Notes

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# Pyrolysis of 1,2-Diethyltetrachlorodisilane

## Young-Woo Kwak* and Kyung-Koo Lee

*Department of Chemistry, Kyungpook National University, Taegu 702-701, Korea*
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Silylenes are cleanly generated from α-elimination of simple disilanes through shift of a hydrogen, halogen, or alkoxy group attached to silicon.[1] Competition between hydrogen and chlorine shifts in the pyrolysis of 1,2-dichloro-1,2-dimethyldisilane had been examined.[1k] The results from this pyrolysis showed hydrogen shift was considerably more favorable than chlorine shift. From thermolysis of 1,2-dimethoxytetramethyldisilane, a silane and a silylene was formed *via* shift of the methoxy group but not the methyl group.[1b] A few results of alkyl group shift in the pyrolyses of disilanes have been reported.[1g,2,3] Davidson and coworkers reported that a methyl group shift in the pyrolysis of hexamethyldisilane requires a higher activation energy.[2] Evidences have been found for hydrogen and methyl shift in the conversion of disilirane (Me$_2$SiSiHMeCH$_2$) to β-silylsilylenes.[1g,3] It was reported that a methyl shift in the disilirane ring opening had a *ca.* 20 kcal/mol higher barrier than a hydrogen shift.[4]

We recently reported that vacuum pyrolysis of 1,2-diethyltetraalkoxydisilane in the presence of diene trapping agent was found to proceed through migration of alkoxy group and no migration of ethyl group attached to silicon.[5] Here, we wish to report silylene generation *via* alkyl group shift in the pyrolysis of 1,2-dialkyltetrachlorodisilane (alkyl= ethyl, methyl). It will be discussed the characteristics of chemical behavior of alkylchlorosilylenes produced in this

report, comparing with that of previously reported ethylmethoxysilylene. In an attempt to elucidate the energetics of thermal decomposition of 1,2-diethyltetrachlorodisilane into ethylchlorosilylene, chlorosilylene, and dichlorosilylene, the temperature dependence of the product distribution was examined and the AM 1 semi-empirical calculations[6] were performed to estimate the heats of formation for the molecules containing silicon.

## Experimental

**General.** All pyrolyses were carried out in a seasoned hot zone consisting of a 10 mm i.d. × 30 cm quartz tube wrapped with nichrome ribbon and covered with asbestos tape. This hot zone was seasoned with hexamethyldisilazane before use. Both residence and pressure were controlled by a 0.8 mm aperture placed at the end of vertical quartz tube which was connected to a vacuum line. The progress of pyrolysis was followed by gas chromatography with a flame ionization detector (FID) using a Hewlett-Packard 5890 instrument on a HP-1 capillary column (cross-linked 5% methylphenylsilicone, 25 m). Products yields were determined by gas chromatography with cyclohexane as an internal standard on the basis of the quantity of 1,2-dialkyltetrachlorodisilane decomposed. Seperation of the products was performed on

a Varian Model 920 GC with a thermal conductivity detector (TCD) using 20% OV-17 column (Chromosorb W 80/100, 1/4 in × 13 ft). The $^1$H NMR and $^{13}$C NMR spectra were recorded on a Hitachi R-1200 60 MHz and Bruker AM-300 NMR spectrometer in CDCl$_3$ with tetramethylsilane (TMS) as an internal standard. Mass spectra were obtained on a Hewlett Packard 5890 Series II GC coupled to a 5970 Series mass selective detector. High resolution mass spectra were obtained by using a Jeol SX-102A double focusing mass spectrometer.

**Materials.** For the synthesis of precursors, aluminum chloride, dichlorodiphenylsilane, 2,3-dimethyl-1,3-butadiene, ethyl bromide, lithium, and magnesium were purchased form Aldrich Chemical Company and used without further purification. All solvents were dried and distilled prior to use. 1,2-Dialkyltetrachlorodisilanes were prepared by known procedures.[7,8]

**Preparation of 1,2-diethyltetrachlorodisilane (1).**

For the preparation of chlorodiphenylethylsilane, to a stirred suspension of 3.90 g (0.16 g-atoms) of Mg turnings in 50 mL of dry ether was slowly added 13.1 g (0.12 mol) of ethyl bromide in 10 mL of dry ether at ice-water temperature. After being stirred for an additional 2 h at room temperature, the liquid was transferred to a dropping funnel by a cannula. The solution was then added dropwise with stirring under nitrogen to 25.2 g (0.10 mol) of dichlorodiphenylsilane in 100 mL of dry ether at room temperature. After addition was completed, the mixture was left overnight followed by filtration of the salts, then fractionally distilled under reduced pressure to afford 16.0 g (64.8 mmol, 65%, b.p. 128 °C/1.5 torr) of chlorodiphenylethylsilane. MS m/z (rel. intensity) : 248 (28), 246 (12) (M$^+$), 219 (37), 217 (100), 199 (12), 181 (11), 165 (1), 163 (2), 141 (4), 139 (2), 121 (3), 105 (3), 91 (4), 77 (4), 65 (4), 63 (8). For the preparation of 1,2-diethyltetraphenyldisilane, to a suspension of 0.35 g (0.05 g-atoms) of Li metals and 7.40 g (30.0 mmol) of chlorodiphenylethylsilane was slowly added 50 mL of dry THF at ice-water temperature. After being stirred for an additional 4 h at room temperature, the organic layer was transferred through a cannula to the reaction flask. The chlorodiphenylethylsilane (7.40 g, 30.0 mmol) in 10 mL of dry THF was placed in dropping funnel, and added to the solution at room temperature.[7] The reaction was exothermic and the mixture was stirred vigorously. After addition was completed, the reaction mixture was stirred overnight at warm temperature followed by filtration of the salts, then the organic layer was treated with water and dried over anhydrous calcium chloride. The volatile solvent was evaporated and the residue was recrystallized in chloroform to afford 8.6 g (20.3 mmol, 68%, mp 116-118 °C) of 1,2-diethyltetraphenyldisilane. $^1$H NMR: δ 1.09 (t, 6H, (SiCH$_2$CH$_3$)$_2$, J=7.0 Hz), 1.33 (q, 4H, (SiCH$_2$CH$_3$)$_2$, J=7.0 Hz), 7.40 (m, 12H, 4Ph), 7.51 (m, 8H, 4Ph). $^{13}$C NMR: δ 5.87, 8.84, 128.23, 129.33, 136.05, 136.28. For the preparation of 1,2-diethyltetrachlorodisilane, 8.0 g (18.9 mmol) of the 1,2-diethyltetraphenyldisilane in 50 mL of dry benzene was placed in a three-necked flask fitted with a stirrer, condenser and gas-inlet which was extended into the liquid nearly to the bottom of flask. To the stirred solution, 0.3 g (2.2 mmol) of sublimed aluminum chloride was added

and dry HCl gas was introduced through the gas-inlet tube.[8] The complete consumption of 1,2-diethyltetraphenyldisilane was checked by GC analysis. After reaction was completed, it was mixed well with a small amount of anhydrous acetone in order to deactivate the aluminum chloride remaining in the reaction mixture and then the solvent was evaporated. Bulb-to-bulb distillation of the mixture followed by preparative gas chromatography on an OV-17 column afforded 4.0 g (15.6 mmol, 82%) of **1**.

Compound 1: $^1$H NMR: δ 0.97 (q, 4H, (SiCH$_2$CH$_3$)$_2$, J= 8.0 Hz), 1.37 (t, 6H, (SiCH$_2$CH$_3$)$_2$, J=8.0 Hz). $^{13}$C NMR: δ 1.75, 6.56. MS m/z (rel. intensity): 260 (2), 258 (7), 256 (13), 254 (10) (M$^+$), 229 (2), 227 (4), 225 (3), 192 (1), 131 (7), 129 (37), 127 (57), 103 (5), 102 (2), 101(23), 100 (8), 99 (35), 98 (9), 94 (52), 92 (100), 66 (3), 65 (31), 64 (7), 63 (76). HRMS cacld for C$_4$H$_{10}$Si$_2$Cl$_4$ (M$^+$) 253.9077, found 253.9063.

**Preparation of 1,2-Dimethyltetrachlorodisilane (3).** 1,2-Dimethyltetraphenyldisilane (2) and 3 were prepared through the same procedure as mentioned above. The spectral properties of these products were as follows.

Compound 2: $^1$H NMR: δ 0.66 (s, 6H, (CH$_3$Si)$_2$), 7.23-7.39 (m, 20H, 4Ph). $^{13}$C NMR: δ −4.11, 127.80, 128.91, 135.18, 136.54.

Compound 3: $^1$H NMR: δ 1.00 (s, 6H, (CH$_3$Si)$_2$). $^{13}$C NMR: δ 5.14. MS m/z (rel. intensity): 232 (1), 230 (2), 228 (4), 226 (3) (M$^+$), 215 (1), 213 (2), 211 (2), 195 (1), 193 (2), 191 (2), 117 (5), 115 (31), 113 (42), 100 (1), 98 (2), 95 (2), 93 (6), 80 (16), 78 (58), 65 (43), 63 (100), 43 (15).

**Pyrolysis of 1,2-Diethyltetrachlorodisilane (1) in the presence of 2,3-dimethyl-1,3-butadiene (4).**

The mixture of 0.3 g (1.2 mmol) of **1** and 1.5 g (18.3 mmol) of **4** as a trapping agent was injected into rubber septum at the inlet of vertical quartz tube, which is connected to a vacuum line, using a gas tight syringe over a period of 3 h. The starting material **1** was almost decomposed in the temperature range from 350 to 450 °C. The pyrolysate was collected in a trap cooled with a liquid nitrogen and separated by preparative gas chromatography. The observed major products were 1-chloro-1-ethyl-3,4-dimethyl-1-silacyclopent-3-ene (5), 1-chloro-1-hydrido-3,4-dimethyl-1-silacyclopent-3-ene (6), and 1,1-dichloro-3,4-dimethyl-1-silacyclopent-3-ene (7) along with ethyltrichlorosilane and dichlorodiethylsilane. The trapped products yields are listed in Table 1.

Compound 5: $^1$H NMR: δ 0.98 (q, 2H, SiCH$_2$CH$_3$, J=7.2 Hz), 1.07 (t, 3H, SiCH$_2$CH$_3$, J=7.2 Hz), 1.61 (bs, 4H, Si (CH$_2$)$_2$), 1.73 (bs, 6H, (CCH$_3$)$_2$). $^{13}$C NMR: δ 6.82, 9.11, 18.94, 25.69, 129.84. MS m/z (rel. intensity): 176 (18), 174 (53) (M$^+$), 161 (1), 159 (2), 147 (36), 145 (100), 138 (15), 131 (11), 117 (13), 109 (46), 105 (15), 93(8), 91 (9), 81 (10), 79 (18), 67 (15), 65 (32), 63 (60), 53 (14).

Compound 6: $^1$H NMR: δ 1.69-1.92 (m, 4H, Si(CH$_2$)$_2$), 1.80 (bs, 6H, (CCH$_3$)$_2$), 5.23 (quin, 1H, SiH, J=1.8 Hz). $^{13}$C NMR: δ 19.17, 25.91, 129.76. MS m/z (rel. intensity): 148 (28), 146 (77) (M$^+$), 133 (31), 131 (87), 120 (9), 118 (25), 110 (41), 105 (24), 104 (32), 95 (44), 93 (8), 91 (13), 81 (13), 79 (23), 67 (37), 65 (55), 63 (100), 53 (21).

Compound 7: $^1$H NMR: δ 1.75 (bs, 6H, (CCH$_3$)$_2$), 1.86 (bs, 4H, Si(CH$_2$)$_2$). $^{13}$C NMR: δ 18.81, 29.29, 129.31. MS m/z (rel. intensity): 184 (8), 182 (43),180 (64) (M$^+$), 169 (7),

167 (38), 165 (57), 154 (11), 152 (16), 146 (13), 144 (39), 142 (4), 140 (20), 138 (29), 131 (12), 129 (34), 113 (11), 112 (9), 98 (12), 82 (49), 81 (16), 79 (12), 67 (100), 65 (34), 63 (61), 53 (17). The formed ethyltrichlorosilane and dichlorodiethylsilane were identified with the MS of authentic samples. A trace of 1,2-dimethylcyclohexene (8) in the reaction mixture was observed and the mass spectra of 8 was identical with that reported earlier.[9]

**Pyrolysis of 1,2-dimethyltetrachlorodisilane (3) in the presence of 2,3-dimethyl-1,3-butadiene (4).**

The pyrolysis of 0.27 g (1.18 mmol) of **3** and 1.50 g (18.26 mmol) of **4** at 450 °C was conducted in the same procedure as described above. The pyrolysate was separated by preparative gas chromatography to afford 1-chloro-1-methyl-3,4-dimethyl-1-silacyclopent-3-ene (**9**, 42%) and a trace of **7** along with methyltrichlorosilane and dichlorodimethylsilane. The reactant **3** was almost decomposed at temperatures from 350 to 450 °C.

Compound **9**: $^1$H NMR: $\delta$ 0.63 (s, 3H, Si$CH_3$), 1.69 (bs, 4H, Si($CH_2)_2$), 1.78 (bs, 6H, (C$CH_3)_2$). $^{13}$C NMR: $\delta$ 1.31, 19.04, 27.54, 129.59. MS m/z (rel. intensity): 162 (19), 160 (55) (M$^+$), 147 (20), 145 (58), 134 (2), 132 (5), 124 (28), 120 (10), 119 (9), 118 (18), 117 (12), 109 (42), 107 (6), 105 (29), 95 (8), 93 (16), 81 (15), 80 (8), 79 (34), 78 (23), 67 (30), 65 (50), 63 (100), 53 (39), 43 (68). The formation of methyltrichlorosilane and dichlorodimethylsilane was observed and confirmed with the MS of authenic samples.

## Results and Discussion

The vacuum pyrolysis of 1,2-diethyltetrachlorodisilane (**1**) in the presence of 15-fold excess of 2,3-dimethyl-1,3-butadiene (**4**) as an efficient trapping agent in the temperature range from 350 to 450 °C affords three major products, 1-chloro-1-ethyl-3,4-dimethyl-1-silacyclopent-3-ene (**5**), 1-chloro-1-hydrido-3,4-dimethyl-1-silacyclopent-3-ene (**6**), 1,1-dichloro-3,4-dimethyl-1-silacyclopent-3-ene (**7**) along with ethyltrichlorosilane and dichlorodiethylsilane.
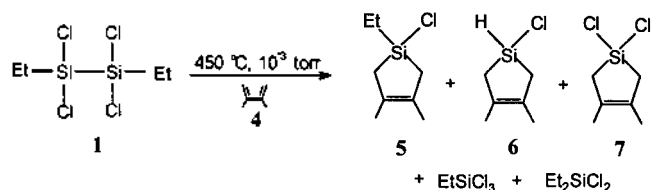


The pyrolysis of **1** is initiated by a conventional α-elimination of ethyltrichlorosilane and dichlorodiethylsilane forming ethylchlorosilylene and dichlorosilylene which are believed to be primary intermediates, respectively.

As suggested in Scheme 1, the observed products **5**, **6**, and **7** might be produced from the addition of ethylchlorosilylene, chlorosilylene, and dichlorosilylene into **4**, respectively under thermolysis condition. The ethylchlorosilylene and dichlorosilylene are generated through the migration of chlorine and ethyl group of the disilane **1**, respectively. Ethyl group shift can be possibly suggested from the formation of dichlorodiethylsilane in the pyrolysis of **1**. These shift reactions occur under the conditions of thermolysis of polysilanes, but not in hydrocarbon pyrolyses, can probably be attributed to the availability of low lying unoccupied orbitals (4s and 3d) on silicon which can
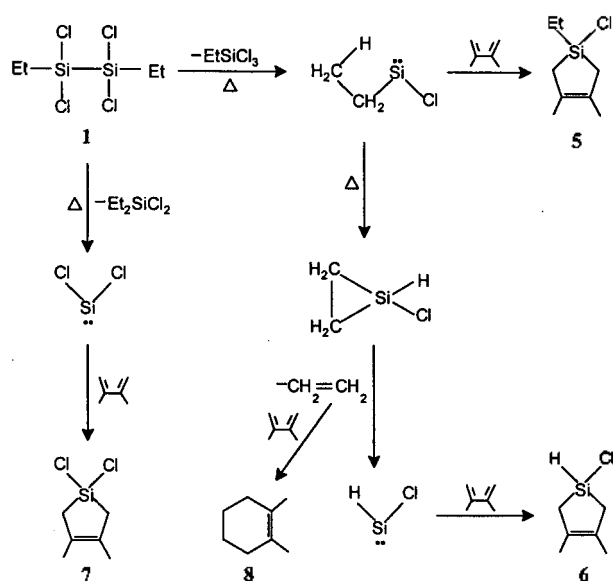


**Scheme 1**

provide appreciable less steric-hindrance for pentavalent silicon in the transition state. The formation of chlorosilylene is proposed from decomposition of 1-chloro-1-silacyclopropane intermediate which derives from an intramolecular silylene insertion into a C-H bond of the ethyl group of ethylchlorosilylene. Thermally induced extrusion of ethylene from the 1-chloro-1-silacyclopropane was confirmed from the observation of 1,2-dimethylcyclohexene (**8**) in the reaction mixture. It is well known that alkylsilylenes are to insert intramolecularly into C-H bonds of alkyl group involving silacyclic intermediates.[1a,10]

Over the temperature range 350-450 °C, the three major products were formed from reactions with **4** as shown in Table 1. In previous work it was found that intramolecular silylene insertion into a C-H bond of the ethyl group of ethylmethoxysilylene was more favorable than direct addition of ethylmethoxysilylene to **4**.[5,10c] In this study, however, it appears that chlorine-substituted silylene leads more predominantly to direct addition of ethylchlorosilylene into **4** than intramolecular C-H insertion of the silylene, since the direct addition may involve a sufficiently low energy barrier compared with the intramolecular silylene insertion. It seems to us that this different behavior may be due to the electronic effects of chlorine and methoxy group on the silylenes.

As the reaction temperature increases, the trapped adduct ratio of **6** to **5** increases. This implies that the decomposition of ethylchlorosilylene into chlorosilylene at

**Table 1.** Temperature dependence of the product ratios from vacuum pyrolysis of Cl$_2$EtSiSiEtCl$_2$ (**1**) and 2,3-dimethyl-1,3-butadiene (**4**)

| Temp (°C) | Yields of products (%) | | | Product ratios | |
|---|---|---|---|---|---|
| | 5 | 6 | 7 | 6.5 | 7/5+6 |
| 350 | 43 | 3 | 1 | 0.07 | 0.02 |
| 400 | 34 | 10 | 2 | 0.29 | 0.05 |
| 450 | 27 | 14 | 4 | 0.52 | 0.10 |

higher temperatures is more predominant than the direct addition of ethylchlorosilylene to **4**. Increasing reaction temperature favors the formation of **7** over **5**. It suggests that the activation barrier of 1,2-ethyl shift is higher than that of 1,2-chlorine shift in pyrolysis of the disilane **1**.

Heats of formation ($\Delta H_f$/kcal mol$^{-1}$) for the molecules containing silicon, $Cl_2EtSiSiEtCl_2$ ($-197.34$), $EtSiCl$ ($-17.3$), $ClHSiCH_2CH_2$ ($-28.2$), $HSiCl$ (10.7), and $SiCl_2$ (-46.7) were obtained by AM 1 semi-empirical calculations. The relative stability of silylenes is in the following order: $SiCl_2$ > EtSiCl > HSiCl. It appears that the product distribution of pyrolysis of **1** is independent on the stability of silylenes. It seems to us that the routes for thermal decomposition of **1** to ethylchlorosilylene and dichlorosilylene, the primary intermediates, depend on their activation barriers.

The ionized ethylchlorosilylene (m/z 92), chlorosilylene (m/z 64), and dichlorosilylene (m/z 98) in the mass spectrum of **1** were shown. The peak intensity of ionized ethylchlorosilylene (base peak) is higher than that of ionized chlorosilylene and dichlorosilylene. It implys that the loss of $EtSiCl_3$ is more favorable process than that of $Et_2SiCl_2$ from the molecular ion.

The pyrolysis employing an alkylchlorosilylene precursor of 1,2-dimethyltetrachlorodisilane (**3**) with **4** at 450 °C affords one major product, 1-chloro-1-methyl-3,4-dimethyl-1-silacyclopent-3-ene (**9**) and a trace amount of **7** along with methyltrichlorosilane and dichlorodimethylsilane. It seems to us that the observed products are also generated by the same route shown in Scheme 1. The trapped adduct **9** was also produced from the trapping reaction of methylchlorosilylene intermediate which might be generated from migration of chlorine group of the disilane **3**. The presence of trapped adduct **7** shows that thermal decomposition of **3** consisted of methyl group shift forming dichlorosilylene. The product **7** in the pyrolysis of **3** at 350 and 400 °C, however, was not observed. This implys that an ethyl group of the disilane **1** is more likely to migrate than a methyl group of the disilane **3**.

## Summary

Vacuum pyrolysis of 1,2-diethyltetrachlorodisilane (**1**) in the presence of **4** resulted in formation of **5**, **6**, and **7**. The observation of ethyltrichlorosilane and diethyldichlorosilane in the reaction mixture demonstrates that this thermal decomposition of the disilane **1** consisted solely of chlorine and ethyl group shifts forming the ethylchlorosilylene and dichlorosilylene, respectively. It was found that the direct addition of ethylchlorosilylene to **4** was more favorable than intramolecular C-H insertion of the silylene at temperatures from 350 to 450 °C. As the reaction temperature increases, the dissocation of ethylchlorosilylene into chlorosilylene and the formation of dichlorosilylene via ethyl group shift from the disilane **1** increase.

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