147.063; $P - 15$ $m/e = 133$ (12.3%), $m/e = 131$ (44%), $m/e = 117$ (23.1%), $m/e = 73$ (100%).

1-Methoxy-1,1,2,2,3,3-hexamethyltrisilane. NMR: δ 3.73 (sept, 1H, J 4.5 Hz), 3.40 (s, 3H), 0.224 (s, 6H), 0.162 (s, 6H), 0.155 ppm (d, 6H, J 4.5 Hz). IR: Si—H 2090, Si—O and C—O 1070 and 1020 cm^{-1}. Mass spectrum: $P - 15$ $m/e = 191$ (4.9%), calcd. $C_6H_{19}OSi_3$ 191.0744; found 191.0763; $P - 31$ $m/e = 175$ (18.2%), calcd. $C_5H_{15}OSi_3$ 175.0430; found 175.0422; $m/e = 133$ (31.6%), *m/e* = 131 (11.7%), *m/e* = 117 (40.1%), *m/e* = 116 (59.5%), *m/e* = 101 (10%), *m/e* = 73 (100%), calcd. C_2H_5OSi 73.0110; found 73.0133.

1-Methoxy-1,1,2,2,3,3,4,4-octamethyltetrasilane. NMR: δ 3.75 (sept, 1H, J 4.5 Hz), 3.40 (s, 3H), 0.224 (s, 6H), 0.167 (s, 6H), 0.154 (s, 6H), 0.147 ppm (d, 6H, J 4.5 Hz). IR: Si—H 2090, Si—O and C—O broad 1060 and 1015 cm^{-1}. UV: λ_{max} 2360 Å (ϵ 10210). Mass spectrum: $P - 15$ *m/e* = 249 (10%), calcd. $C_8H_{25}OSi_4$ 249.0982; found 249.0991; $P - 31$ *m/e* = 233 (3.6%), calcd. $C_7H_{21}OSi_4$ 233.0669; found 233.0679; *m/e* = 175 (18.8%), *m/e* = 147 (13.1%), *m/e* = 131 (15.2%), *m/e* = 117 (12.7%), *m/e* = 116 (13.6%), *m/e* = 89 (11.3%), *m/e* = 73 (100%), calcd. C_2H_5OSi 73.0110; found 73.0127.

Competition reactions of dimethylsilylene with ethoxytrimethylsilane and n-butyldimethylsilane

A solution of dodecamethylcyclohexasilane (46 mg, 0.13 mmol), ethoxytrimethylsilane (319 mg, 2.7 mmol) and n-butyldimethylsilane (313.5 mg, 2.7 mmol) in ether (740 mg, 10 mmol) was placed in a 5 mm quartz NMR tube. This solution was photolyzed as above at 0—5°C for 50 min. GLPC analysis (A) of the resulting colorless solution indicated the formation ethoxypentamethyldisilane [21] (22.2%), 1-ethoxyheptamethyltrisilane [27] (11.1%) and 1-n-butyl-1,1,2,2-tetramethyldisilane (29.2%). The relative reactivity of dimethylsilylene toward Si—O and Si—H single bonds was calculated to be 1.14.

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