

## Halogenodisilanes

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The syntheses of bromo-, chloro-, and fluoro-disilanes are reported, and the preliminary identification of 1-bromo-1-chlorodisilane and 1-bromo-1,1-dichlorodisilane. The  $^1\text{H}$  and  $^{19}\text{F}$  n.m.r. parameters of these and related compounds are reported and discussed.

THE formation of chloro- and bromo-disilanes by direct reaction of disilane with boron trichloride<sup>1</sup> and tribromide<sup>2</sup> has been described in preliminary communications. We have extended this work and also report the identification of some fluorodisilanes and mixed halogen species. The  $^1\text{H}$  and  $^{19}\text{F}$  n.m.r. parameters for these compounds are presented because only limited chemical-shift data have been reported.<sup>1-3</sup> The values of the  $^{29}\text{Si}$ -H coupling constants in these and related disilanyl derivatives are correlated with the 'effective electronegativity' by a quadratic function similar to that used with monosilanes.<sup>4</sup>

### EXPERIMENTAL

Disilane was prepared by the lithium tetrahydroaluminate reduction of hexachlorodisilane.<sup>5</sup> Commercial

Viton A diaphragm) which was used for all experiments. The  $^1\text{H}$  n.m.r. spectra were recorded on a Varian A 60 high-resolution variable-temperature spectrometer and the  $^{19}\text{F}$  n.m.r. spectra on a Varian HA 100 high-resolution spectrometer. The n.m.r. parameters are listed (Table 1) along with those of related compounds (Table 2).

**Formation of Monochlorodisilane.**—Typically,  $\text{Si}_2\text{H}_6$  (4.5 mmoles) was condensed at  $-196^\circ$  with  $\text{BCl}_3$  (1.5 mmoles) into a reaction vessel (ca. 60 ml) and then held at  $0^\circ$  for 8 h. The product was fractionated by trap-to-trap distillation through a trap at  $-63^\circ$  into one at  $-96^\circ$  to give  $\text{Si}_2\text{H}_5\text{Cl}$  (1.7 mmoles).

**Formation of 1,1- and 1,2-Dichlorodisilane.**—Typically,  $\text{Si}_2\text{H}_6$  (4.5 mmoles) and  $\text{BCl}_3$  (2.25 mmoles) were allowed to react as described in the previous experiment. Trap-to-trap distillations gave the dichlorodisilanes (1.8 mmoles) from a trap at  $-45^\circ$ . The  $^1\text{H}$  n.m.r. spectrum was recorded immediately and confirmed the presence of both

TABLE 1  
 $^1\text{H}$  N.m.r. parameters for halogenated disilanes

Compound	$\delta(\text{SiH}_3)$	$\delta(\text{SiH}_2)$	$\delta(\text{SiH})$	$J(\text{H-H})$	$J(^{29}\text{SiH}_3)$	$J(^{29}\text{SiH}_2)$ or $J(^{29}\text{SiH})$	$J(^{29}\text{SiH}_2)$ calc.	$J(^{29}\text{SiH})$ calc.	$J(\text{H-M-MF})$	$J(\text{H-MF})$
$\text{SiH}_3\cdot\text{SiH}_3\text{Cl}^a$	3.47	4.82		3.0	-201.4	-221.2	-203.8	-221.7		
$\text{SiH}_3\cdot\text{SiHCl}_2$	3.53		5.70	2.1	-210.0	-266.3	-209.5	-270.5		
$\text{SiH}_3\cdot\text{SiCl}_3$	3.65				-214.0		-215.0			
$\text{SiH}_2\text{Cl}\cdot\text{SiH}_2\text{Cl}$		4.80		3.0		-233.0		-227.3		
$\text{SiH}_2\text{Cl}\cdot\text{SiHCl}_2$		4.79	5.75	3.0		-237.2		-232.9		
						(-276.6)		-276.1		
$\text{SiHCl}_2\cdot\text{SiHCl}_2$			5.70	b		-280.2		-281.7		
$\text{SiH}_3\cdot\text{SiH}_2\text{Br}^c$	3.61	4.31		3.0	-202.6	-225.8	-203.9	-221.9		
$\text{SiH}_3\cdot\text{SiHBr}_2$	3.90		5.42	2.3	-210.0	-254.2	-209.6	-271.4		
$\text{SiH}_3\cdot\text{SiBr}_3$	4.59				b					
$\text{SiH}_2\text{Br}\cdot\text{SiH}_2\text{Br}$		4.48		3.0		-236.4		-227.5		
$\text{SiH}_2\text{Br}\cdot\text{SiHBr}_2$		4.56	5.43	3.0		-242.0		-233.2		
$\text{SiHBr}_2\cdot\text{SiHBr}_2$			5.40			b				
$\text{SiH}_3\text{SiH}_2\text{F}^d$	3.19	5.30		2.7	b	-217		-222.8	6.6	43.2
$\text{SiH}_3\text{SiHF}_2$	3.28	5.40		2.8	-206.2	b	-210.2		6	53
$\text{SiH}_3\text{SiF}_3$	3.35				b				5.8	
$\text{GeH}_3\text{SiHF}_2^e$	2.72	4.96		3.0	b	b			8.0	54.5
for Ge										
$\text{SiH}_3\text{SiH}_2\text{I}^f$	3.66	3.39		3.0	-204.6	-224.0	-202.8	-217.8		
$\text{SiH}_3\text{SiHClBr}$	3.66		5.66	2.25	-208.0	b	-209.5			
$\text{SiH}_3\text{SiCl}_2\text{Br}$	3.80				b					

<sup>a</sup> A. D. Craig, J. V. Vrenovitch, and A. G. MacDiarmid, *J. Chem. Soc.*, 1962, 548. <sup>b</sup> Not measured, owing to either insufficient concentration or peaks being masked by solvent or compound peaks. <sup>c</sup> M. Abedini, C. H. Van Dyke, and A. G. MacDiarmid, *J. Inorg. Nuclear Chem.*, 1963, **25**, 307. <sup>d</sup> M. Abedini, Ph.D. Thesis, University of Pennsylvania, 1963. <sup>e</sup> Ref. 14. <sup>f</sup> L. G. L. Ward and A. G. MacDiarmid, *J. Amer. Chem. Soc.*, 1960, **82**, 2151.

The values for the chlorodisilanes agree with those reported,<sup>6</sup> when corrected with reference to tetramethylsilane as internal standard. All figures for chemical shifts are relative to internal T.M.S. A downfield shift is considered to be positive.

samples of boron trichloride and tribromide were purified by distillation in a conventional Pyrex-glass vacuum line fitted with greaseless stopcocks (Springham and Co.;

<sup>1</sup> J. E. Drake and N. Goddard, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 385.

<sup>2</sup> J. E. Drake and J. Simpson, *Inorg. Nuclear Chem. Letters*, 1966, **2**, 219.

$\text{SiHCl}_2\cdot\text{SiH}_3$  (5%) and  $\text{SiH}_2\text{Cl}\cdot\text{SiH}_2\text{Cl}$  (95%). After  $\frac{1}{2}$  h at room temperature the spectrum showed 95%  $\text{SiHCl}_2\cdot\text{SiH}_3$ .

<sup>3</sup> A. G. MacDiarmid and M. Abedini, *Inorg. Chem.*, 1963, **2**, 608.

<sup>4</sup> M. A. Jensen, *J. Organometallic Chem.*, 1968, **11**, 423.

<sup>5</sup> G. W. Bethke and M. K. Wilson, *J. Chem. Phys.*, 1957, **26**, 1107.

The i.r. spectra of these chloro-compounds were as reported earlier<sup>6</sup> and further confirmation was provided by their Raman spectra. The main features in the Raman effect are shown (Table 3) along with those of  $\text{SiHF}_2\cdot\text{SiH}_3$ .

**Formation of 1,1,2-Trichlorodisilane and 1,1,2,2-Tetrachlorodisilane.**—Typically,  $\text{Si}_2\text{H}_6$  (4.5 mmoles) and  $\text{BCl}_3$  (4.5 mmoles) were allowed to react as described in the previous experiment. Fractionation gave  $\text{SiHCl}_2\cdot\text{SiH}_2\text{Cl}$

described earlier. After 1 h at room temperature the  $\text{Si}_2\text{H}_6$  (2.1 mmoles) was recovered.

**Formation of 1,1,1-Trifluorodisilane.**—Typically,  $\text{SiHCl}_2\cdot\text{SiH}_3$  (1.0 mmole) was passed at room temperature over  $\text{SbF}_3$  (5 g) supported on glass wool. The volatile constituents were distilled back and forth through the  $\text{SbF}_3$  for 5 min and then fractionated, to give a mixture of  $\text{SiF}_4$  and  $\text{Si}_2\text{F}_6$  (0.52 mmole; identified by i.r. spectra<sup>7,9</sup>)

TABLE 2  
<sup>1</sup>H N.m.r. parameters of disilanyl derivatives

	( $\text{SiH}_3$ )	( $\text{SiH}_2$ )	$J(^{29}\text{SiH}_3)$	$J(^{29}\text{SiH}_3)$ calc.	$J(^{29}\text{SiH}_2)$ or $J(^{29}\text{SiH})$	$J(^{29}\text{SiH}_2)$ or $J(\text{SiH})$ calc.
$\text{SiH}_3\cdot\text{SiH}_3$ <sup>a</sup>	3.25		—198.4			
$\text{SiH}_3\cdot\text{SiH}_2\cdot\text{SiH}_3$ <sup>a</sup>	3.38	3.20	—199.0	—197.0	—193.1	—181.4
$\text{SiH}_3\cdot\text{SiH}(\text{SiH}_3)_2$ <sup>b</sup>	3.40	2.91	—192 ± 5	—195.7	<sup>c</sup>	
$\text{SiH}_3\cdot\text{SiH}_2\cdot\text{SiH}_2\cdot\text{SiH}_3$ <sup>b</sup>	3.34	3.24	—199	—197.0	—197.0	—181.4
$\text{SiH}_3\cdot\text{SiH}_2\cdot\text{Me}$ <sup>d</sup>	3.17	3.67	—191.0	—195.0	—189.0	—185.1
$\text{SiH}_3\cdot\text{SiH}_2\cdot\text{PH}_2$ <sup>e</sup>	3.19	3.57	—201.0	—198.8	<sup>c</sup>	
$(\text{SiH}_3\cdot\text{SiH}_2)_3\text{P}$ <sup>f</sup>	3.40	3.98	<sup>c</sup>	<sup>c</sup>	<sup>c</sup>	
$\text{SiH}_3\cdot\text{SiH}_2\cdot\text{AsH}_2$ <sup>g</sup>	3.45	3.60	—201.0	<sup>h</sup>	<sup>c</sup>	
$\text{SiH}_3\cdot\text{SiH}\cdot\text{NMe}_2$ <sup>d</sup>	3.15	4.74	<sup>c</sup>		—199.8	—199.4
$\text{SiH}_3\cdot\text{SiH}_2(\text{NMe}_2)_2$ <sup>d</sup>	3.30	5.00	—184.5	—200.4	<sup>c</sup>	
$(\text{SiH}_3\cdot\text{SiH}_2)_2\text{NMe}$ <sup>d</sup>	3.19	4.78	<sup>c</sup>		—203.0	—203.5
$(\text{SiH}_3\cdot\text{SiH}_2)_3\text{N}$ <sup>d</sup>	3.28	4.84	<sup>c</sup>		—205.2	—203.5
$\text{SiH}_3\cdot\text{SiH}_2\cdot\text{O}\cdot\text{SiH}_3$ <sup>i</sup>	3.22	5.13	—192.8	—202.1	—210.6	—215.1
$\text{SiH}_3\cdot\text{SiH}_2\cdot\text{OMe}$ <sup>i</sup>	3.17	4.99	—198.2	—201.6	—207.6	—215.1
$(\text{SiH}_3\cdot\text{SiH}_2)_2\text{O}$ <sup>b</sup>	3.20	5.12	—194.4	—201.1	—214.8	—215.1
$(\text{SiH}_3\cdot\text{SiH}_2)_2\text{S}$ <sup>j</sup>	3.39	4.55	—202.0	—201.3	—213.6	—210.8

<sup>a</sup> E. A. V. Ebsworth and J. J. Turner, *Trans. Faraday Soc.*, 1964, **60**, 256. <sup>b</sup> S. D. Gokhale and W. L. Jolly, *Inorg. Chem.*, 1964, **3**, 946. <sup>c</sup> Not measured. <sup>d</sup> Footnote d of Table 1. <sup>e</sup> S. D. Gokhale and W. L. Jolly, *Inorg. Chem.*, 1965, **4**, 597. <sup>f</sup> J. E. Drake and N. Goddard, *J. Chem. Soc. (A)*, 1969, 662. <sup>g</sup> J. E. Drake, N. Goddard, and J. Simpson, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 361. <sup>i</sup> C. H. Van Dyke, Ph.D. Thesis, University of Pennsylvania, 1964. <sup>j</sup> L. G. L. Ward and A. G. MacDiarmid, *J. Inorg. Nuclear Chem.*, 1962, **21**, 287.

(1.8 mmoles) from a trap at  $-23^\circ$ ;  $\text{SiHCl}_2\cdot\text{SiHCl}_2$  (ca. 0.2 mmole) was retained in the trap at that temperature.

**Formation of 1,1-Difluorodisilane.**—Typically,  $\text{SiHCl}_2\cdot\text{SiH}_3$  (2.2 mmoles) was condensed at  $-196^\circ$  in the reaction vessel which contained  $\text{SbF}_3$  (5 g) supported on glass-wool. The vessel was warmed to room temperature and the volatile contents distilled out leaving an antimony mirror. Non-condensable gases (0.2 mmole) were pumped away and the

containing a trace of  $\text{SiF}_3\cdot\text{SiH}_3$  and  $\text{SiHCl}_2\cdot\text{SiH}_3$  (0.2 mmole) with involatile materials.

**Formation of 1-Bromo-1-chlorodisilane.**—Typically  $\text{Si}_2\text{H}_5\text{Cl}$  (1.0 mmole) and  $\text{BBr}_3$  (0.4 mmole) were condensed at  $-196^\circ$  into the 60 ml reaction vessel and held at  $0^\circ$  for 8 h. The noncondensable products were pumped away at  $-196^\circ$  and the remaining volatile products fractionated to give  $\text{SiH}_4$  and  $\text{B}_2\text{H}_6$  (total 0.25 mmole; identified by i.r. spectra<sup>8,10</sup>),  $\text{Si}_2\text{H}_5\text{Cl}$  (0.6 mmole), and  $\text{SiHCl}_2\cdot\text{SiH}_3$  and  $\text{SiHBrCl}\cdot\text{SiH}_3$  (total 0.3 mmole; estimated from integrated <sup>1</sup>H n.m.r. spectrum to be in the ratio 1 : 1).

**Formation of 1-Bromo-1,1-dichlorodisilane.**—Typically,  $\text{SiHCl}_2\cdot\text{SiH}_3$  (0.75 mmoles) and  $\text{BBr}_3$  (0.13 mmole) were condensed together at  $-196^\circ$  into the 60 ml reaction vessel and then maintained at  $0^\circ$  for 6 h. After recooling to  $-196^\circ$  the noncondensable gases (0.12 mmole) were pumped away. Fractionation gave  $\text{SiH}_4$  and  $\text{B}_2\text{H}_6$  in a trap at  $-196^\circ$ . A trap at  $-126^\circ$  contained 0.3 mmole of volatile products identified by the <sup>1</sup>H n.m.r. spectrum as a mixture of  $\text{SiBrCl}_2\cdot\text{SiH}_3$ ,  $\text{SiHCl}_2\cdot\text{SiH}_3$ , and  $\text{SiCl}_2\cdot\text{SiH}_3$  in the ratio ca. 1 : 1 : 0.1. In another series of experiments,  $\text{BCl}_3$  (typically 0.2 mmole) was condensed at  $-196^\circ$  with a 1 : 1 mixture of  $\text{Si}_2\text{H}_5\text{Br}$  and  $\text{Si}_2\text{H}_4\text{Br}_2$  (a total of 0.8 mmole) and held at  $0^\circ$  for 6 h. There was a considerable amount of nonvolatile deposit and fractionation of the volatile products gave  $\text{SiH}_4$  and  $\text{B}_2\text{H}_6$  (total 0.2 mmole) and only unreacted starting material containing a trace of  $\text{SiHBrCl}\cdot\text{SiH}_3$  (total 0.3 mmole) in a trap at  $-126^\circ$ . There was no evidence for the presence of any species such as  $\text{Si}_2\text{H}_3\text{Br}_2\text{Cl}$ .

<sup>8</sup> C. H. Tindal, J. W. Straley, and H. H. Nielsen, *Phys. Rev.*, 1942, **62**, 151.

<sup>9</sup> E. A. Samworth, Ph.D. Thesis, John Hopkins University, 1963.

<sup>10</sup> R. C. Lord and I. Shapiro, *J. Chem. Phys.*, 1951, **19**, 1.

TABLE 3

Main features in the Raman spectrum of some halogeno-disilanes ( $\text{cm}^{-1}$ )

$\text{SiH}_3\cdot\text{SiH}_2\text{Cl}$	$\text{SiH}_3\cdot\text{SiHCl}_2$	$\text{SiH}_2\text{Cl}\cdot\text{SiH}_2\text{Cl}$	$\text{SiH}_3\cdot\text{SiHF}_2$	
2186s(pol)	2162s(pol)	2183s(pol)	2198s(pol)	Si—H str
538m	536m	554m		Si—Cl str
418s(pol)	397s(pol)	410s(pol)	426s(pol)	Si—Si str

(s = strong, m = medium, pol = polarised.)

remaining volatile constituents fractionated through a trap at  $-96^\circ$  into one at  $-196^\circ$ . The latter contained  $\text{SiF}_4$  and  $\text{SiH}_4$  (total 0.9 mmoles; identified by i.r. spectra<sup>7,8</sup>) and the former  $\text{SiHF}_2\cdot\text{SiH}_3$  (1.73 mmoles), identified by <sup>1</sup>H and <sup>19</sup>F n.m.r. spectra (Table 1 and Discussion section). The i.r. spectrum of  $\text{SiHF}_2\cdot\text{SiH}_3$  showed peaks at 2185s, 2175s, 2150sh, 948w, 940m, 930m, 910sh, 825sh, 815vs, and 523w  $\text{cm}^{-1}$ ; the main features in its Raman spectrum are shown in Table 3.

Experiments were also carried out in which  $\text{Si}_2\text{H}_6$  (typically 2.1 mmoles) was condensed on  $\text{SbF}_3$  (5 g) as

<sup>6</sup> R. P. Hollandsworth and M. A. Ring, *Inorg. Chem.*, 1968, **7**, 1635.

<sup>7</sup> P. J. H. Woltz, E. A. Jones, and H. H. Nielsen, *Phys. Rev.*, 1950, **79**, 416.

**Formation of Monobromodisilane.**—Typically,  $\text{Si}_2\text{H}_6$  (1.5 mmoles) and  $\text{BBr}_3$  (0.3 mmole) were condensed at  $-196^\circ$  in a 60 ml reaction vessel and maintained at  $0^\circ$  for 8 h. The products were fractionated and  $\text{Si}_2\text{H}_5\text{Br}$  (0.25 mmole) passed through a trap at  $-63^\circ$ , leaving behind higher-brominated disilanes.

**Formation of 1,1- and 1,2-Dibromodisilane.**—Typically,  $\text{Si}_2\text{H}_6$  (1.2 mmoles) was condensed and allowed to react with  $\text{BBr}_3$  (0.4 mmole) as described in the previous experiment. Fractionation gave  $\text{Si}_2\text{H}_5\text{Br}$  (0.1 mmole) and a mixture of  $\text{SiHBr}_2\cdot\text{SiH}_3$  and  $\text{SiH}_2\text{Br}\cdot\text{SiH}_2\text{Br}$  (0.2 mmole) in the ratio 5:95 as shown by the  $^1\text{H}$  n.m.r. spectrum which was recorded immediately after the separation. There was no evidence of a change in the ratio of these components with time.

**Formation of Polybromodisilanes.**—Typically,  $\text{Si}_2\text{H}_6$  (1.4 mmoles) and  $\text{BBr}_3$  (0.7 mmole) were condensed at  $-196^\circ$  into a 165 ml reaction vessel and held for 8 h at  $0^\circ$ . Fractionation of the products gave  $\text{Si}_2\text{H}_5\text{Br}$  (0.1 mmole),  $\text{Si}_2\text{H}_4\text{Br}_2$  (0.05 mmole), and  $\text{SiH}_2\text{Br}\cdot\text{SiHBr}_2$  (0.4 mmole). The tribromodisilane was collected in a trap at  $-23^\circ$  while the 1,1,2,2-tetrabromodisilane (0.15 mmole) was retained in a trap at  $0^\circ$ .

#### DISCUSSION

The reduction of boron trichloride and tribromide to diborane by disilane takes place fairly readily, both reactions showing similar features. The formation of monohalogenodisilanes is best carried out with a ratio of  $\text{BX}_3$  to  $\text{Si}_2\text{H}_6$  of  $\leq 1:3$ . An increase in the relative amount of  $\text{BX}_3$  leads to more halogenation of disilane with less percentage conversion to mono- and more to poly-halogenodisilanes. If it is increased still further eventually only polyhalogenosilanes of an intractable nature are formed. The size of reaction vessels is fairly important since too low a pressure gives very little conversion of the disilane and too high a pressure leads to a large amount of intractable materials.

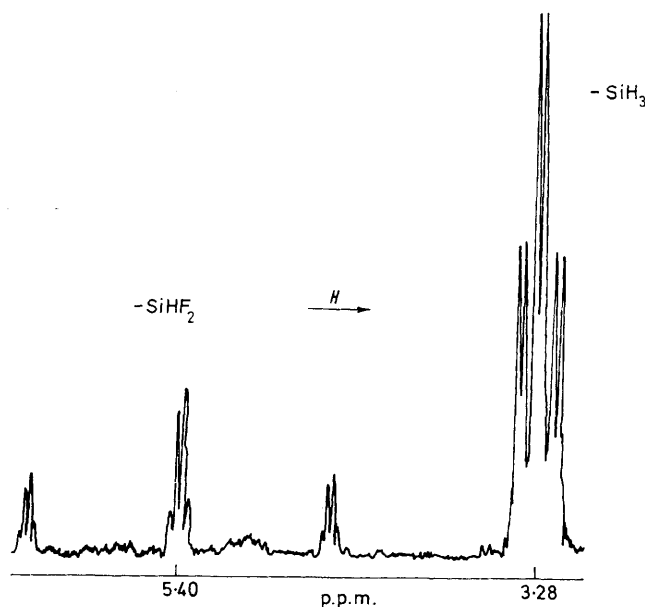
The tendency of halogenodisilanes to both isomerisation and decomposition has been noted for the chloro-<sup>11</sup> and for the bromo-disilanes<sup>12</sup> and attributed to the presence of Lewis acids. We find that there is rapid isomerisation of 1,2- to 1,1-dichlorodisilane while stored samples of mixtures of chlorodisilanes give small amounts of 1,1,1-trichlorodisilane as they slowly decompose. The preparation of bromodisilanes from the aluminium tribromide-catalysed reaction of hydrogen bromide on disilane yielded 1,1- and 1,2-dibromodisilanes in the ratio of *ca.* 8:1 and only the 1,1,1-isomer of the tribromodisilanes. By contrast, the action of  $\text{BBr}_3$  on  $\text{Si}_2\text{H}_6$  gives mainly the 1,2-dibromodisilane and only the 1,1,2-isomer of tribromodisilane. These species did not show the same tendency as did the corresponding chloro-derivatives to disproportionate to the more unsymmetrical forms.

The reaction of 1,1-dichlorodisilane with antimony trifluoride leads to the formation of the new fluoride,

1,1-difluorodisilane. It was not found necessary to use antimony pentachloride as catalyst as was reported for the conversion of chloro- to fluoro-monosilanes.<sup>13</sup>

However, it appears that this is mainly an exchange reaction because  $\text{SbF}_3$  does not fluorinate disilane directly. There is appreciable cleavage of the Si-Si bond resulting in the formation of  $\text{SiF}_4$  and also some further fluorination to give small amounts of 1,1,1-trifluorodisilane, possibly by disproportionation of the difluoride.

The  $^1\text{H}$  n.m.r. spectrum of  $\text{SiH}'\text{F}_2\cdot\text{SiH}_3$  (Table 1, Figure) shows the  $\text{SiH}_3$ - signal as a triplet [ $J(\text{HSi}-\text{SiF})$  6 Hz] of doublets [ $J(\text{HSi}-\text{SiH}')$  2.8 Hz] centred at 3.28 p.p.m. relative to internal tetramethylsilane. The



The  $^1\text{H}$  n.m.r. spectrum of  $\text{SiHF}_2\cdot\text{SiH}_3$

$\text{SiH}'$ - signal of a triplet [ $J(\text{H}'\text{SiF})$  53 Hz] of quartets is centred at 5.4 p.p.m. The spectrum is similar to that of  $\text{GeH}_3\cdot\text{SiHF}_2$ .<sup>14</sup> The  $^{19}\text{F}$  n.m.r. spectrum is also first-order showing a doublet [ $J(\text{FSiH}')$  53 Hz] of triplets [ $J(\text{FSi}-\text{SiH}')$  6 Hz] centred at  $-24.1$  p.p.m. relative to external hexafluorobenzene. The analogous values for  $\text{GeH}_3\cdot\text{SiHF}_2$  were 54.5 and 8.0 Hz respectively.

The  $^{19}\text{F}$  n.m.r. spectrum of  $\text{SiF}_3\cdot\text{SiH}_3$  showed the expected quartet [ $J(\text{FSiH})$  5 Hz] at  $-41.2$  p.p.m. relative to external hexafluorobenzene. Boron tribromide reacts with monochlorodisilane to give a bromine-substituted derivative without halide exchange, namely 1-bromo-1-chlorodisilane. This is confirmed by the  $^1\text{H}$  n.m.r. spectrum of  $\text{SiH}'\text{BrCl}\cdot\text{SiH}_3$  in which the  $\text{SiH}_3$ - and  $\text{SiH}'$ - resonances are seen as the doublet and quartet expected for first-order H-H' coupling. The chemical shifts of the two signals, which are in the

<sup>11</sup> L. G. L. Ward and A. G. MacDiarmid, *J. Inorg. Nuclear Chem.*, 1962, **20**, 345.

<sup>12</sup> J. Cohen, Ph.D. Thesis, University of Pennsylvania, 1967.

<sup>13</sup> A. G. Maddock and H. J. Emeléus, *J. Chem. Soc.*, 1944, 293.

<sup>14</sup> D. Solan and P. L. Timms, *Inorg. Chem.*, 1968, **7**, 2157.

expected intensity ratio of 3:1, lie between those of  $\text{SiHBr}_2\cdot\text{SiH}_3$  and  $\text{SiHCl}_2\cdot\text{SiH}_3$  (Table 1).

Boron tribromide also appears to further brominate 1,1-dichlorodisilane giving 1-bromo-1,1-dichlorodisilane. The singlet at 3.80 p.p.m. in the  $^1\text{H}$  n.m.r. spectrum of  $\text{SiBrCl}_2\cdot\text{SiH}_3$  lies between those of  $\text{SiBr}_3\cdot\text{SiH}_3$  and  $\text{SiCl}_3\cdot\text{SiH}_3$ .

By contrast, there is no evidence that boron trichloride will readily further chlorinate mono- or 1,1-dibromodisilane. However, it is a weaker halogenating agent towards the silicon hydrides, since  $\text{SiH}_4$  is not affected by  $\text{BCl}_3$ , whereas it is brominated by  $\text{BBr}_3$ .

A tabulation of the n.m.r. parameters of the halogenodisilanes showed up some fairly consistent trends. Jensen<sup>4</sup> had found that the  $J(^{13}\text{C}-\text{H})$  and  $J(^{29}\text{Si}-\text{H})$  directly bonded coupling constants in methyl and monosilyl derivatives [ $J(\text{MHXYZ})$ ] can be related (1) to

$$J(\text{MHXYZ}) = J(\text{MH}_4) + A(\alpha_X + \alpha_Y + \alpha_Z) + B(\alpha_X^2 + \alpha_Y^2 + \alpha_Z^2) - C(\alpha_X\alpha_Y + \alpha_Y\alpha_Z + \alpha_Z\alpha_X) \quad (1)$$

the coupling constant in the molecule [ $J(\text{MH}_4)$ ] and an 'effective electronegativity' of each substituent ( $\alpha_X, \alpha_Y, \text{or } \alpha_Z$ ).

We find that for the halogenated disilanes, as well as for all the known disilanyl compounds, the same values of the constants  $A$ ,  $B$ , and  $C$  (*viz.* 18.26, 1.78, and -1.28) can be used as for the silyl compounds. Literature values of  $\alpha$  were utilised with the addition of:  $\alpha_{\text{SiH}_3}$ , 0.57,  $\alpha_{\text{SiH}_2}$ , -1.37,  $\alpha_{\text{N}(\text{SiH}_3)_2}$ , -0.72, and  $\alpha_{\text{PH}_3}$ , -0.32.\* A further adjustment was made in the calculation of  $J(\text{Si}-\text{H})$  for the silicon atom contiguous with the substituted silicon atom (2).

$$J(\text{Si}-\text{H}) = J(\text{SiH})(\text{disilane}) + 2.25\alpha \quad (2)$$

There is good agreement between predicted and experimental  $|J|$  values which were generally not corrected to infinite dilution (Table 2).

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\* On this scale positive values are less electronegative than hydrogen and negative values more.