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Chlorodisilanes. Preparation and Silicon–Hydrogen Stretching Frequencies

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The reaction between disilane and silver chloride has yielded 1,2-dichlorodisilane while the aluminum chloride catalyzed reaction between hydrogen chloride and disilane has yielded 1,1-dichlorodisilane, 1,1,2-trichlorodisilane, and a tetrachlorodisilane. The weighted average of the Si–H stretching frequencies of these and other silanes has been examined, and a correlation of these averages is presented.

Introduction

The aluminum halide catalyzed reaction between silane and the appropriate hydrogen halide at 100° has been the standard preparation for the halosilanes.[1] In 1963, this procedure was extended to the preparation of chloro- and bromodisilane.[2] Following a paper describing the preparation of halogermanes and halodigermanes by the reaction of germane or digermane with silver chloride or bromide at 260°,[3] we examined some reactions of silane and disilane with silver halides.[4]

Monochloro-, dichloro-, and trichlorodisilanes were observed but not isolated as products from the reaction between boron trichloride and disilane[5] while bromodisilane, both dibromodisilanes, 1,1,2-tribromodisilane, and 1,1,2,2-tetrabromodisilane were obtained from the reaction of boron tribromide with disilane.[6]

In this paper we report a more extensive examination of the reactions between disilane and hydrogen chloride (catalyzed) and disilane and silver chloride. We have also obtained weighted averages for the Si–H stretching frequencies in the chlorodisilanes and have correlated these with similar data for substituted silanes and for methyldisilanes.

Experimental Section

The reactions were carried out with standard high-vacuum techniques. Separations were made by trap to trap distillations through traps cooled by standard slush baths. The disilane was prepared by the reduction of hexachlorodisilane with lithium aluminum hydride.[7]

Infrared spectra were obtained on Perkin-Elmer Model 337 and 621 spectrometers in 10-cm gas-phase cells fitted with potassium bromide windows. A Varian A-60 spectrometer was used to obtain proton nmr spectra. Chemical shifts are reported as negative when downfield from TMS at 0.0 as an external standard. Mass spectra were obtained on a Hitachi RMU-6E spectrometer.

(1) **Si_2H_6-AgCl Reaction.**—The reaction between disilane and silver chloride was carried out in a 20 cm long reaction chamber of 1-cm radius surrounded by a water jacket maintained at about 0°. The silver chloride (~15 g) was held in five layers by glass wool plugs and the disilane was circulated through the chamber by a Toepler pump. A trap cooled by a slush bath was used to trap the products.

(a) **Preparation of $ClSi_2H_5$.**—Disilane (2.02 mmol) was circulated through the silver chloride chamber (0°) for 5 hr with the product trap cooled to −95°. The reaction mixture was then passed through a series of cold traps. Hydrogen (2.2 mmol) was obtained. The condensate in the −196° trap was disilane (0.013 mmol), identified from an infrared spectrum which also demonstrated that silane and chlorosilane were absent. The condensate in the −112° trap (after several passes through a −78° trap) was chlorodisilane (1.39 mmol). The chlorodisilane was identified from its infrared spectrum[8] and a proton nmr spectrum of a neat sample which consisted of absorptions at −4.78 (-SiH_2Cl) and −3.32 (-SiH_3) ppm of relative intensity 2.0–3.1. Very strong infrared absorptions of dichlorosilane occur at windows in the spectrum of chlorodisilane, and these absorptions were not observed. The condensate in the −78° trap was a dichlorodisilane mixture (0.11 mmol) identified by infrared spectra.

(b) **Preparation of 1,2-Cl_2SiH_4.**—Disilane was circluated through the silver chloride chamber (0°) with the product trap cooled to −78°. The products were then separated by trap to trap distillation. Infrared spectra of the condensates in the −196 and −95° traps indicated that considerable quantities of chloro- and dichlorosilane were produced. In 10-hr runs, about 0.4 mmol of dichlorodisilanes and about 1.3 mmol of chlorodisilane were obtained from 4 mmol of disilane. The ratio of 1,2-$Cl_2Si_2H_4$ to 1,1-Cl_2SiH_4 varied from 2:1 to 1:2. The best yields of the 1,2 derivative were obtained with fresh silver chloride. The 1,2-Cl_2SiH_4 was purified by repeated distillations through a trap cooled to −78° which passed the chlorodisilane, the 1,1-dichlorodisilane, and the chloromonosilanes.

(c) **Identification of 1,2-Dichlorodisilane.**—The identification of 1,2-dichlorodisilane was based on the following facts. (1) The molecular weight obtained by vapor density was 132.4 compared to a calculated molecular weight of 131.1. (2) The proton nmr spectrum of a neat sample consisted of a singlet at −4.61 ppm (this eliminates Cl_3SiH, $ClSi_2H_5$, 1,1-Cl_2SiH_4, and 1,1,2-$Cl_3Si_2H_3$). (3) The infrared spectrum (Table I) was consistent for 1,2-dichlorodisilane. Strong bands from the following molecules were absent: $ClSi_2H_5$, 1,1-Cl_2Si_2H, Cl_2SiH_2, Cl_3SiH, and $SiCl_4$. (4) The mass spectrum (Table II) was consistent with that expected for a dichlorodisilane. The $SiCl_2$ ions may be due to impurities.

(2) **Si_2H_6-HCl Reaction** (over Al_2Cl_6).—The reaction between disilane and hydrogen chloride was carried out in a 1000-ml reaction flask fitted with a Teflon valve and a standard taper joint. Aluminum chloride (2 g) was added to the reactor and sublimed to coat the walls.

(a) **Preparation of 1,1-$Cl_2Si_2H_4$ and 1,1,2-Trichlorodisilane.**—Disilane (8.06 mmol) and hydrogen chloride (25.2 mmol) were condensed onto the aluminum chloride at −196°. After 4 hr at room temperature, the volatile compounds were distilled

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TABLE I

THE INFRARED SPECTRUM OF THE CHLORODISILANES (CM^{-1})

$ClSi_2H_5$	1,1-$Cl_2Si_2H_4$	1,2-$Cl_2Si_2H_4$[b]	1,1,2-$Cl_3Si_2H_3$
2190 s	2193 s[c]	2191 s[c]	2200 s[d]
2178 s	2178 s	2169 s	2192 s[d]
2170 s	~2178 s	929 s	2180 s[d]
~2170 s	2165 s	835 m	930 s
2153 s	925 m	795 vs	838 s
962 sh[a]	878 s	765 vs	820 m
946 m[a]	810 sh	685 w	785 s
936 m[a]	768 vs	578 m	743 s
888 s[a]	690 w	540 s	705 m
878 s[a]	572 s		590 vs
814 vs[a]	540 s		535 vs
801 vs[a]	510 m		
707 w			
560 sh			
552 m			
522 m			

[a] A. D. Craig, J. V. Urenovitch, and A. G. MacDiarmid, *J. Chem. Soc.*, 548 (1962). [b] With point group C_{2h}, one expects only two active bands. [c] P, Q, and R bands were observed. [d] Q branches were observed.

into the vacuum system. Hydrogen (19.5 mmol) was obtained. The other substances were then separated by fractional condensation. The condensate in the −196° trap (4.55 mmol) was hydrogen chloride with a small amount (about 5%) of disilane. The condensate in the −130° trap (1.49 mmol) was identified by infrared analysis to be a near-equimolar mixture of disilane and chlorosilane. The condensate in the −112° trap (0.47 mmol) was a near-equimolar mixture of disilane, chlorosilane, and dichlorosilane identified by an infrared spectrum. The condensate in the −95° trap (2.87 mmol) was identified from an infrared spectrum to be mainly trichlorosilane with some dichlorosilane and 1,1-dichlorodisilane. The condensate in the −78° trap was now distilled from a trap cooled to −63° into a liquid nitrogen trap for 12 hr. Pure 1,1-dichlorodisilane (2.16 mmol) was found in the liquid nitrogen trap. The fraction that remained in the −63° trap was passed through a −45° trap. The condensate in the −63° trap (0.36 mmol) was 1,1,2-trichlorodisilane while the condensate in the −45° trap (0.16 mmol) which passed through a −23° trap was a mixture of 1,1,2,2-tetrachlorodisilane and 1,1,2-trichlorodisilane.

TABLE II

MASS SPECTRA OF THE CHLORODISILANES (HEAVY-ATOM SKELETON, Si AND Cl)

Compound	Ion	Rel intens	Ion	Rel intens
$ClSi_2H_5$	Si	49	SiCl	100
	Cl	38	Si_2Cl	90
	Si_2	44		
1,1-$Cl_2Si_2H_4$	Si	35	Si_2Cl	20
	Cl	91	$SiCl_2$	46
	Si_2	9	Si_2Cl_2	46
	SiCl	100		
1,2-$Cl_2Si_2H_4$	Si	20	Si_2Cl	30
	Cl	100	$SiCl_2$	4
	Si_2	14	Si_2Cl_2	13
	SiCl	53		
1,1,2-$Cl_3Si_2H_3$	Si	43	Si_2Cl	4.8
	Cl	100	$SiCl_2$	31
	Si_2	6.1	Si_2Cl_2	16
	SiCl	72	Si_2Cl_3	7.7

(b) **Identification of 1,1-$Cl_2Si_2H_4$.**—The identification of 1,1-dichlorodisilane was based on the following facts. (1) The molecular weight obtained by vapor density was 135.8 compared to a calculated molecular weight of 131.1. (2) The proton nmr spectrum of a neat sample consisted of a doublet at −2.88 ppm (–SiH_3) and a quartet at −5.19 ppm (–$SiHCl_2$) of relative intensities 3.0–0.95 (this eliminates Cl_3SiH, $ClSi_2H_5$, 1,2-$Cl_2Si_2H_4$, and 1,1,2-$Cl_3Si_2H_3$). (3) The infrared spectrum (Table I) was consistent with that expected for 1,1-dichlorodisilane and the absence of the very strong 630-cm^{-1} absorption of silicon tetrachloride demonstrates the absence of this compound. (4) The mass spectrum (Table II) was consistent with that expected for 1,1-dichlorodisilane.

(c) **Identification of 1,1,2-$Cl_3Si_2H_3$.**—The identification of 1,1,2-trichlorodisilane was based on the following facts. (1) The proton nmr spectrum of a heat sample consisted of a doublet at −4.87 (–SiH_2Cl) and a triplet at −5.60 (–$SiHCl_2$) ppm of relative intensities 2.00–0.97. (2) The infrared spectrum (Table I) was consistent with that expected for 1,1,2-trichlorodisilane (this infrared spectrum eliminates $SiCl_4$ and 1,1-Cl_2SiH_4). (3) The mass spectrum (Table II) was consistent with that expected for 1,1,2-trichlorodisilane.

(d) **Identification of 1,1,2,2-$Cl_4Si_2H_2$.**—The probable identification of 1,1,2,2-tetrachlorodisilane was based on the infrared spectrum of the disilane obtained from an $LiAlD_4$ reduction of a small fraction of the tetrachlorodisilane which was obtained free of trichlorodisilane by repeated fractionations through a −45° trap. The infrared spectrum indicated the mixture to be mainly 1,1,2,2-$D_4Si_2H_2$ with some Si_2D_5H.[9] A strong absorption of 1,1-$H_2Si_2D_4$ was absent.[9]

Results and Discussion

It has been demonstrated that the chlorodisilanes can be prepared from disilane by either of two methods. The first is the reaction with hydrogen chloride over an aluminum chloride catalyst, and the second is a reaction with silver chloride. The latter reaction is best carried out as a flow method below room temperature.

Our results with the silver chloride reaction suggest that the dichlorodisilane formed is primarily (or completely) the 1,2 derivative followed by catalytic conversion to the 1,1 derivative.

It is interesting to note that in the silver chloride reaction very little silicon–silicon bond rupture occurs with the product trap cooled to −95°; but with the trap cooled to −78°, considerable silicon–silicon bond rupture is observed. Thus, as disilane passes silver chloride, no rupture occurs, but as chlorodisilane passes silver chloride, silicon–silicon bond rupture becomes important.

During this work, the trend shown in Table III was noticed. That, is, the weighted average (doubly deenerate frequencies counted twice, etc.) of the gas-phase silicon–hydrogen stretching frequencies increases with the replacement of a hydrogen by a chlorine atom. Since the stretching frequencies are far removed from the bending modes, coupling should be at a minimum and the frequencies should be proportional to the bond force constants. Thus, it appears that the Si–H bond strengths increase from silane to trichlorosilane. The "s" character of the silicon orbital bonded to hydrogen should increase as chlorine replaces other hydrogen atoms.[10] Overlap calculations by Maccoll show that, for carbon, the overlap integrals are in the order sp > sp^2 > sp^3.[11] Further, experimental data are cited by Maccoll to support the validity of his calculations.

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TABLE III

Si–H STRETCHING FREQUENCIES OF SILANES

Compound	ν, cm⁻¹ [a]	Ref
Cl_3SiH	2262	*b*
Cl_2SiH_2	2216	*c*
$ClSiH_3$	2197	*d*
SiH_4	2182	*e*
CH_3SiH_3	2167	*f*
$(CH_3)_2SiH_2$	2143	*g*
$(CH_3)_3SiH$	2125	*c*

[a] Weighted average. [b] N. A. Chumaevskii, *Opt. Spectry.* (U.S.S.R.), **10,** 33 (1961). [c] This paper. [d] C. Newman, J. K. O. Loane, S. R. Polo, and M. K. Wilson, *J. Chem. Phys.*, **25,** 855 (1956). [e] J. H. Meal and M. K. Wilson, *ibid.*, **24,** 385 (1956). [f] R. E. Wilde, *J. Mol. Spectry.*, **8,** 427 (1962). [g] E. A. V. Ebsworth, M. Oynszchuk, and N. Sheppard, *J. Chem. Soc.*, 1453 (1958).

Thus our results suggest that the Si–H bond strength also increases as the per cent "s" character in the silicon orbitals bonded to hydrogen increases when the silicon is close to an sp^3 hybrid. An alternate explanation for the increase in Si–H bond strength from silane to trichlorosilane could be due to an increase in the ionic character of the Si–H bond (this would assume an inversion in the Si–H polarity). However, since the methyl group is electron donating toward silicon compared to hydrogen,[12,13] the ionic approach would predict an increase in the Si–H stretching frequencies going from silane to trimethylsilane. This is not observed. The "s" character approach does predict a decrease in the Si–H stretching frequencies for silane to trimethylsilane which is observed. Therefore, it appears that the Si–H stretching frequencies in monosilanes can be explained on the basis of hybrid character in the Si–H bond and that ionic effects or mass effects (Cl and CH_3) appear to be negligible.

It should be noted that our model only fits the data where the number of halogen substituents changes. For the series $FSiH_3$, $ClSiH_3$, $BrSiH_3$, and $ISiH_3$ the averaged frequencies are (in cm⁻¹) 2199,[14] 2197,[14] 2197,[14] and 2201.[15] Our model would predict that these frequencies should follow the electronegativities of the halogen.

If one examines the weighted average of the germanium–hydrogen stretching frequencies in the chloro- or methylgermanes[16–20] or the tin–hydrogen stretching frequencies in the methylstannanes,[19–21] one finds the same trends as seen in Table III. Thus, the E–H (E = Si, Ge, or Sn) stretching frequencies are easily correlated with the hybridization of the central atom orbitals bonded to hydrogen.

For methane and the chloromethanes the weighted averages of the carbon–hydrogen stretching frequencies follow the same pattern as in Table III except that the weighted average for methyl chloride is slightly out of line.[22]

The weighted averages of the silicon–hydrogen stretching frequencies for a number of chloro- and methyldisilanes are listed in Table IV. It is apparent that these averaged frequencies can be correlated with the predicted hybridization changes of the silicon orbitals bonded to hydrogen.

TABLE IV

Si–H STRETCHING FREQUENCIES OF DISILANES

Compound	ν, cm⁻¹	Ref
1,1,2,2-$Cl_4Si_2H_2$	2200[a]	*d*
1,1,2-$Cl_3Si_2H_3$	2191[b]	*d*
1,1-$Cl_2Si_2H_4$	2179[b]	*d*
1,2-$Cl_2Si_2H_4$	2180[a]	*d*
$ClSi_2H_5$	2172[b]	*d*
Si_2H_6	2159[b]	*e*
$CH_3Si_2H_5$	2160[c]	*f*
1,2-$(CH_3)_2Si_2H_4$	2150[c]	*g*
1,1-$(CH_3)_2Si_2H_4$	2140[b]	*h*
1,1,2,2-$(CH_3)_4Si_2H_2$	2102[a]	*i*
$(CH_3)_5Si_2H$	2090[b]	*i*

[a] Weighted average (half of bands). [b] Weighted average (all bands). [c] Observed absorption. [d] This paper. [e] G. W. Bethke and M. K. Wilson, *J. Chem. Phys.*, **26,** 1107 (1957). [f] M. Abedini and A. G. MacDiarmid, *Inorg. Chem.*, **5,** 2040 (1966). [g] A. D. Craig and A. G. MacDiarmid, *J. Inorg. Nucl. Chem.*, **24,** 161 (1962). [h] W. M. Ingle, M.S. Thesis, San Diego State College, 1966. [i] J. V. Urenovitch and R. West, *J. Organometal. Chem.* (Amsterdam), **3,** 138 (1965).

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