Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

CHLORAMINOSILANES
II*. PREPARATION AND SPECTROSCOPIC STUDIES ON ALKYL(DIMETHYLAMINO)CHLOROSILANES**

S. S. WASHBURNE AND W. R. PETERSON, JR.
Department of Chemistry, Temple University of the Commonwealth System of Higher Education, Philadelphia, Pennsylvania 19122 (U.S.A.)

(Received May 15th, 1969; in revised form September 2nd, 1969)

SUMMARY

Several new compounds containing both chloro and dimethylamino groups linked to silicon have been prepared. The general method involved reacting a solution of the appropriate polychlorosilane in ether at *ca.* − 50° with a chilled ethereal solution of dimethylamine. Prepared in this fashion were $CH_3Si(NMe_2)Cl_2$, $CH_3Si(NMe_2)_2Cl$, $PhSi(NMe_2)Cl_2$, $PhSi(NMe_2)_2Cl$, $CH_3(H)Si(NMe_2)Cl$, $(CH_3)_2Si(NMe_2)Cl$, $CH_2{=}CH(CH_3)Si(NMe_2)Cl$, and $Ph_2Si(NMe_2)Cl$. Comparison of the spectra of these compounds with those in the perhalo and peramine series showed that replacement of NMe_2 for Cl resulted in an upfield shift of the resonances of the other groups linked to silicon, a shift which parallels that observed upon substitution of CH_3 for Cl. The relationship of ν(Si–H) in the IR and δ(Si–H) in the NMR spectra was linear.

INTRODUCTION

While silicon–nitrogen chemistry has been a field of vigorous interest for many years[1-3], compounds containing both chloro- and amino-functionality have been neglected. Studies have shown that compounds Cl_3SiNR_2, $Cl_2Si(NR_2)_2$, and $ClSi(NR_2)_3$ can be isolated only when extreme precautions against atmospheric moisture are employed[4,5]. Tansjö reported compounds of the general formula $R'Si(NR_2)_2Cl$ and $R'Si(NR_2)Cl_2$ with R′ = Et, Pr, prepared by treatment of alkyltrihalosilane with various primary and secondary amines[6], while Wannagat and Schreiner[7] prepared (monoalkylamino)- and (dialkylamino)-dimethylchlorosilanes from dimethyldichlorosilane and the appropriate amine in petroleum ether. We have previously reported that reaction of dimethylamine with $HSiCl_3$ leads to $HSi(NMe_2)Cl_2$, $HSi(NMe_2)_2Cl$, and $HSi(NMe_2)_3$ (ref. 8).

Chloraminosilanes are difficult to work with because of their extreme sensitivity towards atmospheric moisture[7], this sensitivity varying roughly inversely

---

* For part I see ref. 8.

** Presented in part at the 4th Mid-Atlantic Regional Meeting, American Chemical Society, Washington, D.C., February 12–15, 1969.

with the molecular weight. Although they did not isolate the compounds, Van Wazer and Moedritzer studied (dimethylamino)dimethylchlorosilane, bis(dimethylamino)-methylchlorosilane, and (dimethylamino)methyldichlorosilane as part of a program measuring the exchange of functional groups at organometallic centers[9]. When bis-(dimethylamino)dimethylsilane and dimethyldichlorosilane are mixed, equilibrium is established within three minutes. The equilibrium constant for the reaction

$$Me_2Si(NMe_2)_2+Me_2SiCl_2 \xrightarrow{25^\circ} 2\ Me_2Si(NMe_2)Cl \qquad K_{eq}=6000$$

is such that the mixed species is tremendously favored.

A similar situation was observed in the $MeSiX_3$ series. Most of the other functional group exchanges studied by the Monsanto group showed behavior much closer to randomness.

EXPERIMENTAL

All experiments involving organosilicon compounds were carried out under a blanket of dry nitrogen in dried glassware. Ether was distilled from lithium aluminum hydride, petroleum ether from sodium metal. Experiments using commercial anhydrous grades of solvents usually gave lowered yield. Dimethylamine was Eastman White Label grade used as obtained. Chlorosilanes, purchased from various sources, were distilled before use. Nuclear magnetic resonance spectra (NMR) were determined as *ca.* 20% solutions in deuteriochloroform or carbon tetrachloride containing 2% tetramethylsilane as internal standard on a Varian Associates Model A60A spectrometer. Infrared spectra (IR) were determined as neat liquids on a Perkin–Elmer Model 21 spectrophotometer. Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. and by Mr. I. Pye, Pitman–Dunn Research Laboratories, Frankford Arsenal, Philadelphia, Pennsylvania using a F&M Model 182 CHN Analyser.

(Dimethylamino)phenyldichlorosilane

This procedure illustrates the general method for preparation of Cl–Si–N compounds. In a three-necked, 1-liter flask equipped with condenser, addition funnel, and paddle stirrer were placed 44.6 g (0.2 mole) of phenyltrichlorosilane and 450 ml of ether. The solution was cooled to −50° in a dry-ice/acetone bath and treated with a solution of 18.1 g (0.4 mole) of dimethylamine in 150 ml of ether over a thirty min period, causing formation of a voluminous precipitate of dimethylamine hydrochloride. Filtration under a positive pressure of nitrogen with a filter-stick gave a clear, colorless filtrate which was combined with the ether washings of the amine salts (200 ml), concentrated to *ca.* 50 ml by distillation at atmospheric pressure, transferred to a small distillation flask, and fractionated with 10 cm Vigreux column. The yield of (dimethylamino)phenyldichlorosilane, a clear, colorless liquid, b.p. 118–121° (25 mm), was 33.0 g (75%). It fumed violently on contact with air. An identical reaction employing petroleum ether as solvent afforded 29.7 g (68%) of product. (Found: C, 43.10; H, 5.91; N, 6.01. $C_8H_{11}Cl_2NSi$ calcd.: C, 43.64; H, 5.04; N, 6.36%.)

Table 1 lists compounds prepared in analogous fashion. Two equivalents of

TABLE 1

SILICON–NITROGEN COMPOUNDS PREPARED

Chlorosilane	Product	Yield (%)	B.p. [°C(mm)]	Analysis, found (calcd.) (%)		
				C	H	N
$CH_3(H)SiCl_2$	$CH_3(H)Si(NMe_2)Cl$	69	85–87 (767)	29.30 (29.12)	8.20 (8.15)	11.30 (11.38)
CH_3SiCl_3	$CH_3Si(NMe_2)Cl_2$	85	52–53 (45)	22.50 (22.79)	5.19 (5.74)	8.75 (8.86)
CH_3SiCl_3	$CH_3Si(NMe_2)_2Cl$	60	56–57 (25)	36.13 (36.02)	8.90 (9.07)	16.71 (16.80)
$CH_3(CH_2{=}CH)SiCl_2$	$CH_3(CH_2{=}CH)Si(NMe_2)Cl$	80	128–130 (765)	40.18 (40.12)	7.76 (8.08)	9.56 (9.36)
$(CH_3)_2SiCl_2$	$(CH_3)_2Si(NMe_2)Cl$	67	105 (765)	35.89 (34.88)	8.90 (8.79)	10.26 (10.17)
$C_6H_5SiCl_3$	$C_6H_5Si(NMe_2)Cl_2$	75	118–121 (25)	43.10 (43.64)	5.91 (5.04)	6.01 (6.36)
$C_6H_5SiCl_3$	$C_6H_5Si(NMe_2)_2Cl$	63	127–129 (23)	52.40 (52.49)	7.01 (7.49)	12.12 (12.25)
$(C_6H_5)_2SiCl_2$	$(C_6H_5)_2Si(NMe_2)Cl$	67	137 (1.0)	64.00 (64.22)	6.01 (6.16)	5.00 (5.35)
$CH_3(H)SiCl_2$	$CH_3(H)Si(NMe_2)_2$	75	112–113 (767)	45.39 (45.40)	12.07 (12.19)	21.50 (21.18)
CH_3SiCl_3	$CH_3Si(NMe_2)_3$[a]	83	64.5–65 (25)	47.50 (47.95)	12.00 (12.07)	23.80 (23.96)
$(CH_3)_2SiCl_2$	$(CH_3)_2Si(NMe_2)_2$[a]	66	124–127 (760)			
$CH_3(CH_2{=}CH)SiCl_2$	$CH_3(CH_2{=}CH)Si(NMe_2)_2$	66	147 (771)	53.00 (53.10)	10.98 (11.46)	17.81 (17.70)
$C_6H_5SiCl_3$	$C_6H_5Si(NMe_2)_3$	61	143–144 (32)	60.59 (60.71)	9.70 (9.76)	17.73 (17.70)
$(C_6H_5)_2SiCl_2$	$(C_6H_5)_2Si(NMe_2)_2$	76	138–140 (1.9)	71.10 (71.05)	8.20 (8.20)	10.14 (10.36)

[a] Ref. 4.

Me_2NH were used for each Si–Cl bond to be replaced. Inverse addition was employed for the preparation of completely aminated silanes.

Bis(N,N-dimethyldithiocarbamato)diphenylsilane, $(C_6H_5)_2Si[SC(S)NMe_2]_2$

A 50 ml Erlenmeyer flask with a no-air stopper was charged with 25 mmoles of bis(dimethylamino)diphenylsilane, 25 ml of carbon tetrachloride, and 8.4 g (100 mmoles) of carbon disulfide. The mixture was allowed to stand three days at 25°, during which time it slowly precipitated colorless prisms of bis(*N*,*N*-dimethyldithiocarbamato)diphenylsilane which when filtered, washed with CCl_4, and dried in a stream of nitrogen, had m.p. 120–121°. (Found: C, 51.04; H, 5.07; N, 6.16. $C_{18}H_{22}N_2S_4Si$ calcd.: C, 51.13; H, 5.24; N, 6.65%.) A similar reaction with bis(dimethylamino)methylvinylsilane gave no precipitate after 5 days standing at 25°; however, pale yellow clusters were isolated by chilling the mixture to 0° and filtering. By elemental analysis these wide melting crystals appeared to be a mixture of $CH_3(CH_2{=}CH)Si(NMe_2)SC(S)NMe_2$ and $CH_3(CH_2{=}CH)Si[SC(S)NMe_2]_2$.

RESULTS AND DISCUSSION

All of the chloro-amino and poly-amino silanes produced in this study were colorless liquids of exceedingly high reactivity towards atmospheric moisture. Those containing both chlorine and dimethylamino groups bonded to silicon fumed violently when exposed to the atmosphere. Those with only amine groups did not fume, but were apparently hydrolysing, for the odor of dimethylamine was always present upon opening bottles. Somewhat surprisingly, Cl–Si–NMe_2 compounds appeared more reactive than corresponding Cl–Si–Cl compounds. In the absence of atmospheric moisture, chloraminosilanes are apparently quite stable, for a sample of $HSi(NMe_2)_2Cl$[8] sealed in an NMR tube under N_2 showed essentially no change in the spectrum over a period of nine months.

Table 2 lists pertinent IR and NMR spectral parameters for compounds prepared in this study. It is of interest to examine progressive changes in the NMR spectra as chlorine is replaced by dimethylamino in a series $RSiX_3$ or R_2SiX_2. As can be seen from a cursory examination of Table 2, progressive replacement of chlorine by dimethylamino causes an upfield shift of all NMR resonances, including those of the dimethylamino group. The spectroscopic effect of the dimethylamino group is almost identical with that of the methyl group, *i.e.*, the methyl group of tris(dimethylamino)methylsilane resonates at −0.03 ppm while tetramethylsilane is at 0.00; methyl(dimethylamino)dichlorosilane resonates at 0.76 ppm while dimethyldichlorosilane is at 0.77 ppm. Since in the carbon series protons α to nitrogen are shifted downfield relative to those α to a methyl group, presumably via inductive withdrawal of electron density by nitrogen, the apparent spectroscopic equivalence of methyl and dimethylamino in the silicon series provides further confirmation of the

TABLE 2

Compound	NMR resonances (ppm downfield from TMS, δ)[a]					IR frequencies
	CH_3–Si	H–Si	CH_3–N	C_6H_5–Si	CH_2=CH–Si	(cm^{-1})
$MeHSi(NMe_2)Cl$	0.50 d	5.01 q	2.58			2190, 1262, 1002
$MeHSi(NMe_2)_2$	0.04 d	4.31 q	2.47			2125, 1256, 991
$MeSi(NMe_2)Cl_2$	0.76		2.59			1270, 1172, 997
$MeSi(NMe_2)_2Cl$	0.35		2.50			1263, 1173, 994
$MeSi(NMe_2)_3$	−0.03		2.42			1258, 1183, 986
$Me_2Si(NMe_2)Cl$	0.43		2.45			1292, 995
$Me_2Si(NMe_2)_2$	−0.03		2.34			1288, 983
$Me(CH_2{=}CH)Si(NMe_2)Cl$	0.48		2.54		6.15 s	1262, 1172, 995
$Me(CH_2{=}CH)Si(NMe_2)_2$	0.04		2.45		5.81–5.94 m	1255, 1178, 985
$PhSi(NMe_2)Cl_2$			2.59	7.2–7.9		1302, 1120, 997
$PhSi(NMe_2)_2Cl$			2.54	7.2–7.8		1298, 1118, 995
$PhSi(NMe_2)_3$			2.54	7.2–7.75		1292, 1117, 994
$Ph_2Si(NMe_2)Cl$			2.58	7.2–7.9		1438, 1165, 994
$Ph_2Si(NMe_2)_2$			2.45	7.2–7.9		1434, 1165, 993

[a] s, singlet; d, doublet; q, quartet; m, multiplet.

ability of nitrogen to donate electrons to silicon through a d_π–p_π interaction*. This effect appears to be additive, for successive replacement of one, two, and three of the chlorines of methyltrichlorosilane by dimethylamino gives incremental upfield shifts of 36, 31, and 38 Hz in the methyl resonance.

Comparison can be made of the relationship of NMR and IR absorption frequencies of substituents on silicon. Webster[11] found a linear relationship for trisubstituted Si–H compounds which did not contain phenyl groups. An upfield shift of the NMR resonance was accompanied by a shift to longer wavelength in the IR. Fig. 1 shows the relationship of ν(Si–H) in the IR and δ(Si–H) in the NMR for

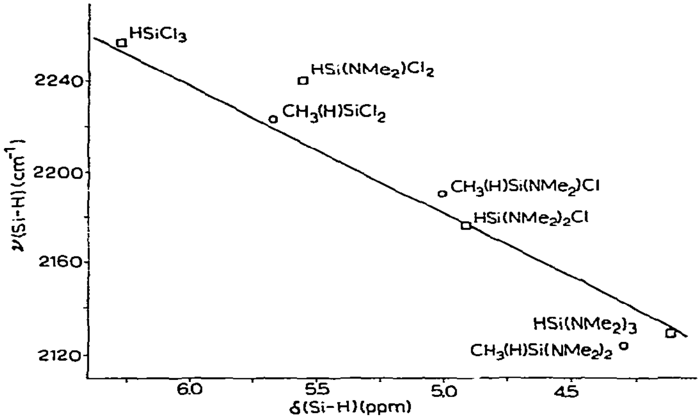
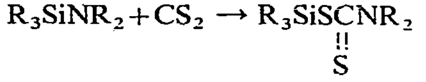


Fig. 1. The relationship of IR and NMR absorptions of chloraminosilanes. The correlation line is that of Webster, ref. 11.

compounds of the $CH_3(H)SiX_2$ and $HSiX_3$ series[8], X = Cl or NMe_2, and the correlation line of Webster[11]. This implies that the chemical shift and stretching frequency of the Si–H proton are affected by similar factors.

We studied the reactions of aminosilanes with CS_2. Si–NR_2 compounds are known to react smoothly with CS_2 to form dithiocarbamates[12].



$$R_3SiNR_2 + CS_2 \rightarrow R_3SiS\underset{\underset{S}{\|}}{C}NR_2$$

We found that $Ph_2Si(NMe_2)_2$ reacted with CS_2 to give $Ph_2Si[SC(S)NMe_2]_2$, but $CH_2{=}CH(CH_3)Si(NMe_2)_2$ gave a mixture of mono- and bis-dithiocarbamate derivatives. In the $RSi(NMe_2)_3$ series, R = H, CH_3, Ph, reaction with CS_2 was observed (formation of crystals or yellowing of the solutions), the rate of which appeared to be inversely proportional to the size of the R group, but the products were not simple; their structures will be the subject of a future communication.

In accord with the finding that the reaction of Me_3SiNMe_2 with CS_2 was inhibited by added Me_3SiCl[12], we found that reaction of CS_2 with chloraminosilanes was sluggish and ill-defined.

---

* See *e.g.* ref. 10.

Study of the bonding in Cl–Si–N compounds, with particular emphasis upon the nature of $\mathrm{N{\overset{\pm}{=}}Si{=}Cl^{-}}$ interactions, is under active investigation in these laboratories.

REFERENCES

1 R. Fessenden and J. S. Fessenden, *Chem. Rev.*, 61 (1960) 361.
2 W. Fink, *Angew. Chem. Int. Ed. Engl.*, 5 (1966) 760.
3 B. J. Aylett, *Organometal. Chem. Rev.*, *A*, 3 (1968) 151.
4 H. Breederveld and H. I. Waterman, *Research (London)*, 5 (1952) 537.
5 W. R. Peterson, Jr., unpublished work.
6 L. Tansjö, *Acta Chem. Scand.*, 11 (1957) 1613; 13 (1959) 35.
7 U. Wannagat and G. Schreiner, *Monatsh. Chem.*, 96 (1965) 1889.
8 S. S. Washburne and W. R. Peterson, Jr., *Inorg. Nucl. Chem. Lett.*, 5 (1969) 17.
9 K. Moedritzer, *Advan. Organometal. Chem.*, 6 (1968) 171, and references therein.
10 V. Chvalovsky, *Pure Appl. Chem.*, 13 (1966) 231.
11 D. E. Webster, *J. Chem. Soc.*, (1960) 5132.
12 H. Breederveld, *Recl. Trav. Chim. Pays-Bas*, 81 (1962) 276.