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SYNTHESIS AND CHARACTERIZATION OF THE (HALOSILYL)METHYLSILANES

J.A. MORRISON and J.M. BELLAMA*
Department of Chemistry, University of Maryland, College Park, Maryland 20742 (U.S.A.)
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Summary

The previously unreported (halosilyl)methylsilanes, $XSiH_2CH_2SiH_3$ (X = F, Cl, Br, and I), were synthesized and characterized by PMR, infrared, mass spectra, vapor pressure data, and melting points. In addition, a new preparation of the parent hydride, disilylmethane, is described.

Introduction

Although the alkyl halides have been extensively studied, much less information is available about the analogous compounds formed when one or more of the carbon atoms is replaced by a lower member of Group IVA. Both metal-functional [1-3] and carbon-functional [2,4] isomeric series which are analogous to the ethyl halides have been investigated; however, little is known about the analogous series which are isomeric to propyl halides. Only Si_3H_7X derivatives [5,6] and $GeH_3CH_2SiH_2Cl$ [7] have been previously reported. We have undertaken a more extensive study of such compounds and report here the synthesis and characterization of a series of silicon-functional species in which two of the skeletal atoms are silicon. Additionally, we report a new preparation of the parent hydride, disilylmethane.

Experimental

With the exception of the preparation of bis(trichlorosilyl)methane, the work in this investigation was carried out under vacuum using standard techniques. The PMR spectral data were obtained with a Varian Associates A-60-A spectrometer. Chemical shifts were determined in 10% and 90% (v/v) cyclohexane solutions, and the values were extrapolated to infinite dilution. Mass spectra were obtained with a DuPont Model 21-492 spectrometer operating at 75 eV and 50 μA; exact masses were determined using standard peak matching techniques. Gas phase infrared spectra were recorded on a Perkin—Elmer Model 337 spectrometer. Melting points were ascertained using a Stock magnetic plunger apparatus [8]. Temperatures below 0°C were measured by an iron-constantan thermocouple vs. an ice water reference junction. Pressures were read from a mercury manometer with the aid of a cathetometer. The hydrogen halides and the lead(II) fluoride were prepared by standard reactions; all other chemicals were obtained commercially.

Preparation of (chloro-, bromo-, and iodosilyl)methylsilane; $ClSiH_2CH_2SiH_3$, $BrSiH_2CH_2SiH_3$, and $ISiH_2CH_2SiH_3$

These compounds were prepared by a method analogous to the classic work of Stock [9]. A small amount of the appropriate aluminum halide was sublimed onto the walls of a one liter vessel. Disilylmethane (synthesis given below) and hydrogen halide in a 3/1 molar ratio were vacuum distilled into the vessel, and the reagents were allowed to react at room temperature for one hour. The contents of the flask were then distilled. Hydrogen was removed, and material which passed a —95° trap (unreacted $(SiH_3)_2CH_2$ and a small amount of HX) was returned to the reaction vessel with enough HX to reconstitute a 3/1 molar ratio. This process was repeated until most of the disilylmethane had been consumed. The combined condensates from the —95° trap were then distilled from a low-temperature still with the results described in Table 1.

Preparation of (fluorosilyl)methylsilane, $FSiH_2CH_2SiH_3$

This compound was prepared by the reaction of (bromosilyl)methylsilane with lead(II) fluoride. Two grams of freshly prepared PbF_2 and a stirring bar were placed into a 200 ml flask which was then evacuated. (Bromosilyl)methylsilane, 0.95 g (6.1 mmol) was distilled into the vessel and allowed to react at room temperature. After two hours the volatile contents of the flask were condensed into a low temperature still from which 0.30 g $FSiH_2CH_2SiH_3$ (3.2 mmol, 51% yield) was collected at —109°C.

Preparation of disilylmethane, $SiH_3CH_2SiH_3$

Large amounts of disilylmethane (see Discussion) were conveniently prepared by the base catalyzed reaction [10] of $HSiCl_3$ with $HCCl_3$; the $CH_2(SiCl_3)_2$ produced was then reduced with $LiAlH_4$. To a 250 ml flask were added 31.1 g

TABLE 1

YIELDS AND SEPARATION OF THE $XSiH_2CH_2SiH_3$ COMPOUNDS

X	$(SiH_3)_2CH_2$ used g (mmol)	$XSiH_2CH_2SiH_3$ recovered g (mmol)	Yield[a] (%)	Distil. temp. (°C)
Cl	0.60 (7.9)	0.64 (5.8)	73	−78
Br[b]	1.34 (17.6)	1.87 (12.0)	68	−66 to −62
I	0.40 (5.2)	0.88 (4.4)	83	−50 to −48

[a] Yields from small scale reactions using a 5/1 molar ratio of $(SiH_3)_2CH_2/HX$ were virtually quantitative.

[b] (Bromosilyl)methylsilane was also prepared in 60% yield by the low temperature bromination of $(SiH_3)_2CH_2$ with Br_2, a method similar to that used by Norman [6] for analogous preparations.

(0.168 mol) of freshly distilled tri-n-butyl amine, 9.68 g (0.081 mol) redistilled $HCCl_3$ and 55.0 g (0.406 mol) $HSiCl_3$. A $CaCl_2$ drying tube was attached to the condenser and the mixture was refluxed for twelve hours. The contents of the vessel were cooled to 0°, and as 100 ml of heptane was added a solid precipitated. After filtration, the solvent and excess starting materials were removed under vacuum at —10°. The liquid which remained was then treated with 4.50 g (0.118 mol) $LiAlH_4$, and the products separated under vacuum. Disilylmethane, identified by its IR [11], PMR [12], and mass [13] spectra, as well as its extrapolated b.p., 15.1° (lit. [14]: 15.3°), distilled from the low temperature still at —113 to —110° in 50.9% yield (3.14 g, 0.412 mol). The melting point is —134.0°.

Results

(Fluorosilyl)methylsilane, Dumas mol. wt. 94.6 (calcd. 94.2), melts at —129.9°C. The exact mass of the $FSiCSiH_6^+$ ion was measured as 92.99979 (calcd. 92.99921; error 6.2 ppm). Major IR absorptions occur at 2920vw; 2179vs; 1357w; 1058s; 960vs(br); 916vs; 880s; 768m and 739w. Mass spectral peaks more intense than 7.5% of the base peak occur at the following *m/e* values (% abundance): 94 (14.5), 93 (100.0), 92 (58.3), 91 (16.3), 90 (23.4), 89 (9.0) $FSiCSiH_n^+$; 75 (18.3), 74 (13.1), 73 (8.0), 72 (10.9) $SiCSiH_n^+$; 63 (19.6), 62 (10.4) $FSiCH_n^+$; 47 (33.8) FSi^+; 45 (22.8), 44 (26.1) and 43 (28.3) $CSiH_n^+$. The PMR data are given in Tables 2 and 3.

(Chlorosilyl)methylsilane, Dumas mol. wt. 110.3 (calcd. 110.7), melts at —120.0°C. The exact mass of the $^{35}ClSiCSiH_6^+$ ion is 108.97016 (calcd. 108.97066; error 4.6 ppm). The vapor pressure data determined over the range 0 to +23°C fit the equation $\log p = -1674.13/T(K) + 7.83841$; the experimentally determined vapor pressure at 0°C is 50.7 mm. The extrapolated b.p. is 64.5°, $\Delta H_v = 7.660$ kcal/mol, and $\Delta S_v = 22.7$ eu. Major IR absorptions occur at 2935w; 2165vs; 1352m; 1059s; 939vs; 872vs; 774s; 695m(br); 576vw; 523m and 487vw cm^{-1}. Mass spectral peaks greater than 7.5% of the base peak occur at the following *m/e* values (% abundance): 111 (37.1), 110 (24.0), 109 (100.0), 108 (42.6), 107 (13.1), 106 (21.5) $ClSiCSiH_n^+$; 79 (13.1), 78 (10.4) $^{35}ClSiCH_n^+$; 65 (8.7), 63 (21.2) $ClSi^+$; 45 (17.5), 44 (8.9) and 43 (17.5) $SiCH_n^+$. The PMR data for this compound are presented in Tables 2 and 3.

(Bromosilyl)methylsilane, Dumas mol. wt. 155.1 (calcd. 155.1), melts at —177.6°C. The exact mass of the $^{81}BrSiCSiH_6^+$ ion is 154.9182 (calcd. 154.9171;

TABLE 2

PROTON CHEMICAL SHIFTS[a] OF THE (HALOSILYL)METHYLSILANES

Compound	$\delta(SiH_2)$	$\delta(CH_2)$	$\delta(SiH_3)$
$FSiH_2CH_2SiH_3$	4.81	0.18	3.63
$ClSiH_2CH_2SiH_3$	4.78	0.27	3.69
$BrSiH_2CH_2SiH_3$	4.56	0.41	3.69
$ISiH_2CH_2SiH_3$	4.18	0.60	3.70
$HSiH_2CH_2SiH_3$[b]		—0.16	3.66

[a] Values given at infinite dilution in cyclohexane solvent: δ (ppm) to low field of tetramethylsilane. δ = ±0.01 ppm. [b] Lit. [12] (20% in CCl_4). $\delta(CH_2)$ —0.08. $\delta(SiH_3)$ 3.63.

TABLE 3

COUPLING CONSTANTS[a] OF THE (HALOSILYL)METHYLSILANES

Compound	$^1J(^{29}SiH_2)$	$^1J(^{29}SiH_3)$	$J(H-H')(SiH_2)$	$J(H-H')(SiH_3)$
$FSiH_2CH_2SiH_3$[b]	228.1	201.7	3.32	4.64
$ClSiH_2CH_2SiH_3$	234.5	203.2	3.60	4.49
$BrSiH_2CH_2SiH_3$	235 9	203.5	3.69	4.45
$ISiH_2CH_2SiH_3$	235 0	203 5	3 86	4.38
$HSiH_2CH_2SiH_3$		199.2		4.51

[a] $^1J(^{29}SiH)$ ±0.1-0.2 Hz; $J(H-H')$ 0 04 Hz. [b] $^2J(^{19}FSiH)$ 50 1. $^3J(^{19}FSiCH)$ 7.3; $^4J(^{19}FSiCSiH)$ 1.42 Hz. [c] Lit. [12]: $J(H-H')(SiH_3)$ 4.5 Hz.

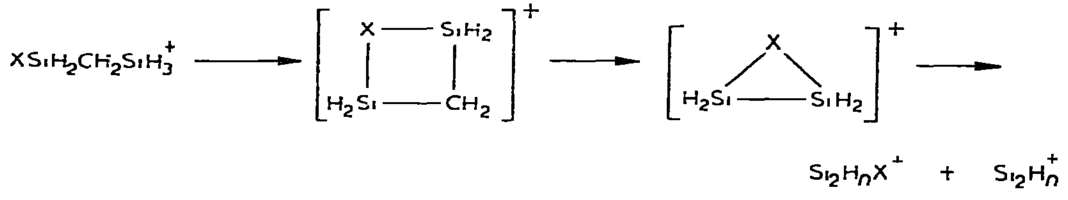
error 7.1 ppm). The vapor pressure at 0°C is 16.8 mm. Major IR absorptions occur at 2923vw; 2167vs; 1355w; 1058s; 1009vw; 940vs; 856vs; 774s; 703m(br); 671w; 572w(br); 431s and 416s cm^{-1}. In addition to intense peaks corresponding to $SiCSiH_n^+$, $SiCH_n^+$ and SiH_n^+ ions for which n = 1 to 7, the mass spectrum of this compound contains peaks at the following m/e values (% abundance): 156 (12.6), 155 (95.2), 154 (46.2), 153 (100.0), 152 (49.7), 151 (12.4), 150 (18.3) $BrSiCSiH_n^+$; 125 (8.2), 124 (8.2), 123 (18.8), 122 (22.9), 121 (12.7) $BrSiCH_n^+$; 111 (12.2), 110 (8.2), 109 (34.7), 108 (12.9) and 107 (28.9) $BrSiH_n^+$. The PMR data for this compound are shown in Tables 2 and 3.

(Iodosilyl)methylsilane, exact mass of the molecular ion 201.91307 (calcd. 201.91329; error −1.1 ppm), melts at −106.7°. The vapor pressure at 0°C is 4.0 mm. Major IR absorptions occur at 2961vw; 2172vs; 1353w; 1056s; 1012w; 936vs; 881w; 834vs; 768s; 698w; 643vw and 564vw(br) cm^{-1}. In addition to intense peaks corresponding to the ions $SiCSiH_n^+$, $SiCH_n^+$ and SiH_n^+ for which n = 1 to 7, the mass spectrum of (iodosilyl)methylsilane contains peaks at the following m/e values (% abundance): 202 (100.0), 201 (53.7), 200 (16.3), 199 (12.8), 198 (20.2), 197 (16.7) $ISiCSiH_n^+$; 171 (5.1), 170 (3.4), 169 (2.4) $ISiCH_n^+$; 157 (14.5), 156 (9.8) $ISiH_n^+$ and 127 (9.2) I^+. The PMR data for $ISiH_2CH_2SiH_3$ are summarized in Tables 2 and 3.

Discussion

Mass spectra

In addition to the major peaks reported in the Results section, the mass spectra of each of the (halosilyl)methylsilanes and the parent hydride contain smaller intensities corresponding to the $XSi_2H_n^+$ and $Si_2H_n^+$ ions. The latter species can most easily be explained by a four-centered intermediate which expels a methylene group and forms a metal—metal bond in the manner shown below.



The mass spectrum [15] of the related $(GeH_3)_2CH_2$ compound similarly contains peaks due to the $Ge_2H_n^+$ species which results from the loss of a CH_2 and the formation of a metal—metal bond.

PMR spectra

The trends seen in Table 2 for the proton chemical shifts of the $XSiH_2CH_2$-SiH_3 compounds are similar to those found in the alkyl halide and the $XSiH_2CH_3$ homologs [1]. Except for the fluoride derivative, the chemical shifts of the α protons (SiH_2) are linearly related to the Huggins electronegativity of the halogen, and the β protons (CH_2) are primarily controlled by anisotropic effects. The chemical shifts and vicinal ^{29}Si—H coupling constants of the γ protons (SiH_3) appear little affected by a change in the halogen substituent four bonds away. With the exception of the hydride, the vicinal coupling constants of the $XSiH_2$ protons in the substituted disilylmethanes in Table 3 are identical to the $XSiH_2$ proton coupling constants of the corresponding $XSiH_2CH_3$ compound [1]. Both the small increase, 5 ± 1 Hz, in the $^1J(^{29}Si{-}H)(SiH_2)$ values and the slight shielding of the carbon bound protons, 0.26 ± 0.07 ppm in the (halosilyl)methylsilanes relative to the $XSiH_2CH_3$ compounds can be viewed as evidence that the silyl group is electron donating compared to a proton; a result which might be expected in view of their respective electronegativities.

Synthesis of disilylmethane

Previous syntheses of disilylmethane have involved the laborious preparation of hexachlorodisilylmethane by the pyrolysis of methylchlorosilane, or the "direct synthesis" reaction of CH_2Cl_2 with Si/Cu at elevated temperatures [12, 14]. In order to develop a more efficient preparation, several preliminary experiments were carried out in which the reactions of $KSiH_3$ [16] with CH_2Cl_2, $CHCl_3$ and CH_2Br_2 were examined. Reactions were carried out at room temperature without solvent, in monoglyme (dimethoxyethane) at room temperature and at −78°C, and in hexamethylphosphoramide at 0°C. Each of these methods produced disilylmethane in approximately 30% yield based upon the amount of $KSiH_3$ present, and each was found suitable for small scale preparations of $(SiH_3)_2CH_2$. However, attempts to prepare this hydride on a larger scale at room temperature without solvent usually resulted in detonation, perhaps due to the localized heating generated by the reaction. For generation of significant quantities of this hydride, a base-catalyzed reaction of $HCCl_3$ and $HSiCl_3$, followed by reduction of the $(SiCl_3)_2CH_2$ produced, was found quite suitable (see Experimental section).

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References

1 E.A.V. Ebsworth and S G. Frankiss, Trans. Faraday Soc., 59 (1963) 1518.
2 J M. Bellama and C.J. McCormick, Inorg. Nucl. Chem. Lett. 7 (1971) 533.
3 J.M. Bellama and R.A. Gsell, unpublished observations.

4 J.M. Bellama and A.G. MacDiarmid, J. Organometal. Chem., 18 (1969) 275.
5 F. Fehér, P. Plichta and R. Guillery, Chem. Ber., 103 (1970) 3028; Inorg. Chem., 10 (1971) 606.
6 T.C. Geisler, C.G. Cooper and A.D. Norman, Inorg. Chem., 11 (1972) 1710.
7 G.A. Gibbon, E.W. Kifer and C.H. Van Dyke, Inorg. Nucl. Chem. Lett., 6 (1970) 617.
8 A. Stock, Hydrides of Boron and Silicon, Cornell Univ. Press, Ithaca, N.Y., 1933, p. 183
9 A. Stock and C. Somieski, Chem. Ber., 53 (1930) 759.
10 R.A. Benkeser, J.M. Gaul and W.E. Smith, J. Amer. Chem. Soc., 91 (1961) 3666.
11 D.C. McKean, G. Davidson and L.A. Woodward, Spectrochim. Acta A, 26 (1970) 1815.
12 G. Fritz, H.J. Buhl and D. Kummer, Z. Anorg. Allgem. Chem., 327 (1964) 165.
13 F. Aulinger and W. Reerink, Z. Anal. Chem., 197 (1963) 24
14 M.I. Beteuv, V.A. Ponomarenko, A.D. Matveeva and A.D. Petrov, Dokl. Akad. Nauk SSSR, 95 (1954) 805.
15 R.M. Dreyfuss and W.L. Jolly, Inorg. Chem., 10 (1971) 2567.
16 M.A. Ring and D.M. Ritter, J. Amer. Chem. Soc., 83 (1961) 802; S. Craddock, G.A. Gibbon and C.H. Van Dyke, Inorg. Chem., 6 (1971) 1751.