

104. *The Preparation and Properties of Silylacetylene, and the Structures of Silyl Cyanides.*

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Silylacetylene has been prepared and characterised, and its ultraviolet and nuclear magnetic resonance spectra have been recorded, with those of trimethylsilylacetylene and triethoxysilylacetylene. The nuclear magnetic resonance spectra of silyl cyanide and the methyl-silyl cyanides indicate that these compounds have the "normal" cyanide structures, though the possibility of the presence of small amounts of isocyanides cannot be excluded.

WE have prepared silylacetylene, $\text{SiH}_3\cdot\text{C}\equiv\text{CH}$, by reaction between silyl iodide and ethynylmagnesium bromide in tetrahydrofuran in ~15% yield. Attempts to improve the yield proved unsuccessful. Earlier attempts to prepare the compound by reducing triethoxysilylacetylene with lithium aluminium hydride under a variety of conditions produced silylacetylene in yields of $\gt 2\%$, the main product of the reduction being monosilane.

Silylacetylene is a colourless gas, stable at room temperature; its Trouton constant gives no indication of association in the liquid phase. The contours of the vapour-phase

infrared bands are typical of those expected of a symmetric top molecule with a small moment of inertia about the top axis, and the perpendicular bands show "strong, weak, weak, strong" rotational detail with sub-branch separation of about 5 cm.⁻¹; the high-resolution infrared spectrum will be described elsewhere. A detailed examination of the microwave spectrum is also in progress. The series of sharp maxima in the ultraviolet spectrum between 2285 and 2040 Å have a roughly constant separation of about 750 cm.⁻¹, consistent with the excitation of the (CH) bending mode in the transition; three other maxima were distinguished between 2040 Å and the high-frequency limit of the instrument. No maxima were observed in the spectrum of methylacetylene in the same region.

Silylacetylene reacts quantitatively with 40% aqueous potassium hydroxide at room temperature, giving hydrogen (from the Si-H groups) and acetylene. No exchange between the acetylenic-hydrogen atom and heavy water was observed in 60 hr. at room temperature; under these conditions silylacetylene decomposes slowly.

The expected AX₃ peaks were observed in the nuclear magnetic resonance spectrum, with the directly bound ¹³CH and ²⁹SiH satellites. The ¹³CH coupling of 240.9 c./sec. is 6.7 c./sec. less than in methylacetylene,¹ while the acetylenic CH couplings in the related molecules trimethylsilylacetylene and triethoxysilylacetylene are less than 240 c./sec. (see Table 1). This indicates that the presence of silicon bound to the acetylene group may reduce the s-character of the remote CH bonding orbital.² In silylacetylene the CH resonance is 0.4 p.p.m. to low field of the acetylenic CH resonance of methylacetylene; part of the shift can be accounted for if the magnetic anisotropy ($\Delta\chi = \chi_{||} - \chi_{\perp}$) of the SiC bond is greater than that of the C:C bond, though a difference of 12×10^{-30} cm.² per bond would be needed to account for all of it. A small reduction in the magnitude of the (C:C) bond anisotropy (which is negative), caused by the presence of the silicon atom, would also cause a shift in the required direction. The (C)H-(Si)H coupling is less in silylacetylene than in methylacetylene;¹ the CH dilution shift is in the same direction and is of the same order as the analogous dilution shifts in alkylacetylenes,³ and the ²⁹SiH

TABLE I.
Acetylenic chemical shifts and ¹³CH coupling constants in some monosubstituted acetylenes.

Compound	τ (¹³ CH) (p.p.m.)	J (¹³ CH) (c./sec.)	Compound	τ (¹³ CH) (p.p.m.)	J (¹³ CH) (c./sec.)
HC≡CH *	8.20	249.0	SiH ₃ -C≡CH §¶	7.81	240.9
Me-C≡CH †	8.21	247.6	Me ₃ Si-C≡CH §	7.89	236.6
PhC≡CH ‡	7.26	251	(EtO) ₃ Si-C≡CH §	7.96	239.5
Me ₃ C-C≡CH §	8.21	247.0			

* Lynden-Bell and Sheppard, personal communication. † Shoolery, Johnson, and Anderson, *J. Mol. Spectroscopy*, 1960, **5**, 110 [J (HH') in Me-C≡CH = 2.93 c./sec.]. ‡ Hatton and Richards, *Trans. Faraday Soc.*, 1961, **57**, 28; Muller and Pritchard, *J. Chem. Phys.*, 1959, **31**, 768. § This work. ¶ J (HH') = 1.47 c./sec.

coupling constant is 24 c./sec. greater in silylacetylene than in methylsilane,⁴ a change in the same direction as the change in ¹³CH coupling from ethane to methylacetylene.^{1,2} Most of the differences between the spectra of methylacetylene and silylacetylene could be explained if an ethylenic state makes a larger contribution to the ground state of the silyl compound.

The proton chemical shift for a compound SiH₃X, where X is an atom or group, is sensitive to changes in the atom bound to silicon, but is relatively insensitive to changes in the rest of the molecule.^{4,5}

¹ Shoolery, Johnson, and Anderson, *J. Mol. Spectroscopy*, 1960, **5**, 110.

² Muller and Pritchard, *J. Chem. Phys.*, 1959, **31**, 768 and 1471.

³ Hatton and Richards, *Trans. Faraday Soc.*, 1961, **57**, 28.

⁴ Ebsworth and Frankiss, unpublished observations.

⁵ Ebsworth and Turner, unpublished observations.

Thus a comparison of the proton chemical shifts for silyl cyanide, silylacetylene, and $\text{SiH}_3\cdot\text{N}$ compounds such as silyl isocyanate, silyl isothiocyanate, and disilylcarbodi-imide might be expected to provide additional evidence whether the silicon atom in silyl cyanide in solution in cyclohexane is bound to nitrogen or to carbon. The possibility of distinguishing between the two structures in this way is reinforced by the observation that the proton resonance in methyl cyanide⁶ is close to the CH_3 -proton resonance in methylacetylene,¹ but more than 1 p.p.m. to high field of the proton resonances in methyl isocyanide, methyl isocyanate, and methyl isothiocyanate. The SiH -proton resonance in silylacetylene is only 0.02 p.p.m. to high field of that of silyl cyanide, but over 0.7 p.p.m. to high field of the resonances in $\text{Si}\cdot\text{N}$ compounds⁵ (see Table 2), affording strong evidence for the $\text{SiH}_3\cdot\text{C}$ structure that has been established by microwave spectroscopy for the vapour of the compound.⁷ Moreover, spin coupling has been observed between the ^{14}N atom and the α - and β -alkyl protons⁸ in the spectra of all alkyl isocyanides so far studied;

TABLE 2.

MH_3^- chemical shifts in $\text{MH}_3\cdot\text{C}\equiv$ and $\text{MH}_3\cdot\text{N}=\text{}$ compounds.

Compound	τ (CH_3) (p.p.m.)	Compound	τ (SiH_3) (p.p.m.)
$\text{CH}_3\cdot\text{C}\equiv\text{CH}$ *	8.238	$\text{SiH}_3\cdot\text{C}\equiv\text{CH}$ ‡	6.20
$\text{CH}_3\cdot\text{CN}$ †	8.34	$\text{SiH}_3\cdot\text{CN}$ ‡	6.18
$\text{CH}_3\cdot\text{NC}$ ‡	6.99		
$\text{CH}_3\cdot\text{NCO}$ ‡	7.125	$\text{SiH}_3\cdot\text{NCO}$ §	5.58
$\text{CH}_3\cdot\text{NCS}$ ‡	6.89	$\text{SiH}_3\cdot\text{NCS}$ ¶	5.54
		$\text{SiH}_3\cdot\text{N}\cdot\text{C}\equiv\text{N}\cdot\text{SiH}_3$ ¶	5.55

* Hatton and Richards, *Trans. Faraday Soc.*, 1961, **59**, 28. † Spiesecke and Schneider, *J. Chem. Phys.*, 1961, **35**, 722. ‡ This work. § Ebsworth and Mays, unpublished work. ¶ Ebsworth and Mays, *J.*, 1961, 4484.

we were unable to detect any such coupling in the spectra of any of the compounds $\text{H}_x\text{SiMe}_{3-x}\cdot\text{CN}$ (where x is 0—3), under experimental conditions that should have resolved splittings of less than 0.1 c./sec. In the methyl-silyl cyanides the proton chemical shifts and coupling constants vary in the same way with increasing methyl substitution as in the series $\text{H}_x\text{SiMe}_{3-x}\cdot\text{Y}$ (where Y is I, Cl, or CH_3);^{4,9} in all the series studied the ^{13}C coupling constant decreases by 1—2 c./sec. with each successive methyl group, while the few measurements that have been made of analogous carbon compounds $\text{H}_x\text{C}(\text{CH}_3)_{3-x}\cdot\text{Y}$ show rather smaller changes in the same direction.^{2,10,11} The ^{29}SiH coupling constants of many silyl compounds decrease by about 8—10 c./sec. with each additional methyl group.⁴ As the ^{13}CH coupling constants in methyl cyanide² and methyl isocyanide differ by 9 c./sec., the regular decrease in ^{29}SiH coupling constant with increasing methyl substitution in the Si -methyl-silyl cyanides indicates that in all these compounds the same atom is bound to silicon. While it is impossible to preclude the possibility that small amounts of isocyanide are present in all of these compounds in labile equilibrium with the "normal" cyanides at room temperature, no signs of exchange (such as line broadening or abnormal dilution shifts) were observed; the small dilution shifts that were observed for the silyl cyanides imply that the intermolecular forces are not strong for these compounds in the liquid phase, even though the SiH resonance is not very sensitive to dilution.^{4,5,12}

The $\text{C}\equiv\text{C}$ and $\text{C}\equiv\text{N}$ bonds are likely to have similar magnetic anisotropies. Using the dipolar approximation, we have estimated that this anisotropy contributes about +0.59 p.p.m. to the shielding of the SiH protons in silylacetylene and silyl cyanide, giving "corrected" chemical shifts for the two compounds of 5.61 and 5.59 p.p.m., respectively,

⁶ Spiesecke and Schneider, *J. Chem. Phys.*, 1961, **35**, 722.

⁷ Sheridan and Turner, *Proc. Chem. Soc.*, 1960, 21.

⁸ Kuntz, von Schleyer, and Allerhand, *J. Chem. Phys.*, 1961, **35**, 1533.

⁹ Webster, *J.*, 1960, 5132.

¹⁰ Malinowski, *J. Amer. Chem. Soc.*, 1961, **83**, 4479.

¹¹ Sheppard and Turner, *Proc. Roy. Soc.*, 1959, *A*, **252**, 506.

¹² Huggins and Carpenter, *J. Phys. Chem.*, 1959, **63**, 238.

both some 0.9 p.p.m. less than for the silyl protons of methylsilane. This in turn indicates that $\tau(\text{SiH})$ in Si-C compounds is more sensitive to changes in hybridisation at the carbon atom than it is to changes in *N*-hybridisation in analogous $\text{SiH}_3\cdot\text{N}$ compounds.

EXPERIMENTAL

Silylacetylene.—Iodosilane (6.2 g.) in dry, degassed tetrahydrofuran (~10 ml.) was added during 2 hr. to a stirred solution of ethynylmagnesium bromide (from 2.5 g. of magnesium) in tetrahydrofuran (110 ml.) at room temperature under dry nitrogen at 30 cm. pressure. After $\frac{1}{2}$ hour's stirring, the pressure was reduced until the solution boiled; volatile products were collected in five traps at -196° . Dry nitrogen was reintroduced to 30 cm. pressure and after a further 12 hours' stirring, volatile products were collected as before. From the combined volatile products *silylacetylene* was isolated by fractional distillation at low temperatures (Found: Si-H, 5.4%; *M*, 56. $\text{C}_2\text{H}_4\text{Si}$ requires Si-H, 5.4%; *M*, 56); 0.034 g. of this compound, when shaken with concentrated aqueous sodium hydroxide, gave 0.0156 g. of acetylene (theor., 0.0158 g.) (Found: *M*, 26.7; v. p. at -116.7° , 40.3 mm. Calc. for C_2H_2 : *M*, 26.0; v. p. at -116.3° , 40.0 mm.¹³).

Silylacetylene was obtained in 1–2% yield by reducing triethoxyethynylsilane with lithium aluminium hydride in dibutyl ether, the main product being monosilane. No reduction was observed with sodium borohydride, lithium borohydride or lithium tri-*t*-butoxyaluminium hydride in dibutyl ether or diethylene glycol dimethyl ether.

Physical properties of silylacetylene were determined for samples that had been repeatedly distilled at -112° and condensed at -132° . The m. p. is $-90.7^\circ \pm 0.5^\circ$; the b. p. (extrapolated over 0.3°) is $-22.4^\circ \pm 0.5^\circ$; v. p.s between -58° and the b. p. are given by: $\log_{10} p$ (mm.) = $7.465 - 1150/T$; the v. p. at -63.5° is 80.3 mm.; the latent heat between -50° and the b. p. is 5240 ± 50 cal./mole, and Trouton's constant is 20.9.

The compound was recovered unchanged after 3 months' storage in a sealed tube in the vapour phase at room temperature and after 3 hours' heating at 45° .

Preparation of Other Compounds.—Trimethylsilylacetylene,¹⁴ triethoxysilylacetylene,¹⁵ 3,3-dimethylbut-1-yne,¹⁶ 3,3-dimethylbutyl cyanide,¹⁷ trimethylsilyl cyanide,¹⁸ methyl isocyanate,¹⁹ methyl isothiocyanate,²⁰ and ethyl²¹ and methyl²¹ isocyanide were prepared by standard methods and purified by fractional distillation. Silyl,²² methylsilyl,²³ and dimethylsilyl²⁴ cyanide were prepared in a high-vacuum apparatus and purified by low-temperature fractional distillation, purity being checked by measurements of vapour pressure and molecular weight.

Ultraviolet Spectra.—The ultraviolet spectra of vapours were recorded with a Cary model 14M50 recording spectrophotometer, slit width 0.72 mm. at 2000 Å, flooded with dry nitrogen. Silylacetylene showed a series of well-defined maxima between 2285 and 2040 Å, with mean separation of 35 Å (~750 cm^{-1}), ϵ rising from 0.2 at 2285 to 35 at 2040 Å. Maxima were also observed at 1985 (ϵ 390), 1954 (ϵ 350), and 1896 Å (ϵ 670). Trimethylsilylacetylene gave absorption between 2300 Å and the low-frequency limit of the instrument, with maxima at 1962 (ϵ 260) and 1904 Å (ϵ 420); triethoxysilylacetylene gave a very weak maximum at 2620 Å ($\epsilon \sim 1$). No maxima were observed at wavelengths higher than 1850 Å for methylacetylene; absorption at 2200 Å corresponded to ϵ 1.3, and at 2050 Å to ϵ 18. Maxima were observed for 3,3-dimethylbut-1-yne at 2202 (ϵ 198), 2142 (ϵ 184), and 1900 Å (ϵ 330).

Nuclear Magnetic Resonance Spectra.—These were recorded on a Varian Associates V4300B

¹³ Burrell and Robertson, *U.S. Bur. Min.*, 1916, Bull. 142.

¹⁴ Minh, Billote, and Cadiot, *Compt. rend.*, 1960, **251**, 730.

¹⁵ Boldebuck, U.S. Patent 2,551,924 (1951); *Chem. Abs.*, 1952, **46**, 130e.

¹⁶ Bartlett and Rosen, *J. Amer. Chem. Soc.*, 1942, **64**, 543.

¹⁷ Mann and Saunders, "Practical Organic Chemistry," Longmans, Green and Co., London, 1960, p. 120.

¹⁸ Evers, Freitag, Keith, Kriner, MacDiarmid, and Sujishi, *J. Amer. Chem. Soc.*, 1959, **81**, 4493.

¹⁹ Slotta and Lorenz, *Ber.*, 1925, **58**, 1320.

²⁰ Moore and Crossley, *Org. Synth.*, 1941, **21**, 81.

²¹ Gautier, *Ann. Chim. Phys.*, 1869, **17**, 203.

²² MacDiarmid, *J. Inorg. Nuclear Chem.*, 1956, **2**, 88.

²³ Emel us, Onyszchuck, and Kuchen, *Z. anorg. Chem.*, 1956, **283**, 74.

²⁴ Kuchen, *Z. anorg. Chem.*, 1956, **288**, 101.

spectrometer operating at 40 Mc./sec. with flux stabilisation and sample spinning; measurements were made by sidebands generated with a Muirhead-Wigan D695A decade oscillator. Samples were held in Pyrex tubing of 5 mm. outside diameter; cyclohexane or tetramethylsilane was used as solvent and internal standard. The results are summarised in Table 3; each measurement is the mean of at least eight readings, and errors quoted are mean errors. At least two solutions of known concentration ($\sim 95\%$ and $\sim 5\%$ by volume) were studied, and chemical shifts quoted are obtained by extrapolation to infinite dilution.

TABLE 3.

Nuclear magnetic resonance parameters in cyanides, acetylenes, and related compounds.

Compound	$\tau^\circ(\text{SiH})$ ± 0.01	$\tau^\circ(\text{CH}_3)$ ± 0.01	$J(\text{HH}')$ (c./sec.)	$J(^{29}\text{SiH})$ (c./sec.)	$J(^{13}\text{CH}_3)$ (c./sec.)	Dilution shift SiH (c./sec.)	Dilution shift CH_3 (c./sec.)
$\text{SiH}_3\cdot\text{CN}$	6.18	—	—	240.2 ± 0.4	—	$+0.2 \pm 0.1$	—
$\text{CH}_3\cdot\text{SiH}_2\cdot\text{CN}$	6.01	9.60	4.27 ± 0.06	228.5 ± 0.3	125.0 ± 0.3	$+0.7 \pm 0.2$	-2.0 ± 0.3
$(\text{CH}_3)_2\text{SiH}\cdot\text{CN}$...	5.83	9.67	3.88 ± 0.05	218.0 ± 0.5	124.1 ± 0.3	$+2.0 \pm 0.4$	-2.8 ± 0.2
$(\text{CH}_3)_3\text{Si}\cdot\text{CN}$	—	9.73	—	—	121.8 ± 0.2	—	-0.9 ± 0.3
$\text{SiH}_3\text{C}\equiv\text{CH}$	6.20	—	1.47 ± 0.04	218.6 ± 0.2	—	-0.1 ± 0.2	—

Compound	$\tau^\circ(\ddot{\text{C}}\text{H})$ (± 0.01)	$\tau^\circ(\text{CH}_3)$ (± 0.01)	$J(\ddot{\text{C}}^{\text{13}}\text{CH})$ (± 0.4 c./sec.)	$J(^{13}\text{CH}_3)$	Dilution shift $\ddot{\text{C}}\text{H}$ (c./sec.)	Dilution shift CH_3 (c./sec.)
$\text{SiH}_2\text{C}\equiv\text{CH}$	7.81	—	240.9	—	-6.8 ± 1	—
$\text{Me}_3\text{SiC}\equiv\text{CH}$	7.89	9.86	236.6	120.1 ± 0.2	-8.5 ± 1	-0.7 ± 0.4
$(\text{EO})_3\text{SiC}\equiv\text{CH}^*$...	7.96	8.86	239.5	126.0 ± 0.4	-21 ± 3	-1.8 ± 0.5
$\text{Me}_3\text{C}\equiv\text{CH}$	8.21	8.80	247.0	127.2 ± 0.2	-8.5 ± 1	-0.4 ± 0.1

Compound	$\tau^\circ(\text{CH}_3)$	$J(^{13}\text{CH}_3)$	Dilution shift CH_3 (c./sec.)	$^{13}\text{CH}_3$ isotope shift (c./sec.)
$\text{CH}_3\cdot\text{NC}^\dagger$	6.99 ± 0.01	144.8 ± 0.2	-1.9 ± 0.4	0.01 ± 0.13
$\text{C}_2\text{H}_5\cdot\text{NC}^\ddagger$	8.74 ± 0.01	129.4 ± 0.2	-0.5 ± 0.2	—
$\text{CH}_3\cdot\text{NCS}$	6.89 ± 0.01	144.5 ± 0.4	$(-7.6 \pm 1)^\S$	—
$\text{CH}_3\cdot\text{NCO}$	7.125 ± 0.005	143.3 ± 0.2	-3.1 ± 0.4	0.14 ± 0.11
$(\text{CH}_3)_3\text{C}\cdot\text{CN}$	8.740 ± 0.003	129.0 ± 0.2	-2.1 ± 0.2	0.19 ± 0.12
$(\text{CH}_3)_3\text{CCl}$	8.447 ± 0.003	127.4 ± 0.2	-1.1 ± 0.4	0.19 ± 0.19

τ° are τ values extrapolated to infinite dilution in cyclohexane or tetramethylsilane; errors are estimated for the extrapolated values. τ° for cyclohexane = 8.56.

Error quoted is the mean error of at least eight measurements. Dilution shift is $\Delta\nu$ (pure compound — infinitely dilute compound) (c./sec.). $^{13}\text{CH}_3$ isotope shift = $\Delta\nu(^{13}\text{CH}_3\text{X} - ^{12}\text{CH}_3\text{X})$ (c./sec.).

* $J(^{13}\text{CH}_2)$ 141 ± 1 c./sec. $\dagger J(^{14}\text{NH})$ 2.26 ± 0.02 c./sec. $\ddagger J(\text{HH}')$ 7.28 ± 0.06 c./sec.; $J(^{13}\text{CH}_2)$ 143.6 ± 0.6 c./sec.; $\tau^\circ(\text{CH}_2)$ 6.72 ± 0.01 ; dilution shift CH_2 , -5.7 ± 0.6 c./sec.; $J(^{14}\text{N}\cdot\text{CH}_3)$ 2.40 ± 0.05 c./sec.; $J(^{14}\text{N}\cdot\text{CH}_2)$ 1.91 ± 0.06 c./sec. \S Dilution shift (50—0%).

Starting Materials.—Iodosilane was prepared from monosilane and hydrogen iodide.¹⁶ Tetrahydrofuran was refluxed over sodium wire for 8 hr. and fractionally distilled. To prepare ethylmagnesium bromide, a solution of ethylmagnesium bromide was prepared under dry nitrogen, filtered, and added slowly to tetrahydrofuran that was continuously saturated with acetylene;¹⁷ the solution was then cooled to 0°, the brown supernatant liquid was decanted, and fresh tetrahydrofuran added. Acetylene was purified by passing it through concentrated aqueous sodium hydrogen sulphite, over sodium hydroxide, through concentrated aqueous potassium permanganate, through a trap at -80° , and over calcium chloride, active charcoal, and phosphoric oxide. Nitrogen was dried by passage through concentrated sulphuric acid and over a molecular sieve.

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