Bis(trimethylsilyl)-, Trimethylsilyltrimethylgermyl-, and Bis(trimethylgermyl)diazomethane. Synthesis and Chemistry of Quantitative Silene and Germene Precursors

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Abstract: Convenient syntheses of bis(trimethylsilyl)diazomethane (**1**), trimethylsilyltrimethylgermyldiazomethane (**22**), and bis(trimethylgermyl)diazomethane (**31**), utilizing diazo transfer from tosyl azide to the carbanion derived from the corresponding bis(trimethylmetallo)methane or -chloromethane, are described. Both photolysis and thermolysis of **1** produce a carbene which rearranges via methyl migration to silene **3**, which dimerizes. Trapping results with methanol, benzaldehyde, 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, and D_2O indicate that silene formation is essentially quantitative. Thermolysis of **23** produces only products from silene intermediacy, but photolysis and trapping with MeOD reveal a competition between silene and germene formation which favors the silene by a factor of 4. Both photolysis and pyrolysis of **31** produce only products from the germene resulting from methyl migration to carbon.

Introduction

Since 1973 it has become established that the intramolecular reaction of α-silylcarbenes produces silenes (compounds containing a (p-p)π carbon-silicon double bond).[1-6] However, the systems studied to date have been complicated by a variety of alternate reaction pathways. For example, the gas-phase, thermal generation of phenyltrimethylsilylcarbene yields products from carbene-carbene interconversion, carbene dimerization, and apparent C-H insertion, along with the desired silene products.[6] We report here a convenient synthesis[7] and some chemistry of bis(trimethylsilyl)diazomethane (**1**), a molecule which cleanly affords silene products of either thermal or photochemical origin. We also report the syntheses of trimethylsilyltrimethylgermyldiazomethane (**22**), a compound which produces a carbene providing the opportunity for competitive silene or germene formation, and bis(trimethylgermyl)diazomethane (**31**), a germene precursor.

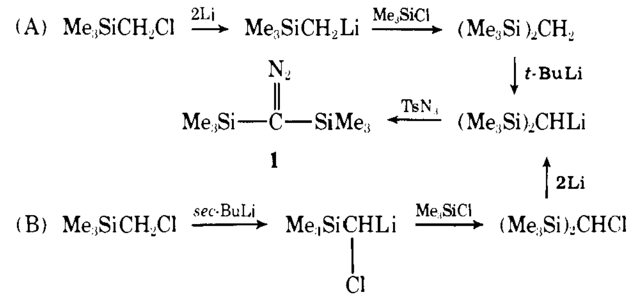
Results and Discussion

Synthesis, Pyrolysis, and Photolysis of Bis(trimethylsilyl)diazomethane (1). Our synthesis (Scheme I) of **1** was accomplished (route A) by lithiation of readily available chloromethyltrimethylsilane (Et_2O, −23 °C, 2 h) followed by quenching with trimethylchlorosilane to afford bis(trimethylsilyl)methane in 75% yield.[9] Metalation with *tert*-butyllithium (THF/HMPA, −78 °C, 2.5 h) followed by addition of tosyl azide produced upon workup a 57% yield of **1**. A modification of this synthesis (route B) was carried out by *sec*-butyllithium-induced deprotonation of chloromethyltrimethylsilane, quenching with trimethylsilyl chloride to form bis(trimethysilyl) chloromethane (70%), followed by sequential reaction with lithium and tosyl azide to yield **1** (37%).

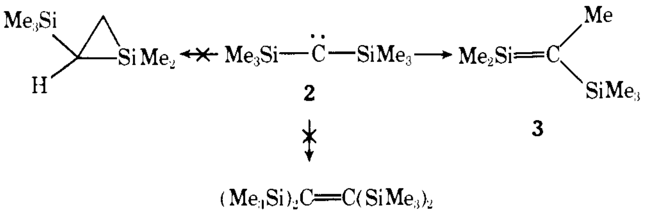
The carbene (**2**) produced from N_2 extrusion from **1** presents an interesting potential competition (Scheme II) between C-H insertion to form a silacyclopropane and methyl migration to generate a silene. Although there is some rather suggestive evidence in the literature[6] for the former process, in none of the reactions of **2** have we ever seen any evidence for such an insertion process. Also, as expected, we have never observed tetrakis(trimethylsilyl)ethene, the formal product of carbene dimerization.

Carbene generation through a nitrogen-flow pyrolysis of **1** at 400 °C (Scheme III) produced as the major products 1,3-disilacyclobutanes **4a** and **4b** in a combined yield of 46%. Essentially equal amounts of the cis and trans isomers were formed in this reaction. Also formed are disilane **5** (22%) and disilazane **6** (10%). The three major products (**4a**, **4b**, and **5**) are most economically rationalized as arising from methyl migration in **2** to afford **3**. Silene **3** would by precedent[10] be expected to dimerize in a head-to-tail fashion, which here produces **4**. However, there are two cases in the literature[11,12] where sterically hindered silenes dimerize in a head-to-head manner. Thus, it is not surprising that **3** also dimerizes head-to-head to form diradical **7**, which intramolecularly abstracts a hydrogen to produce **5**. The formation of disilazane **6** is quite surprising, and to our knowledge is without precedent. We suggest a route involving reaction of **3** and **1**, one possibility of which is shown in Scheme IV. Of course, the details are purely speculative, but reaction of **3** and **1** as the origin of **6** is supported both by the observation of Me_3SiCN as a product of this pyrolysis and by the fact that the considerably higher dilution conditions of a vacuum pyrolysis (500 °C, 0.05 Torr) of **1** produces only **4** (60%) and **5** (23%) with no detectable amount of **6**.

Scheme I



Scheme II



Intermediacy of silene **3** in the thermolysis of **1** was further established through a variety of trapping reactions (Scheme V). Copyrolysis of a 5% solution of **1** in benzaldehyde (400 °C, N_2 flow) dramatically affords only three products in a total yield of 97% with a 98% mass balance. Each of these products clearly arises from the intermediacy of **3**. Addition of silene

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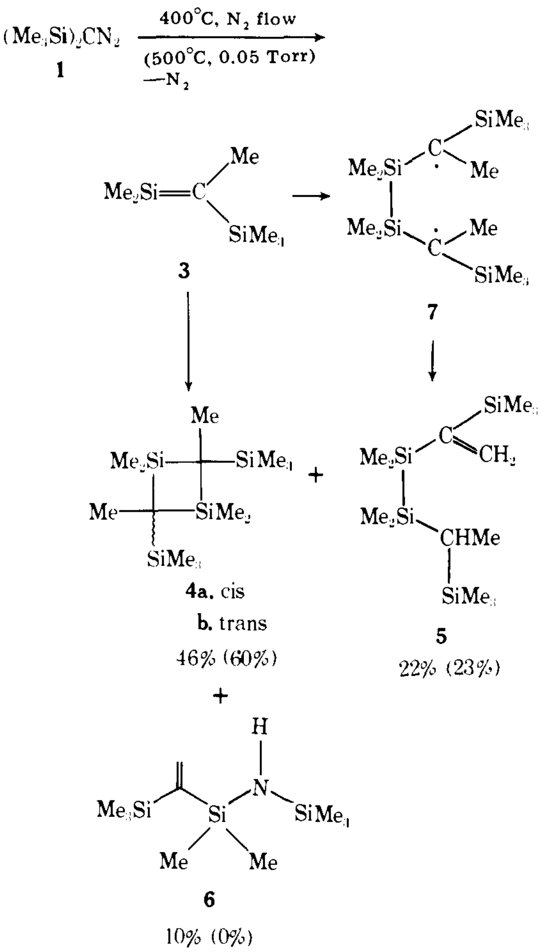
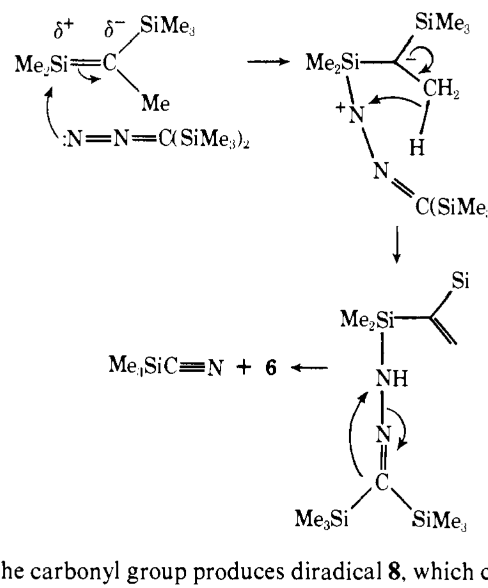
Scheme III



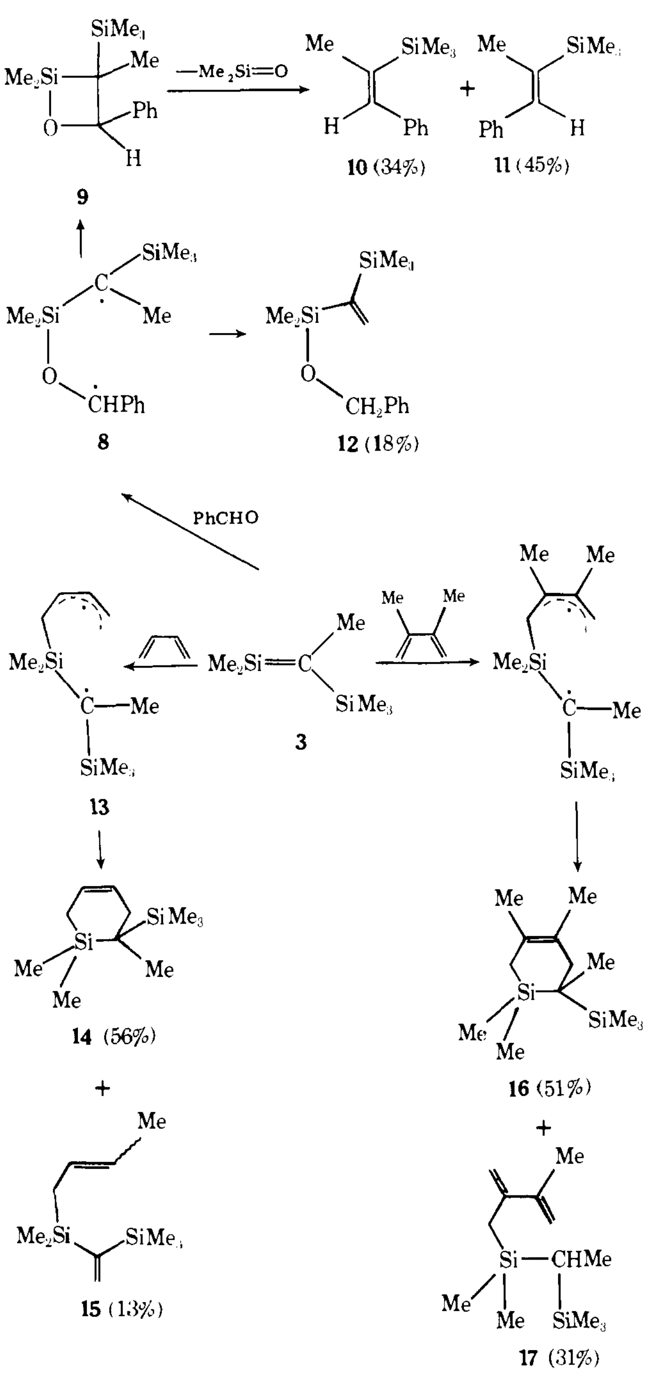
Scheme IV. Possible Origin of Disilazane 6



3 to the carbonyl group produces diradical **8**, which can either close to silaoxetane **9** and extrude dimethylsilanone to yield olefins **10** and **11** or can intramolecularly abstract a hydrogen atom to form the benzyl ether **12**.

Flow pyrolysis of **1** at 400 °C with 1,3-butadiene as the carrier gas produced the expected, formal Diels-Alder adduct **14** in 56% yield. In addition, a linear adduct, **15**, was formed in 13% yield. Both of these products can be rationalized as arising from silene addition to butadiene to produce diradical **13**, which either closes to **41** or undergoes hydrogen migration to give **15**.

Scheme V. Trapping of Thermally Generated 3

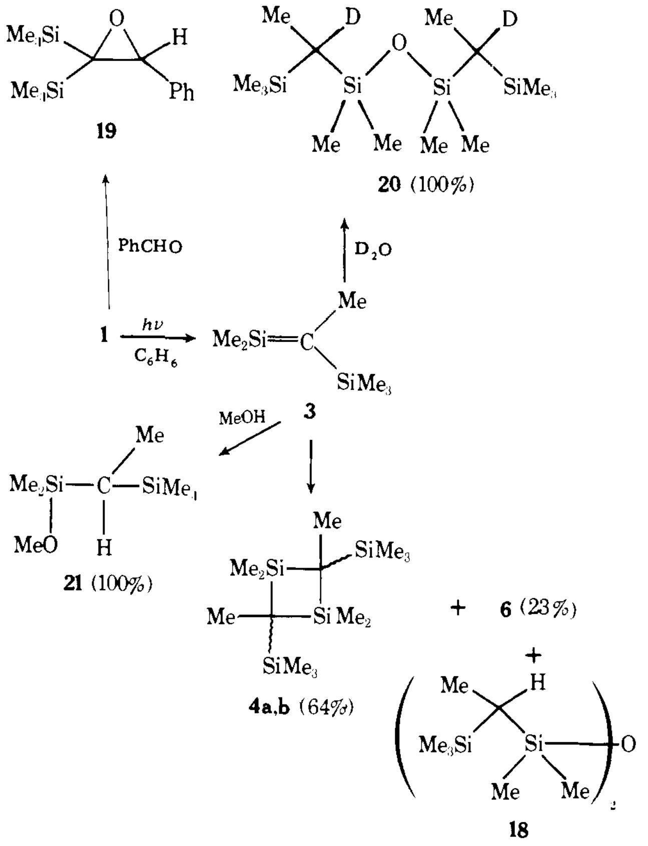


Similar results[13] were obtained from a flow copyrolysis of **1** and 2,3-dimethyl-1,3-butadiene. This reaction afforded the cyclic adduct **16** in 51% yield and the linear adduct **17** in 31% yield.

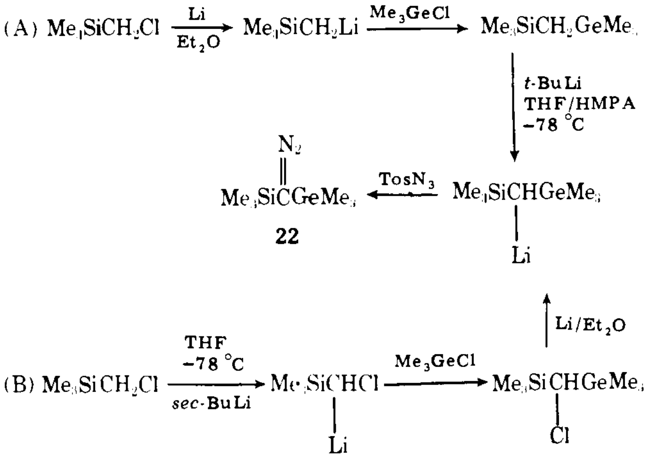
Photolysis of **1** in benzene (Scheme VI) resulted in rather rapid (<3 h) complete disappearance of **1** and the formation of equal amounts of 1,3-disilacyclobutanes **4a** and **4b** in combined yield of 64% and disilazane **6** in 10% yield. Trace amounts of siloxane **18** were sometimes observed. Again the products appear to arise from the intermediacy of silene **3**, with **18** possibly being the condensation product of the silanol produced from trace water reacting with **3**. It is interesting to note the oomplete absence of the head-to-head dimer **5** produced in the thermolysis of **1**.

Although photolysis of **1** in the presence of benzaldehyde (5% in C_6H_6 with 1.1 equiv of PhCHO) yielded only epoxide **19** as an identifiable product, other trapping reactions con-

Scheme VI. Photochemical Generation of Silene 3



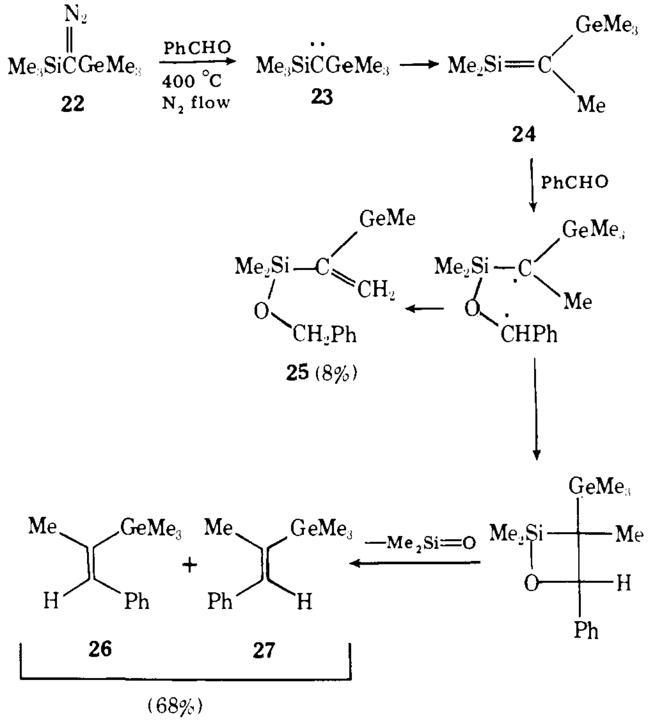
Scheme VII



firmed the transient presence of silene **3**. Irradiation for 2.5 h of a 5% solution of **1** in benzene with a threefold excess of D_2O quantitatively afforded disiloxane **20**. Likewise, quantitative formation of methoxysilane **21** was realized when methanol was substituted for D_2O. These results clearly demonstrate that **1** is a superb photochemical silene generator.

Synthesis, Pyrolysis, and Photolysis of Trimethylsilyltrimethylgermyldiazomethane (22). In order to set up a competition between silene and germene formation, we undertook the synthesis of the mixed diazo compound (**22**). This was accomplished by the two routes outlined in Scheme VII. Again, both routes are initiated through metalation of chloromethyltrimethylsilane, and both terminate with a diazo transfer from tosyl azide. The yield of **22** in route A was 48% in the final step, with an overall yield of 35%. The yield of **22** from route B was only ca. 10%. The bright green, liquid **22** proved to be quite stable, and was purified by preparative GC.

Scheme VIII



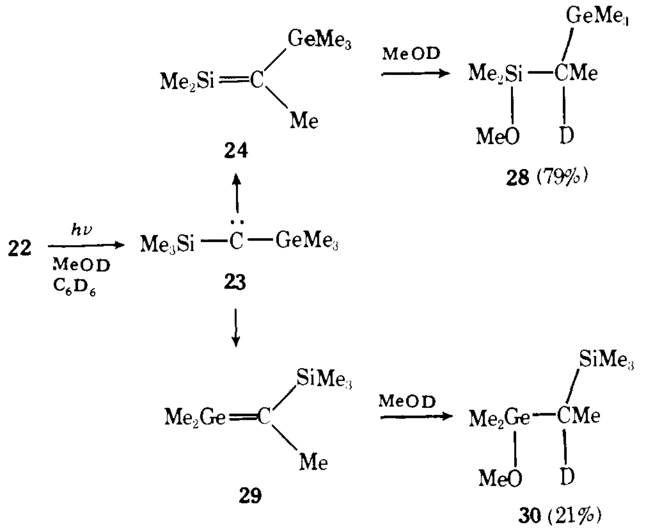
The carbene **23** produced from N_2 extrusion from **22** could either undergo methyl migration from silicon to produce a silene or from germanium to afford a germene. In order to determine the preferred rearrangement, a copyrolysis of **22** and benzaldehyde was conducted at 400 °C in a nitrogen-flow system. The only products observed were approximately equal amounts of cis and trans olefins **26** and **27** (combined yield of 68%) and silyl ether **25** (8%). The germyl alkenes **26** and **27** were isolated by preparative GC and identified by their NMR and mass spectra. Ether **25** was identified from the NMR spectrum of the reaction mixture and from its GC/MS, which was very similar to the spectrum of **12**. Thus, it would appear that the mechanism shown in Scheme VIII is operating, and only methyl migration from silicon to produce silene **24** is occurring. As 24% of the reaction mixture is unaccounted for, it is still possible that some of the germene is formed, but there is no reason to suspect that this is the case.

Photochemical generation of carbene **23** was conducted in benzene-d_6 with a sixfold excess of methanol-*O*-*d* present as a silene/germene trap. The reaction was extremely clean with only ethers **28** and **30** being formed in combined yield of >95% (NMR). Precedent[10] dictates that **28** arises from addition of MeOD across the π bond of silene **24**, and **30** is produced from the corresponding reaction with germene **29**. Thus, under these conditions silene production is favored over germene formation by a factor of 4.

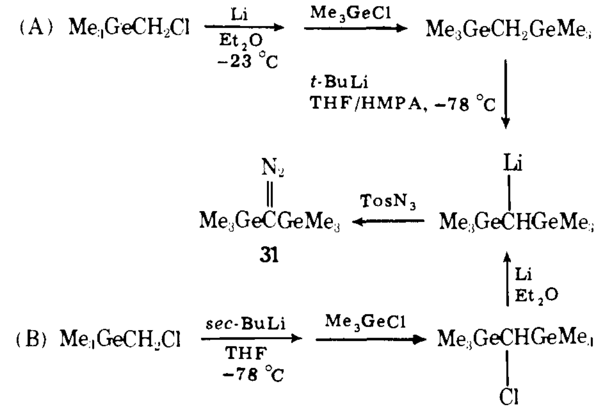
Synthesis, Pyrolysis, and Photolysis of Bis(trimethylgermyl)diazomethane (31). Synthesis of **31** was accomplished in the same fashion as for the other two title compounds, and is outlined in Scheme X. Route A produced **31** in 32% yield, while route B afforded only a trace amount of **31**. However, **31** proved to be much less stable than either **1** or **22**. It was not stable in the reaction mixture and had to be removed immediately. Indeed, **31** reacted with CCl_4, thus necessitating the use of benzene-d_6 for NMR solutions. However, once purified by preparative GC, **31** can be stored at −10 °C for months without decomposition.

Bis(trimethylgermyl)diazomethane (**31**) was pyrolyzed as a 5% solution in benzene in a nitrogen-flow system at 400 °C. Two major products were obtained, each in ca. 32% yield. Dimer **32** was isolated and identified by IR, NMR, and

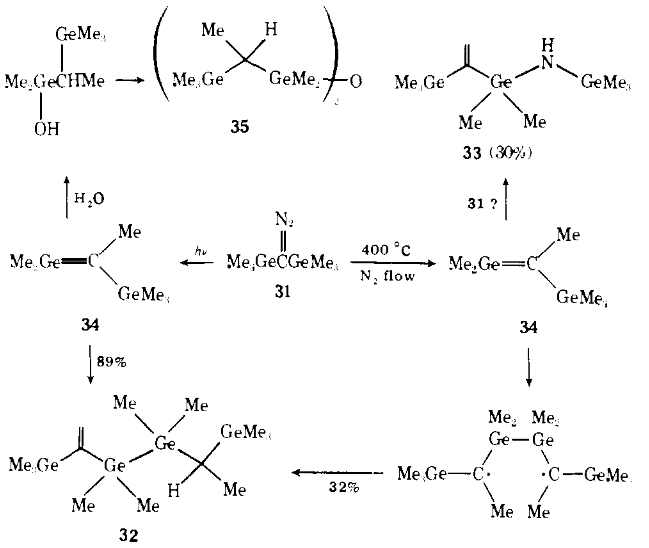
Scheme IX



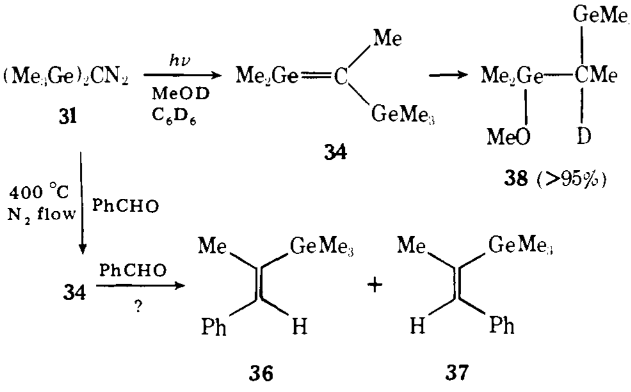
Scheme X



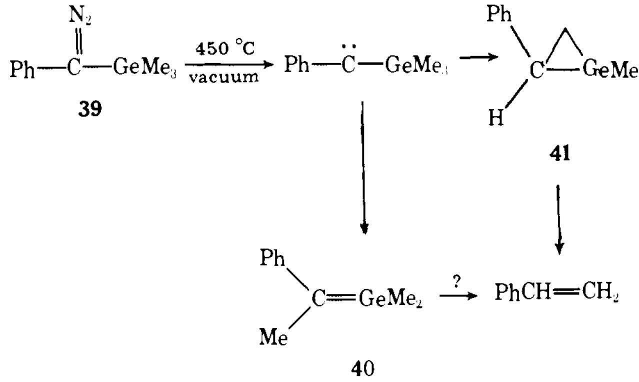
Scheme XI



Scheme XII



Scheme XIII



GC/MS. The second product was not isolated in pure form, but produced a mass spectrum consistent with that expected for germazane **33**. Thus, it would appear that **31** is a rather efficient generator of germene **34** as illustrated in Scheme XI. Photochemical generation of **34** is even more efficient. Irradiation of **31** (5% in C_6H_6, 2 h) produced germene dimer **32** in 89% along with a small amount of germoxane **35**. It is interesting to note that **32** arises from a head-to-head addition, while the dimerization of 2-methyl-2-germapropene occurs in a head-to-tail fashion.[11] Presumably this is due to the added steric influence of the trimethylgermyl group.

Confirmation of the formation of **34** in the photolysis of **31** was obtained by conducting the photolysis in the presence of a sixfold excess of MeOD. Two hours of irradiation in benzene-d_6 produced the expected adduct **38** in >95% yield. Thus, in this case the chemistry of the germene parallels that of silenes. However, a flow copyrolysis of **31** and benzaldehyde produced a complex mixture of organogermanium products for which separation proved impossible. GC/MS analysis revealed two products, each <5%, whose mass spectra were consistent with the expected olefins **36** and **37**, but definite assignments are impossible at this time. Previous attempts in our laboratory to trap germenes with the carbonyl group have also proved unsuccessful.[14]

It is of interest to compare our results with those found in the literature for phenyltrimethylgermyldiazomethane (**39**). Jones[15] has made the reasonable claim that the formation of styrene (15%) in the gas-phase pyrolysis of **39** is evidence for the intermediacy of germirane **41**. The analogous carbene insertion is definitely not taking place in the photochemistry of **31** (or **1** or **22**). There appears to be no reason to suspect such a process in the thermolysis of **31**, although our mass balances are rather low, and a variety of minor processes could be taking place unbeknownst to us. However, in view of our results we would suggest the possibility that the origin of styrene is not **41**, but the germene **40**. The various paths which one can write (including that of decomposition of **41**) are indistinguishable without the trapping of the actual intermediates, which should be done.

Experimental Section

NMR spectra were recorded on a Varian A-60 or HA 100 spectrometer. IR spectra were obtained on a Beckman IR 4250. Mass spectra were determined using either a Finnegan Model 4000 or an AEI MS 902, with exact masses obtained on the latter instrument.

Gas chromatographic analyses and separations were performed on Varian Models 3700 and 920 and Aerograph Model A-90-P. GC yields were determined with internal standards after determination of the relevant response factors. Photolyses were carried out at room temperature in a Rayonet photochemical reactor equipped with 2537-Å lamps. Pyrolyses, unless otherwise noted, were carried out in a vertical flow system consisting of a $^5/_8$ in. × 2 ft quartz tube inside a 1-ft tube furnace. The tube was packed with quartz chips, and a carrier gas (N_2 unless otherwise stated) was passed through the system at a rate of ca. 30 mL/min. The reaction mixtures were introduced into the tube dropwise via motor-driven syringe, and the products were collected in traps cooled by liquid nitrogen.

Bis(trimethylsilyl)chloromethane. Chloromethyltrimethylsilane in THF solution was metalated by *sec*-butyllithium in 10 min at −78 °C. The general procedure was that of Magnus,[16] although it was not necessary to employ TMEDA. To the stirred anion solution at −78 °C was added dropwise 1 equiv of neat trimethylchlorosilane. After completion of addition the temperature was allowed to rise to room temperature. The THF was removed in vacuo, and the residue was dissolved in hexane. The hexane solution was extracted several times with water, dried over Na_2SO_4, and distilled to afford bis(trimethylsilyl)chloromethane in 70%: bp 177–179 °C (lit.[17] 178.5 °C); NMR (CCl_4) δ 0.16 (s, 18 H), 2.37 (s, 1 H); IR (thin film) 2960 (s), 2900 (m), 1410 (m, br), 1255 (s), 1040 (s, br), 770 cm^{-1} (m).

Bis(trimethylsilyl)methane.[9] An excess of lithium dispersion in paraffin oil was placed in a three-neck flask equipped with a Hirsch stirrer and then washed three times with 40 mL of ether. After a final addition of 60 mL of ether, the solution was cooled to −23 °C (CO_2/CCl_4 bath). After addition of 5.0 mL (4.4 g, 36 mmol) of chloromethyltrimethylsilane, the mixture was stirred for 2 h, followed by addition of 1 equiv of trimethylchlorosilane via syringe. After the mixture was slowly warmed to room temperature, it was extracted three times with H_2O, dried over Na_2SO_4, and distilled to afford 4.3 g of bis(trimethylsilyl)methane (75%): bp 133–135 °C; NMR (CCl_4) δ −0.25 (s, 2 H), 0.02 (s, 18 H) (lit.[18] δ −0.28, 0,01); IR (film) 2970 (s), 2910 (m), 2870 (w), 1260 (s), 1060 (s), 845 (s, br), 790 (w), 770 (w), 735 (w), 690 cm^{-1} (m).

Bis(trimethylsilyl)diazomethane (1) from Bis(trimethylsilyl)chloromethane. Metalation was by essentially the procedure of Lappert.[19] To an excess of Li in 60 mL of ether was added 3.0 g of bis(trimethylsilyl)chloromethane, and this mixture was refluxed for 20 h. The resulting mixture was cooled and filtered (glass wool, under N_2). To the filtered solution at 0 °C was added via syringe 1 equiv of tosyl azide in ether. The temperature was maintained at 0 °C for 4 h, and then at room temperature overnight. Salts were removed by centrifugation, and the ether was removed by distillation. Distillation of the remainder afforded **1** at 25 °C (0.1 mm). The yield of **1** was found by GC on either an SE-30 or XF 1150 column: NMR (CCl_4) δ 0.12 (s); IR (film) 2960 (s), 2910 (m), 2040 (s), 1260 (s), 1250 (s), 1220 (s), 930 (s), 840 cm^{-1} (s, br); mass spectrum *m/e* (rel intensity) 186 (parent ion, 73), 171 (41), 144 (67), 143 (67), 85 (80), 83 (67), 74 (80), 73 (100). Both the NMR and IR spectra are in close agreement with those reported by Seyferth.[20]

Bis(trimethylsilyl)diazomethane (1) from Bis(trimethylsilyl)methane. Metalation was by a variation of the procedure of Gröbel and Seebach.[21] THF (6 mL), HMPA (0.3 mL), and bis(trimethylsilyl)methane (0.213 g, 1.33 mmol) were cooled to −78 °C in a 10-mL flask. To this solution was added, via syringe, 1 equiv of *tert*-butyllithium in *n*-pentane to immediately produce a bright yellow color. After the solution was stirred for 2.5 h, 1 equiv of tosyl azide was added without solvent. The solution immediately darkened, but within 10 s lightened to a yellow-orange color. The temperature was maintained at −78 °C for 2 h, and then allowed to rise to room temperature where stirring was continued overnight. The reaction mixture was diluted with 100 mL of hexane and then extracted several times with slightly alkaline H_2O (pH ~9). After drying (Na_2SO_4), the solvents were removed to leave **1**, which was purified by GC. The GC-determined yield of **1** was 57%.

Photolysis of 1. A 5% solution of **1** in benzene (0.0281 g of **1** in 0.560 g of benzene) was placed in a quartz NMR tube, repeatedly degassed by the freeze-thaw method, and sealed under vacuum. After irradiation for 2.5 h the NMR spectrum revealed the complete absence of **1**. The products were isolated by preparative GC on a 10-ft, 15% poly-*m*-phenyl ether column. Silene dimers **4a** (cis) and **4b** (trans) were formed in ca. equal amounts (by NMR) in a combined yield of 64% (GC). Disilazane **6** was formed in 23% yield (GC), and disiloxane **18** was often observed in <5% yield due to trapping of the silene with H_2O.

4a: NMR (D_6C_6) δ 0.10 (s, 18 H), 0.17 (s, 6 H), 0.38 (s, 6 H), 1.35 (s, 6H); mass spectrum *m/e* (rel intensity) 316 (parent ion, 2), 301 (3), 242 (18), 227 (12), 213 (6), 201 (1), 185 (2), 169 (3), 159 (18), 155 (19), 141 (8), 131 (17), 117 (6), 85 (34), 73 (100), 59 (15).

4b: NMR (D_6C_6) δ 0.13 (s, 18 H), 0.25 (s, 12 H), 1.23 (s, 6 H); *m/e* (rel intensity) 316 (12), 301 (14), 242 (1), 227 (20), 213 (20), 201 (3), 185 (4), 169 (6), 159 (5), 155 (15), 141 (12), 131 (14), 85 (10), 73 (100), 59 (18); calcd for $C_{14}H_{36}Si_4$ 316.1894, measured 316.1885.

IR of **4a,b** mixture (film): 2960 (s), 2910 (m), 2870 (m), 1465 (m), 1410 (m), 1265 (sh), 1250 (s), 1080 m, 1050 (w), 995 (m), 975 (m), 870 (sh), 840 (s, br), 790 (w), 760 (m), 700 (w), 675 cm^{-1} (m).

6: NMR (CCl_4) δ 0.08 (s, 9 H), 0.13 (s, 9 H), 6.32 (AB quartet center, 2 H, J_{AB} = 5 Hz), NH not observed; IR (CCl_4) 3370 (w), 3000 (w), 2950 (s), 2910 (w), 2880 (w), 1610 (w), 1400 (m, br), 1250 (sh), 1240 (s), 1210 (s), 1170 (s), 1140 (m), 1105 (w), 1080 (w), 960 (m), 925 (s), 860 (sh), 840 (s, br); GC/MS *m/e* (rel intensity) 245 (parent ion, 4), 230 (11), 214 (3), 172 (10), 156 (4), 146 (100), 142 (57), 132 (15), 130 (26), 116 (7), 100 (7), 73 (51), 59 (6), 45 (11); calcd for $C_{10}H_{27}NSi_3$ 245.1451, measured 245.1456.

18: NMR (CCl_4) δ −0.04 (s, 18 H), 0.04 (br s, 12 H), 0.97 (d, 6 H, J = 8 Hz), the remaining 2 H's appeared as a quartet partially obscured by the SiMe resonances, and the chemical shift was determined to be δ 0–0.12 by decoupling the doublet at δ 0.97; GC/MS *m/e* (rel intensity) 334 (parent ion, <1), 319 (21), 247 (10), 233 (98), 217 (5), 203 (5), 189 (7), 175 (6), 173 (6), 159 (26), 147 (27), 145 (23), 133 (27), 131 (22), 117 (12), 85 (35), 73 (100), 59 (17).

Photolysis of 1 with D_2O. To a 5% solution of **1** in benzene in a quartz NMR tube was added a threefold excess of D_2O. The solution was degassed repeatedly, and the tube was sealed under vacuum. During irradiation the tube was shaken vigorously every few minutes to ensure saturation. After 2.5 h of irradiation the NMR spectrum showed complete conversion of **1** to disiloxane **20** (a colorless liquid): NMR (CCl_4) δ −0.06 (s, 18 H), 0.00 (s, 12 H), 0.94 (br s, 6 H); GC/MS *m/e* (rel intensity) 336 (parent, <1), 321 (10), 247 (2), 234 (52), 218 (3), 204 (3), 189 (4), 175 (3), 160 (14), 147 (16), 146 (13), 133 (15), 131 (13), 117 (8), 86 (28), 73 (100), 59 (16).

Photolysis of 1 with MeOH. A degassed 5% solution of **1** in benzene containing a threefold molar excess of MeOH was sealed in a quartz NMR tube in vacuo. After 2.5 h of irradiation, the NMR spectrum revealed total conversion of **1** to **21** (a colorless liquid): NMR (CCl_4) δ 0.00 (s, 9 H), 0.06 (s, 6 H), 1.00 (d, 3 H, J = 8 Hz), 3.34 (s, 3 H), the remaining methine H appears as a quartet partially obscured by the SiMe absorption, the chemical shift was determined to be δ −0.08 by decoupling the doublet at δ 1.00; GC/MS *m/e* (rel intensity) 190 (parent ion, 2), 175 (100), 161 (7), 145 (10), 133 (7), 117 (11), 101 (6), 89 (82), 86 (19), 73 (35), 59 (40), 45 (11); calcd for $C_8H_{22}OSi_2$ 190.1209, measured *m/e* 190.1218.

Nitrogen-Flow Pyrolysis of 1. A 5% solution of **1** in benzene (0.121 g of **1** in 2.4 g of benzene) was introduced dropwise into a vertical, quartz-packed tube heated at 400 °C and continuously swept by a nitrogen stream. Products were isolated by preparative GC. Both NMR and GC measurements showed **4a** and **4b** to be formed in equal amounts; the combined GC yield was 46%. The GC yield of **6** was 23%. Products **4a**, **4b**, and **6** had NMR, GC/MS, and IR spectra identical with those reported above. Disilane **5**, a colorless liquid, was formed in 10% yield: NMR (CCl_4) δ 0.00 (s, 9 H), 0.06 (s, 3 H), 0.10 (s, 12 H), 0.18 (s, 3 H), 0.20 (s, 3 H), 1.02 (d, J = 7.5 Hz, 3 H), 6.26 (AB q center, J = 4.7 Hz, 2 H), the chemical shift of the remaining proton was determined to be ca. δ 0.02 by double irradiation; IR (film) 3000 (w), 2950 (s), 2900 (m), 2860 (m), 2815 (w), 1400 (m, br), 1310 (sh), 1300 (s), 1140 (w), 1100 (m), 1000 (sh), 990 (m), 950 (m), 850 (sh), 830 (s), 790 (s), 780 (s), 760 (s), 720 (w), 680 cm^{-1} (m); mass spectrum *m/e* (rel intensity) 316 (parent ion, 2), 301 (3), 242 (24), 227 (13), 213 (5), 201 (2), 185 (3), 169 (4), 159 (16), 155 (16), 131 (14), 117 (5), 101 (3), 85 (52), 73 (100), 59 (16); calcd for $C_{14}H_{36}Si_2$ 316.1894, measured *m/e* 316.1899.

Vacuum-Flow Pyrolysis of 1. A 0.0914-g sample of neat **1** was slowly distilled through a horizontal, unpacked quartz tube ($^5/_8$ in. × 2 ft) in a 1-ft tube furnace at 500 °C and a vacuum of 0.05 mmHg. The sample flask was held at 0 °C to ensure slow vaporization, and the two collection traps were respectively cooled to 0 and −78 °C. All the products (which made it through) were collected in the 0 °C trap. Identification of **4a** (30%), **4b** (30%), and **5** (23%) was made by GC/MS comparisons.

Nitrogen-Flow Copyrolysis of 1 and Benzaldehyde. A solution of **1** (0.0532 g) in pure PhCHO (1.1 g) was pyrolyzed in the vertical, N_2-flow system at 400 °C. The products isolated by preparative GC were **10** (3), **11** (45%), and **12** (18%), with yields determined by GC. A trace amount of hexamethylcyclotrisiloxane (D_3) was observed by GC/MS, and, when the percentage of **1** in PhCHO was increased, the amount of D_3 also increased. Presumably the D_3 arises from trimerization of extruded dimethylsilanone.

10: NMR (CCl_4) δ −0.08 (s, 9 H), 1.95 (d, J = 1.5 Hz, 3 H), 7.14 (br s, 6 H); IR (film) 3030 (w, br), 3010 (w), 2960 (s), 2900 (m), 2850 (w), 1710 (s), 1595 (s), 1590 (sh), 1490 (s), 1475 (m), 1260 (s), 1250 (s), 1210 (m), 1205 (sh), 1125 (s), 1080 (s, br), 1030 (s), 985 (m), 920 (m), 850 (sh), 840 (s), 790 (m, br), 745 (s), 695 cm^{-1} (s); mass spectrum m/e (rel intensity) 190 (parent ion, 39), 175 (91), 159 (19), 135 (100), 115 (12), 105 (7), 73 (96), 59 (56), 45 (24), 43 (42).

11: NMR (CCl_4) δ 0.15 (s, 9 H), 1.90 (d, J = 1.5 Hz, 3 H), 6.66 (q, J = 1.5 Hz, 1 H), 7.20 (s, 5 H); IR (film) 3080 (sh), 3060 (w), 3020 (w), 2960 (s), 2900 (m), 2850 (w), 1710 (s), 1600 (m), 1575 (w), 1490 (m), 1445 (m), 1400 (w), 1370 (w), 1310 (w), 1260 (sh), 1250 (s), 1200 (w), 1125 (m), 1070 (m), 1025 (m, br), 960 (s), 915 (m), 850 (s), 835 (s), 755 (s), 745 (m), 710 (m), 690 cm^{-1} (s); mass spectrum m/e (rel intensity) 190 (33), 175 (70), 159 (11), 135 (100), 115 (10), 105 (5), 73 (86), 59 (49), 45 (21), 43 (24); calcd for $C_{12}H_{18}Si$ (from mixture of **10** and **11**) 190.1178, measured m/e 190.1175.

12: NMR (CCl_4) δ 0.08 (s, 9 H), 0.16 (s, 6 H), 4.62 (s, 2 H), 6.34 (center of AB q, J_{AB} = 5.0 Hz, 2 H), 7.20 (br s, 5 H); IR (film) 3080 (w), 3020 (w), 2960 (s), 2915 (w), 2900 (w), 1705 (m), 1495 (w), 1455 (m), 1260 (sh), 1255 (s), 1210 (m), 1150 (m), 1125 (s), 1090 (s), 1070 (s), 1030 (s), 850 (s), 780 (m), 730 (m), 695 cm^{-1} (m); mass spectrum m/e (rel intensity) 249 (parent − Me, 5), 207 (1), 190 (1), 165 (5), 147 (4), 135 (7), 91 (100), 73 (11), 65 (5), 59 (3).

Nitrogen-Flow Copyrolysis of 1 and 2,3-Dimethyl-1,3-butadiene.[13] A 5% solution of **1** (0.0879 g) in 2,3-dimethyl-1,3-butadiene (1.7 g) was pyrolyzed in standard fashion at 400 °C in the N_2-flow system. Three products were isolated: **16** (51%), **17** (31%), and i (10%). Separation of i was accomplished by GC using an SE-30 or OV 101 column. Separation of **16** and **17** required an XF 1150 column. All three products are colorless liquids.

16: NMR (CCl_4) δ 0.00 (s, 12 H0, 0.06 (s, 3 H), 0.96 (s, 3 H), 1.10 (m, 2 H), 1.70 (m, 6 H), 2.1 (center of AB q, J = 16 Hz, 2 H); IR (film) 2960 (s), 2920 (m), 2900 (m), 2860 (s), 1460 (w), 1450 (m), 1260 (sh), 1250 (s), 1060 (m), 1045 (m), 920 (m), 905 (m), 850 (s), 830 (s), 740 (m), 750 (m), 675 cm^{-1} (m); mass spectrum m/e (rel intensity) 240 (parent, 12), 225 (7), 211 (1), 198 (1), 184 (2), 171 (16), 166 (20), 158 (26), 152 (15), 143 (33), 137 (12), 97 (23), 85 (14), 73 (100), 59 (43); calcd for $C_{13}H_{28}Si_2$ 240.1730, measured m/e 240.1728.

17: NMR (CCl_4) δ 0.02 and 0.06 (s, s, 16 H), 1.06 (d, J = 7.5 Hz, 3 H), 1.80 (br s, 2 H), 1.94 (br s, 3 H), 4.75 and 4.96 (m, m, 4 H); IR (film) 3100 (w), 2960 (s), 2900 (m), 2870 (m), 1590 (m), 1250 (s), 1160 (m), 990 (m), 885 (m), 875 (m), 855 (s), 830 (s), 760 (m), 675 (m); mass spectrum m/e (rel intensity) 240 (parent, 4), 225 (7), 166 (5), 159 (46), 152 (4), 143 (4), 131 (13), 97 (6), 85 (67), 73 (100), 59 (26).

i: NMR (D_6C_6) δ 0.10 (s, 9 H), 0.25 (brd s, 6 H), 1.12 (d, J = 9 Hz, 3 H), 1.18 (s, 9 H), 4.04 (d, J = 1.5, 1 H), 4.21 (d, J = 1.5 Hz, 1 H), remaining H hidden under SiMe resonances, with the chemical shift of δ 0.05 determined by double irradiation; IR (film) 3080 (w), 2960 (s), 2910 (s), 1635 (m), 1440 (s, br), 1365 (m), 1250 (s), 1205 (m), 1140 (m), 1105 (w), 1040 (br w), 995 (m), 885 (s), 830 (s), 680 cm^{-1} (m); m/e (rel intensity) 258 (parent, 1), 243 (10), 201 (76), 185 (22), 161 (30), 158 (28), 147 (11), 143 (52), 133 (10), 129 (12), 117 (8), 99 (7), 85 (51), 75 (98), 73 (100), 59 (33), 55 (30).

Nitrogen-Flow Copyrolysis of 1 and 1,3-Butadiene. Using 1,3-butadiene as the carrier gas (30 mL/min) in the vertical-flow pyrolysis system, a 5% solution of **1** in benzene was pyrolyzed at 400 °C. GC/MS analysis showed the pyrolysate to contain four isomeric products: **14** (56%), **15** (13%), and two in combined yield of ca. 20% for which separation could not be effected. Products **14** and **15** were isolated by preparative GC, and were colorless liquids.

14: NMR (CCl_4) δ 0.00, 0.04, 0.08 (s, s, s, 15 H), 1.04 (s, 3 H), 1.15 (m, 2 H), 5.50 (m, 2 H), 2.12 (center of AB q, J = 16 Hz, 2 H); IR (film) 3005 (m), 2960 (s), 2900 (m), 2865 (m), 1650 (w), 1455 (w), 1255 (s), 1170 (m), 1050 (m), 890 (m), 860 (s), 835 (s), 755 (m), 715 (m), 685 (m); m/e (rel intensity) 212 (parent, 4), 197 (4), 171 (5), 158 (7), 143 (11), 138 (24), 123 (12), 109 (14), 98 (19), 85 (8), 83 (9), 73 (100), 59 (33).

15: NMR (CCl_4) δ 0.08 and 0.12 (br s and s, 15 H), 1.55 (m, 5 H), 5.34 (m, 2 H), 6.28 (s, 2 H, presumably a tight AB q); IR (film) 3010 (m), 2960 (s), 1650 (w), 1400 (br), 1255 (s), 1150 (m), 1050 (br m), 995 (m), 965 (m), 840 (s, br), 760 (m), 675 (m); m/e (rel intensity) 212 (parent, 2), 197 (2), 169 (2), 157 (25), 141 (3), 124 (4), 113 (3), 97 (3), 85 (5), 83 (8), 73 (100), 59 (17).

Synthesis of Trimethylsilyltrimethylgermyldiazomethane (22). Route A. A suspension of 80 mmol of Li in 60 mL of Et_2O was cooled to −23 °C (CO_2/CCl_4 bath). After addition of 5.0 mL of chloromethyltrimethylsilane (36 mmol), vigorous stirring (Hirsch) was continued for 2.5 h, and then 28.3 mmol of trimethylchlorogermane was added by syringe. The reaction mixture was allowed to warm to room temperature, drained through a stopcock on the bottom of the flask (leaving behind the excess Li), diluted with 150 mL of Et_2O, washed with saturated NH_4Cl, and dried over Na_2SO_4, and the solvent was evaporated. Trimethylsilyltrimethylgermylmethane was isolated in 72% yield after distillation: bp 140–142 °C (lit.[22,23] 139 °C); NMR (CCl_4) δ −0.15 (s, 2 H), 0.03 (s, 9 H), 0.18 (s, 9 H); IR matches spectra reported in ref 22 and 23. A solution of this material (0.229 g), THF (6.0 mL), and HMPA (0.5 mL) was cooled to −78 °C. One equivalent of t-BuLi in pentane was added to immediately produce a bright yellow color. After the solution was stirred for 45 min at −78 °C, 1 equiv of tosyl azide was added, and the mixture was kept at −78 °C for an additional 1 h before it was allowed to warm to room temperature for 2 h. The reaction mixture was diluted with n-hexane (100 mL), extracted several times with slightly alkaline H_2O (pH ~9), and dried over Na_2SO_4, and the solvent was largely removed by distillation. GC analysis revealed a 48% yield of **22** accompanied by 24% unreacted starting material. Purification of bright green, liquid **22** was by preparative GC on a glass SE-30 column: NMR (C_6D_6) δ 0.18 (s, 9 H), 0.30 (s, 9 H); IR (film) 2970 (s), 2920 (m), 2880 (sh), 2040 (s), 1410 (br, m), 1250 (s), 1230 (s), 925 (m), 900 (m), 835 (s, br), 820 (sh), 760 cm^{-1} (m); m/e (rel intensity) 228 (parent ion for ^{70}Ge isomer, 2), 213 (1), 185 (2), 143 (7), 115 (42), 99 (14), 89 (22), 85 (51), 73 (100), 59 (32), the appropriate isotopic patterns were observed.

Route B. To a solution of 3.0 mL (2.66 g, 22 mmol) of chloromethyltrimethylsilane in 50 mL of THF at −78 °C was added 1 equiv of sec-butyllithium in cyclohexane by syringe. After stirring for 30 min, 1 equiv of neat trimethylchlorogermane was added, and the temperature was allowed to slowly rise to room temperature. The solvent volume was reduced by evaporation to ca. 10 mL, diluted with 100 mL of n-hexane, and extracted several times with H_2O. After drying (Na_2SO_4) and removal of solvent in vacuo, 3.66 g of colorless liquid trimethylsilyltrimethylgermylchloromethane[24] remained, 70% yield. GC analysis showed the purity to be >95%. Thus, it was used without further purification: NMR (CCl_4) δ 0.13 (s, 9 H), 0.28 (s, 9 H), 2.55 (s, 1 H); IR (film) 2970 (s), 2910 (m), 1410 (br, m), 1260 (m), 1245 (s), 1230 (m), 1030 (s), 860 (s), 830 (s), 815 (s), 760 (m), 690 (m); m/e (rel intensity) 236 (parent for ^{70}Ge, <1), 221 (1), 159 (39), 115 (53), 103 (26), 85 (64), 73 (100), 59 (12), the appropriate isotopic patterns were present. Metalation of the chloride was accomplished by vigorously stirring for 7 h a refluxing solution of 0.50 mL of trimethylsilyltrimethylgermylchloromethane and 1.5 excess of Li dispersion in 50 mL of Et_2O. The resulting mixture was filtered through a glass-wool plug in the bottom directly into a second N_2-filled flask. After sitting overnight at 0 °C the anion solution was added by syringe to a solution containing a slight excess of tosyl azide in 20 mL of Et_2O at 0 °C. After 2 h at 0 °C and overnight at room temperature, the mixture was filtered and the majority of the Et_2O was evaporated. GC analysis showed that **22** was present in ca. 10% along with many other products.

Nitrogen-Flow Copyrolysis of 22 and Benzaldehyde. A 5% solution of **22** (0.0242 g) in benzaldehyde (0.52 g) was pyrolyzed at 400 °C in the N_2-flow system. The only major products observed were **26**, **27** (equal amounts by NMR and GC, combined yield 68%), and **25** (8%). Neither NMR nor GC/MS analysis showed any evidence of products derived from a germene. Products **26** and **27** were isolated by preparative GC as colorless liquids. Ether **25** was formed in insufficient quantity to isolate, and was identified solely from its GC/MS spectrum and subtraction of **26** and **27** from the NMR spectrum of the product mixture.

26 (Z isomer): NMR (CCl_4) δ 0.13 (s, 9 H), 2.06 (d, J = 1.6 Hz, 3 H), 7.18 (center of m, 6 H); m/e (rel intensity) 232 (parent ion for ^{70}Ge, 10), 217 (97), 201 (10), 177 (31), 147 (22), 131 (41), 115 (39), 101 (96), 87 (100), 73 (25), 65 (27), 51 (28), appropriate isotopic patterns for one Ge were present.

27 (*E* isomer): NMR (CCl_4) δ 0.35 (s, 9 H), 2.07 (d, J = 1.6 Hz, 3 H), 6.64 (q, J = 1.6 Hz, 1 H), 7.27 (s, 5 H); the mass spectra of **26** and **27** are virtually identical.

25: GC/MS (parent ion not observed) *m/e* 291 (P − Me for ^{70}Ge, 15), 215 (1), 199 (2), 189 (13), 159 (4), 145 (4), 115 (33), 90 (100), 77 (6), 73 (58), 65 (44), 59 (16).

Photolysis of 22 and MeOD. In a quartz NMR tube was placed 400 μL of a 5% solution of **22** in C_6D_6, and a sixfold molar excess of MeOD was added. The solution was repeatedly degassed and then sealed under vacuum. After 2.5 h of irradiation the NMR spectrum showed complete conversion to **28** and **30.** Based on the NMR spectrum **28** predominated by a factor of 4. Assuming identical response factors, the GC ratio of **28:30** was 79:21.

28:[24] NMR (CCl_4) δ 0.07 (s, 6 H), 0.15 (s, 9 H), 1.07 (br s, 3 H), 3.37 (s, 3 H); *m/e* (rel intensity) (parent ion not observed), 218 (P − Me for ^{70}Ge, 38), 188 (5), 159 (5), 128 (6), 115 (24), 89 (100), 73 (25), 59 (62).

30:[24] NMR (CCl_4) δ 0.03 (s, 9 H), 0.31 (slightly br s, 6 H), 1.11 (br s, 3 H), 3.38 (s, 3 H); *m/e* (rel intensity) (parent ion not observed) 218 (P − Me for ^{70}Ge, 29), 188 (4), 159 (6), 143 (2), 131 (22), 128 (7), 115 (8), 105 (33), 101 (21), 89 (100), 86 (41), 73 (55), 59 (39).

Synthesis of Bis(trimethylgermyl)diazomethane (31). Route A. To a cooled (−23 °C, CO_2/CCl_4 bath) suspension of 85 mmol of Li dispersion in 60 mL of Et_2O was added 4.70 g (28 mmol) of Me_3GeCH_2Cl[25,26] by syringe. The mixture was vigorously stirred for 2 h, after which time 28 mmol of neat Me_3GeCl was added. After the solution was separated from the excess Li, it was diluted with 150 mL of Et_2O, extracted several times with saturated aqueous NH_4Cl, then with H_2O, and finally dried over Na_2SO_4. Evaporation of the Et_2O left a colorless liquid, which was shown by GC to be >95% pure (isolated yield, 69%) bis(trimethylgermyl)methane: bp 152–155 °C (lit.[27] 156–157 °C); NMR (CCl_4) δ 0.21 (s, 18 H), 0.00 (s, 2 H); IR (film) 2980 (s), 2915 (s), 2895 (m), 1410 (br, m), 1240 (s), 1045 (s), 820 (s), 780 (m), 770 (sh), 685 (s); *m/e* (rel intensity) (parent ion not observed) 235 (P − Me for most intense peak in that ensemble in which all of the required isotope peaks for a fragment ion with Ge_2 are observed, 32), 119 (100), 105 (11), 89 (27). To a solution containing $(Me_3Ge)_2CH_2$ (0.240 g), THF (5 mL), and HMPA (0.25 mL) at −78 °C was slowly added 1 equiv of *tert*-butyllithium. After the solution was stirred for 30 min, 1 equiv of neat tosyl azide was added to almost immediately change the solution from bright yellow to dark brown to a light yellow-orange color. The temperature was allowed to rise to 0 °C, at which point the reaction mixture was poured into 100 mL of *n*-hexane and then extracted several times with slightly alkaline H_2O (pH ~9). The organic solution was dried (Na_2SO_4) and then evaporated to leave a mixture containing **31** (32%), $Me_3GeCH_2GeMe_2$-*t*-Bu (8%), $(Me_3Ge)_2CH_2$, Me_3Ge-*t*-Bu, $(Me_3Ge)_2O$, and several unidentified minor components. It was discovered that **31** is not stable in the reaction mixture, and must be removed as quickly as possible. Purification of **31** was by preparative GC on a 6-ft, 15% SE-30 glass column with a column temperature of 120 °C. After purification, **31** is a bright green liquid which can be stored at −10 °C for months without decomposition. When the synthesis of **31** is performed on a larger scale, we obtain better results with an inverse addition, that is, anion solution to tosyl azide. **31:**[24] NMR (C_6D_6, **31** is not stable in CCl_4) δ 0.28 (s) (lit. δ 0.15[28] and 0.22[29]); IR (film) 2950 (s), 2920 (m), 2890 (sh), 2850 (w), 2040 (s) (lit.[28] 2050 for CN_2), 1250 (s), 1220 (s), 925 (s), 830 (s, br), 750 (m), 680 cm^{-1} (m); *m/e* (rel intensity) 276 (most intense peak for P − Me fragment ion cluster, 9), 261 (5), 233 (10), 191 (26), 175 (8), 145 (20), 131 (18), 119 (100), 89 (63).

Route B. A solution of Me_3GeCH_2Cl (0.50 g) in 10 mL of THF was cooled to −78 °C before addition of 1 equiv of *sec*-butyllithium in hexane. After the solution was stirred for 30 min, 1 equiv of Me_3GeCl was added by syringe. The temperature was allowed to rise to room temperature and the solution was poured into 100 mL of hexane. After extracting several times with H_2O, drying over Na_2SO_4, and evaporation of solvents, colorless liquid bis(trimethylgermyl)chloromethane was isolated in 60% yield with >95% GC-determined purity. This material was used without further purification. **$(Me_3Ge)_2CHCl$:** NMR (CCl_4) δ 0.27 (s, 18 H), 2.72 (s, 1 H); IR (film) 2980 (s), 2910 (s), 2810 (w), 1415 (w, br), 1245 (s), 1035 (m), 820 (s, br), 760 (m), 695 cm^{-1} (m); *m/e* (rel intensity) 284 (P + 6 for $^{70}Ge_2$, <1), 269 (2), 152 (6), 131 (13), 119 (100), 105 (17), 89 (21). Metalation was accomplished by refluxing for 5 h a mixture of $(Me_3Ge)_2CHCl$ (0.6 mL), 1.5-fold excess of Li dispersion, and 60 mL of Et_2O. The mixture was filtered through a glass-wool plug at the bottom of the flask into a second flask, and then added via syringe to a solution of 1 equiv of tosyl azide in 20 mL of Et_2O at 0 °C. After stirring at 0 °C for 4 h, the mixture was filtered and the solvent evaporated, and GC/MS analysis showed only ca. 1% yield of **31**.

Nitrogen-Flow Pyrolysis of 31. A 5% solution of **31** (0.0206 g) in benzene (0.40 g) was pyrolyzed in the N_2-flow system at 400 °C. Two major products were formed. Digermazane **33** (ca. 30%) was not isolated, and was tentatively identified on the basis of the similarity of its mass spectrum with that of disilazane **6.** Digermane **32** (32%) was isolated as a colorless liquid by preparative GC:[24] NMR (CCl_4) δ 0.12 (s, 9 H), 0.22 (s, 12 H), 0.23 (s, 3 H), 0.33 (s, 3 H), 0.34 (s, 3 H) 1.16 (d, J = 7.5 Hz, 3 H), 6.12 (center of AB q, J = 3.5 Hz), methine quartet not observed owing to low concentration; IR (film) 2980 (s), 2945 (s), 2910 (s), 2870 (m), 2810 (w), 1680 (w), 1460 (w), 1420 (m, br), 1260 (m), 1245 (s), 1130 (m), 1100 (m, br), 1010 (m, br), 950 (m), 830 (s), 785 (s), 670 (s), 600 cm^{-1} (s); *m/e* (rel intensity) 494 (P^+ + 10 for $^{70}Ge_4$, <1), 479 (<1), 377 (3), 347 (2), 319 (3), 247 (13), 207 (10), 191 (5), 175 (2), 159 (2), 145 (4), 131 (18), 119 (100), 105 (14), 89 (18).

Photolysis of 31. A solution of **31** (0.0270 g) in benzene (0.50 g) was repeatedly degassed in an NMR tube, and the tube was then sealed under vacuum. Photolysis was carried out for 2 h, after which time GC analysis revealed an 89% yield of **32** and ca. 1% of **35:** NMR (CCl_4) 0.20 (s, 18 H), 0.32 (s, 6 H), 0.33 (s, 6 H), 1.22 (d, J = 8.0 Hz, 6 H), the remaining 2 H q was not observed owing to low S/N; *m/e* (rel intensity) 497 (parent − Me + 10 for $^{70}Ge_2$, 8), 367 (9), 249 (13), 235 (8), 221 (7), 207 (10), 191 (3), 175 (2), 161 (2), 145 (3), 131 (28), 119 (100), 105 (21), 89 (13), 73 (3).

Photolysis of 31 and MeOD. To 0.50 mL of a 5% solution of **31** in C_6D_6 was added a sixfold excess of MeOD. This solution was repeatedly degassed, and the NMR tube was then sealed in vacuo. After 2 h of irradiation, both NMR and GC analysis showed complete conversion of **31** to **38:** NMR (CCl_4) δ 0.15 (s, 9 H), 0.31 (s, 3 H), 0.32 (s, 3 H), 1.17 (br s, 3 H), 3.36 (s, 3 H); *m/e* (rel intensity) 266 (parent − Me + 6 for $^{70}Ge_2$, 66), 236 (42), 207 (43), 191 (18), 149 (10), 132 (69), 119 (100), 105 (97), 89 (58), the appropriate isotopic clusters were present.

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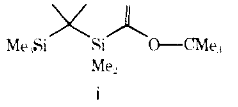

i

action of **3** and some unidentified impurity in the commercial diene, although careful drying and fractional distillation of the diene did not eliminate the formation of i. However, use of a different commercial sample of the diene resulted in a significant reduction in the yield of i, and photolysis of **1** (5% in C_6H_6) in the presence of a threefold excess of 2,3-dimethyl-1,3-butadiene resulted in exclusive formation of **16** and **17**, and no i. Spectral characteristics of i are presented in the Experimental Section.

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Gas-Phase Heats of Formation of Keto and Enol Ions of Carbonyl Compounds

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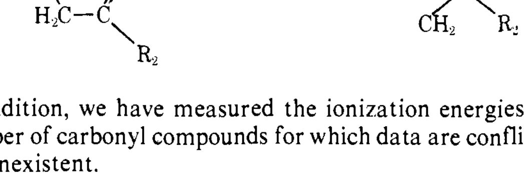
Abstract: The gas-phase heats of formation of 13 enol positive ions of aliphatic aldehydes, ketones, acids, and esters have been measured and are compared with those of the corresponding keto ions. The enolic ions are all much more stable thermodynamically, by amounts ranging from 14 to 31 kcal mol^{-1}. This is in marked contrast to the neutral tautomers, in which the keto forms are generally the more stable. Enol ions have often been postulated as product structures in ionic fragmentations, but quantitative thermochemical data for such ions have not been available.

Introduction

In recent papers we have reported measurements of the gas-phase heats of formation of the enol ions of methyl acetate[2a] and of acetic acid.[2b] These measurements, made by impact of energy-selected electrons, showed that the enol forms of ionized methyl acetate and acetic acid, formed by dissociative ionization of appropriate precursor molecules, are more stable by 24 and 22 kcal mol^{-1}, respectively, than the corresponding carbonyl forms of the ions.

This is consistent with an earlier study[3] which showed that the molecular ion of vinyl alcohol, produced by dissociative ionization processes, is more stable than the tautomeric acetaldehyde ion by 15 kcal mol^{-1}. For the neutral enol and keto forms of C_2H_4O, the thermodynamic stabilities are in the reverse order by 12–13 kcal mol^{-1}.[3,4] According to energies calculated by ab initio MO theory there is an activation energy barrier of some 85 kcal mol^{-1} for the isomerization vinyl alcohol → acetaldehyde. Although it is found experimentally that enols are thermodynamically less stable than their carbonyl forms,[5] enol intermediates have been detected by NMR.[6] Vinyl alcohol has recently been prepared in the gas phase[7] by thermolysis of ethylene glycol at 1000 °C; it had a half-life in Pyrex of ca. 30 min. As pointed out by Radom et al.,[4] this observation is hard to reconcile with the large energy barrier calculated for unimolecular isomerization to acetaldehyde, and so the short half-life may be attributed to intermolecular and/or heterogeneous reactions. Whatever the explanation, it is noteworthy that, in spite of their unfavorable thermodynamic stability, the proposed participation by enol forms in oxidation–reduction[8] and in photochemical reactions (the Norrish type II reaction) is not uncommon.

The condition for participation of enolic molecular ions in ionic reactions is, as a consequence of their relative stability, much more favorable than for their neutral counterparts. The well-known McLafferty rearrangement[9,10] which plays an important role in the mass spectra of aldehydes, ketones, acids, and esters has as its motive force this favorable stability. Because this enhanced stabilization may well be a general phenomenon, we have undertaken an extended study of the thermochemistry of $C_nH_{2n}O^{+\cdot}$ and $C_nH_{2n}O_2^{+\cdot}$ ions, comparing the heats of formation of product ions of these formulas with those of their ionized isomeric carbonyl compounds. The existing quantitative data for such comparisons are fragmentary, and in many cases too inaccurate to be useful. We have measured the appearance energies of $C_2H_4O_2^{+\cdot}$, $C_3H_6O^{+\cdot}$, $C_4H_8O^{+\cdot}$, $C_3H_6O_2^{+\cdot}$, and $C_4H_8O_2^{+\cdot}$ ions formed in the fragmentation of aldehydes, ketones, esters, and acids (in whose mass spectra these ions are major or prominent peaks) by elimination of a neutral olefin via a six-centered activated complex, e.g.



In addition, we have measured the ionization energies of a number of carbonyl compounds for which data are conflicting or nonexistent.

Experimental Section

Appearance energies (AE) were measured by impact of an energy-resolved electron beam from an electrostatic electron monochromator,[11] together with a quadrupole mass spectrometer and minicomputer data system.[12] All the compounds were of research grade, carefully purified where necessary by GLC. In this work, the purity was of particular importance, since appearance energies for $C_nH_{2n}O^{+\cdot}$ and $C_nH_{2n}O_2^{+\cdot}$ product ions were in some cases quite close to the ionization energies of possible isomeric impurities.

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