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The Bromination of Silanes and Germane

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Recently, Feher and coworkers[3] described large-scale halogenations of silanes (Si_2H_6, Si_3H_8, and n-Si_4H_{10}) using molecular chlorine or bromine in Freon solvents. For the preparation of relatively small quantities of monobromo derivatives we have found that direct bromination reactions at low temperature in the absence of a solvent are more convenient. By working with molar deficiencies of Br_2 at low temperatures, the reaction is moderated sufficiently to allow formation of monobromo derivatives principally and to minimize its reportedly violent nature.[4,5] In the studies described below, reactions of Br_2 with Si_2H_6, Si_3H_8, $CH_3Si_2H_5$, and GeH_4 to yield the monobromo derivatives are described. In addition we present complete characterization data for 1- and 2-$BrSi_3H_7$, which have not been reported previously.[3,6]

Experimental Section

Apparatus and Techniques.—All work was performed in standard vacuum line apparatus.[7,8] High-vacuum fractional distillations were effected using a column similar to ones described previously.[9,10] Infrared spectra were obtained on Perkin-Elmer 337 and Beckman IR-12 spectrometers on gaseous samples in 10-cm cells fitted with KBr windows. Proton nmr spectra were recorded at 60 and 100 MHz on Varian A-60A and HA-100 spectrometers, respectively. Samples were diluted to 20–50% with carbon disulfide, tetramethylsilane, or cyclohexane. Chemical shifts were measured relative to internal tetramethylsilane or cyclohexane and are reported relative to tetramethylsilane ($\delta_{C_6H_{12}}$ −1.49 ppm relative to $(CH_3)_4Si$). A computer of average transients (CAT) was used to obtain the ^{29}Si satellite spectrum of 1-$BrSi_3H_7$. Mass spectra were obtained at 70 eV on a Varian MAT CH-5 spectrometer. Melting points were determined by the Stock method.

Materials.—Di- and trisilanes were prepared by the $LiAlH_4$ reduction of Si_2Cl_6[11] and Si_3Cl_8[12] (Alfa Inorganics), respectively. Methyldisilane was prepared by the low-temperature reaction between CH_3Li (Foote Mineral Co.) and $BrSi_2H_5$, described below. Germane[13] was prepared using standard procedures. Bromine (reagent grade, Matheson Coleman and Bell) was used as obtained.

Synthesis of $CH_3Si_2H_5$.—In a typical preparation, CH_3Li (10 mmol) in diethyl ether was syringed into a 100-ml flask fitted with a stopcock adapter. The flask was cooled and evacuated, and $BrSi_2H_5$ (10.8 mmol) was condensed in at −196°. The mixture was allowed to react at −63° for 10 min. The volatile reaction materials were then condensed into the vacuum line leaving a white solid (presumed to be mainly LiBr) in the reaction flask. High-vacuum column distillation of the volatile products yielded Si_2H_6[14] (0.52 mmol) which from the ir spectrum was seen to contain traces of SiH_4[15] and $CH_3Si_2H_5$[16] and $CH_3Si_2H_5$ (6.13 mmol, 61% yield based on CH_3Li; confirmed by ir spectrum and 0° vapor tension). Lower volatility material, including the solvent-containing fraction, was not examined further.

Bromination Reactions.—Typical bromination reaction conditions are shown in Table I. In each case the bromine was syringed into a 100-ml Pyrex reaction tube fitted with a ground joint and stopcock. Due to the inaccuracies associated with measuring bromine using the syringe technique, the quantities of bromine reported in Table I are given to *ca.* ±0.2 mmol. The tube was cooled to −196° and evacuated. The appropriate hydride was condensed into the tube and the contents was allowed to warm to the indicated reaction temperature. Reaction was allowed to proceed, with occasional shaking of the tube, to completion as evidenced by the disappearance of the brown bromine color. *Caution! During several attempted large-scale brominations of disilane and germane (>25 mmol of Si_2H_6 or >15 mmol of GeH_4), the reaction spontaneously inflamed. This was caused by inadequate cooling of the mixture as the reactions are very exothermic. These reactions should be performed with adequate mixing in a fume hood behind a safety shield.* Reaction materials were removed to the vacuum line, separated, and characterized as outlined below. The following known reaction products were characterized by comparison of their physical and spectral properties with literature values (confirmation methods in parentheses): HBr (ir spectrum[17]), SiH_4 (ir spectrum[15]), Si_2H_6 (ir spectrum[14]), $BrSi_2H_5$ (ir[18] and nmr[19] spectra and 0° vapor

Table I

Typical Bromination Reactions

Reactants (mmol)	Time, min (temp, °C)	Products (mmol)
Si_2H_6 (19.7) Br_2 (10)	30 (−95)	HBr (11.5)[a] Si_2H_6 (10.1)[b] Si_2H_5Br (7.8; 82% yield[c]) $Si_2H_4Br_2$[d] (~1.8)
Si_3H_8 (3.54) Br_2 (1.8)	45 (−112)	HBr (1.87)[e] Si_3H_8 (1.94)[b] 1-$BrSi_3H_7$ (0.20; 12% yield[c]) 2-$BrSi_3H_7$ (1.20; 75% yield[c]) $Si_3H_{8-x}Br_x$[f]
$CH_3Si_2H_5$ (7.11) Br_2 (3.6)	20 (−130)	HBr (4.17) $CH_3Si_2H_5$ (3.08)[b] 1-Br-1-$CH_3Si_2H_4$ (3.52; 87% yield[c]) 2-Br-1-$CH_3Si_2H_4$ (0.39; 10% yield[c]) $CH_3Si_2H_{5-x}Br_x$[f]
GeH_4 (11.7) Br_2 (3.4)	30 (−112) and 30 (−95)	HBr (3.56) GeH_4 (8.15)[b] GeH_3Br (3.42; 96% yield[c]) GeH_2Br_2 (0.02)

[a] Contained traces of SiH_4 and Si_2H_6. [b] Recovered starting material. [c] Yield based on amount of reacted hydride. [d] Contained 85% 1,2-$Br_2Si_2H_4$ as shown by the ^{1}H nmr spectrum. [e] Contained traces of SiH_4. [f] Yield and composition not determined.

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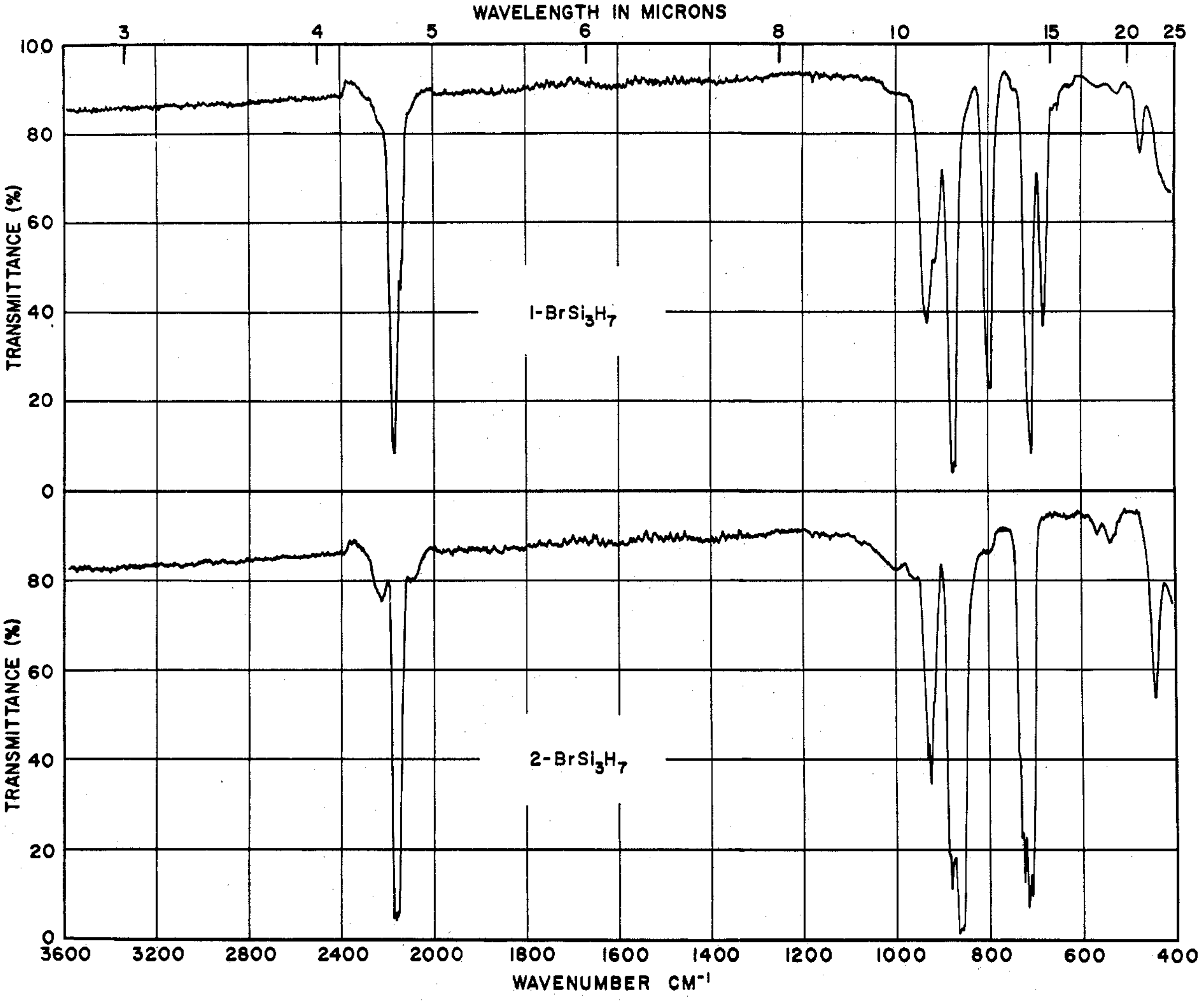

Figure 1.—Infrared spectra of 1-BrSi$_3$H$_7$ and 2-BrSi$_3$H$_7$.

tension[18]), 1,1-Br$_2$Si$_2$H$_4$ and 1,2-Br$_2$Si$_2$H$_4$ (nmr spectra[20]), Si$_3$H$_8$ (ir spectrum[21] and 0° vapor tension), CH$_3$Si$_2$H$_5$ (ir spectrum[16]), GeH$_4$ (ir spectrum[22]), GeH$_3$Br (ir spectrum[23] and 0° vapor tension[24]), and GeH$_2$Br$_2$ (ir spectrum[23]). No hydrogen was formed in any of the reactions.

(A) Si$_2$H$_6$–Br$_2$.—Separation was achieved by fractional condensation of reaction materials through a series of traps at -63, -112, -130, and $-196°$. The contents of the traps were as follows: $-196°$, HBr along with traces of SiH$_4$ and Si$_2$H$_6$; $-130°$, Si$_2$H$_6$; 112°; Si$_2$H$_5$Br; $-63°$, dibromodisilanes. The ^{1}H nmr spectrum of the fraction which condensed at $-63°$ indicated the fraction contained 85% 1,2-Br$_2$Si$_2$H$_4$ and 15% 1,1-Br$_2$Si$_2$H$_4$. No attempt was made to separate this isomer mixture. More highly brominated disilanes were not detected.

(B) Si$_3$H$_8$–Br$_2$.—Reaction materials were passed through a $-130°$ trap into a $-196°$ trap to remove HBr and traces of SiH$_4$. The mixture which condensed at $-130°$ was first separated by rapid-passage low-temperature column distillation into Si$_3$H$_8$, a mixture of 1- and 2-BrSi$_3$H$_7$, and a small quantity (<0.2 mmol) of polybrominated trisilanes. By examination of the ^{1}H nmr spectrum, the BrSi$_3$H$_7$ mixture was found to contain 14 and 86% of the 1 and 2 isomers, respectively. Repeated slow passage distillation of this mixture yielded pure samples of 1-BrSi$_3$H$_7$ and 2-BrSi$_3$H$_7$. Isomer purity was established by vapor tension and ^{1}H nmr spectral data. The polybrominated trisilane mixture was not examined further.

The 2-BrSi$_3$H$_7$ melts at $-88.5 \pm 0.1°$ and has a 0° vapor tension of 6.5 ± 0.5 mm. The 1-BrSi$_3$H$_7$ melts at $-94.2 \pm 0.2°$ and has a 0° vapor tension of 4.0 ± 0.5 mm. A vapor density molecular weight of 176 (calcd 171.0) was obtained for 2-BrSi$_3$H$_7$. Attempts to obtain a vapor density molecular weight of 1-BrSi$_3$H$_7$ and vapor tension *vs.* temperature data for either isomer were unsuccessful due to the thermal instability of the samples above 0°.

The mass spectra of 1- and 2-BrSi$_3$H$_7$ consist of peak envelopes at *m/e* 176–163, 144–135, 112–107, 96–84, 63–56, and 33–28. The eight most intense peaks and the highest mass peak in the spectra (per cent relative intensities in parentheses) occur at

TABLE II

^{1}H NMR SPECTRAL PARAMETERS[a]

	SiH'$_2$BrSi-H''$_2$SiH'''$_3$	SiH'$_3$SiH''-BrSiH'$_3$	CH$_3$SiH'-BrSiH''$_3$	BrSiH'$_2$-SiH''$_2$CH$_3$
δ(SiH)	...	-4.43	-4.75	...
δ(SiH'$_2$)	-4.42	...	...	-4.32
δ(SiH''$_2$)	-3.5[b]	...	...	-3.90
δ(SiH$_3$)	...	-3.69	-3.54	...
δ(CH$_3$)	...	...	-0.86	-0.33
$J_{\mathrm{H'SiSiH''}}$	2.60	3.20	2.72	2.50
J_{HSiCH}	...	...	4.28	4.90
$J_{^{29}\mathrm{SiH'}}$	225	205	*d*	*d*
$J_{^{29}\mathrm{SiH''}}$	*d*	214[c]		
$J_{^{29}\mathrm{SiH'''}}$	204	...		

[a] Chemical shifts in ppm and coupling constants in Hz. [b] Center of Si$_2$H$_5$ multiplet. [c] Obtained by doubling the distance from the downfield satellite to the main resonance, since the high-field satellite is obscured by the SiH$_3$ resonance. [d] Silicon-29 satellite data not measured.

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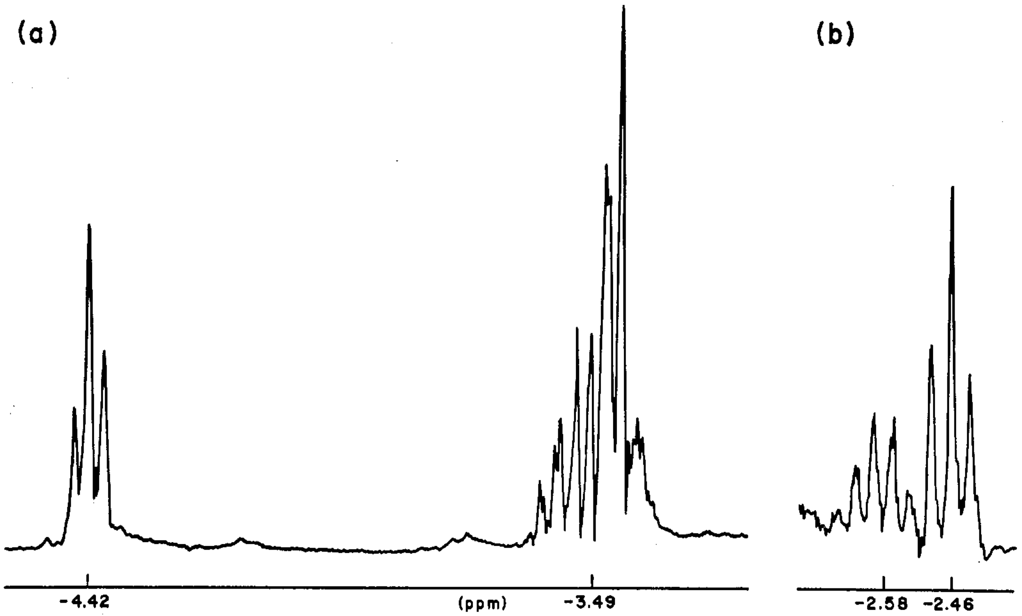


Figure 2.—Proton nmr spectrum of 1-$BrSi_3H_7$ at 100.0 MHz: (a) main spectrum; (b) high-field ^{21}Si satellite resonance.

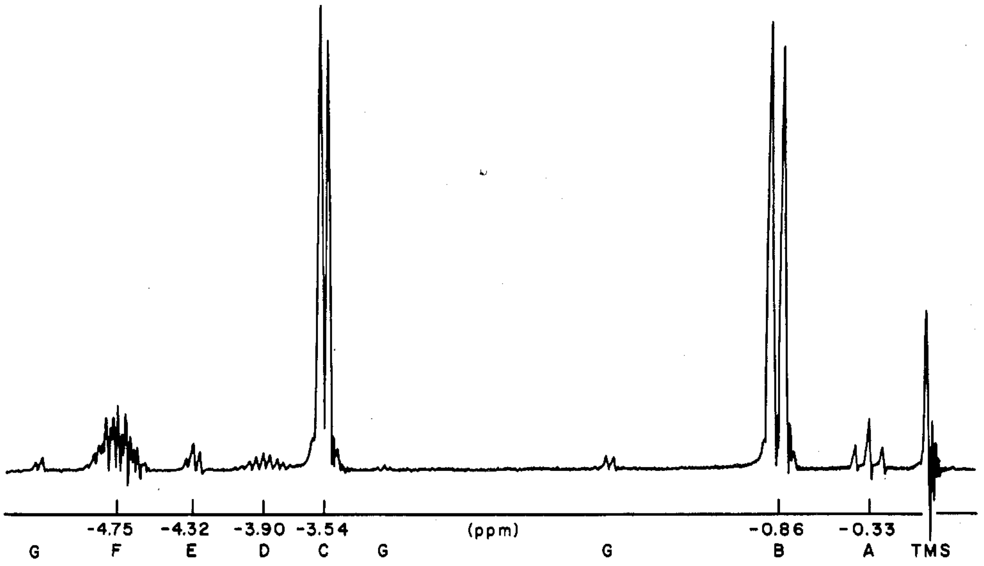


Figure 3.—Proton nmr spectrum at 60 MHz of the $CH_3Si_2H_4Br$ isomer mixture.

m/e 60 (100), 138 (79.9), 140 (72.0), 109 (52.4), 107 (49.7), 58 (46.5), 57 (28.8), 139 (28.2), and 176 (0.1) for 1-$BrSi_3H_7$, and at *m/e* 138 (100), 140 (87.7), 107 (55.6), 109 (55.6), 60 (48.7), 58 (33.9), 139 (31.4), 170 (29.2), and 176 (0.1) for 2-$BrSi_3H_7$.

Infrared spectra in the range 4000–400 cm^{-1} were obtained on gaseous samples at 4 mm pressure (Figure 1). The infrared spectrum of 1-$BrSi_3H_7$ shows absorptions at 2170 (vs), 2146 (sh), 932 (m), 879 (vs), 803 (m), 799 (s), 702 (vs), 685 (m), and 470 cm^{-1} (w). The spectrum of 2-$BrSi_3H_7$ shows absorptions at 2230 (sh), 2160 (vs), 2100 (sh), 1008 (w), 962 (w), 937 (m), 930 (m), 891 (s, sh), 885 (s), 865 (vs); 805 (w), 740 (sh), 735 (s, sh), 730 (s), 720 (s), 712 (vs), 563 (w), 534 (w), and 443 cm^{-1} (m).

The ^1H nmr spectrum of 2-$BrSi_3H_7$ at both 60 and 100 MHz consists of a high-field doublet (area 6) arising from the SiH_3 protons, and a low-field septet (area 1) arising from the SiHBr proton. Nmr spectral parameters are given in Table II.

The ^1H nmr spectrum of 1-$BrSi_3H_7$ at both 60 and 100 MHz cannot be interpreted in terms of first-order coupling. It consists of a low-field triplet (area 2) assigned to the SiH_2Br protons and a high-field multiplet (area 5) resulting from the overlap of the SiH_2 and SiH_3 resonances. Spectral parameters are given in Table II. The 100-MHz spectrum of 1-$BrSi_3H_7$ is shown in Figure 2a. The 100-MHz high-field ^{29}Si satellite spectrum of the multiplet (CAT spectrum, 49 scans) consists of a triplet, resulting from the $^{29}SiH_3$ protons, and a sextet, resulting from the $^{29}SiH_2$ protons, consistent with first-order couplings. This spectrum is shown in Figure 2b.

(C) **$CH_3Si_2H_5$–Br_2.**—Reaction materials were passed through a −130° trap into a −196° trap to remove HBr. Low-temperature column distillation of the material which condensed at −130° yielded $CH_3Si_2H_5$, a mixture of $CH_3Si_2H_4Br$ isomers, and a trace (<0.1 mmol) of polybrominated methyldisilanes which was not examined further. The 60-MHz nmr spectrum of the $CH_3Si_2H_4Br$ mixture is shown in Figure 3 and spectral parameters are given in Table II. Resonances A, D, and E arise from the CH_3, SiH_2, and SiH_2Br groups, respectively, of CH_3SiH_2Br. Relative areas of A:D:E are 3.0:2.0:2.0 (calcd 2.0:2.0:2.0). Resonances B, C, and F arise from the CH_3, SiH_3, and SiHBr groups, respectively, of $CH_3SiHBrSiH_3$. Relative areas of B:C:F are 3.16:2.97:1.00 (calcd 3.0:3.0:1.0). The ^{29}Si satellite data were not measured. An isomer distribution of *ca.* 10% $CH_3SiH_2SiH_2Br$ and 90% $CH_3SiHBrSiH_3$ (determined from the integration of resonances A and B) was observed in typical experiments.

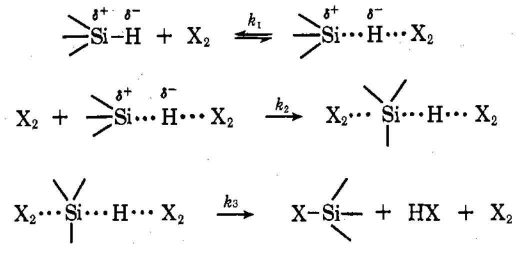
(D) **GeH_4–Br_2.**—Reaction materials were passed through a series of traps at −78 and −130° into a −196° trap. Germane and HBr were trapped at −196°. Traces of GeH_2Br_2 were trapped at −78° and were not examined further. Repeated fractionation of the material which collected at −130° yielded pure GeH_3Br.

Discussion

The spectral and physical property data shown above allow for the complete characterization of the $BrSi_3H_7$ isomers. The ^1H nmr spectra for both 1- and 2-$BrSi_3H_7$ are consistent with the proposed structures. The peaks at 2160 and 2170 cm^{-1} in the infrared spectra of 2-$BrSi_3H_7$ and 1-$BrSi_3H_7$, respectively, are characteristic of the Si–H stretching absorption.[17] Due to the complexity of the spectra, further assignments were not attempted. The mass spectra of both 1- and 2-$BrSi_3H_7$ exhibit fragmentation patterns of the type expected for bromotrisilanes. The mass spectra for both compounds consist of envelopes at (assignments in parentheses) m/e 176–163 ($BrSi_3H_x^+$), 144–135 ($BrSi_2H_x^+$), 112–107 ($BrSiH_x^+$), 96–84 ($Si_3H_x^+$), 63–56 ($Si_2H_x^+$), and 33–28 (SiH_x^+). A strong molecular ion envelope was observed for both isomers. The two most intense peaks in the mass spectrum of 2-$BrSi_3H_7$ occur at m/e 138 and 140, corresponding to the loss of a neutral SiH_4 from the molecular ions $^{79}Br^{28}Si_3H_7^+$ and $^{81}Br^{28}Si_3H_7^+$. The most intense peak in the spectrum of 1-$BrSi_3H_7$ occurs at m/e 60, corresponding to the loss of a neutral $BrSiH_3$ from the molecular ion $Br^{28}Si_3H_7^+$. This fragmentation is consistent with the proposed structural assignment of the isomers and with the observed fragmentation of trisilane.[12] The most intense peak in the mass spectrum of trisilane occurs at m/e 60 resulting from the loss of a neutral SiH_4 from the molecular ion $^{28}Si_3H_7^+$.

The isomers of $CH_3Si_2H_4Br$ were also prepared in this study; however, since we were interested only in isomer distribution of the monobromo products, they were not separated for complete characterization. The ^1H nmr spectra of the mixture provides clear evidence for the presence of both the 1 and 2 isomers. As shown by the spectrum in Figure 3, the 1-Br-1-$CH_3Si_2H_4$ isomer predominates in the product mixtures.

The mechanisms of the silane bromination reactions appear analogous to those proposed for the bromination[25] and iodination[26] of trisubstituted silane. In these cases, the kinetics of the halogenation reactions were consistent with electrophilic attack on H by the halogen



where $k_1 < k_3 \ll k_2$. Electron-donating groups on silicon were found to enhance the rate of substitution. Thus, for disilane, substitution of one hydrogen by a bromine should decrease the rate of further bromination and direct the second bromine atom to the adjacent silicon atom. Analysis of the polybromodisilanes formed in our studies indicate the predominance of 1,2-$Br_2Si_2H_4$ over 1,1-$Br_2Si_2H_4$. Substitution of electron-donating groups CH_3[27,28] and SiH_3[29] for H on Si_2H_6 should enhance the rate of bromination of the substituted silicon; thus, we observe the predominance of 2-$BrSi_3H_7$ over 1-$BrSi_3H_7$ and 1-Br-1-$CH_3Si_2H_4$ over 2-Br-1-$CH_3Si_2H_4$ in the brominations of Si_3H_8 and $CH_3Si_2H_5$, respectively.

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Preparation and Characterization of μ-Superoxo-bis[bis(L-histidinato)cobalt(III)] Salts[1]

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In a previous note,[3] preparation and electron paramagnetic resonance studies in solution of a previously unknown μ-superoxo-bis[bis(L-histidinato)cobalt(III)] complex were reported. Herein, we describe the preparation of salts of this ion and summarize our findings as to its molecular weight, charge, and unpaired electron content.

Experimental Section

Preparation of μ-Superoxo-bis[bis(L-histidinato)cobalt(III)] Trinitrate.—As a starting material, μ-peroxo-bis[bis(L-histidinato)cobalt(III)] was prepared,[4] and about 5 g was slowly added to 10 ml of 15 *M* HNO_3, with stirring on a cold plate at *ca.* −10°. The temperature was not allowed to exceed 0°. During the addition, the color changed to dark green. The solution was diluted to 200 ml and poured onto a 40-cm ion-exchange column containing *ca.* 650 cm^3 of Dowex 50-X-2 resin. The column was washed with successive additions of 1 *M* HNO_3 (which produced a pale pink eluent, presumably Co^{2+}) and then 2 *M* HNO_3, and finally the dark green band was removed with 3 *M* HNO_3. This green fraction was evaporated under vacuum, the residue taken up with a minimum of 2 *M* HNO_3, and the solution refrigerated. A dark green solid (*ca.* 2.3 g) was obtained which was filtered, washed with ethanol, and air-dried. Recrystallization was carried out by dissolving the solid in a minimum of 2 *M* HNO_3 at 35°, filtering, and refrigerating the filtrate overnight. The resulting green solid was filtered, washed with ethanol, and stored over $CaCl_2$ in the refrigerator (yield *ca.* 1.2 g). The solubility of the salt is *ca.* 1 g/ml in H_2O or dilute HNO_3, and it dissolves to give acidic solutions (pH ~2.2). Solutions are unstable at pH >5 at room temperature and under intense light. *Anal.* Calcd for $\{[Co(C_6H_9O_2N_3)(C_6H_8O_2N_3)]_2O_2\}(NO_3)_3\cdot 2H_2O$ (990.56): Co, 11.89; C, 29.1; N, 21.15; H, 3.83; NO_3^-, 18.7; wt loss *in vacuo* (H_2O), 3.64. Found: Co, 11.52; C, 28.0; N, 20.92; H, 3.68; NO_3^-, 19.15; wt loss *in vacuo*, 3.61.

Preparation of μ-Superoxo-bis[bis(L-histidinato)cobalt(III)] Trichloride.—The preparation of the chloride salt was identical with that of the nitrate except that elution of the Dowex-50 column was carried out with various concentrations of HCl. The dark green band was removed with 6 *M* HCl, the eluent was evaporated, and the solid obtained was recrystallized from 1 *M* HCl at 35°. *Anal.* Calcd for $\{[Co(C_6H_9O_2N_3)(C_6H_8O_2N_3)]_2O_2\}Cl_3\cdot 4H_2O$: Co, 12.45; C, 30.45; N, 17.75; H, 4.44; Cl, 11.25;

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