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SILENE GENERATION FROM A SILYL 1,3-MIGRATION

THOMAS J. BARTON and WILLIAM D. WULFF

Gilman Hall, Department of Chemistry, Iowa State University, Ames, Iowa 50011 (U.S.A.)

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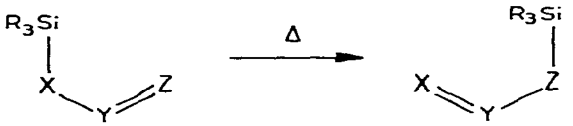
Summary

To probe for a thermally-induced 1,3-migration of silicon from silicon to produce a silicon—carbon double bond, 1,2-divinyl-1,1,2,2-tetramethyldisilane was pyrolyzed in a nitrogen-flow system at 620°C. All cyclic products can be rationalized as arising from an initial 1,3-migration to form the intermediate silene, 2,5-disila-2,5,5-trimethyl-2,6-heptadiene. The major product, 1,1,3,3-tetramethyl-1,3-disilacyclobutane, is shown to arise from the dimerization of 2-sila-2-methylpropene. All other cyclic products appear to arise from various cleavages of an intermediate 2,5-disilabicyclo[2.1.1]hexane.

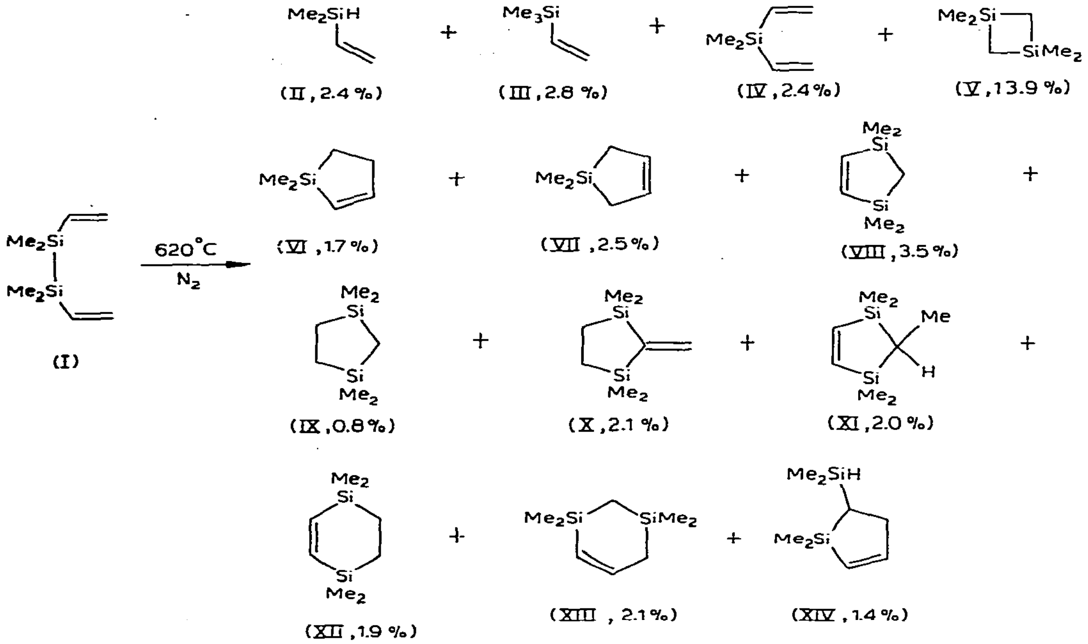
Thermally induced 1,3-migrations of silyl groups have been observed for a variety of allylic and heteroallylic silanes as illustrated here by the generalized equation:



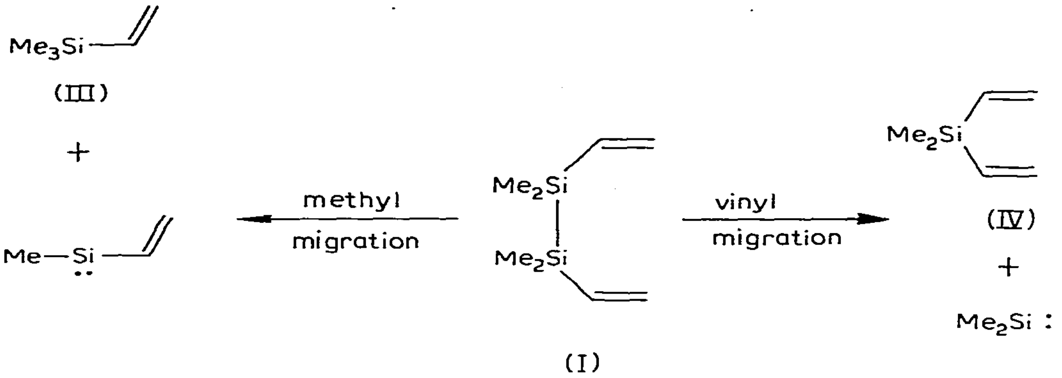
X	Y	Z	References (not comprehensive)
C	C	C	1
C	C	O	2, 3
N	C	O	4, 5, 6
N	S	O	7
N	N	N	6, 8
N	C	S	6
O	C	N	4
N	P	O	9

We report here the examination of a reaction which appears to proceed via a 1,3-migration of this type where X is also a silicon atom, thus creating a silicon—carbon double bond.

In order to maximize the possibility of the desired rearrangement, the symmetrical system 1,2-divinyl-1,1,2,2-tetramethyldisilane (I) was chosen. Pyrolysis of I was carried out in a vertical nitrogen-flow system * at 620° C. The reaction produced a complex array of products from which the 13 major compounds (II—XIV) were isolated by preparative gas chromatography and identified through GCMS, NMR, IR and, when possible, spectral comparison with authentic samples.



Product II likely arises from homolytic cleavage of the Si—Si bond of I followed by intermolecular hydrogen abstraction by the dimethylvinylsilyl radical. Products III and IV are also not entirely unexpected as they presumably arise from α-eliminations [10] on silicon to produce methylvinylsilylene and dimethylsilylene.



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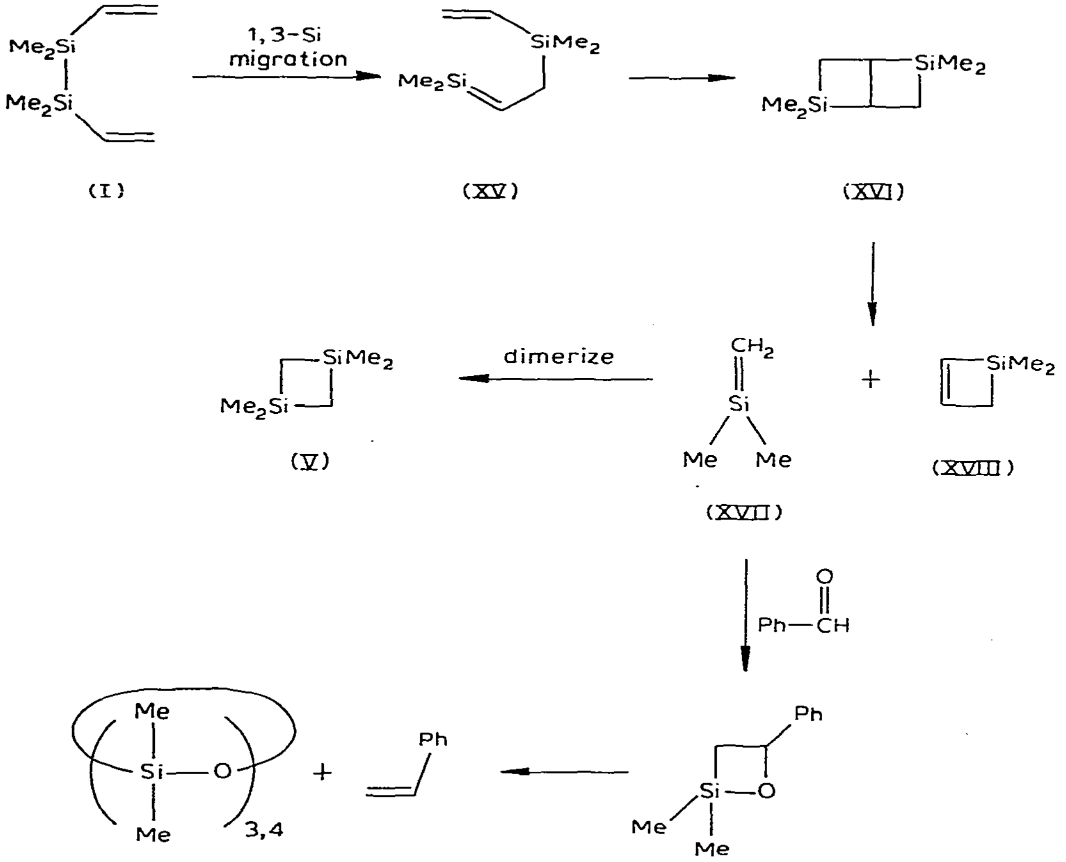
* A single sealed-tube pyrolysis at 238°C (7 h) afforded no reaction. In the flow system there was no reaction at 460°C and only 20% conversion at 525°C.

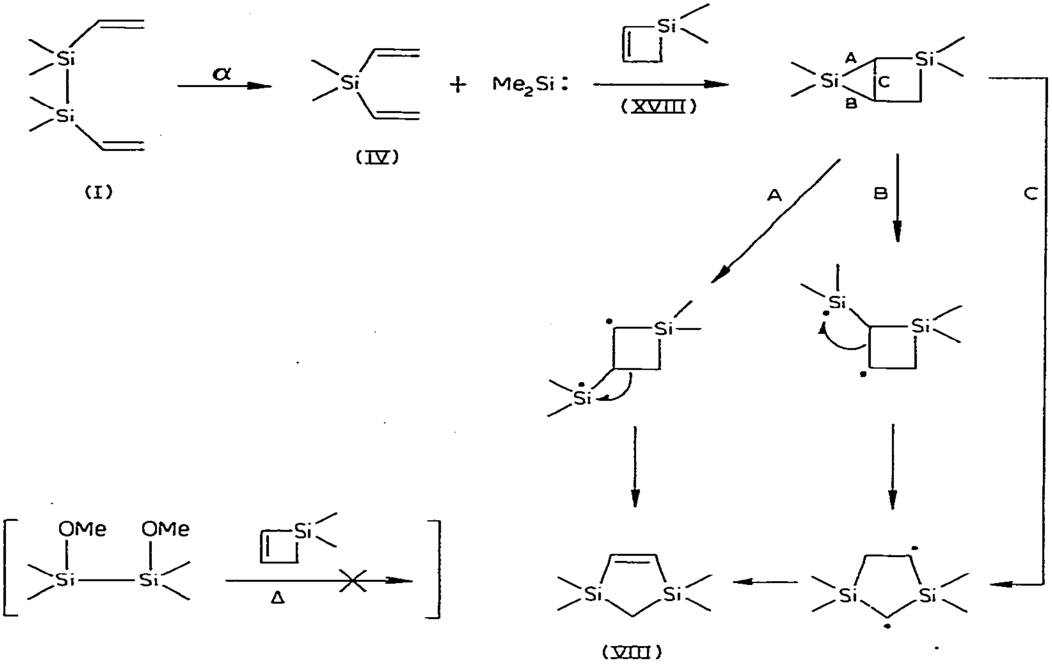
Product V, (1,1,3,3-tetramethyl-1,3-disilacyclobutane) is usually the major product when 2-methyl-2-silapropene (XVII, a silene) is produced under these conditions in the absence of added silene trapping agents [11]. Its formation is generally accepted as evidence for silene intermediacy in such reactions. Examination of the reaction options of silene XV, the product of a 1,3-silyl shift in I, suggests a possible source of silene XVII. It is well established [12] that silenes will cycloadd to olefins to form silacyclobutanes although this bimolecular reaction has only been observed as a very minor pathway. However, intramolecular cyclization of XV might be expected to be more efficient in the production of 3,3,6,6-tetramethyl-3,6-disilabicyclo[2.2.0]hexane (XVI). Far more extensively established is the fact that silacyclobutanes undergo thermal cleavage in the gas phase to afford silenes and olefins [13]. Thus, XVI should serve as a generator of silene XVII, the source of the major product V through head-to-tail dimerization.

Silenes are efficiently trapped by aldehydes and ketones [11]. This reaction is believed to proceed through an intermediate silaoxetane which suffers thermal cleavage to olefin and silanone ($R_2Si{=}O$), the latter product undergoing cyclic oligomerization. Thus, to probe for the intermediacy of XVII, we conducted the flow pyrolysis of I with a 6-fold excess of benzaldehyde. Analysis of the resulting product mixture revealed a dramatic decrease in V



and the appearance of styrene (20.2%), hexamethylcyclotrisiloxane (3.6%), and octamethylcyclotetrasiloxane (4.3%), the expected products from reaction of benzaldehyde and XVII [13].

A possible origin of VIII is from insertion of dimethylsilylene, produced from the α-elimination of I to IV, into silete XVIII. Silylene ring expansions of this type are wellprecedented for both three- [14] and five-membered [15] rings. The ring expansion can take place via rupture of any of three bonds in the intermediate silacyclopropane.



As attractive as this mechanism for the formation of VIII might be, we are quite distrustful of it. Copyrolysis of the dimethylsilylene generator, 1,2-dimethoxytetramethyldisilane, and silete XVIII (3/1) at 615°C in a nitrogen flow system produced no 1,3-disilacyclopentene (VIII). Thus, we favor a route involving initial 1,3-silyl migration followed by 2 + 2 intramolecular cycloaddition to produce disilabicyclo[2.1.1]hexane (XIX), methylene extrusion and transannular hydrogen abstraction (vide infra).

Our experiments do not allow us to comment on whether or not a reversible Cope rearrangement of I is occurring. If indeed this is happening, we are unable to efficiently bleed off the Cope product through benzaldehyde trapping * [17]. However, products XIII and XIV are easily rationalized as originating from an initial Cope rearrangement followed by radical closure and either hydrogen migration (Path A), or ring migration (Path B).

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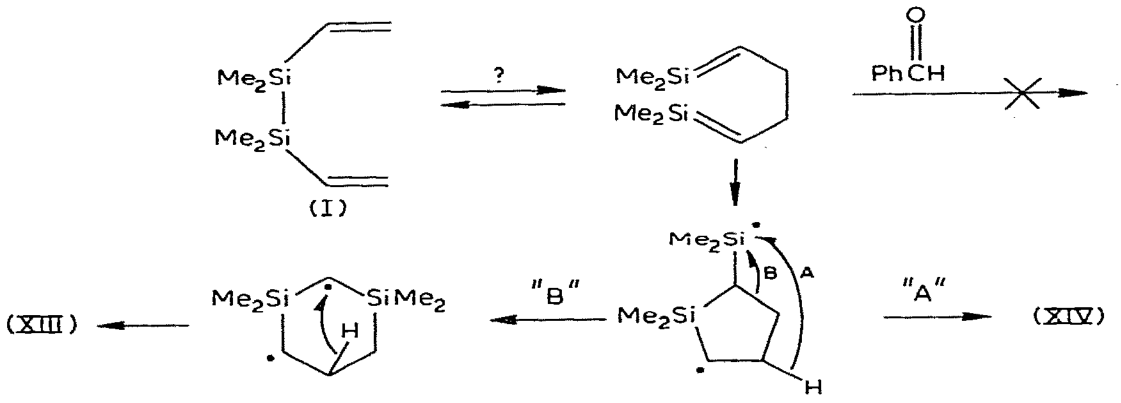
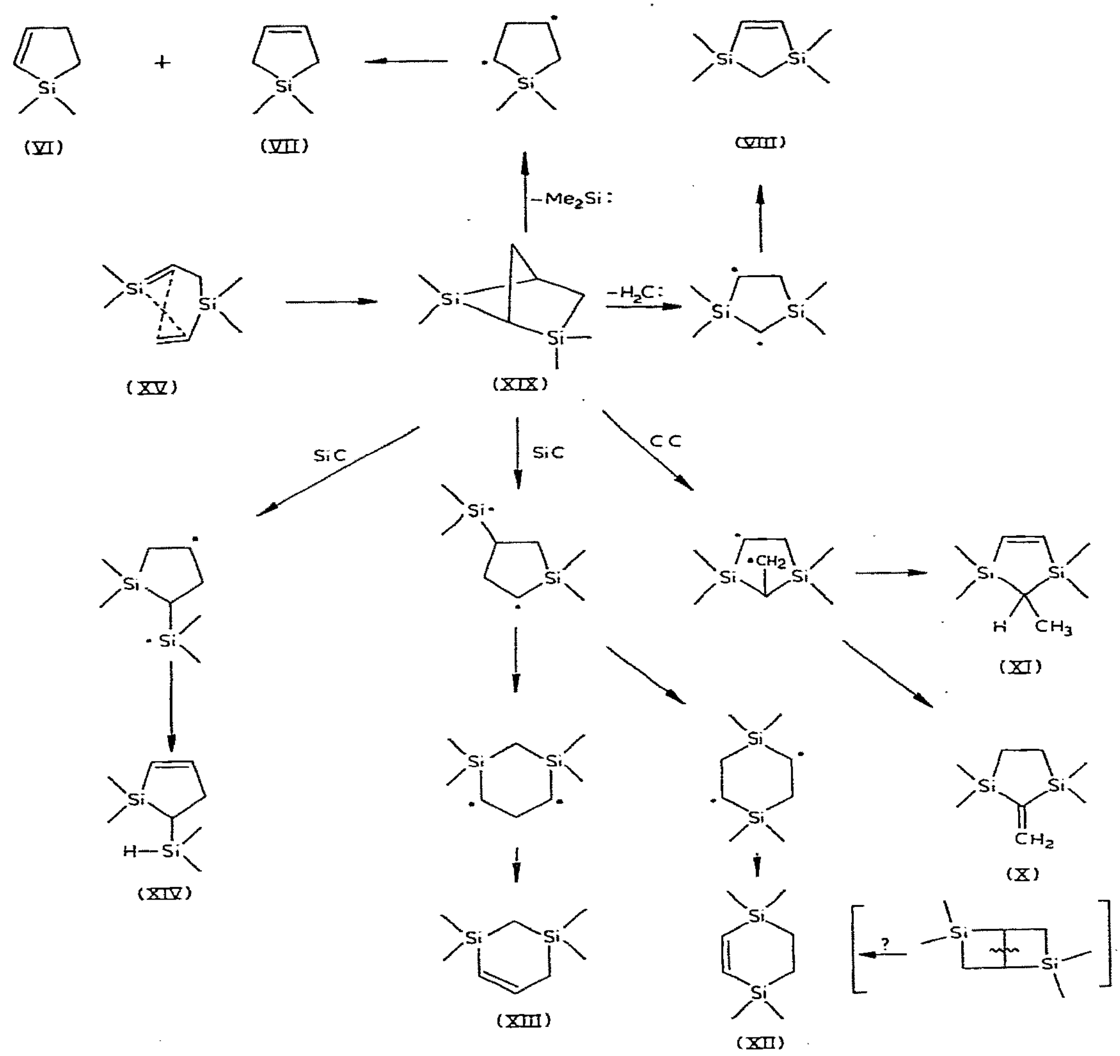
* It would be of considerable interest to see if dimethylvinylallylsilane, a system which has been shown to undergo reversible Cope rearrangement, allows carbonyl trapping.


Me₂Si
Me₂Si
(I)
?
Me₂Si
Me₂Si
PhCH
O
Me₂Si
B
A
Me₂Si
H
"B"
"A"
(XIV)
Me₂Si
SiMe₂
H
(XIII)


Si
(VI)
+
Si
(VII)
Si
Si
Si
(VIII)
−Me₂Si:
Si
Si
(XV)
Si
Si
(XIX)
−H₂C:
Si
Si
SiC
SiC
CC
Si
Si
Si
Si
Si
•CH₂
Si
Si
Si
H
CH₃
(XI)
Si
H—Si
(XIV)
Si
Si
Si
Si
Si
Si
CH₂
(X)
Si
Si
(XIII)
Si
Si
(XII)
?
Si
Si

It is not necessary to invoke a Cope rearrangement as the most economical mechanistic rationalization for all of the products of this reaction simply involves 1,3-silyl migration in I to form silene XV. Closure to XVI ultimately affords the major product V, while closure to XIX will produce VI and VII from dimethylsilylene extrusion, VIII from methylene extrusion, X and XI from C—C homolysis, and XII, XIII and XIV from Si—C bond rupture.

In summary we find that thermal 1,3-migration of silicon, from silicon, to carbon does occur. However, it is not likely that this ultimately complex reaction will be of any synthetic usefulness except, perhaps, in a very special situation.

Experimental

Starting materials

1,2-Dichloro-1,1,2,2-tetramethyldisilane was prepared by the photochemical coupling of dimethylchlorosilane [17]. To a refluxing solution of vinylmagnesium bromide (200 ml THF, 0.24 mol Grignard reagent) was added, as a rate sufficient to maintain reflux, 20 g (0.107 mol) of the dichlorodisilane in 350 ml hexane. After completion of addition the solution was cooled to 0°C, hydrolyzed with 5% HCl, the organic layer separated, washed with water and dried over Na_2SO_4. After removal of solvents, distillation yielded 8.5 g (51%) of 1,2-divinyl-1,1,2,2-tetramethyldisilane (I): b.p. 63—65°C/35 mmHg; NMR (CCl_4) δ (ppm) 0.13 (s, 12 H), 5.2—6.7 (vinyl mult., 6 H); mass spectrum (*m/e*, % relative intensity) 156 (12), 155 (46), 127 (10), 95 (12), 85 (53), 73 (43), 71 (12), 59 (100), 58 (10).

Pyrolysis of 1,2-divinyl-1,1,2,2-tetramethyldisilane (I)

The pyrolysis was conducted in a vertical one foot quartz tube filled with quartz chips and enclosed in a tube furnace. Disilane I was mechanically added at a rate of 2.2 ml/h concomitant with a nitrogen flow of 26 ml/min. With the temperature at 460°C there was no reaction, at 525°C there was ca. 20% conversion of I, and at 630°C only 4.4% of I remained in the product mixture. Analysis of the product mixture was conducted on a Varian Model gas chromatograph 920 with all products being isolated on a 12 ft, 20% DC-550/Chromosorb P column at 95°C. Yields were determined by gas chromatography using undecane as a standard. Response factors (RF) were determined for products II, III, IV, V and VIII. For products VI and VII the RF of IV was assumed, for IX the RF of VIII was used, and for X, XI, XII, XIII and XIV the RF of I was assumed valid. Products were largely identified by NMR spectra and gas chromatographic-mass spectra (GCMS). The instruments used, respectively, were a Varian HA100 and a Finnegan Model 2000 quadrupole mass spectrometer.

Dimethylvinylsilane (II). NMR (CCl_4) δ (ppm) 0.15 (d, 6 H, J 7 Hz), 4.08 (m, 1 H), 5.4—6.4 (vinyl m, 3 H), spectrum identical to that of an authentic sample prepared from $LiAlH_4$ reduction of dimethylethoxyvinylsilane; GCMS, *m/e* (% rel. int.) 86 (11), 71 (37), 59 (32), 58 (100), 45 (37), 43 (37); yield, 2.4%.

Trimethylvinylsilane (III). NMR (CCl_4) δ (ppm) 0.06 (s, 9 H), 5.4—6.4

(vinyl m, 3 H); GCMS, *m/e* (% rel. int.) 100 (9), 85 (100), 73 (13), 59 (84), 43 (47), matched with spectrum of authentic material; yield, 2.8%.

Dimethyldivinylsilane (IV). NMR (CCl_4) δ (ppm) 0.13 (s, 6 H), 5.4–6.4) (vinyl m, 6 H); GCMS, *m/e* (% rel. int.) 112 (<1), 97 (100), 59 (31), 43 (21); yield, 2.4%.

1,1,3,3-Tetramethyl-1,3-disilacyclobutane (V). NMR (CCl_4) δ (ppm) −0.02 (s, 4 H), 0.27 (s, 12 H); GCMS, *m/e* (% rel. int.) 144 (23), 130 (15), 129 (100), 101 (20), 73 (13), 59 (25), calculated for $C_6H_{16}Si_2$ *m/e* 144.07906, measured 144.07841; the IR spectrum matched the published spectrum [18]; yield, 13.9%.

3,3-Dimethyl-3-silacyclopentene (VI). NMR ($DCCl_3$) δ (ppm) 0.03 (s, 6 H), 0.57 (m, 2 H, CH_2 in ring α to Si), 2.38 (m, 2 H_C, allylic), 5.87 (d of t, 1 H_A, vinyl α to Si, J_{AB} 11 Hz, J_{AC} 2 Hz), 6.76 (d of t, 1 H_B, vinyl β to Si, J_{BC} 3 Hz); GCMS, *m/e* (% rel. int.) 112 (12), 98 (11), 97 (100), 95 (26), 69 (10); yield 1.7%.

4,4-Dimethyl-4-silacyclopentene (VII). NMR ($CDCl_3$) δ (ppm) 0.02 (s, 6 H), 1.17 (broad s, 4 H), 5.82 (board s, 2 H); GCMS, *m/e* (% rel. int.) 112 (31), 98 (11), 97 (100), 95 (26), 71 (13), 59 (15), 58 (30), 55 (11); yield, 2.5%.

3,3,5,5-Tetramethyl-3,5-disilacyclopentene (VIII). NMR ($CDCl_3$) δ (ppm) −0.38 (s, 2 H), 0.16 (s, 12 H), 7.15 (s, 2 H); GCMS, *m/e* (% rel. int.) 156 (29), 143 (13), 141 (100), 113 (15), 73 (25), 63 (17), 59 (17), 45 (14), 43 (23); yield, 3.5%. Both the NMR and mass spectra match those published by Fritz [19].

1,1,3,3-Tetramethyl-1,3-disilacyclopentane (IX). NMR (CCl_4) δ (ppm) 0.48 (s, 2 H), 0.08 (s, 12 H), 0.63 ppm (s, 4 H); GCMS, *m/e* (% rel. int.) 158 (25), 144 (14), 143 (85), 130 (34), 115 (100), 73 (27), 59 (33); yield, 0.8%. Both the NMR and mass spectra match those published by Fritz [20].

1,1,3,3-Tetramethyl-1,3-disila-2-methylidenecyclopentane (X). NMR ($CDCl_3$) δ (ppm) −0.02 (s, 12 H), 0.65 (s, 4 H), 6.34 (s, 2 H); GCMS, *m/e* (% rel. int.) 171 (11), 170 (61), 155 (91), 142 (28), 129 (24), 127 (100), 97 (25), 96 (21), 95 (31), 85 (27), 83 (23), 73 (87), 59 (63), 45 (26), 43 (50); IR (neat 3040, 2955, 2910, 1590, 1240, 830, 775 cm^{-1}; yield, 2.1%.

3,3,4,5,5-Pentamethyl-3,5-disilacyclopentene (XI). NMR ($CDCl_3$) δ (ppm) −0.27 (q, 1 H_A, J_{AB} 8 Hz), −0.06 (s, 6 H), 0.00 (s, 6 H), 0.92 (d, 3 H_B, Me, $h\nu$ at −0.27 collapses to singlet), 7.02 (s, 2 H); GCMS, *m/e* (% rel. int.) 170 (32), 156 (17), 155 (100), 127 (49), 95 (50), 73 (47), 59 (50), 45 (16), 43 (31); IR (neat 2960, 1250, 830, 785 cm^{-1}; yield, 2.0%.

3,3,6,6-Tetramethyl-3,6-disilacyclohexene (XII). NMR ($CDCl_3$) δ (ppm) 0.05 (s, 12 H), 0.82 (s, 4 H), 6.84 (s, 2 H); GCMS, *m/e* (% rel. int.) 170 (45), 156 (12), 155 (90), 142 (20), 129 (28), 128 (18), 127 (100), 97 (62), 96 (74), 95 (61), 73 (83), 59 (72), 58 (20), 55 (16), 45 (25), 43 (59); IR (neat) 2950, 2920, 2900, 1410, 1245, 1050, 820, 780, 685 cm^{-1}; ^{13}C NMR, δ (ppm) −2.27, 7.74, 150.68; yield, 1.9%.

3,3,5,5-Tetramethyl-3,5-disilacyclohexene (XIII). NMR ($CDCl_3$) δ (ppm) −0.19 (s, 2 H), 0.06 (s, 6 H), 0.08 (s, 6 H), 1.32 (d of d, 2 H_C, allylic CH_2), 5.51 (d of t, 1 H_A, $=CH_A{-}Si$, J_{AC} 1.4 Hz), 6.73 (d of t, 1 H_B, $CH_B{=}CH_A{-}Si$, J_{BC} 5.4 Hz, J_{AB} 15 Hz), $h\nu$ at δ 1.32 ppm collapses both H_A and H_B to doublets, J 15 Hz; GCMS, *m/e* (% rel. int.) 170 (37), 156 (25), 155 (100), 142

(23), 129 (24), 128 (10), 127 (68), 95 (33), 73 (40), 59 (44), 45 (21), 43 (36); both NMR and mass spectra match those published by Fritz [20]; IR (neat) 3040, 2960, 2900, 1580, 1245, 1020, 860, 830, 805, 785 cm^{-1}; yield, 2.1%.

3,3-Dimethyl-3-sila-4-dimethylsilylcyclopentene (XIV). NMR (C_6D_6) δ (ppm) 0.07 (d, 6 H, J 4 Hz), 0.20 (s, 6 H), 2.47 (m, 2 H_B, allylic CH_2, J_{AB} 9 Hz, H_A methine H is hidden by SiMe's as $h\nu$ at 0.10 reduces H_{BB}, to AB quartet of triplets), 4.22 (m, 1 H, Si—H_E, J (E—SiMe) 4 Hz), 6.08 (d of t, 1 H_D, $CH_C{=}CH_D$—Si, J_{CD} 10 Hz, J_{BD} 3 Hz, $h\nu$ at 2.47 collapses both H_D and H_C to doublets J 10 Hz), 6.85 (d of t, 1 H_C, J_{BC} 2 Hz, J_{CD} 10 Hz); GCMS, *m/e* (% rel. int.) 170 (10), 156 (19), 155 (100), 129 (36), 128 (7), 127 (43), 97 (24), 96 (80), 95 (77), 73 (68), 59 (84); IR (neat 3040, 2970, 2920, 2110, 1570, 1250, 1035, 990, 890, 845, 775 cm^{-1}; yield, 1.4%.

Copyrolysis of I and benzaldehyde. A solution of I dissolved in a six-molar excess of benzaldehyde was pyrolyzed, as described above, with an addition rate of 2.2 ml/h, a nitrogen flow of 20 ml/min, and a furnace temperature of 630° C. Gas chromatographic analysis was performed as described above and response factors (RF) were obtained for all products. Yields are based on unrecovered I and an assumed 1/1 stoichometry. The products and yield were II (2.0%), III (1.5%), IV (7.9%), V (3.9%), hexamethylcyclotrisiloxane (3.6%), I (11.9%), octamethylcyclotetrasiloxane (4.3%) and styrene (20.2%). An undetermined amount of benzene from decarbonylation of benzaldehyde was also observed. All peaks in the GC trace matched the retention times of authentic samples. Only styrene was actually isolated for NMR analysis.

Copyrolysis of 1,2-dimethoxy-1,1,2,2-tetramethyldisilane and 3,3-dimethyl-3-silacyclobutene. Dimethylsilete (prepared by the method of Block [21]) was dissolved in a three-fold molar excess of dimethoxytetramethyldisilane [17] and pyrolyzed in a vertical-flow system (2.2 ml/h, N_2-flow 25 ml/min, 620° C). Mass recovery was 82%. Only one peak in the GC trace was near the retention time of XIII, and this compound was shown by NMR not to be XIII.

Acknowledgment

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