lutions of coupler II, R. Cameron of these laboratories for the preparation of coupler II, and R. Bent for the preparation of the *p*-phenylenediamines.

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Gas-Phase Pyrolysis of Phenyltrimethylsilyldiazomethane. Intramolecular Chemistry of Phenyltrimethylsilylcarbene[1,2a]

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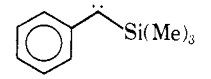
Abstract: The gas-phase generation of phenyltrimethylsilylcarbene through the pyrolysis of phenyltrimethylsilyldiazomethane yields ditrimethylsilylstilbene (13%), 1,1-dimethyl-1-silabenzocyclopentene (15-20%), benzyltrimethylsilane (2%), and styrene (2-5%). The major product arises through a carbene-to-carbene rearrangement. The styrene is probably formed by decomposition of the product of carbon-hydrogen insertion, 1,1-dimethyl-2-phenylsilirane. The product of carbon-silicon insertion, 1,2,2-trimethyl-1-phenylsilene, can be trapped with methanol, carbonyl compounds, and dienes.

Interest has quickened over the last few years in the synthesis of silenes[3-5] and siliranes.[6,7] It is now clear that such compounds are accessible, if reactive, species. One attractive route for the generation of both such intermediates is the intramolecular reaction of α-silylcarbenes. We report here the details of our investigations of the chemistry of one such potential precursor, phenyltrimethylsilylcarbene (**1**). If the all-carbon analogue, phenyl-*tert*-butylcarbene (**2**), is taken as a model, **1** seems a likely source indeed. Gas-phase generation of carbene **2** gives 1-phenyl-2,2-dimethylcyclopropane and 2-methyl-3-phenylbutene in the ratio 85/15. Of course carbene **2** need not be a perfect model for **1**, as it is reasonable to expect formation of species containing sp^2-hybridized silicons to be more difficult than in the corresponding carbon case. Thus it seemed important to minimize the intermolecular reactions of **1** by generating the carbene in the gas phase where difficult intramolecular reactions might prevail.



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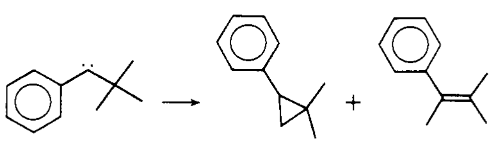

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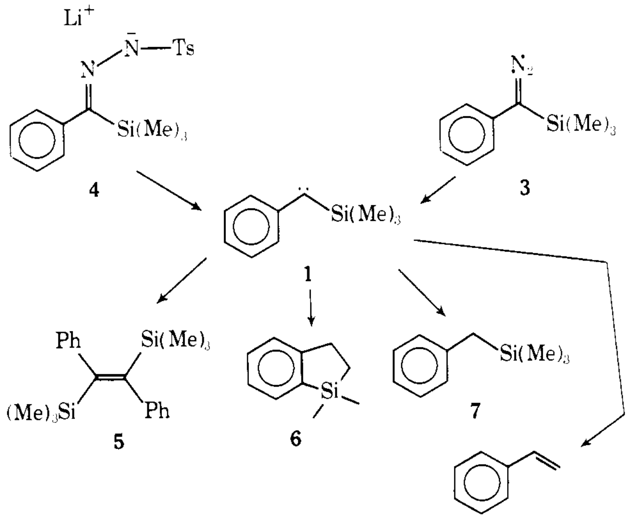
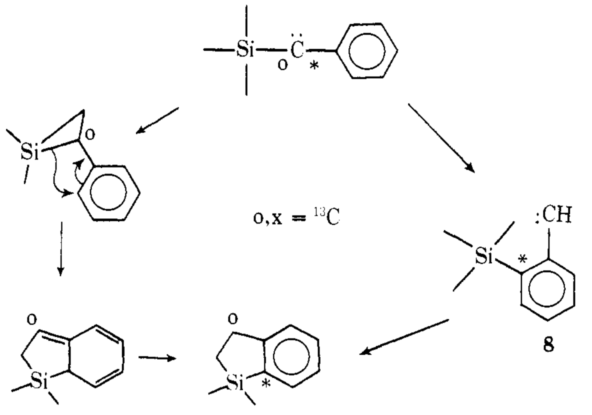
Carbene **1** was generated in three ways. The diazo compound **3** was carried with a stream of nitrogen in a vertical flowing system through a 28 × 1 cm Pyrex tube packed with Pyrex chips at a rate of 30 mL/min (method A). The products were condensed in a trap and analyzed. Alternatively, the diazo compound could be decomposed in the inlet of a gas chromatograph held at 300 °C (method B). A third method involved the flash pyrolysis of the lithium salt of the tosylhydrazone of phenyl trimethylsilyl ketone **4** (method C).



Method A gave four products, ditrimethylsilylstilbene (**5**, 13%), 1,1-dimethyl-1-silabenzocyclopentene (**6**, 15%), benzyltrimethylsilane (**7**, 2%), and styrene (2%). Method B gave similar results and method C gave **6** (20%) and styrene (5%). Compound **5** is easily rationalized as the product of either dimerization of **1** or reaction of **1** with **3**. Compound **7** involves abstraction of hydrogen by **1** and is a typical minor product of carbene reactions.

Interestingly, neither **6**, the major product, nor styrene finds analogy in the gas-phase reactions of **2**. Phenylcarbenes are known to undergo rearrangement in the gas phase,[8,9] and it seemed likely that isomerization of **1** to **8** followed by a conventional carbon–hydrogen insertion reaction was the mechanism leading to **6**. A ^{13}C labeling experiment was consistent with this postulate and in particular ruled out an earlier suggestion[4] that a silirane was involved. A sample of ^{13}C-labeled benzoic acid (24.3% ^{13}C) was prepared from phenylmagnesium bromide and labeled CO$_2$ and then converted to labeled **3** by the method of Brook and Jones.[10] Decomposition by method B led to labeled **6**. A sample of labeled **4** (12.8% ^{13}C) was prepared from ^{13}C-labeled methyl benzoate by the method of Picard and co-workers.[11] Decomposition via method C gave another supply of labeled **6** (13% ^{13}C).



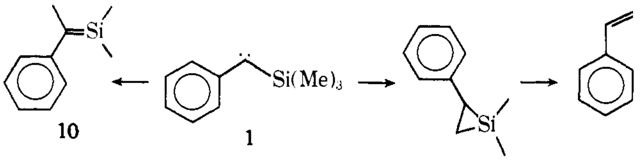
6

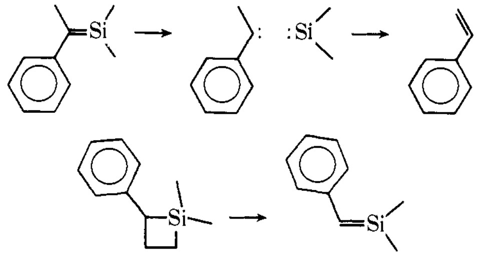
The ^{13}C NMR spectrum of unlabeled **6** shows three aliphatic carbon absorptions at 31.80, 11.47, and −1.59 ppm from Me$_4$Si. In addition, a group of signals for the aromatic carbons appears at lower field, of which two, at 153.1 and 139.9 ppm from Me$_4$Si, are of low intensity in the hydrogen-decoupled Fourier transform spectrum and can confidently be attributed to the two quaternary carbons in **6**.[12] Moreover, it is the upfield member of the pair that is adjacent to the silicon atom.[13]

The ^{13}C NMR spectrum of labeled **6** shows no enhancement of the aliphatic carbon absorbances (as it must were the silirane mechanism operative) and it is the absorbance of the quaternary carbon α to silicon that is increased, as predicted by the phenylcarbene rearrangement mechanism. Comparable results are obtained with **6** produced by either method B or C. So the formation of **6** can be confidently attributed to a carbene-to-carbene rearrangement.

Clearly carbene **1** is "avoiding" paths taken by its carbon analogue **2**. The question is why? It is reasonable to assume that the normally difficult route of reaction with the benzene ring is taken because activation barriers to the carbon–hydrogen and carbon–silicon insertions leading to siliranes and silenes are relatively high. Presumably the formation of **6** in the silicon case reflects the relative "badness" of the siliranes and silenes.

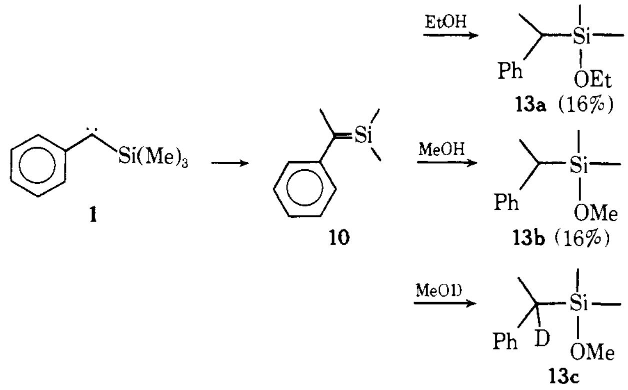
But are they formed at all in this reaction? One would not expect either **9** or **10**, the products of carbon–hydrogen and carbon–silicon insertions of **1**, respectively, to be stable to the reaction conditions. Siliranes are now known[14] to extrude dimethylsilylene at very low temperatures. One would expect **9** to yield styrene and we attribute the 2–5% of styrene formed in our reaction to this pathway. Since our work was completed, we have been informed by Professor H. Shechter that trimethylsilylcarbene itself yields small amounts of 1,1-dimethylsilirane, which in turn produces ethylene and dimethylsilylene which can be trapped.[15] So it seems that small amounts of siliranes are formed. There is another potential source of styrene, however, and that is the dissociation of **10** to dimethylsilylene and methylphenylcarbene, which subsequently yields styrene. Although we cannot rule such a pathway out absolutely, we can note that related species have been generated in our laboratories many times without the detection of carbene products. For example, **11** is the product of the gas-phase decomposition of **12** and none of the products associated with the gas-phase chemistry of phenylcarbene[8] are detected.





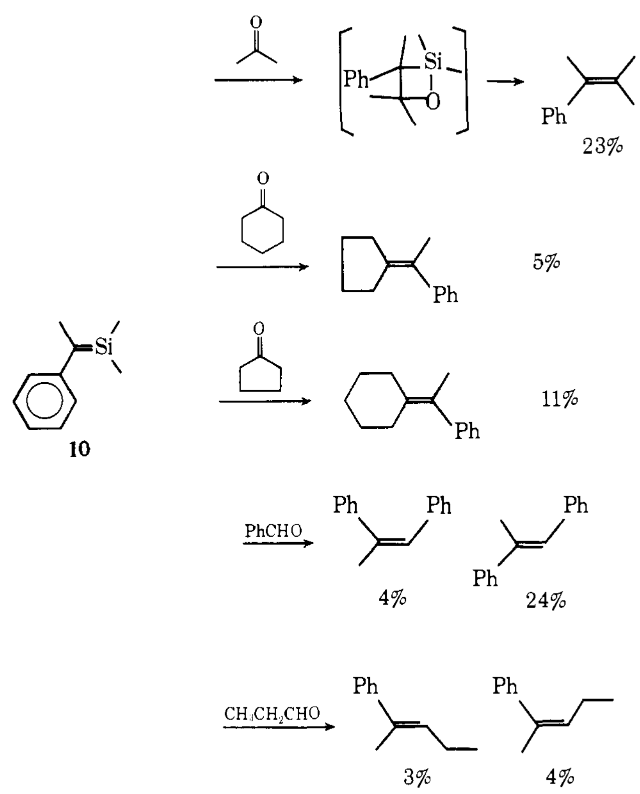
However, silene **10** is also formed in the reaction! Its presence is revealed by a number of experiments in which **1** is generated by method A in the presence of a trapping agent.

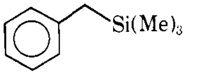
In addition to **6** and **7**, silyl ethers **13a–c** are formed when **1** is generated in the presence of alcohols. Although one must be wary of the intrusion of a mechanism in which alcohol attacks a silicon adjacent to the carbene with simultaneous or subsequent methyl migration, the above results are certainly consistent with the intervention of **10**.



Even more convincing is the evidence for silene formation of olefins when carbonyls are used as traps for **10**. Silenes are known[16-18] to react with carbonyl-containing compounds to generate olefins through the intermediacy of labile siloxycyclobutanes.

Finally and most convincingly, **10** can be trapped in Diels–Alder fashion with 2,3-dimethylbutadiene. Formation of **14**, the conventional product of reaction of **1** with a conjugated diene, and **15**, the product of thermal rearrangement of **14**, is accompanied by 8% of **16**, the product of [2 + 4] cycloaddition of **10** and the diene. Although we were concerned initially about the isomerization of **14** and/or **15** to **16** under the conditions of the reaction, at 500 °C **14** led only to **15**. No **16** could be isolated. At 700 °C several minor products are formed in addition to **15** along with substantial amounts of polymer and charred material. However, no **16** can be found. Thus it appears that **16** must be formed by Diels–Alder reaction of **10**.





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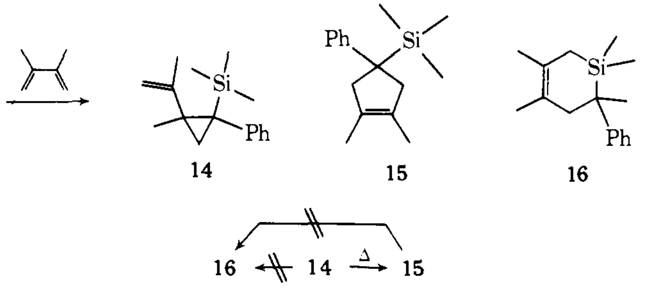

In conclusion we note that carbene **1** does undergo the reactions anticipated by analogy to the all-carbon case **2**. However, these reactions are not nearly as favorable in the silicon-containing case and a new reaction not encountered in the chemistry of carbene **2** dominates.

Experimental Section

General Procedures. ^{1}H NMR spectra were obtained on either a Varian A-60D or A-60A spectrometer. ^{13}C NMR spectra were obtained on a Brucker 90 NMR machine. Infrared spectra were obtained using either a Hitachi spectrometer or a Perkin-Elmer Model 237B grating infrared spectrometer. Mass spectra were obtained on a Nippon Denshi or an AEI 902 high-resolution mass spectrometer. Preparative gas chromatographic separations were made under the following conditions: Conditon A, 2 m × 5 mm, 15% SF-96 on Celite 545 column used in an Ohkura gas chromatograph; condition B, 8 ft × 1/4 in. 20% SE-30 on Chromosorb P in a F and M Model 500 gas chromatograph; condition C, 6 ft × 1/4 in. 10% Carbowax 20M on 60/80 mesh Chromosorb W in an Aerograph A90P gas chromatograph; condition D, 6 ft × 1/4 in. 12% DC710 on 60/80 mesh Chromosorb P in an Aerograph A90P chromatograph.

General Pyrolysis Procedures. Method A. Vertical Tube Oven. The pyrolysis apparatus consisted of a 28 × 1 cm Pyrex glass tube packed with Pyrex chips. The upper end of the tube was equipped with a rubber cap for a syringe introduction of the sample and a nitrogen gas inlet. The pyrolysis tube was maintained at 500–550 °C and the nitrogen flow rate was 30 mL/min. The sample was introduced drop by drop by using a 1-mL syringe. We estimate contact times using this apparatus at ca. 7 s. The collection trap was cooled with liquid nitrogen or dry ice/acetone. The pyrolysate was concentrated and then analyzed by preparative gas chromatography using condition A.

Method B. Gas Chromatographic Decomposition. Phenyltrimethylsilyldiazomethane was injected into a gas chromatograph with the inlet port at 300 °C and an SE-30 column at 175 °C (condition B).

Method C. Flash Pyrolysis. The pyrolysis was conducted by slowly dropping the solid tosylhydrazone salt onto a hot Pyrex surface under vacuum and trapping the pyrolysate on a cold finger. The cold finger was situated at the end of a tube leading from the reaction vessel ~250 mm from the site of pyrolysis. The Pyrex vessel was constructed from a three-necked, 500-mL flask with 24/40 standard taper joints. The flask was wrapped in wire and asbestos tape impregnated with plaster. The solids addition device consisted of a bent glass tube connected to the 24/40 joint in such a way that it could be extended into the flask, allowing the salt to be dropped directly onto the hot surface. When the solid was to be dropped, the device was rotated at the joint so that the end containing tosylhydrazone salt was raised above the level of the joint. Slight tapping caused the solid to fall into the pyrolysis flask. The pyrolysis apparatus should be shielded at all times, although we have never experienced an explosion.

Phenyl *tert*-Butyl Ketone Tosylhydrazone. *p*-Toluenesulfonylhydrazine (12.65 g, 0.068 mol, 1.1 equiv) was covered with methanol and warmed on a hot plate until all the *p*-toluenesulfonylhydrazine had dissolved. To this was added dropwise a solution of 10 g (0.062 mol) of phenyl *tert*-butyl ketone[19] in 5 mL of methanol. The flask was then scratched and stored in the freezer overnight. The white tosylhydrazone crystals were collected by filtration and air dried, yield 14.5 g (0.0455 mol, 73%). From the mother liquor another 4.82 g was isolated. The two crops were combined and pumped (0.2 mm) overnight, total yield 19.32 g (0.0607 mol, 98%), mp 158–160 °C (lit.[10] 161–162 °C).

Lithium Salt of the Tosylhydrazone of Phenyl *tert*-Butyl Ketone. Phenyl *tert*-butyl ketone tosylhydrazone (3 g, 0.0094 mol) was dissolved in 40 mL of tetrahydrofuran (THF) and cooled in a dry ice/acetone bath to −78 °C. To this was added 3.7 mL of *n*-butyllithium (2.4 M). The solution was stirred at −78 °C for 1 h and then the green-yellow solution was warmed to room temperature. The THF was stripped off by rotary evaporation, leaving a white salt. The salt was pumped (0.2 mm) overnight, yield 2.65 g (0.0083 mol, 88.7%).

Pyrolysis of the Lithium Salt of Phenyl *tert*-Butyl Ketone Tosylhydrazone Using Method C. Tosylhydrazone salt (1.5 g) was pyrolyzed at 360 °C. Analysis by gas chromatography under condition C at 130 °C led to 1-phenyl-2,2-dimethylcyclopropane (85%)[20] and 2-methyl-3-phenylbutene (15%),[21] in ca. 25% absolute yield.

Pyrolysis of Phenyltrimethylsilyldiazomethane by Method A. A benzene solution of phenyltrimethylsilyldiazomethane (0.244 g) was pyrolyzed at 500 °C. An additional 1 mL of benzene was slowly passed through the heated tube as a wash. Separation of the product mixture by preparative gas chromatography (condition A) gave 1,2-ditrimethylsilylstilbene (13%), 1,1-dimethyl-1-silabenzocyclopentene (15%), benzyltrimethylsilane, and styrene in 2–3% yield. Benzyltrimethylsilane and styrene were identified by comparison of their NMR and IR spectra and retention time with those of authentic samples.

1,1-Dimethyl-1-silabenzocyclopentene was identified by its NMR, IR, and mass spectra. NMR (CCl$_4$) δ 0.27 (6 H, s, SiCH$_3$), 0.95 (2 H, t, SiCH$_2$, J = 7 Hz), 3.05 (2 H, t, ArCH$_2$, J = 7 Hz), and 6.9–7.5 (4 H, m, Ar H); IR (neat) 1441 (Si-Ph), 1251 (SiCH$_3$), and 1122 cm^{-1} (Si-Ph); mass spectrum *m/e* (rel intensity) 162 (26, parent ion), 147 (100), 145 (32); high-resolution mass *m/e* 162.0919 (calcd for $C_{10}H_{14}Si$, 162.0820).

1,2-Ditrimethylsilylstilbene was identified by its NMR, IR, and mass spectra. NMR (CCl$_4$) δ −0.38 (18 H, s, SiCH$_3$) and 6.8–7.4 (10 H, m, Ar H); IR (KBr) 1247 cm^{-1} (SiCH$_3$); mass spectrum *m/e* (rel intensity) 324 (14, parent ion), 309 (14), 251 (18), 221 (45), 159 (57), 135 (55), and 73 (100); high-resolution mass *m/e* 324.1762 (calcd for $C_{20}H_{28}Si_2$, 324.1729).

Copyrolysis of Phenyltrimethylsilyldiazomethane and Methanol. A mixture of 0.72 g of methanol and 0.17 g of phenyltrimethylsilyldiazomethane was pyrolyzed at 500 °C using method A. Compound **6** (15%) and methoxysilane **13b** (16%) were obtained as major products. Methoxysilane **13b** was identified by its NMR and IR spectra and elemental analysis. NMR (CCl$_4$) δ 0.02 (6 H, s, SiCH$_3$), 1.38 (3 H, d, CCH, J = 7.5 Hz), 2.22 (1 H, q, CH, J = 7.5 Hz), 3.35 (3 H, s, OCH_3), and 7.0-7.5 (5 H, m, ArH); IR (neat) 1225 ($SiCH_3$), 1093 and 1035 cm^{-1} (Si-O-C). Anal. Calcd for $C_{11}H_{18}SiO$: C, 67.98; H, 9.34. Found: C, 68.48; H, 9.41.

Copyrolysis of Phenyltrimethylsilyldiazomethane and Methanol-*O-d*. A mixture of 2 mL of methanol-*O-d* and 0.5 mL of phenyltrimethylsilyldiazomethane was pyrolyzed at 500 °C using method A. Deuteriomethoxysilane **13c** was identified by its NMR and IR spectra. NMR (CCl_4) δ 0.02 (6 H, s, $SiCH_3$), 1.37 (3 H, br s, CCH_3), 3.33 (3 H, s, OCH_3), and 6.9-7.3 (5 H, m, ArH).

Copyrolysis of Phenyltrimethylsilyldiazomethane and Ethanol. A mixture of 2 mL of ethanol and 0.5 mL of phenyltrimethylsilyldiazomethane was pyrolyzed at 500 °C using method A. A 16% yield of ethoxysilane **13a** was obtained. Ethoxysilane **13a** was identified by its NMR, IR, and mass spectra. NMR (CCl_4) δ 0.02 (6 H, s, $SiCH_3$), 1.10 (3 H, t, $OCCH_3$, $J = 7$ Hz), 1.35 (3 H, d, CCH_3, $J = 7$ Hz), 2.18 (1 H, q, CH, $J \approx 7$ Hz), 3.55 (2 H, q, OCH_2, $J = 7$ Hz), and 6.9-7.3 (5 H, m, ArH); IR (neat) 1225 ($SiCH_3$) and 1065 cm^{-1} (Si-O-C); mass spectrum 208 *m/e* (rel intensity) 208 (8, parent ion), 105 (13), 104 (13), 103 (100), and 75 (34); high-resolution mass *m/e* 208.1339 (calcd for $C_{12}H_{20}SiO$, 208.1283).

Copyrolysis of Phenyltrimethylsilyldiazomethane and Acetone. A mixture of 5.19 g of acetone and 0.20 g of phenyltrimethylsilyldiazomethane was pyrolyzed at 500 °C using method A. Trimethylstyrene was obtained in 23% yield together with 37% **6** and 2% benzyltrimethylsilane. Trimethylstyrene was identified by comparison of its NMR and IR spectra and retention time with those of an authentic sample.

Copyrolysis of Phenyltrimethylsilyldiazomethane and Cyclohexanone. A mixture of 5.02 g of cyclohexanone and 0.194 g of phenyltrimethylsilyldiazomethane was pyrolyzed at 500 °C using method A. α-Methyl-β-pentamethylenestyrene was obtained in 11% yield together with 13% **6** and 8% benzyltrimethylsilane. The product was identified by comparison of its NMR, IR, and mass spectra with those of an authentic sample.

Copyrolysis of Phenyltrimethylsilyldiazomethane and Cyclopentanone. A mixture of 4.89 g of cyclopentanone and 0.174 g of phenyltrimethylsilyldiazomethane was pyrolyzed at 500 °C using method A. α-Methyl-β-tetramethylenestyrene was obtained in 5% yield together with 10% **6** and 6% benzyltrimethylsilane. The product was identified by comparison of its NMR, IR, and mass spectra with those of an authentic sample.

Copyrolysis of Phenyltrimethylsilyldiazomethane and Benzaldehyde. A mixture of 5.49 g of benzaldehyde and 0.187 g of phenyltrimethylsilyldiazomethane was pyrolyzed at 500 °C using method A. 1,2-Diphenyl-1-propene (28%, cis 4%, trans 24%) was obtained. 1,2-Diphenyl-1-propene was identified by comparison of its NMR, IR, and mass spectra with those of an authentic sample.

Copyrolysis of Phenyltrimethylsilyldiazomethane and Propionaldehyde. A mixture of 4.21 g of propionaldehyde and 0.204 g of phenyltrimethylsilyldiazomethane was pyrolyzed at 500 °C using method A. 2-Phenyl-2-pentene (two isomers) was obtained in 7% yield together with 10% **6** and 9% benzyltrimethylsilane. The 2-phenyl-2-pentenes were identified by comparison of their NMR, IR, and mass spectra with those of authentic samples.

Copyrolysis of Phenyltrimethylsilyldiazomethane and 2,3-Dimethyl-1,3-butadiene. A mixture of 1.40 g of 2,3-dimethyl-1,3-butadiene and 0.252 g of phenyltrimethylsilyldiazomethane was pyrolyzed at 500 °C using method A. Silacyclohexene **16** was obtained in 8% yield together with 22% **6**, 2% **14** and 25% **15**.

Cyclopentene **15** was identified by its NMR, IR, and mass spectra and elemental analysis. NMR (CCl_4) δ −0.18 (9 H, s, $SiCH_3$), 1.62 (6 H, s, $C{=}CCH_3$), 2.77 (4 H, s, $C{=}CCH_2$), and 6.9-7.4 (5 H, m, ArH); IR (neat) 1251 cm^{-1} ($SiCH_3$); mass spectrum *m/e* (rel intensity) 244 (8, parent ion), 171 (27), 170 (100), 155 (29), and 73 (57). Anal. Calcd for $C_{16}H_{24}Si$: C, 78.62; H, 9.90. Found: C, 78.90; H, 9.97.

Cyclopropane **14** was identified by its NMR, IR, and mass spectra. NMR (CCl_4) δ −0.03 and −0.15 (9 H, s, $SiCH_3$), 0.76 and 1.4 (3 H, s, CCH_3), 0.80-1.60 (2 H, m, CCH_2C), 1.36 and 1.88 (3 H, m, $C{=}CCH_3$), 4.4-4.5 and 4.7-4.9 (2 H, m, $C{=}CH_2$), 6.9-7.3 (5 H, m, ArH); (neat) 1245 cm^{-1} ($SiCH_3$); mass spectrum *m/e* (rel intensity) 244 (9, parent ion), 171 (48), 170 (100), 155 (46), 135 (31), and 73 (100).

Silacyclohexene **16** was identified by its NMR, IR, and mass spectra. NMR (CCl_4) δ −0.27 (3 H, s, $SiCH_3$), 0.00 (3 H, s, $SiCH_3$), 1.0-1.4 (2 H, m, $SiCH_2$), 1.28 (3 H, s, CCH_3), 1.72 (6 H, br s, $C{=}CCH_3$), 2.1-2.3 and 2.5-2.8 (2 H, m, $C{=}CCH_2$), and 7.00 (5 H, br s, ArH); IR (neat) 1252 cm^{-1} ($SiCH_3$); mass spectrum *m/e* (rel intensity) 244 (56, parent ion), 175 (36), 163 (40), 162 (100), and 147 (79); high-resolution mass *m/e* 244.1639 (calcd for $C_{16}H_{24}Si$, 244.1647).

Pyrolysis of Phenyltrimethylsilyldiazomethane by Method B. Phenyltrimethylsilyldiazomethane was injected into a gas chromatograph with the inlet port at 300 °C and an SE-30 column at 175 °C (condition B). The major product, 1,2-dimethyl-1-silabenzocyclopentene, was isolated by cold trap at −78 °C. ^{13}C NMR from Me_4Si (intensity) 153.14 (317 440), 139.86 (227 456), 131.93 (1 388 928), 129.20 (1 673 984), 125.56 (2 893 056), 31.80 (652 416), 11.47 (360 448), −1.59 (551 936).

Phenyl Trimethylsilyl Ketone Tosylhydrazone. Phenyl trimethylsilyl ketone[11] (5.84 g) and 6.1 g of recrystallized tosylhydrazide were suspended in 75 mL of dry *p*-dioxane. The mixture was stirred at room temperature overnight and the yellow color disappeared. Addition of cold water yielded a white solid which was recrystallized from ethanol to yield 5.57 g (49%), mp 117-119 °C (lit. 124-125 °C dec).[10] This material decomposes upon prolonged standing at room temperature and should be stored under refrigeration. Attempts to prepare the tosylhydrazone in alcohol failed. Brook and Jones report the preparation of the tosylhydrazone in hot glacial acetic acid.[10]

Lithium Salt of Phenyl Trimethylsilyl Ketone Tosylhydrazone. A solution of 5.57 g of phenyl trimethylsilyl ketone tosylhydrazone was dissolved in 6.8 mL of distilled tetrahydrofuran and cooled in a dry ice/acetone bath to −78 °C. The addition of 6.9 mL of 2.4 M butyllithium/hexane was accomplished with stirring under nitrogen. The temperature was not allowed to rise above −50 °C. After 1 h of stirring the tetrahydrofuran was removed using a vacuum pump to leave an orange solid (quantitative yield) which was pumped dry overnight and stored under vacuum in a freezer.

Flash Pyrolysis of the Lithium Salt of Phenyl Trimethylsilyl Ketone Tosylhydrazone by Method C. Into the solid addition device was placed 2.59 g of the tosylhydrazone salt. The pyrolysis flask was heated to 420 °C (measured before pyrolysis using a thermocouple). The solid salt was added via the solids addition device in as small amounts as could be managed under vacuum. The pyrolysate was trapped at −196 °C. After the pyrolysis the material trapped on the cold finger was washed off with pentane and analyzed by gas chromatography under condition B at 140 °C. Preparative gas chromatography yielded 20% **6** and 5% styrene.

Photolysis of Phenyltrimethylsilyldiazomethane in 2,3-Dimethyl-1,3-butadiene. A 0.55-g sample of phenyltrimethylsilyldiazomethane was dissolved in 10 mL of 2,3-dimethyl-1,3-butadiene and irradiated for 3 h through Pyrex using a 450-W medium-pressure Hanovia mercury arc. Excess butadiene was removed on a rotary evaporator and the residue analyzed by gas chromatography under condition D at 140 °C. Cyclopropane **14** and a trace amount of cyclopentene **15** were isolated by preparative gas chromatography.

Pyrolysis of 1-Phenyl-1-trimethylsilyl-2-methyl-2-(2-propenyl)-cyclopropane. A sample of **14** was passed through a quartz tube maintained at 500 °C using a stream of nitrogen at 30 mL/min. The sample was gently heated in order to vaporize it into the hot zone. The pyrolysate was collected in a trap cooled in a dry ice/acetone bath. Gas chromatographic analysis on column D at 170 °C showed only cyclopentene **15**. A similar pyrolysis conducted at 700 °C (50 mL/min N_2) showed after analysis under condition D at 170 °C seven components in addition to **15**. No **16** was seen and much of the material was lost to polymer or carbonized.

Preparation of ^{13}C-Labeled Phenyl Trimethylsilyl Ketone Tosylhydrazone. Phenylmagnesium bromide and 20% ^{13}C-labeled carbon dioxide were allowed to react to produce benzoic acid. The benzoic acid was converted to phenyl trimethylsilyl ketone tosylhydrazone according to the method of Brook and Jones.[10] NMR ($CDCl_3$) δ 0.08 (9 H, s), 2.41 (3 H, s), 7.80-6.75 (9 H, m); mass spectrum (70 eV) *m/e* (rel intensity) 346 (6) M^+, 228 (36), 191 (34), 91 (90), 73 (100), *m/e* (measured intensity) 346 (45.0), 347 (22.5). The ^{13}C content was measured at 24.3%. An NMR spectrum of the intermediate benzyl chloride shows the α carbon to have 20% ^{13}C label: NMR δ 4.14 (1.6 H, s), 4.14 (4 H, d), 7.10 (5 H, s).

Preparation of ^{13}C-Labeled Phenyltrimethylsilyldiazomethane. ^{13}C-Enriched phenyltrimethylsilyldiazomethane was made from ^{13}C-enriched benzoyltrimethylsilane *p*-toluenesulfonylhydrazone according to the method of Shechter and co-workers.[22] Distillation at 80-135 °C (0.3 mm) yielded a red liquid.

Pyrolysis of ^{13}C-Enriched Phenyltrimethylsilyldiazomethane. ^{13}C-Enriched phenyltrimethylsilyldiazomethane was injected into a gas chromatograph under condition B. The product, ^{13}C-enriched 1,1-dimethyl-1-silabenzocyclopentene, was isolated in a cold trap at −78 °C: NMR (CCl_4) δ 0.31 (6 H, s), 1.00 (2 H, t), 3.02 (2 H, t), 6.95–7.51 (4 H, m); mass spectrum (70 eV) *m/e* (measured intensity) 163 (13.2), 162 (32.5), 120 (2.1), 119 (5.5); mass spectrum *m/e* 119.0318 ± 0.0006 (calcd for C_7H_7Si, *m/e* 119.0317); ^{13}C NMR from Me_4Si (intensity) 153.11 (124 992), 139.86 (1 183 552), 131.93 (495 616), 129.20 (608 256), 125.56 (1 042 816), 31.80 (288 640), 11.47 (177 600), −1.59 (230 336).

Pyrolysis of ^{13}C-Enriched Phenyl Trimethylsilyl Ketone Tosylhydrazone Salt. Enriched (12.8% ^{13}C) salt was flash-pyrolyzed by method C to produce, after isolation by gas chromatography under condition B, enriched (13.0% ^{13}C) **6**.

References and Notes

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(2) (a) Portions of this work were communicated previously[3,4] and others are taken from the Ph.D. Theses of R.R.G. (Princeton, 1976) and J.A.K. (Iowa State, 1976) and the A.B. Thesis of A.J.R. (Princeton, 1975). (b) The University of Tsukuba. (c) Princeton University. (d) Iowa State University.

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Effects of Charge Delocalization on Hydrogen Bonding to Negative Ions and Solvation of Negative Ions. Substituted Phenols and Phenoxide Anions

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Abstract: Measurements of gas phase ion equilibria with a pulsed electron beam high ion source pressure mass spectrometer lead to the $\Delta G°$ and $\Delta H°$ values for the reactions $AHCl^- = AH + Cl^-$ and $AHCl^- = A^- + HCl$, where AH stands for substituted phenols. These results show that the hydrogen bond energies in $AHCl^-$ (for dissociation to $Cl^- + HA$) increase linearly with the gas phase acidity of the phenols. The hydrogen bond energies for dissociation of $AHCl^-$ to $A^- + HCl$ increase linearly with increase of the (gas phase) basicity of the phenoxide ions A^-. Comparison with investigations of the $AHCl^-$ complexes in acetonitrile by Kolthoff and Chantooni shows that the substituent effects in acetonitrile are strongly attenuated. It is suggested that in acetonitrile the extent of proton transfer on formation of $AHCl^-$ from AH and Cl^- is much smaller than that occurring in the gas phase. Proton transfer leads to charge dispersal in $AHCl^-$ which would decrease the solvation of $AHCl^-$. The decrease of hydrogen bonding in A^-–HCl with decreasing basicity of A^-, i.e., increasing acidity of AH, is related to an expected decrease of hydrogen bonding in A^-–$(HOH)_n$ which is responsible for the attenuation of the acidities of phenols in aqueous solution.

Earlier studies of the gas phase equilibrium

$$BHR^- = B^- + HR \qquad (1)$$

executed in this laboratory[1-5] showed that the strength of the hydrogen bond (i.e., $\Delta H_1°$ and $\Delta G_1°$) increased with the (gas phase) acidity of HR and the basicity of B^-. For example, study of the series[3] where $B^- = Cl^-$ and HR = HOH, CH_3OH, $(CH_3)_3COH$, Cl_3CH, C_6H_5OH, CH_3COOH, HCOOH gave $\Delta H_1°$ and $\Delta G_1°$, values which were found to increase in the order shown above, which is also the order of increasing gas phase acidity.[6] In another series[4] where HR = H_2O was kept constant and B^- was changed, it was found that the hydrogen bond strengths increased almost linearly with the basicity of $B^- = I^-, Br^-, NO_3^-, Cl^-, NO_2^-, F^-, OH^-$.

Results involving positive ions B_1H^+ like H_3O^+, $CH_3OH_2^+$, $(CH_3)_2OH^+$, NH_4^+, $CH_3NH_3^+$, etc., and molecules B_2 like H_2O, CH_3OH, $(CH_3)_2O$, NH_3, CH_3NH_2, etc., also showed[7-10] that the strength of the hydrogen bond in $B_1HB_2^+$ increases with the acidity of B_1H^+ and the basicity of B_2.

The existence of homoconjugated (AHA^-) and heteroconjugated (BHA^-) complexes in solution has been long known. These complexes are particularly stable in aprotic solvents and have been subjected to numerous studies[11] in these media. On the whole, considerable parallels exist regarding stabilities of the complexes in the gas phase[1-5] and in aprotic solvents. Thus, Gordon[12] found that the stabilities of the complexes AHA^- (log *K* values in acetonitrile, AH benzoic acids) increased linearly with the aqueous acidities of the acids