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Silicon–Carbon Unsaturated Compounds. 28. Regiochemistry in the Photochemical Formation of Silenes from Dihydropyranyl-Substituted Phenyldisilanes

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The photochemical behavior of 1-(3,4-dihydro-2*H*-6-pyranyl)-1-phenyltetramethyldisilane (1) and 1-(3,4-dihydro-2*H*-6-pyranyl)-2-phenyltetramethyldisilane (2) in the presence of methanol, acetone, and isobutene has been studied. Irradiation of 1 in the presence of methanol gave a mixture of adducts formed from the reaction of two different silenes arising from a 1,3-trimethylsilyl shift to a pyranyl moiety (silene A) and to a phenyl ring (silene B) with methanol. Similarly, photolysis of 1 in the presence of acetone afforded products derived from the reaction of both A and B with acetone. In the presence of isobutene, however, photolysis gave only the adduct produced from the silene B. Irradiation of 2 afforded two types of silenes, C (1,3-silyl shift to the pyranyl ring) and D (1,3-silyl shift to the phenyl ring), analogous to A and B. The photolysis of 2 in the presence of methanol afforded a mixture of products formed from the silenes C and D. In the presence of acetone, 2 afforded an adduct derived from the silene D, while in the presence of isobutene, an adduct arising from the silene C was obtained. In the photolysis of 2, appreciable amounts of products derived from homolytic scission of a silicon–silicon bond were also observed. Reactivities of the trapping agents toward the silenes have been examined in the photolysis of 1 in the presence of two different trapping agents and found to be, in decreasing order, methanol, acetone, and isobutene.

Introduction

A π-electron-system-substituted disilanyl group acts as a chromophore. Indeed, aryl-[1,2] alkenyl-,[1,3,4] alkynyl-,[1,5–7] and acyl-substituted polysilanes[8–10] are photoactive under ultraviolet irradiation, and their photochemical behavior has been extensively studied. We have found that the photolysis of benzenoid aromatic disilanes and alkenyldisilanes by irradiation with a low-pressure mercury lamp in a hydrocarbon solution affords silenes produced from a 1,3-shift of a silyl group to the π-electron system.[1] We have also reported that the photolysis of disilanes having both phenyl and vinyl groups, 1-phenyl-1-vinyltetramethyldisilane and 1-phenyl-2-vinyltetramethyldisilane, in the presence of methanol gives only the product formed from the reaction of the silene arising from migration of a silyl group to the vinyl moiety with methanol. No products originating from migration of the silyl group to the phenyl ring were observed in the reaction mixture[3] (Scheme I).

In order to learn much more about the regiochemistry in the formation of the silenes, we have now initiated a systematic investigation on the photolysis of disilanes bearing two different types of π-electron systems in the molecule. In this paper, we report that the photolysis of 1-(3,4-dihydro-2*H*-6-pyranyl)-1-phenyltetramethyldisilane and 1-(3,4-dihydro-2*H*-6-pyranyl)-2-phenyltetramethyldisilane produces two types of silene intermediates and distribution of the products derived from the resulting silenes depends highly on the trapping agent used.

Results and Discussion

The starting disilanes 1-(3,4-dihydro-2*H*-6-pyranyl)-1-phenyltetramethyldisilane (1) and 1-(3,4-dihydro-2*H*-6-pyranyl)-2-phenyltetramethyldisilane (2) were synthesized by the reaction of (3,4-dihydro-2*H*-6-pyranyl)lithium with 1-chloro-1-phenyltetramethyldisilane[11] and 1-chloro-2-phenyltetramethyldisilane.[12]

Photolysis of 1. When a solution of 1 in the presence of a large excess of methanol in hexane was photolyzed by irradiating with a low-pressure mercury lamp for 2 h, 73% of the starting compound 1 was photolyzed, and 2-(methoxymethylphenylsilyl)-3-(trimethylsilyl)tetrahydropyran (3) was obtained in 49% yield, in addition to 32% of the product whose molecular weight is calculated to be identical with that of 3. Compound 3 could be separated from its isomer in a pure form by preparative GLC. The structure of 3 was verified by IR, mass, and ^{1}H and ^{13}C NMR spectroscopic analysis, as well as by elemental analysis (see Experimental Section). The formation of 3 can best be understood in terms of the reaction of the silene arising from a 1,3-trimethylsilyl shift to the dihydropyranyl ring (silene A) with methanol. Compound 3 has three chiral centers and could exist as four diastereomers. However, GLC analysis and also spectroscopic analysis of the resulting products show that no other diastereomers are detected. Presumably, the photochemical isomerization of 1, giving the silene A, and also addition of methanol to this silene proceed with high stereospecificity. Indeed, in the ^{1}H NMR spectrum of 3, the coupling constant of hydrogen on the methoxysilyl-substituted carbon is determined to be $J = 10.2$ Hz, corresponding to the axial–axial coupling constant. If this is true, both silyl groups on the perhydropyranyl ring should be trans to each other. Presumably, methanol approaches the silicon–

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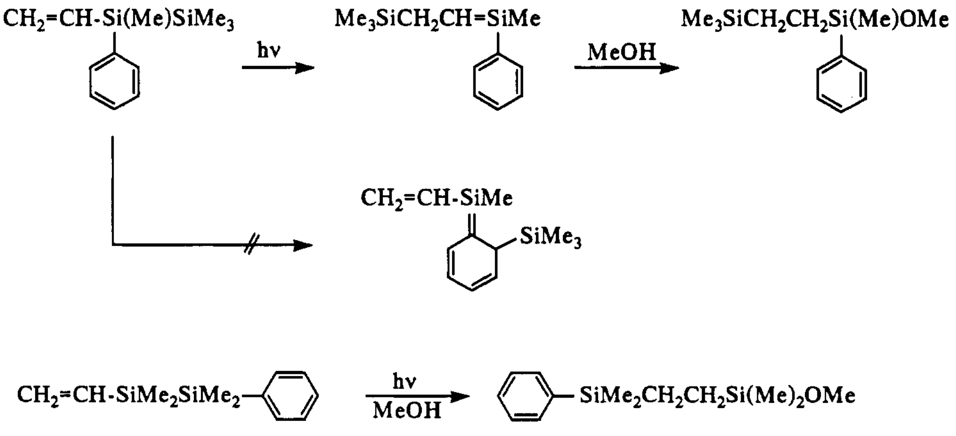
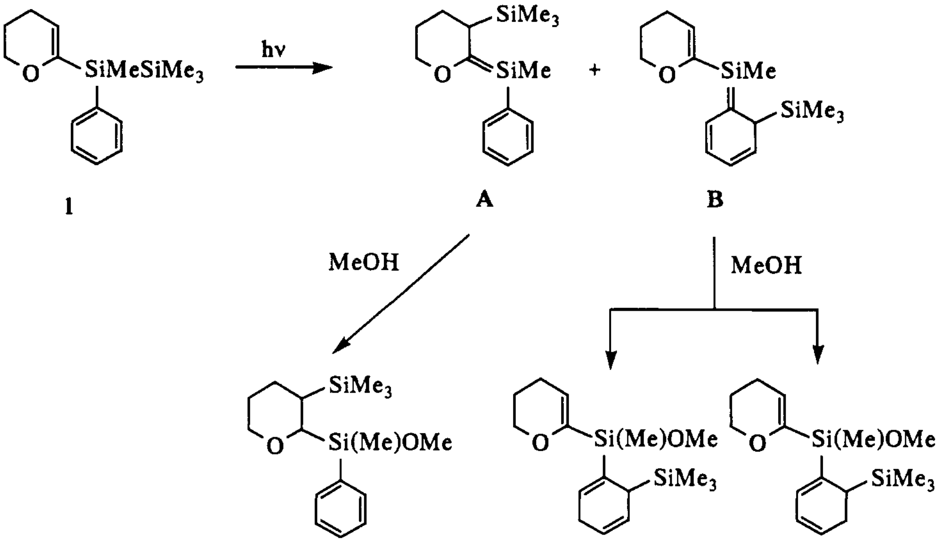
Scheme I



Scheme II



1 A B 3 4a 4b

carbon double bond of the silene A from the opposite side of the trimethylsilyl group on the perhydropyranyl ring and addition of methanol proceeds in an anti fashion. Both stereospecific addition[13] and nonstereospecific addition[10] of methanol have been reported to date.

The ^{1}H NMR spectrum of the other product, the isomer of **3**, showed it to be a mixture of two products (**4a,b**). The ratio of the products was calculated to be approximately 1:1 on the basis of the integral ratio of methylsilyl protons of **4a** (at 0.22 ppm) and **4b** (at 0.25 ppm). Unfortunately, all attempts to separate these isomers in a pure form were unsuccessful. A mixture consisting of a small amount of **3** and two isomers was always obtained. However, the 600-MHz ^{1}H NMR spectrum of this mixture clearly showed the presence of the cyclohexadienyl protons and a vinylic proton in a dihydropyranyl group. The resonances at 113.6, 114.4, and 156.6 (two carbons) ppm in the ^{13}C NMR spectrum of the mixture also revealed the presence of vinylic carbons in the dihydropyranyl ring. Therefore, we tentatively assigned these products to the bis(silyl)-substituted cyclohexadiene derivatives **4a,b**, which were produced from the reaction of the silene arising from a 1,3-trimethylsilyl shift to the phenyl ring (silene B) with methanol. Compounds **4a,b** have two chiral centers, and hence, it might be considered that **4a,b** are the diastereomers of one of the proposed structures. However, bis(silyl)cyclohexadienes analogous to **4a,b** have been obtained in the photolysis of tolylpentamethyldisilane in the presence of alcohols.[14,15] In these photolyses, both 1,4- and 1,6-adducts have been isolated, but no 1,2-adduct has been obtained to date. If our assignment for **4a,b** is correct, the photolysis of **1** must involve two different types of silenes, A and B (Scheme II).

Next, we carried out the photolysis of **1** in the presence of acetone and isobutene. The photolysis of **1** in the presence of a large excess of acetone afforded two products, 6-(dimethylmethylene)-5-(trimethylsilyl)tetrahydropyran (**5**) and 1-[(3,4-dihydro-2*H*-6-pyranyl)isopropoxymethylsilyl]-2-(trimethylsilyl)benzene (**6**) in 22 and 23% yields, respectively, in addition to 13% of the starting compound **1**. The formation of the products **5** and **6** can be best understood in terms of the reaction of two different types of the silene with acetone. The [2 + 2] cycloaddition of acetone to the silene A, followed by splitting off a silanone from the resulting silaoxetane, gives **5**, while the ene reaction of the silene B with acetone affords compound **6** (Scheme III). The reactions of the silene analogous to B with trapping agents such as olefins[15] and carbonyl com-

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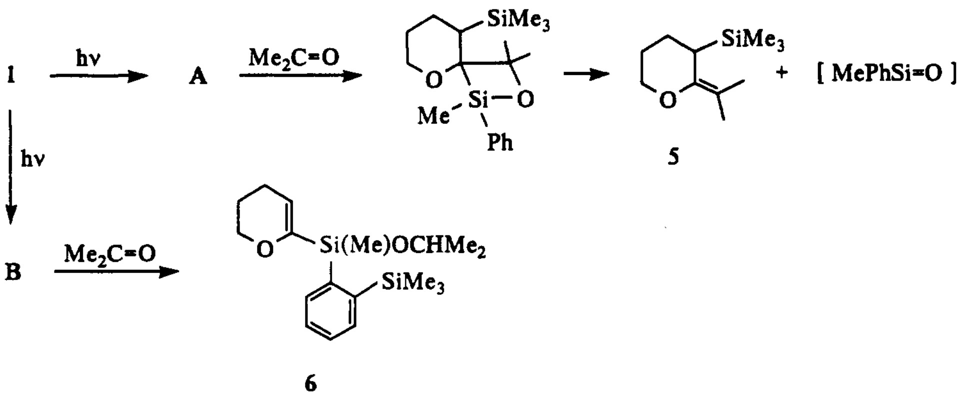
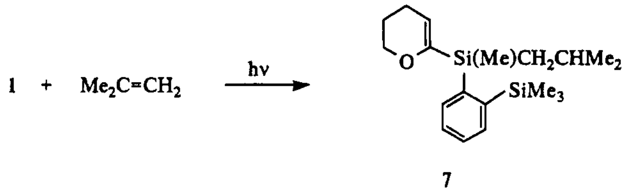
Scheme III



Scheme IV



pounds[16] reported to date always afford the product arising from the ene reaction. The fact that no [2 + 2] cycloadducts are produced in these reactions can be ascribed to a great tendency of the silene B to stabilize itself by restoring the aromatic sextet via the ene reaction.

Interestingly, when isobutene is used as a trapping agent, the adduct produced from the reaction of the silene B with isobutene is obtained as the sole product. Thus, irradiation of 1 with a large excess of isobutene gave 1-[(3,4-dihydro-2*H*-6-pyranyl)isobutylmethylsilyl]-2-(trimethylsilyl)benzene (7) in 38% yield, together with 15% of the starting compound 1 (Scheme IV). In this case, no product derived from the reaction of the silene A with isobutene was detected by either spectroscopic analysis or GLC analysis. These results indicate that the photolysis of 1 produces two photoisomers, silenes A and B. Methanol and acetone react with both silenes A and B, while isobutene reacts only with the silene B, under the conditions used.

In order to learn much more about the reactivity of the trapping agent toward the silenes, we carried out the photolysis of 1 in the presence of two different trapping agents. Irradiation of a hexane solution of 1 in the presence of approximately equimolar amounts of methanol and acetone gave products derived from the reaction of both silenes A and B with methanol, 3 (36%), **4a** (12%), and **4b** (12%), along with a small amount of 6 (8%) produced from the silene B and acetone. No product arising from the reaction of the silene A with acetone was detected in the photolysis mixture. Similar photolysis of 1 in the presence of methanol and isobutene afforded products 3 (39%), **4a** (13%) and **4b** (13%), produced from the addition of methanol to the silenes A and B. No isobutene adduct such as 7 was observed in the photolysis mixture by spectrometric analysis. In the presence of acetone and isobutene, the silenes A and B reacted with only acetone to give 5 and 6 in 24 and 30% yields, respectively. Again, no isobutene adduct was detected in the mixture. On the basis of the results obtained, the reactivities of three different types of the trapping agents toward the silenes A and B are in decreasing order, methanol, acetone, and isobutene.

Photolysis of 2. Two regioisomers of the silene are also produced in the photolysis of 2; one involves a 1,3-dimethylphenylsilyl shift to the dihydropyranyl ring (silene C) and the other comprises a 1,3-(dihydropyranyl)dimethylsilyl shift to the phenyl ring (silene D). In addition, the photolysis of 2 affords methylphenylsilene arising from homolytic scission of a silicon–silicon bond, followed by redistribution of the resulting radicals. Thus, when a hexane solution of 2 in the presence of methanol was photolyzed under the same conditions, 3-(dimethylphenylsilyl)-2-(methoxydimethylsilyl)tetrahydropyran (8; 35% yield) and a mixture of isomers (**9a,b**; 34% combined yield) were obtained, along with 12% of the starting compound 2. In this photolysis, dimethylphenylsilane and methoxydimethylphenylsilane derived from homolytic scission of a silicon–silicon bond were obtained in 11 and 16% yields, respectively. Compound 8 could be separated from the mixture of isomers by preparative GLC. The structure of 8 was verified by mass, IR, and ^{1}H and ^{13}C NMR spectra (see Experimental Section). Again, no other stereoisomers of 8 were detected in the reaction mixture. The formation of 8 can be explained in terms of the reaction of silene C with methanol. Although all attempts to isolate the isomers **9a,b** in a pure form were unsuccessful, the 600-MHz ^{1}H NMR spectrum of the isomers revealed the presence of a vinylic proton in the pyranyl ring at δ 4.86–5.36 ppm. Although the assignment of the structures of **9a,b** is tentative, it seems likely that **9a,b** are the disilyl-substituted cyclohexadiene derivatives expected to be produced from the reaction of silene D with methanol (Scheme V).

The photolysis of 2 in the presence of acetone gave dimethylphenylsilane, dimethylphenyl(α-propenyloxy)silane (10), and 1-(isopropoxydimethylsilyl)-2-[(3,4-dihydro-2*H*-6-pyranyl)dimethylsilyl]benzene (11) in 13, 8, and 29% yields, together with 12% of an unidentified product whose molecular weight is calculated to be 319, corresponding to $[C_{18}H_{30}Si_2O_2 - CH_3]$. All attempts to isolate this compound by use of preparative GLC were unsuccessful; always decomposition products were obtained. The formation of compound 10 can be explained in terms of the ene reaction of methylphenylsilene with acetone, while 11 may be understood by the ene reaction of the silene D with acetone (Scheme VI).

In marked contrast to the photolysis of 1 in the presence of isobutene, in which only the product derived from the silene B arising from a 1,3-trimethylsilyl shift to the phenyl ring was obtained, similar irradiation of 2 with isobutene under the same conditions afforded dimethylphenylsilane and 6-[dimethyl(2-methylpropen-3-yl)silyl]-5-(dimethylphenylsilyl)-3,4-dihydropyran (12) in 10 and 7% yields,

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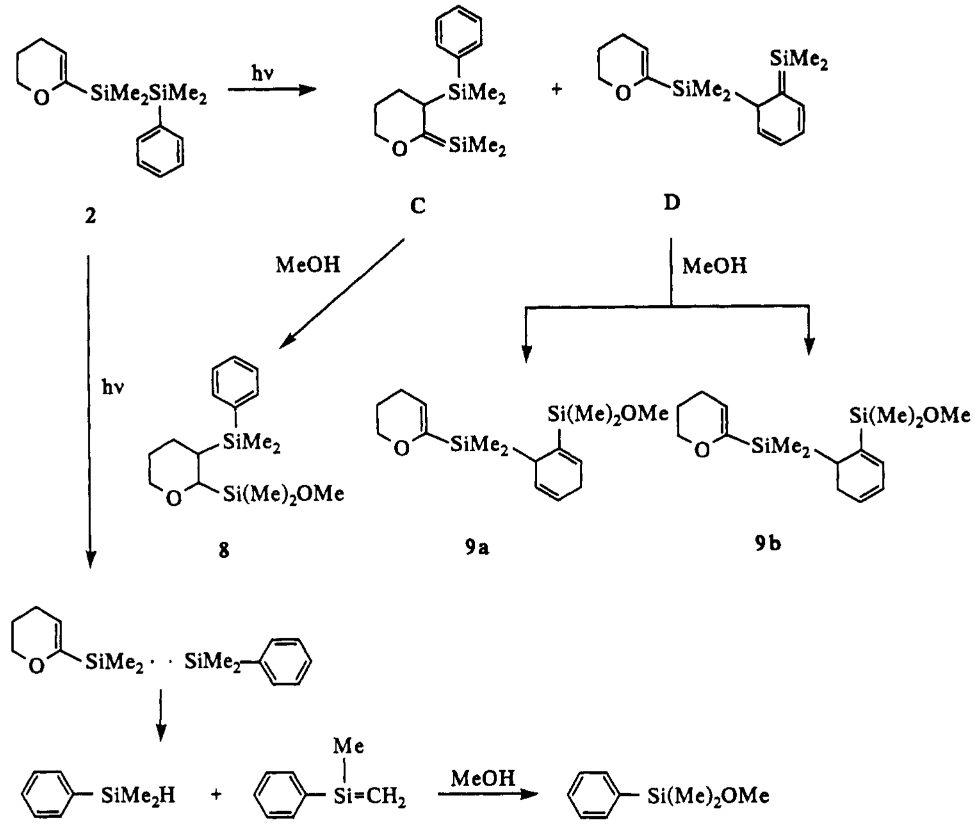
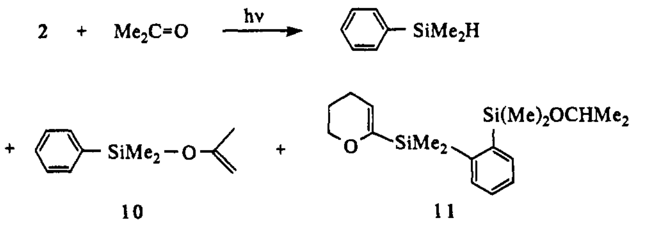
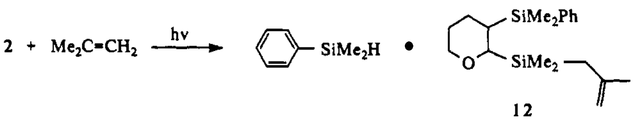
Scheme V



Scheme VI



Scheme VII



as the volatile products. Neither the product derived from the reaction of methylphenylsilene with isobutene nor the product arising from the silene D with isobutene was detected either by spectrometric analysis or by GLC analysis (Scheme VII). Both silenes probably are formed in this photolysis, but they would be transformed into nonvolatile products, because of the low quenching ability of isobutene. The low yield of the adduct **12** can also be explained by the same reason.

In conclusion, the photolysis of (dihydropyranyl)phenyldisilanes produces two isomers of the silene; one involves a 1,3-silyl shift to the pyranyl ring, and the other comprises a 1,3-silyl shift to the phenyl ring. The ratio of the products derived from both silenes highly depends on the trapping agent used.

Experimental Section

General Procedure. All reactions were carried out under an atmosphere of dry nitrogen. Infrared spectra were recorded on a Perkin-Elmer 1600 FT-infrared spectrometer. UV spectra were determined with a Hitachi 150-20 spectrophotometer. Mass spectra were measured on a Shimadzu Model GCMS-QP-1000 instrument. ^{1}H NMR and ^{13}C NMR spectra of all compounds with the exception of **3**, **4**, and **8** were determined on a JEOL Model JNM-FX-90A spectrometer. ^{1}H NMR spectra of **3**, **4**, and **8** were measured on a Bruker AM-600 spectrometer.

The yields of products were determined by GLC with an internal standard on the basis of the unrecovered starting disilanes **1** and **2**.

Tetrahydrofuran and hexane used as solvents were dried over lithium aluminum hydride and distilled before use.

Preparation of 1-(3,4-Dihydro-2*H*-6-pyranyl)-1-phenyltetramethyldisilane (1). In a 300-mL three-necked flask fitted with a reflux condenser, dropping funnel, and stirrer was placed 10.08 g (0.120 mol) of 3,4-dihydro-2*H*-pyran dissolved in 50 mL of THF. To this was added 120 mL (0.09 mol) of a *tert*-butyllithium–pentane solution over 1 h at −78 °C. The mixture was stirred for 4 h at room temperature, and then 20.0 g (0.088 mol) of 1-chloro-1-phenyltetramethyldisilane was added to the lithiated compound with ice cooling. The reaction mixture was stirred for 10 h at room temperature and hydrolyzed with a saturated sodium chloride solution. The organic layer was separated, and the aqueous layer was extracted with hexane. The organic layer and extracts were combined and washed with water and dried over potassium carbonate. After evaporation of the solvents, the residue was fractionally distilled under reduced pressure to give 16.4 g (68% yield) of **1**: bp 105–108 °C (0.5 Torr); MS *m*/*e* 261 ($M^+ - 15$); IR 1613, 1428, 1272, 1244, 1225, 1105 cm^{-1}; UV λ_{max} (cyclohexane) 204 nm (ϵ = 22 500), 222 (19 400); ^{1}H NMR (δ, in $CDCl_3$) 0.11 (s, 9 H, Me_3Si), 0.38 (s, 3 H, MeSi), 1.72–2.14 (m, 4 H, CH_2CH_2), 3.92 (br t, 2 H, CH_2O, J = 4.8 Hz), 4.99 (br t, 1 H, HC=C(O), J = 3.6 Hz), 7.20–7.59 (m, 5 H, phenyl ring protons); ^{13}C NMR (δ, in $CDCl_3$) −6.5 (MeSi), −1.8 (Me_3Si), 21.2, 22.9 (CH_2CH_2), 65.7 (CH_2O), 112.6 (CH=C—O), 127.7, 128.5, 134.5, 136.9 (phenyl ring carbons), 158.5 (O—C=CH). Anal. Calcd for $C_{15}H_{24}OSi_2$: C, 65.15; H, 8.75. Found: C, 65.25; H, 8.75.

Preparation of 1-(3,4-Dihydro-2*H*-6-pyranyl)-2-phenyltetramethyldisilane (2). In a 200-mL three-necked flask was placed 5.6 g (0.067 mol) of 3,4-dihydropyran in 60 mL of THF. To this was added 40 mL (0.068 mol) of a *tert*-butyllithium–pentane solution over 30 min at −78 °C. The mixture was then warmed to room temperature and stirred for 3 h. To this solution was added 9.2 g (0.040 mol) of 1-chloro-2-phenyltetramethyldisilane at 0 °C. The mixture was stirred for 10 h at room temperature. The solvent THF was distilled off, 20 mL of hexane was added to the mixture, and lithium chloride was filtered off. The solvents were evaporated, and the residue was distilled under reduced pressure to give 6.02 g (54% yield) of **2**: bp 105–107 °C (3 Torr); MS *m/e* 261 ($M^+ - Me$); IR 1614, 1427, 1405, 1272, 1244, 1225, 1106 cm^{-1}; UV λ_{max} (cyclohexane) 210 nm (ϵ = 14 000), 231 (13 500); ^1H NMR (δ, in $CDCl_3$) 0.10 (s, 6 H, Me_2Si), 0.35 (s, 6 H, Me_2Si), 1.71–2.15 (m, 4 H, CH_2CH_2), 3.85 (br t, 2 H, CH_2O, *J* = 4.8 Hz), 4.88 (br t, 1 H, HC=C(O), *J* = 3.6 Hz); 7.23–7.63 (m, 5 H, phenyl ring protons); ^{13}C NMR (δ, in $CDCl_3$) −5.0 (Me_2Si), −3.6 (Me_2Si), 21.0, 22.9 (CH_2CH_2), 65.6, (CH_2O), 111.0 (HC=C—O), 127.6, 128.2, 133.9, 139.5 (phenyl ring carbons), 159.5 (C(O)=CH). Anal. Calcd for $C_{15}H_{24}OSi_2$: C, 65.15; H, 8.75. Found: C, 64.95; H, 8.65.

Photolysis of 1 in the Presence of Methanol. In a 70-mL reaction vessel fitted internally with a low-pressure mercury lamp bearing a Vycor filter was placed a solution of 0.7003 g (2.54 mmol) of **1**, 0.8106 g (25.3 mmol) of methanol, and 0.2100 g (1.14 mmol) of tridecane as an internal standard in 60 mL of hexane. The solution was irradiated at room temperature with a slow stream of nitrogen bubbling through the mixture. After 2 h of irradiation, 73% of the starting compound **1** was photolyzed. After the hexane solvent was distilled off, the residue was analyzed by GLC as being 2-(methyoxymethylphenylsilyl)-3-(trimethylsilyl)tetrahydropyran (**3**) (49% yield) and two isomers of 1-[(3,4-dihydro-2*H*-6-pyranyl)methoxymethylsilyl]-2-(trimethylsilyl)cyclohexadiene (**4a,b**; 32% combined yield). Compound **3** and a mixture of **4a,b** were isolated by preparative GLC. For **3**: MS *m/e* 308 (M^+); IR 2949, 2834, 1615, 1428, 1188, 1083 cm^{-1}; ^1H NMR (δ, in $CDCl_3$) 0.04 (s, 9 H, Me_3Si), 0.45 (s, 3 H, MeSi), 1.18–1.23 (m, 1 H, HC(Si)—C), 1.38–1.90 (m, 4 H, CH_2CH_2), 3.29 (dt, 1 H, OCH_a, *J* = 11.0, 2.4 Hz), 3.38 (s, 3 H, CH_3O), 3.45 (d, 1 H, OCH(Si), *J* = 10.2 Hz), 3.85 (br d, 1 H, OCH_b, *J* = 11.0 Hz), 7.34–7.68 (m, 5 H, phenyl ring protons); ^{13}C NMR (δ, in C_6D_6) −6.8 (MeSi), −1.5 (Me_3Si), 27.0 (CH_2), 27.1 (CH_2), 28.2 (CHSi), 50.2 (CH_3O), 69.6 (CH(Si)—O), 72.8 (CH_2O), 127.8, 129.6, 134.5, 136.6 (phenyl ring carbons). Anal. Calcd for $C_{16}H_{28}O_2Si_2$: C, 62.28, H, 9.15. Found: C, 62.64; H, 9.37. For **4a,b** (1:1 mixture contaminated with 29% of **3**): MS *m/e* 308 (M^+); IR 2974, 2884, 1623, 1435, 1271, 1091 cm^{-1}; ^1H NMR (δ, in $CDCl_3$) 0.00 (s, Me_3Si), 0.22, 0.25 (s, MeSi), 1.45–2.73 (m, CH_2CH_2, CH_2—C=C, HC=$SiMe_3$), 3.47 (s, MeO), 3.92 (br t, CH_2O, *J* = 4.8 Hz), 4.95–5.23 (m, HC=C(O)—Si), 5.36–6.23 (m, olefinic protons).

Photolysis of 1 in the Presence of Acetone. A solution of 0.9700 g (3.51 mmol) of **1**, 1.2818 g (22.1 mmol) of acetone, and 0.1711 g (0.96 mmol) of tridecane as an internal standard in 60 mL of hexane was irradiated for 2 h. The solvent was distilled off, and the residue was then analyzed by GLC as being 6-(dimethylmethylene)-5-(trimethylsilyl)tetrahydropyran (**5**; 22% yield), 1-[(3,4-dihydro-2*H*-6-pyranyl)isopropoxymethylsilyl]-2-(trimethylsilyl)benzene (**6**; 23% yield), and 13% of the starting **1**. Compounds **5** and **6** were isolated by preparative GLC. For **5**: MS *m/e* 198 (M^+); IR 1674, 1613, 1453, 1368, 1336, 1286, 1278, 1247, 1207, 1140, 1104 cm^{-1}; ^1H NMR (δ, in $CDCl_3$) 0.04 (s, 9 H, Me_3Si), 1.21–2.17 (m, 5 H, $CH_2CH_2CH(Si)$), 1.54 (s, 3 H, Me), 1.64 (s, 3 H, Me), 3.24–3.60 (m, 1 H, CH_a—O), 3.88–4.16 (m, 1 H, CH_b—O); ^{13}C NMR (δ, in $CDCl_3$) −0.9 (Me_3Si), 16.7 (Me), 18.9 (Me), 24.1, 24.7, 25.8 ($CH_2CH_2CH(Si)$), 69.7 (CH_2—O), 108.4, 147.7 (olefinic carbons). Anal. Calcd for $C_{11}H_{22}OSi$: C, 66.60; H, 11.18. Found: C, 66.51; H, 10.92. For **6**: MS *m/e* 334 (M^+); IR 1616, 1447, 1416, 1382, 1368, 1274, 1249, 1226, 1172, 1119, 1101 cm^{-1}; ^1H NMR (δ, in $CDCl_3$) 0.38 (s, 9 H, Me_3Si), 0.45 (s, 3 H, MeSi), 1.25 (d, 3 H, $Me_aCH(Me_b)$, *J* = 6.2 Hz), 1.26 (d, 3 H, $Me_bCH(Me_a)$, *J* = 6.2 Hz), 1.70–2.18 (m, 4 H, CH_2CH_2), 3.95 (br t, 2 H, CH_2O, *J* = 5.0 Hz), 4.26 (sep, 1 H, $HCMe_2$, *J* = 6.2 Hz), 5.06 (br t, 1 H, HC=C(O), *J* = 3.6 Hz), 7.20–7.84 (m, 4 H, phenyl ring protons); ^{13}C NMR (δ, in $CDCl_3$) −1.4 (MeSi), 1.6 (Me_3Si), 20.8, 22.7 (CH_2CH_2), 25.3 (Me), 25.6 (Me), 65.6 (CH_2—O), 66.4 ($CHMe_2$), 114.2 (CH=C(O)), 127.4, 128.3, 134.9, 135.3, 141.8, 146.9 (phenyl ring carbons), 158.5 (C(O)=CH). Anal. Calcd for $C_{18}H_{30}O_2Si_2$: C, 64.51; H, 9.04. Found: C, 64.50; H, 9.00.

Photolysis of 1 in the Presence of Isobutene. A solution of 0.8906 g (3.23 mmol) of **1**, 1.64 g (29.3 mmol) of isobutene, and 0.0929 g (0.505 mmol) of tridecane as an internal standard in 60 mL of hexane was photolyzed for 3 h. The solvent was evaporated, and the residue was analyzed by GLC as being 1-[(3,4-dihydro-2*H*-6-pyranyl)isobutylmethylsilyl]-2-(trimethylsilyl)benzene (**7**; 38% yield) and 15% of the starting **1**. For **7**: MS *m/e* 332 (M^+); IR 1616, 1462, 1447, 1415, 1249, 1225, 1115 cm^{-1}; ^1H NMR (δ, in $CDCl_3$) 0.37 (s, 9 H, Me_3Si), 0.48 (s, 3 H, MeSi), 0.92 (d, 3 H, $Me_aCH(Me_b)$, *J* = 6.4 Hz), 0.96 (d, 3 H, $Me_bCH(Me_a)$, *J* = 6.4 Hz), 0.98 (d, 2 H, CH_2Si, *J* = 6.4 Hz), 1.41–2.13 (m, 5 H, CH_2CH_2, $HCMe_2$), 3.96 (br t, 2 H, CH_2O, *J* = 4.5 Hz), 4.96 (t, 1 H, HC=C(O), *J* = 3.6 Hz), 7.30–7.81 (m, 4 H, phenyl ring protons); ^{13}C NMR (δ, $CDCl_3$) −1.8 (MeSi), 2.1 (Me_3Si), 20.9, 22.7 (CH_2CH_2), 24.9, 25.1, 26.2 (CH_2CHMe_2), 65.7 (CH_2O), 113.1 (HC=C(Si)), 127.5, 127.9, 135.5, 136.3, 142.7, 146.8 (phenyl ring carbons), 159.5 (C(O)=CH). Anal. Calcd for $C_{19}H_{32}OSi_2$: C, 68.61; H, 9.70. Found: C, 68.34; H, 9.60.

Photolysis of 1 in the Presence of Methanol and Acetone. A solution of 0.3370 g (1.22 mmol) of **1**, 0.2328 g (7.27 mmol) of methanol, 0.4212 g (7.26 mmol) of acetone, and 0.0987 g (0.54 mmol) of tridecane as an internal standard in 20 mL of hexane was photolyzed for 1 h. The solvent was evaporated, and the residue was analyzed by GLC as being **3** (36% yield), **4a,b** (24% combined yield), **6** (8% yield), and 20% of the starting **1**.

Photolysis of 1 in the Presence of Methanol and Isobutene. A solution of 0.3412 g (1.24 mmol) of **1**, 0.4127 g (12.9 mmol) of methanol, 1.65 g (29.5 mmol) of isobutene, and 0.1052 g (0.57 mmol) of tridecane as an internal standard in 20 mL of hexane was photolyzed for 1.5 h. The solvent was evaporated, and the residue was analyzed by GLC as being **3** (39% yield), **4a,b** (26% combined yield), and 15% of the starting **1**.

Photolysis of 1 in the Presence of Acetone and Isobutene. A solution of 0.3426 g (1.24 mmol) of **1**, 0.9336 g (16.1 mmol) of acetone, 1.37 g (24.5 mmol) of isobutene, and 0.0894 g (0.49 mmol) of tridecane as an internal standard in 20 mL of hexane was photolyzed for 1 h. The solvent was evaporated, and the residue was analyzed by GLC as being **5** (24% yield), **6** (30% yield), and 17% of the starting **1**.

Photolysis of 2 in the Presence of Methanol. A solution of 0.3658 g (1.33 mmol) of **2**, 0.3133 g (9.79 mmol) of methanol, and 0.0800 g (0.43 mmol) of tridecane as an internal standard in 20 mL of hexane was photolyzed for 45 min. The solvent was evaporated, and the residue was analyzed by GLC as being **8** (35% yield), **9a,b** (34% combined yield), dimethylphenylsilane (11% yield), methoxydimethylphenylsilane (16% yield), and 12% of the unreacted **2**. Products **8** and a mixture of isomers were separated by preparative GLC. For **8**: MS *m/e* 308 (M^+); IR 1615, 1428, 1370, 1248, 1189, 1086 cm^{-1}; ^1H NMR (δ, in $CDCl_3$) 0.06 (s, 3 H, MeSi), 0.10 (s, 3 H, MeSi), 0.30 (s, 3 H, MeSi), 0.35 (s, 3 H, MeSi), 1.32–1.70 (m, 5 H, CH_2CH_2CHSi), 3.22 (d, 1 H, OCH(Si), *J* = 10.0 Hz), 3.29 (s, 3 H, OMe), 3.33 (dt, 1 H, OCH_a, *J* = 11.0, 2.6 Hz), 3.88 (br d, 1 H, OCH_b, *J* = 11.0 Hz), 7.31–7.58 (m, 5 H, phenyl ring protons). Anal. Calcd for $C_{16}H_{28}O_2Si_2$: C, 62.28; H, 9.15. Found: C, 62.25; H, 9.15. For **9a,b** (1:1 mixture contaminated with 8% of **2**); MS *m/e* 308; IR 1616, 1429, 1249, 1089 cm^{-1}; ^1H NMR (δ, in $CDCl_3$) 0.15 (br s, Me_2Si), 1.67–2.54 (m, CH_2CH_2, -CH_2C=C, CH(Si)), 3.40 (s, MeO), 3.90 (br t, CH_2O, *J* = 4.8 Hz), 4.86–5.36 (m, HC=C(O)Si), 5.50–6.36 (m, olefinic protons).

All spectral data obtained for dimethylphenylsilane and methoxydimethylphenylsilane were identical for authentic samples.

Photolysis of 2 in the Presence of Acetone. A mixture of 0.3917 g (1.42 mmol) of **2**, 0.4654 g (8.02 mmol) of acetone, and 0.1176 g (0.63 mmol) of tridecane as an internal standard in 20 mL of hexane was photolyzed for 45 min. The GLC analysis of the resulting mixture showed the presence of dimethylphenylsilane (13% yield), **10** (8% yield), and **11** (29% yield), in addition to 21% of the unreacted **2**. For **10**: MS *m/e* (M^+); IR 1637, 1489, 1427, 1276, 1120 cm^{-1}; ^1H NMR (δ, in $CDCl_3$) 0.51 (s, 6 H, Me_2Si), 1.78 (s, 3 H, Me), 4.01 (br s, 2 H, CH_2), 7.14–7.67 (m, 5 H, phenyl ring protons); ^{13}C NMR (δ, in $CDCl_3$) −1.2 (Me_2Si), 22.8 (Me), 91.8 (CH_2=C(Me)O), 127.9, 129.7, 133.3, 137.7 (phenyl ring carbons), 155.8 (OC(Me)=CH_2). Anal. Calcd for $C_{11}H_{16}OSi$: C, 68.69; H, 8.38. Found: C, 68.46; H, 8.35. For **11**: MS *m/e* 319 ($M^+ - Me$); IR 1616, 1449, 1415, 1381, 1368, 1250, 1226, 1171, 1119 cm^{-1}; ^1H NMR (δ, in $CDCl_3$) 0.45 (s, 6 H, Me_2Si), 0.52 (s, 6 H, Me_2Si), 1.24 (d, 6 H, Me_2CH, *J* = 6.1 Hz), 1.71–2.20 (m, 4 H, CH_2CH_2), 4.08 (br t, 2 H, CH_2O, *J* = 5.5 Hz), 4.14 (sep, 1 H, $OCHMe_2$), 5.06 (br t, 1 H, HC=C(Si), J = 3.8 Hz), 7.29–7.90 (m, 4 H, phenyl ring protons); ^{13}C NMR (δ, in CDCl$_3$) −1.0 (Me$_2$Si), 1.4 (Me$_2$Si), 20.9, 22.8 (CH$_2$CH$_2$), 25.7 (Me$_2$C), 65.6, 65.7 (CH$_2$O and CH(O)Me$_2$), 112.3 (HC=C(Si)), 127.8, 128.1, 134.7, 136.2, 143.3, 145.2 (phenyl ring carbons), 160.3 (C(O)=C). Anal. Calcd for $C_{18}H_{30}O_2Si_2$: C, 64.61; H, 9.04. Found: C, 64.44; H, 8.80.

The retention time for GLC and the mass spectrum of dimethylphenylsilane were identical with those of an authentic sample.

Photolysis of 2 in the Presence of Isobutene. A mixture of 0.3669 g (1.33 mmol) of **2**, 1.18 g (21.1 mmol) of isobutene, and 0.0819 g (0.64 mmol) of tridecane in 20 mL of hexane was photolyzed for 45 min. The GLC analysis of the mixture showed the presence of dimethylphenylsilane (10% yield), **12** (7% yield), and the starting **2** (9% yield). Product **12** was isolated by preparative GLC: MS m/e 332 (M$^+$); IR 1635, 1428, 1372, 1248, 1153, 1108 cm^{-1}; ^{1}H NMR (δ, in C$_6$D$_6$) 0.02 (s, 3 H, MeSi), 0.14 (s, 3 H, MeSi), 0.41 (s, 3 H, MeSi), 0.54 (s, 3 H, MeSi), 0.89–2.07 (m, 5 H, CH$_2$CH$_2$CHSi), 1.60 (br s, 2 H, CH$_2$Si), 1.67 (br s, 3 H, MeC=C), 3.20–4.07 (m, 2 H, CH$_2$O), 3.48 (br d, 1 H, HC(O)Si, J = 2.9 Hz), 4.63 (br s, 1 H, H$_a$CH=C), 4.75 (br s, 1 H, H$_b$CH=C), 7.11–7.71 (m, 5 H, phenyl ring protons); ^{13}C NMR (δ, in C$_6$D$_6$) −3.6 (MeSi), −3.2 (MeSi), −0.3 (Me$_2$Si), 25.3 (CHSiMe$_2$Ph), 26.1, 26.4 (Me and CH$_2$Si), 27.1, 29.6 (CH$_2$CH$_2$), 71.0 (CH$_2$O), 77.4 (CH(Si)O), 109.0 (CH$_2$=C), 128.0, 129.0, 134.3, 140.0 (phenyl ring carbons), 143.4 (C(Me)=C). Anal. Calcd for $C_{19}H_{32}OSi_2$: C, 68.61; H, 9.70. Found: C, 68.56; H, 9.70.

The retention time for GLC and the mass spectrum of dimethylphenylsilane were identical with those of an authentic sample.

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Electrochemistry of Organosilicon Compounds. 1. Synthesis of Di- and Trisilanes with Use of Mercury and Silver Electrode Systems

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Electrochemical formation of an Si–Si bond has been examined. Electrolysis of monochlorosilanes in 1,2-dimethoxyethane using a platinum cathode and a mercury anode gave disilanes in high yield, while the electrolysis of a mixture of two different monochlorosilanes produced unsymmetrical disilanes as main products. Similar treatment of a mixture of monochlorosilanes and dichlorosilanes gave trisilanes. The use of silver as the anode also gave the di- and trisilanes in high yields.

Introduction

In recent years, the rapid development of material science has led to extensive investigation of polymeric organosilicon compounds having silicon–silicon bonds in the polymer backbone. In this field, the silicon–silicon bond formation is of considerable importance for building up these molecules. However, the practical method used for the formation of the silicon–silicon bonds is limited to the alkali-metal condensation of chlorosilanes.[1–5]

A few papers concerning the silicon–silicon bond formation that involves no alkali-metal condensation have been published to date.[6–9] Hengge and his co-workers have reported that the electrochemical reduction of chlorosilanes using a Pt cathode and a Hg anode in dimethoxyethane led to the formation of coupling products.[6] Corriu et al. have demonstrated that chlorotriphenylsilane could be electrochemically coupled, but they found that large quantities of disiloxanes were formed even when the reaction was carried out under controlled-potential conditions.[7] More recently, Boudjouk has summarized the electroreductive coupling including dimerization of functionally substituted chlorosilanes,[8] but no detailed procedure is described. In this paper, we report electrochemical high-yield syntheses of disilanes and trisilanes from chlorosilanes.

Results and Discussion

The synthesis of polysilane oligomers by electrochemical reduction using mercury as a "sacrificial" anode was originally reported by Hengge and his co-workers.[6] First, we have followed this method for the Si–Si bond formation using chlorodimethylphenylsilane in an H-shaped divided cell having a sintered glass diaphragm, as reported by Hengge.[6] However, as the reaction progressed, mercury

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