Reactions of Carbon Vapor Constituents with Trimethylsilane

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Abstract: The C_1, C_2, and C_3 products obtained from the simultaneous codeposition of trimethylsilane and carbon vapor on a liquid nitrogen cooled surface under vacuum are described. A comparison is made between the product mixtures obtained from carbon vapor produced in a low intensity carbon arc and from thermally produced carbon vapor. The latter is in accord with what might be expected from reactions of largely ground-state precursors.

Reports of the reactivity of silicon–hydrogen bonds to carbene insertions[1,2] have led us to examine the reaction of carbon vapor with trimethylsilane. We have reported previously that the reaction of atomic silicon with trimethylsilane produced 1,1,1,3,3,3-hexamethyltrisilane as the only major volatile product in ~30% yield.[3] The reaction of carbon vapor with silane has been reported to produce low yields of methylsilane, disilane, acetylene, diacetylene, and benzene.[4] The reactions of carbon vapor with a wide variety of substrates have recently been reviewed.[5]

The apparatus and general procedure for carrying out the trimethylsilane reaction were similar to that described previously for other carbon vapor reactions studied in this laboratory.[6] Carbon was vaporized by means of a 16-V arc struck between graphite electrodes, or thermally vaporized by resistively heating a graphite electrode to temperatures in excess of 2200°. The carbon vapor thus produced was simultaneously cocondensed with a large excess of trimethylsilane on a liquid nitrogen cooled surface. Codepositions were carried out at pressures below 1×10^{-4} Torr, precluding vapor-phase collisions of carbon vapor species and substrate molecules during their flight to the walls of the system. Reaction occurs in the cold condensed phase on the walls of the container.

Carbon vapor produced from a low voltage arc under vacuum has been estimated by chlorine trapping[7] to contain 68% C_1, 24% C_2, 7% C_3, and 1% C_4 (mol %). The metastable ^1S and ^1D states and the ^3P ground state of C_1, the triplet ($a\,^3\Pi_u$) and singlet ($X\,^1\Sigma_g^+$) states of C_2, and triplet ($^3\Pi_u$) and singlet ($X\,^1\Sigma_g^+$) states of C_3 from arc produced carbon vapor are all expected to survive their flight to the walls of the system (~10^{-5} sec) and thus might enter into reactions with the substrate. Chemical reactions of the molecular species C_4 have also been observed from arc generated carbon vapor,[8] but no products corresponding to a C_4 precursor were observed in the trimethylsilane reaction.

Chlorine trapping experiments done in this laboratory[9] have indicated that thermally produced carbon vapor contains 54% C_1, 11% C_2, and 35% C_3 (mol %). It was expected that vaporization of carbon from a resistively heated electrode would produce largely ground-state species, with only the negligible population of excited state species predicted by the Boltzmann relation. Thus, only the ^3P ground state of C_1 and the singlet states of C_2 and C_3 should be available for reaction at the walls of the system. The additional substances produced when an arc is used as the source of carbon must be attributed to excited state precursors.

Results and Discussion

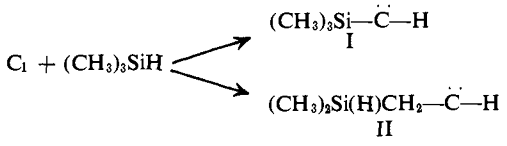
A. C_1 Products. It was assumed that products having a molecular composition corresponding to one or two molecules of trimethylsilane plus one carbon atom were derived from a C_1 precursor. These products and their yields are listed in Table I.

Table I. Products Resulting from Reactions of C_1

	% yield[a]	
Product	16-V arc	Thermal vaporization
$(CH_3)_4Si$	1.36	1.31
$(CH_3)_2Si(H)C{\equiv}CH$	1.87	Trace
$(CH_3)_2Si(H)CH{=}CH_2$	12.2	1.36
$(CH_3)_2Si(H)CH_2CH_3$	0.89	0.12
$(CH_3)_3SiCH_2Si(CH_3)_3$	0.70	0.00

[a] Yields are based on total C_1 reaching the reaction zone.

Surprisingly little product is isolated from the C_1 generated in thermal vaporization; tetramethylsilane only is implicated as a ^3P product. Arc produced C_1 product yields are greater, and two of the products are particularly interesting: dimethylvinylsilane and bis(trimethylsilyl)methane. The formation of these two products is readily explained by postulating insertion of singlet C_1 to form the corresponding carbenes.



$$C_1 + (CH_3)_3SiH \rightarrow (CH_3)_3Si\text{—}\ddot{C}\text{—}H \ \ \text{I}$$
$$C_1 + (CH_3)_3SiH \rightarrow (CH_3)_2Si(H)CH_2\text{—}\ddot{C}\text{—}H \ \ \text{II}$$

I forms a stable product by insertion into another molecule of substrate, II by a rearrangement. Both of these reactions are characteristic of singlet carbenes.

$$\text{I} \xrightarrow{(CH_3)_3SiH} (CH_3)_3SiCH_2Si(CH_3)_3$$
$$\text{II} \longrightarrow (CH_3)_2Si(H)CH{=}CH_2$$

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[1] K. A. W. Kramer and A. N. Wright, *J. Chem. Soc.*, 3604 (1963).

[2] D. Seyferth, J. M. Burtlitch, H. Dertouzos, and H. D. Simmons, Jr., *J. Organometal. Chem.*, 7, 405 (1967); C. J. Mazac and J. W. Simons, *J. Amer. Chem. Soc.*, **90**, 2484 (1968).

[3] P. S. Skell and P. W. Owen, *ibid.*, **89**, 3933 (1967).

[4] J. Binenboym and R. Schaeffer, *Inorg. Chem.*, **9**, 1581 (1970).

[5] G. Czichocki, *Z. Chem.*, **10**, 423 (1970).

[6] P. S. Skell, L. Wescott, Jr., J.-P. Golstein, and R. R. Engel, *J. Amer. Chem. Soc.*, **87**, 2829 (1965).

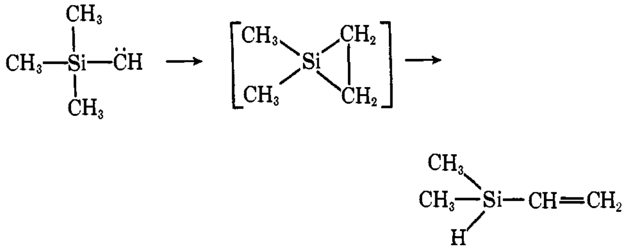
[7] R. F. Harris, Ph.D. Thesis, The Pennsylvania State University, University Park, Pa., 1968.

[8] R. F. Harris and P. S. Skell, *J. Amer. Chem. Soc.*, **90**, 4172 (1968).

[9] P. S. Skell, J. Havel, J. Plonka, J. Villaume, and K. Klabunde, unpublished result.

Rearrangement of I has little driving force since a product with an Si=C linkage would result.

Trimethylsilylcarbene (I) has been generated previously,[10,11] and shown to rearrange to dimethylvinylsilane *via* a silacyclopropane intermediate.[10] To distinguish between the alternate pathways for the formation of this product from C_1, a reaction of arc-produced carbon vapor and trimethyldeuteriosilane was run. If the product resulted from an initial silicon–hydrogen bond insertion to form I, followed by rearrangement through a silacyclopropane, it should contain approximately 75% of the deuterium bonded to carbon and 25% bonded to silicon. If it resulted from an initial insertion of C_1 into a carbon–hydrogen bond to form II, followed by rearrangement to the double bond, the resulting product should contain 100% of the deuterium bonded into silicon. Infrared and nmr analysis of the resulting dimethylvinylsilane obtained from 99.16% Me_3SiD-d_1 showed that it contained 97.6% Si–D. There was only a small peak at 4.7 μ for the Si–H absorption. Comparison of the relative peak areas of the SiH (4.7 μ) and SiD (6.5 μ) absorptions to a series of known Me_3SiH-Me_3SiD mixtures indicated about 2.4% $Me_2(CH_2{=}CH)SiH$ was present. It was concluded that the product was almost entirely derived from an initial carbon–hydrogen bond insertion.



The formation of dimethylvinylsilane from I in this system is apparently precluded by the activation energy required for a carbene C–H bond insertion at liquid nitrogen temperature. This conclusion is supported by the fact that no products were observed that would require an intermolecular carbon–hydrogen bond insertion by either of the carbenes I or II. The previous observation of the intermediacy of a silacyclopropane was from the generation of I at much higher temperature.

Thus, bis(trimethylsilyl)methane is a product derived from I, and vinyldimethylsilane from II. The origins of the minor products are not clear; ethynyldimethylsilane may result from elimination of H_2 from singlet II in a "hot" reaction; ethyldimethylsilane may result from singlet or triplet (preferred) II by a series of H abstractions.

The C_1 products obtained from thermally vaporized carbon are in accord with what might be expected from reactions of ground-state ^3P carbon atoms. Approximately equivalent amounts of tetramethylsilane and dimethylvinylsilane are essentially the only C_1 products formed. It is felt they are derived from the triplet states of the carbenes I and II, thus reflecting approximately a 9:1 preference for insertion of a carbon atom into the weaker Si–H bond. Abstraction of hydrogen by I and rearrangement to the double bond by II are considered reasonable reaction pathways for the triplet states of these carbenes under conditions of high dilution and low temperature. Thus, it appears that dimethylvinylsilane is a product of both the singlet and triplet states of II.

Using the data in Table I, the per hydrogen ratio of relative reactivities of Si–H to C–H bonds for arc-produced C_1 insertion calculates to be 1.2/1.0. In view of the fact that the bond dissociation (D(Si–H) = 81 $\pm$ 2 kcal mol^{-1})[12] is almost 20 kcal mol^{-1} less than that of carbon–hydrogen bonds in methyl groups, it must be concluded that ^1S and/or ^1D carbon atoms from arc-vaporized C_1 are relatively indiscriminate reagents.

The observation of indiscriminate behavior from arc-produced C_1 and discriminate behavior from thermally produced C_1 is in accord with previous results from this laboratory that ^3P carbon atoms showed a marked preference for attack at the weakest C–H bonds in the formation of nondeoxygenative products from aldehydes and ketones.[13] With carbonyl substrates it was concluded that ^1D and ^1S carbon atoms were all entering into the deoxygenation reaction to produce carbon monoxide.

B. C_2 Products. The products derived from reactions of C_2 are listed in Table II.

Table II. Products Resulting from Reactions of C_2

Product	% yield[a] 16-V arc	Thermal vaporization
$HC{\equiv}CH$	56	10
$H_2C{=}CH_2$	1.5	<0.3
$H_3C{-}CH_3$	<0.1	<0.3
$(CH_3)_3SiC{\equiv}CH$	3.1	0.6
$(CH_3)_3SiCH{=}CH_2$	5.1	<0.3
$(CH_3)_3SiCH_2CH_3$	2.1	<0.3
$(CH_3)_2Si(H)CH{=}C{=}CH_2$	1.3	0.4
$(CH_3)_3SiCH{=}CHSi(CH_3)_3$		
Trans	5.2	0.0
Cis	3.6	0.0

[a] Based on mmoles of C_2 reaching the reaction zone.

The formation of acetylene, ethylene, and ethane by hydrogen abstraction has been observed with many substrates in our laboratories. It has been shown that C_2 is indeed the precursor for these products through the use of ^{14}C-enriched electrodes for generating carbon vapor.[14]

Both singlet and triplet C_2 are involved in the formation of acetylene from acetone and toluene.[15] Thus, the formation of some acetylene from the thermal vaporization reaction would not be unexpected.

The products corresponding to addition of C_2 to one or two molecules of trimethylsilane may all be explained in terms of an initial silicon–hydrogen insertion, with the exception of dimethylsilylallene (eq 1). Singlet

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(10) P. S. Skell and E. J. Goldstein, *J. Amer. Chem. Soc.*, **86**, 1442 (1964).

(11) D. Seyferth, A. W. Dow, H. Menzel, and T. C. Flood, *ibid.*, **90**, 1080 (1968).

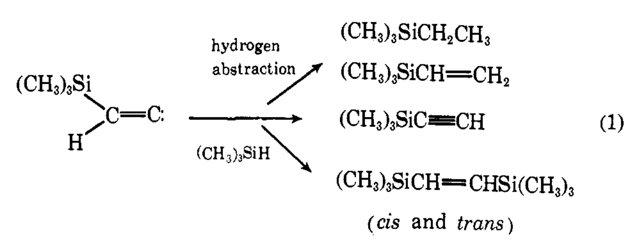
(12) I. M. T. Davidson and I. L. Stephenson, *J. Chem. Soc. A*, 287 (1968).

(13) P. S. Skell, J. H. Plonka, and L. S. Wood, *Chem. Commun.*, 710 (1970).

(14) P. S. Skell and R. F. Harris, *J. Amer. Chem. Soc.*, **88**, 5933 (1966).

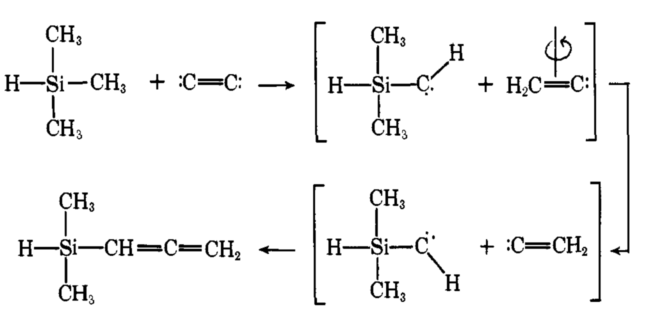
(15) P. S. Skell, J. H. Plonka, and R. F. Harris, *Chem. Commun.*, 689 (1970).

$C_2 + (CH_3)_3Si{-}H \longrightarrow$



(1)

C_2 has been shown to react with alkanes and ethers to produce, among other products, substituted allenes.[16] A mechanism based on the results of deuterium and ^{14}C labeling experiments has been proposed for the formation of these products. It involves abstraction of two hydrogen atoms from a substrate molecule by C_2 to form a carbene–methylenecarbene pair. After suitable rotation of the methylenecarbene, coupling of the two intermediates leads to the substituted allene. It is assumed that dimethylsilylallene is formed by the same process from trimethylsilane.



The *cis-* and *trans*-1,2-bis(trimethylsilyl)ethylenes formed may also have arisen from dimerization of the carbene I. These isomers are obtained from coupling of trimethylsilylcarbene generated by the cuprous chloride catalyzed decomposition of trimethylsilyldiazomethane in benzene.[11] Dimerization of trimethylsilylcarbene (I) is unlikely in this study as it is produced at low concentration in a trimethylsilane matrix (>300-fold weight excess of substrate over carbon vaporized) and remains at 77°K (1–2 hr) before warm-up. Since reaction with a second molecule of trimethylsilane occurs with good efficiency (*vide supra*), survival of the carbene is precluded. Thus, it is considered more likely that these isomers are C_2 products.

The formation of trimethylethynylsilane, trimethylvinylsilane, and trimethylethylsilane is analogous to the formation of methoxyacetylene, methoxyethylene, and methyl ethyl ether reported by Harris[7] from the reaction of C_2 and methanol. The products are rationalized by an initial insertion of singlet and/or triplet C_2 into the Si–H bond followed by rearrangement and/or hydrogen abstraction.

The low yield of C_2 accounted for in the thermal vaporization reaction (12% *vs.* 78% from arc-produced C_2) raises the possibility that ground-state C_2 molecules are relatively unreactive with trimethylsilane.

C. C_3 Products. The products resulting from the reactions of C_3 with trimethylsilane are listed in Table III.

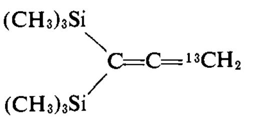
Table III. Products Resulting from Reactions of C_3

	% yield[a]	
Product[b]	16-V arc	Thermal vaporization
$CH_3CH_2CH_3$	1.2	0.1
$CH_3CH{=}CH_2$	1.6	0.1
$(CH_3)_3SiC_3H_7$	4.4	0.0
$(CH_3)_3SiCH{=}C{=}CHSi(CH_3)_3$	21.2	13.0

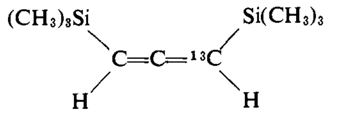
[a] Based on total mmoles of C_3 reaching the reaction zone. [b] Normally allene and propyne are also isolated among the products resulting from C_3. In some arc-produced C_3 reactions with trimethylsilane, small amounts of allene were observed by retention time. A blank experiment showed that propyne could not be recovered from the excess trimethylsilane and allene was recovered in only 3% yield.

No report has been made of the isolation or properties of the major C_3 product, 1,3-bis(trimethylsilyl)allene. It was identified by its mass spectrum (parent peak at *m/e* 184, base peak *m/e* 169), vapor infrared spectrum (3.4 (m), 5.22 (s), 7.1 (w), 7.98 (s), 8.75 (m), 11.8 (vs), 14.3 μ (m)) and nmr spectrum (CCl_4, 100 Mc) which showed two singlets at τ 9.93 and 5.68 of area ratio 8.85:1.00, respectively. Unfortunately it was not possible to tell if the 850-cm^{-1} absorption characteristic of terminal allenes[17] was present in the ir as this region was covered by the trimethylsilyl group absorption.

To distinguish between the 1,1 and 1,3 isomers of this compound, the ^{13}C satellites of the τ 5.68 (=CH–) nmr absorption were examined. One would predict that the ^{13}C–H satellite absorptions in compound III would appear as singlets. In the case of the isomer



III



IV

IV, however, since probability dictates that most of the ^{13}C-containing molecules will contain only one ^{13}C atom, the two hydrogens should no longer be equivalent, and should thus be split into doublets by the long-range coupling of C–H hydrogens across the allene π system.

The 100-Mc nmr spectrum did, in fact, show two doublets [$J(^{13}C\text{–}H)$ = 147 Hz and J(H–H) = 7 Hz] to either side of the τ 5.68 singlet, conclusively identifying the compound as the 1,3 isomer.

The small amounts of C_3 hydrocarbons and olefins formed are also found from carbon vapor reactions with many other substrates. They have been shown to result from hydrogen abstraction by a C_3 precursor through the use of ^{14}C-enriched electrodes.[18] Normally allene and propyne are observed in 1–2% yield as C_3 hydrogen abstraction products. Allene was observed in small quantity in this study. However, the attempted separation of known small amounts of allene and propyne from a large excess of trimethylsilane showed that these materials could not be analyzed; none of the propyne was recovered and only 3% of the allene was found.

The absence of propyltrimethylsilane as a product from the thermal vaporization reaction suggests that it is formed from an excited-state C_3 precursor. The

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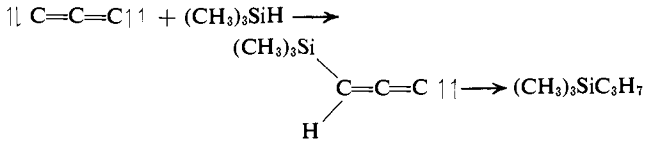
(16) P. S. Skell, F. A. Fagone, and K. J. Klabunde, unpublished results.

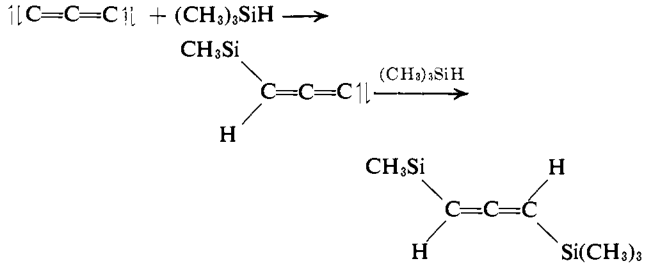
(17) H. Wotiz and D. E. Mancuso, *J. Org. Chem.*, **22**, 207 (1957).

(18) P. S. Skell and R. F. Harris, *J. Amer. Chem. Soc.*, **91**, 699 (1969)

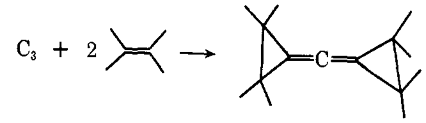
product is most easily rationalized as coming from an initial insertion into the silicon–hydrogen bond followed by abstraction of hydrogens, suggesting the precursor may have been the excited triplet ($^3\Pi_u$) state of C_3.



The isolation of a relatively high yield of 1,3-bis(trimethylsilyl)allene from thermally vaporized carbon suggests that this product is derived from the ground state ($X^1\Sigma_g$) of C_3, a conclusion supported by the fact that its formation is most easily rationalized by two insertions into Si–H bonds.



This conclusion is in agreement with the conclusions of Skell, Wescott, Engel, and Golstein[6] that ground-state (singlet) C_3 adds stereospecifically to double bonds to form bisethanoallenes.



D. Radical Recombination Products. Both $(CH_3)_6Si_2$ (V) and $(CH_3)_3SiCH_2Si(CH_3)_2H$ (VI) were present in low yield in the product mixture from arc-produced carbon vapor and trimethylsilane, formed by coupling of $(CH_3)_3Si\cdot$ and $(CH_3)_2Si(H)CH_2\cdot$ radicals. Presumably $(CH_3)_2Si(H)CH_2CH_2Si(CH_3)_2H$ was also present among some of the higher unidentified products. The mole ratio of VI to V was $\sim$1.7:1.0, indicating a slight excess of $(CH_3)_3Si\cdot$ radicals. The only radical coupling product present in significant quantity from the thermal vaporization reaction was V, indicating an increased preference for abstraction of more weakly bonded Si–H hydrogens by thermally vaporized species.

Experimental Section

Trimethylsilane was obtained from Peninsular ChemResearch and used without further purification.

Reaction of Arc-Produced Carbon Vapor and Trimethylsilane. Over a period of 70 min, carbon (64.0 mg, 5.33 mmol) vaporized from a 16-V carbon arc and trimethylsilane ($\sim$20 g) were continuously codeposited on the liquid nitrogen cooled walls of an evacuated (5×10^{-5} Torr) reaction flask. After completion of the codeposition, the contents of the flask was transferred to a standard vacuum line where bulk separations of products from the excess substrate were achieved by trap-to-trap fractionation and vacuum distillations. Products were isolated by vapor phase chromatography and identified by their infrared spectra, mass spectra, comparison of retention times with those of authentic materials, and, in some cases, nmr spectra.

Reaction of Thermally Vaporized Carbon with Trimethylsilane. Over a period of 120 min, carbon (62.3 mg, 5.19 mmol) vaporized from a resistively heated (200–250 A ac) graphite electrode and trimethylsilane ($\sim$20 g) were simultaneously deposited on the liquid nitrogen cooled walls of an evacuated (3×10^{-5} Torr) reaction flask. The analytical procedures used for this reaction were kept as nearly identical as possible with those used for arc-produced carbon vapor reactions. The results of these reactions are presented in Table IV.

Table IV. Products Obtained from Reactions of Arc-Produced and Thermally Produced Carbon Vapor with Trimethylsilane

Product	16-V arc[a] (mmol)	Thermal vaporization[b] (mmol)
CH_3CH_3	<0.001	<0.001
$CH_2{=}CH_2$	0.011	<0.001
$CH{\equiv}CH$	0.420	0.034
$CH_3CH_2CH_3$	0.003	<0.001
$CH_3CH{=}CH_2$	0.004	<0.001
$(CH_3)_4Si$	0.029	0.021
$(CH_3)_2Si(H)C{\equiv}CH$	0.040	Trace
$(CH_3)_2Si(H)CH{=}CH_2$	0.262	0.022
$(CH_3)_2Si(H)CH_2CH_3$	0.019	0.002
$(CH_3)_3SiC{\equiv}CH$	0.023	0.002
$(CH_3)_3SiCH{=}CH_2$	0.038	0.001
$(CH_3)_3SiCH_2CH_3$	0.016	0.001
$(CH_3)_2Si(H)CH{=}C{=}CH_2$	0.010	0.001
$(CH_3)_3SiC_3H_7$	0.011	0.000
$(CH_3)_3SiCH_2(CH_3)_3$	0.015	0.000
$(CH_3)_3SiCH{=}CHSi(CH_3)_3$		
Trans	0.039	0.000
Cis	0.027	0.000
$(CH_3)_3SiCH{=}C{=}CHSi(CH_3)_3$	0.053	0.126
$(CH_3)_3SiOSi(CH_3)$	0.025	0.000
$(CH_3)_3SiSi(CH_3)_3$	0.006	0.005
$(CH_3)_3SiCH_2Si(CH_3)_2H$	0.010	0.000

[a] Obtained from a total of 64 mg (5.33 mmol) of carbon vapor reaching the reaction zone. [b] Obtained from a total of 62.3 mg (5.19 mmol) of carbon vapor reaching the reaction zone.

Most of the products obtained were identified by comparison of their spectra and retention time with those of authentic materials. The spectral data used for the identification of products for which authentic materials were not available are summarized below. The identification of 1,3-bis(trimethylsilyl)allene is presented in the Results and Discussion section.

Dimethylsilylallene was identified by its vapor infrared spectrum [strong Si–H stretch (4.69 μ) and allene absorptions (5.17 and 11.88 μ)] and mass spectrum (parent peak, *m/e* 98; base peak, *m/e* 59 (Me_2SiH^+).

Dimethylethynylsilane was identified from its vapor infrared spectrum [acetylenic hydrogen at 3.02 μ, SiH stretch (4.67 μ) and monosubstituted triple bond stretch (4.90 μ)] and mass spectrum (70 eV: parent peak, *m/e* 84; base peak, *m/e* 69; other large peaks at *m/e* 83 and 58).

Trimethylethynylsilane was identified from its vapor infrared spectrum (acetylenic absorptions at 3.01 and 4.89 μ, no Si–H absorption) and mass spectrum (parent peak, *m/e* 98; base peak, *m/e* 83).

Trimethylpropylsilane was identified from its vapor infrared spectrum (no SiH or olefinic hydrogen stretch absorptions) and mass spectrum (parent peak, *m/e* 116; base peak, *m/e* 73).

cis-1,2-Bis(trimethylsilyl)ethylene was identified by comparison of its infrared spectrum, mass spectrum (parent peak, *m/e* 172; base peak, *m/e* 73), and 100-Mc nmr spectrum (CH_3 protons at τ 9.89, olefinic $=$CH at τ 3.32; lit. CH_3 protons at τ 9.86, olefinic $=$CH at τ 3.32) with those in the literature.[20]

trans-1,2-Bis(trimethylsilyl)ethylene was identified by comparison of its infrared spectrum, mass spectrum (parent *m/e* 172; base, *m/e* 73), and 100-Mc nmr spectrum (CH_3 protons at τ 9.94, olefinic $=$CH at τ 3.49; lit. CH_3 protons at τ 9.94, olefinic $=$CH at τ 3.45) with those in the literature.[19]

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(19) J. Cudlin, J. Schraml, and V. Chvalosky, *Collect. Czech. Chem. Commun.*, **29**, 1476 (1964).

Synthesis of $(CH_3)_3SiD$. Diglyme was dried by distillation from lithium aluminum hydride. Over a period of 60 min, trimethylchlorosilane (83.4 g, 0.77 mol) in 100 ml of dry diglyme was added dropwise, under nitrogen, to a stirred solution of lithium aluminum deuteride (0.096 mol) in 200 ml of dry diglyme. The resulting solution was then refluxed under nitrogen for 30 min (cold water condensor) and the volatile product swept into a −78° trap by a slow purge of dry nitrogen. Distillation of the −78° trap material yielded 16.8 g (0.227 mol, 59%) of $(CH_3)_3SiD$. Mass spectral analysis indicated the product was >99.1% d_1. The infrared showed an Si–H absorption whose area was 0.69% of the Si–D absorption area.

Recovery Efficiencies of Allene, Propyne, and Tetramethylsilane from Trimethylsilane. Allene (0.167 mmol), propyne (0.137 mmol), and tetramethylsilane (0.138 mmol) were combined with trimethylsilane (~20 g, ~230 mmol or >1000-fold excess). The mixture was subjected to the normal work-up procedure for carbon vapor reactions with trimethylsilane. Vpc analysis of the appropriate fractions indicated tetramethylsilane was recovered in 88% yield and allene in 3% yield. No propyne was recovered.

Acknowledgment. We gratefully acknowledge the financial support of the Air Force Office of Scientific Research (Grant No. 4057).

Fluorine-19 Substituent Chemical Shifts of Fluorophenylsilanes. Substituent Effects on Silicon

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Abstract: The ^{19}F substituent chemical shift (SCS) of a series of fluorophenylsilanes, FC_6H_4SiXYZ, have afforded a measure of the inductive and π components in the interaction of the silicon atom with the ring and with the substituents X, Y, and Z. Correlations of high precision have been obtained from (1) para *vs.* meta SCS ($SCS_p = \rho_1 SCS_m + \rho_2$) and (2) from para and meta SCS *vs.* the sum of inductive substituent constants, $\Sigma\sigma_I$, on silicon ($SCS = \rho_1\Sigma\sigma_I + \rho_2$). Substitution of first row donors on silicon, especially trisubstitution, leads to considerable deviations from relations 1 and 2. In the case of substitution with non-first-row donors, the extent of mesomeric interaction of silicon with para fluorine is linearly related to the electron density on silicon resulting from the inductive effects of the substituents X, Y, and Z. Use of a π substituent constant in linear combination with an inductive constant for substituents on silicon affords correlations of high precision for the full range of substituents, including first row donors. Higher precision is obtained using a π *donor* substituent content (eq 9) rather than a general resonance constant (eq 8). The *donor* substituent constant ($\sigma_p^+ - \sigma_p$) appears to be a better measure of donor ability to silicon than does $\sigma_R°$ for first-row donors. A large variation in the inductive (or polar) effect of the tris(3,3,3-trifluoropropyl)silyl substituent with solvent has been observed. The SCS of *p*-fluorophenyl(2,2′-2′′-nitrilotriethoxy)silane, in which the electron density on silicon is increased by pentacoordination, is 5.1 ppm more shielded than is *p*-fluorophenyltriethoxysilane.

There has been much recent interest in correlating chemical and physical properties of organosilicon compounds with substituent constants of groups on the silicon atom.[1–6] The Taft σ^* parameter[7] has been most widely used in these correlations, which include infrared stretching frequencies[2a–c] and infrared intensities[2d] of silyl hydrides, rates of halogenation[3] and solvolysis[4] of silyl hydrides, ^{1}H nmr chemical shifts of silanols[5a] and silyl hydrides,[5b] ^{19}F nmr chemical shifts of fluorosilanes,[5c] and ^{35}Cl nqr frequencies of chlorosilanes.[6] These linear correlations do not necessarily hold for first-row substituents (O, N, F) capable of (p–d)π interactions with silicon.[2a,2c,8] Some correlations are further complicated by anisotropy effects[5a,b] or steric effects[4] of uncertain magnitude. The kinetic methods[3,4] utilized for substituent effect studies are hampered by undesirable side reactions of those first-row substituents which would be expected to exhibit unique properties on silicon.

In view of the need for a sensitive and synthetically accessible probe for the study of substituent effects on silicon, the ^{19}F substituent chemical shift (SCS) of a series of fluorophenylsilanes, FC_6H_4SiXYZ, has been utilized. The SCS has been shown[9,10] to be a sensitive

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