Anal. Calcd. for $C_9H_{11}O_4NS$: C, 47.15; H, 4.84. Found: C, 47.36; H, 4.97.

(B).—To a solution of 2.74 g. (0.049 mole) of potassium hydroxide in 35 ml. of absolute ethanol, 6.21 g. (0.050 mole), of *p*-thiocresol was added. The mixture was cooled to 0° and a solution of 4.4 ml. (0.050 mole) of 1-chloro-1-nitroethane in 15 ml. of absolute ethanol at 0° was added. The mixture was set aside at 0° for 15 hours, then filtered, yielding 2.10 g. of potassium chloride. Dilution of the filtrate with 200 ml. of water precipitated 6 g. of an oil. Oxidation of the oil with hydrogen peroxide in glacial acetic acid, as above, gave a 15% yield of the same sulfone (affirmed by physical appearance, alkali solubility, melting point and mixed melting point) as resulted by oxidation of the product obtained *via* *p*-toluenesulfenyl chloride and 1-chloro-1-nitroethane. The low yield of sulfone is associated with the presence of considerable *p*-tolyl disulfide in the oily product subjected to oxidation. The disulfide was separated and its identity confirmed by melting point and mixed melting point with authentic *p*-tolyl disulfide.

(C).—α-Nitroethyl *p*-tolyl sulfone also resulted (71% yield) by interaction of 7.06 g. (0.033 mole) of sodium *p*-toluenesulfinate dihydrate with 2.19 ml. (0.025 mole) of 1-chloro-1-nitroethane in methanol (75 ml), at reflux temperature for three hours. The crystalline product was obtained by collecting the precipitated sodium chloride and removing excess solvent. It was identical (solubility in alkali, melting point and mixed melting point) with the sulfone obtained by methods (A) and (B) above.

LOS ANGELES, CALIFORNIA RECEIVED APRIL 6, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Preparation of Aminomethylsilicon Compounds and their Derivatives

BY JOHN E. NOLL,[1] JOHN L. SPEIER[2] AND B. F. DAUBERT

The reaction of various chloro- and bromomethylsilicon compounds with amines and ammonia to prepare aminomethylsilane derivatives is described. The quantitative removal of one methyl group from trimethylsilylmethylamines by sodium amide in ammonia to form N-methyl-(trimethylsilyl)-amine is demonstrated. Some twenty-three new silicon-containing amines are described along with their derivatives.

In continuation of the work in these laboratories aimed at a determination of the effect of organosilicon substituents on organic functional compounds, a series of amines has been prepared containing the linkages Si–C–N with alkyl, alkoxy, oxy and aryl groups on the silicon atoms and hydrogen, alkyl and aryl groups attached to the nitrogen atoms.

The most convenient method for the preparation of moderately large quantities of such amines was found to consist of treating anhydrous ammonia or amines with compounds of the formula R_3SiCH_2X, where R was any combination of alkyl, aryl, alkoxy or siloxy groups and X was chlorine or bromine. Solvents neither were necessary nor showed any advantages as a medium for the reaction. Water and alcohol were found to promote the cleavage of the halomethyl group from silicon and were therefore avoided.[3]

The reactions were generally carried out with about a 20-fold excess of ammonia or a two- to threefold excess of amine at temperatures of from 60 to 120° under pressure when necessary.

Halomethylsilanes with approximately a 20-fold excess of liquid ammonia usually formed about 50–70% primary amine, 20–30% secondary amine and a small amount of unstable material which probably was tertiary amine. Compounds of the type $(R_3SiCH_2)_3N$ were never isolated and identified as such. Repeated efforts to isolate such products led only to the production of very unstable and reactive materials which vigorously decomposed when heated and which reacted rapidly with the atmosphere to form an unstable solid of variable composition. A product thought to have been tris-(trimethylsilylmethyl)-amine was spilled upon a piece of paper and found to cause its spontaneous ignition a few seconds later.

The amines also reacted with halomethylsilanes. A two- to threefold excess of primary amine usually resulted in from 50–88% of secondary amines of the formula R_3SiCH_2NHR', with the remainder usually accounted for approximately as tertiary amines, $(R_3SiCH_2)_2NR$. Secondary amines yielded tertiary amines and probably quaternary salts. Tertiary amines reacted very sluggishly to yield quaternary salts. Ethanolamine resulted in the formation chiefly of N-methylethanolamine indicating that the halomethyl group was cleaved from the silicon.

A most interesting cleavage of a chloromethyl group occurred when chloromethyltrimethylsilane reacted with sodium amide in liquid ammonia. Cleavage and rearrangement appeared to be almost instantaneous with the formation of N-methyl-(trimethylsilyl)-amine. This product on distillation eliminated methylamine and formed N-methylhexamethyldisilazane in excellent yield. These reactions might be represented according to the equations

$$Me_3SiCH_2Cl + NaNH_2 \longrightarrow Me_3SiNHMe + NaCl$$
$$2Me_3SiNHMe \longrightarrow (Me_3Si)_2NMe + MeNH_2$$

The preparation of amines containing the linkages Si–O–Si–C–N– was effected in three different ways. First, and least successful, bis-(chloromethyl)-tetramethyldisiloxane was treated with ammonia or an amine. The difunctionality of the bis-chloromethyl compound led to the production of a mixture of products that could not be satisfactorily separated. The second method was more successful. It consisted of the hydrolysis of an alkoxysilylmethylamine in aqueous or aqueous alcoholic solution. Siloxane-methylamines were easily obtained. Methyldiethoxysilylmethylamine yielded a thermoplastic polymer, soluble in water, which reacted rapidly in air to form what appeared to be a bicarbonate salt. Triethoxysilylmethylamine yielded a white amorphous powder, which was water soluble.

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[1] Submitted in partial fulfillment of the requirements for the degree of M.Sc.

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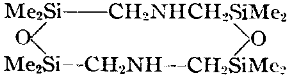
[3] R. H. Krieble and J. R. Elliott, THIS JOURNAL, **67**, 1810 (1945).

TABLE I: REACTION PRODUCTS OF HALOMETHYLSILANES AND AMMONIA

	Name of compound	Formula	Yield, %	B.p.,		n^{25}D	d^{25}_4	Sp. ref.		Element	Analyses, %	
				°C.	Mm.			Found	Calcd.[3]		Found	Calcd.
										MW[a]	102.5, 104.3	103.2
1	Trimethylsilylmethylamine	$Me_3SiCH_2NH_2$	50	93.0	736.8	1.4139	0.7646	0.3268	0.3270	NE	105.3, 105.0	103.2
	Water azeotrope			83	750	1.4161	.815			NE	119.8, 120.1	
	Hydrochloride	$Me_3SiCH_2NH_2 \cdot HCl$		M.p. 240-241						Si	20.21, 20.24	20.09
										C	34.95, 35.17	34.41
										H	10.21, 10.16	10.12
										N	9.53, 9.82	10.03
										Cl	25.36, 25.42	24.38
	Bicarbonate	$Me_3SiCH_2NH_2 \cdot H_2CO_3$		Sublimes at room temp.						Si	17.0	17.0
										NE	163	165
	Sulfate			M.p. 213-216 (dec.)						SO_4	32.38	32.22
	p-Nitrobenzamide	$Me_3SiCH_2NHCOC_6H_4NO_2$-*p*		M.p. 123.5-124						Si	11.16	11.12
										C	52.69	52.36
										H	6.26	6.39
										N	11.35	11.10
2	Bis-(trimethylsilylmethyl)-amine	$(Me_3SiCH_2)_2NH$	19	170.5	736.8	1.4217	.773	.3286	.3277	Si	29.1, 29.2	29.63
										NE	190.0	189.4
	Hydrochloride[c]			M.p. 158.5-159						Si	24.6	24.8
										Cl	15.3, 15.4	15.7
3	Dimethylphenylsilylmethylamine	$C_6H_5SiMe_2CH_2NH_2$	68	226.5	744.1	1.5202	.940	.3235	.3241	Si	16.76, 16.74	16.98
										NE	169.6, 170.5	165.3
	Hydrochloride			M.p. 198 200						Cl	17.66, 17.53	17.54
4	Bis-(dimethylphenylsilylmethyl)-amine	$(C_6H_5SiMe_2CH_2)_2NH$	28	215.2	23	1.5332	.958	.3239	.3244	Si	17.91, 17.73	17.90
										NE	320, 323	313.5
	Hydrochloride			M.p. 121-126						Cl	9.73, 9.73	10.13
5	Ethoxydimethylsilylmethylamine	$EtOSiMe_2CH_2NH_2$	37	131.8	740	1.411	.849	.292	.2938	Si	19.0, 19.4	21.06
										NE	144.3, 144.8	133.2
	Hydrochloride			M.p. 183-187						Cl	21.01, 20.86	20.92
6	Tetramethyldisiloxane-1,3-bismethylamine	$O[SiMe_2CH_2NH_2]_2$										
	Dihydrochloride			M.p. 247-249						Si	21.2	21.15
										Cl	26.68, 26.69	26.73
7	Bis-(ethoxydimethylsilylmethyl)amine	$(EtOSiMe_2CH_2)_2NH$	37	160-170	24	1.433	.892	.292	.2920	Si	22.8, 22.7	22.5
8		$(Me_2SiCH_2NHCH_2SiMe_2O)_x$	100			1.4488	.946			Si	32.01, 32.18	32.10
9	2,2,6,6,8,8,12,12-Octamethyl-1,7-oxa-2,6,8,12-sila-4,10-azacyclododecane									NE	175.7	175.33
				152	23	M.p. 45-49				MW[b]	359	351
10	Diethoxymethylsilylmethylamine	$(EtO)_2SiMeCH_2NH_2$	50	67.5	24	1.4120-6	.914-6	.272	.2697	Si	16.93, 16.90	17.06
										NE	165.5, 165.8	163.4
11	Triethoxysilylmethylamine	$(EtO)_3SiCH_2NH_2$	51	93	26	1.4080	.955	.2583	.2583	Si	14.48, 14.52	14.52
										NE	197, 196.7	193.3
12	Bis-(triethoxysilylmethyl)-amine	$[(EtO)_3SiCH_2]_2NH$	25	117	0.4	1.4132	.973	.2563	.2555	Si	15.35, 15.41	15.18
										NE	383.4, 364.1	369.6

[a] Molecular weight determined cryoscopically in benzene. [b] Molecular weight determined ebulliometrically in benzene. [c] Bis-(trimethylsilylmethyl)-amine hydrochloride exists in at least two forms. As usually obtained from acid solutions, it formed very fine platelets m.p. 158.5–159°. By precipitation of the amine from petroleum ether with dry hydrogen chloride, it was obtained in the form of thick rods with sharp edges, m.p. 175.5–176°. If the 159° form was maintained at 160° for a time, it resolidified at this temperature and then approached the m.p. of 176°. A mechanical mixture of the 159° form and the 176° form also melted always at 164°. The 176° form after standing at room temperature several days melted at 164° but did not change in appearance.

The ethoxysilylmethylamines are surprisingly resistant to hydrolysis in acidic media. In one case, ethoxydimethylsilylmethylamine hydrochloride was made by evaporating to dryness a solution of the amine in aqueous hydrochloric acid.

A third procedure utilized a reaction recently discovered by L. H. Sommer and co-workers at Pennsylvania State College who noted that under proper conditions concentrated sulfuric acid was capable of cleaving only one methyl group from certain trimethylsilyl-organic structures.[4] This process was easily carried out. A compound of the type Me_3Si–CH_2–NR_2, where R could be another Me_3SiCH_2, H or alkyl group, was dissolved in excess sulfuric acid and heated to 100–111° for 6 to 36 hours. Exactly one molar equivalent of methane was evolved for each trimethylsilylmethyl group present. Treatment of the sulfuric acid solution with alkali then freed a siloxane-methylamine in nearly quantitative yields.

By these various procedures the compounds listed in Table I and II were prepared. The basic dissociation constants of the amines have been determined and will be the subject of a forthcoming publication.

In these tables the calculated specific refractions were obtained by the use of Warrick's data.[5] The neutral equivalents were determined to the methyl red end-point.

Experimental

The examples that follow illustrate the general methods used to prepare the amines of Tables I and II.

Reaction of Chloromethyldimethylphenylsilane and Ammonia.—Chloromethyldimethylphenylsilane was prepared from chloromethyldimethylchlorosilane[1] and phenylmagnesium bromide in ether in a yield of 77%. The following properties were determined: b.p. 121° at 24 mm., n^{25}_{D} 1.5186, d^{25}_4 1.023; sp. ref. 0.2965, calcd.[5] sp. ref. 0.2974. *Anal.* Calcd. for $C_9H_{13}ClSi$: Si, 15.19. Found: Si, 15.08, 15.13.

Chloromethyldimethylphenylsilane (193 g., 1.05 moles) was heated in an autoclave with liquid ammonia (425 g., 25 moles) to 103° over a two-hour period and cooled slowly to 25°. The excess ammonia was permitted to escape and the non-volatile residue was mixed with 52 g. of sodium hydroxide in 300 cc. of water. The water insoluble layer was separated, dried over anhydrous Na_2SO_4 and distilled in a still of about ten plates to give 68% yield (126 ml.) of dimethylphenylsilylmethylamine and 28% yield (48 ml.) of bis-(dimethylphenylsilylmethyl)-amine.

Chloromethyltriethoxysilane and Ammonia.—Methyltrichlorosilane was chlorinated in the liquid phase to yield chloromethyltrichlorosilane b.p. 118°. *Anal.* Calcd. for CH_2Cl_4Si: titratable Cl, 57.7. Found: Cl, 56.3. Ethoxylation of this yielded chloromethyltriethoxysilane, b.p. 91° at 25 mm., n^{25}_{D} 1.4065, d^{25}_4 1.022; sp. ref. 0.2406, calcd.[5] sp. ref. 0.2411. *Anal.* Calcd. for $C_7H_{17}O_3ClSi$: Si, 13.16. Found: Si, 13.21, 13.17.

Chloromethyltriethoxysilane (326 g., 1.53 moles) was heated in an autoclave with liquid ammonia (572 g., 33.7 moles) between 100 and 120° for six hours. The excess ammonia was released. The products were shaken with benzene and filtered free of salts. The filtrate was distilled in a still of about ten plates to give 51% yield (157 ml.) of triethoxysilylmethylamine and 25% yield (74 ml.) of bis-(triethoxysilylmethyl)-amine. Both of these compounds hydrolyze on exposure to moisture to form a silica-like material.

Chloromethyltrimethylsilane and Cyclohexylamine.—Chloromethyltrimethylsilane[6] (61 g., 0.5 mole) was mixed with cyclohexylamine (149 g., 1.5 moles) and heated to reflux. The reflux temperature rose slowly from 97 to 133° during four hours of heating. A large amount of crystalline precipitate, m.p. 200–201°, formed, which was identified as cyclohexylamine hydrochloride, m.p. 206–207°, by a mixed melting point. The reaction mixture was made strongly alkaline with 15% aqueous potassium hydroxide and extracted with benzene. The benzene solution was dried and distilled in a still of about ten plates to give a 90% yield (99 ml.) of N-cyclohexyl-(trimethylsilylmethyl)-amine.

By a similar procedure using aniline, N-(trimethylsilylmethyl)-aniline was obtained. This was hydrogenated over a Raney nickel catalyst without difficulty and yielded N-cyclohexyl-(trimethylsilylmethyl)-amine identical to the above.

Reaction of Trimethylsilylmethylamines with Sulfuric Acid. N,N′-Dicyclohexyl-(tetramethyldisiloxane)-1,3-bismethylamine.—N-Cyclohexyl-(trimethylsilylmethyl)-amine (10.47 g., 0.0565 mole) was dissolved in 27 ml. of concentrated sulfuric acid in a flask connected to a 2000-ml. gas buret and heated at about 100° for 6.5 hours. After this time no further evolution of gas was detectable. The volume of gas corrected to standard conditions corresponded to 0.0561 mole. This is very closely stoichiometric to the quantity of amine used. The reaction that occurred is given by the equation

$$Me_3SiCH_2NHC_6H_{11} + H_2SO_4 \longrightarrow HOSO_3SiMe_2CH_2NHC_6H_{11} + CH_4$$

The sulfuric acid solution was diluted with ice, made alkaline with sodium hydroxide, and extracted with ether. The ether layer was acidified with dry hydrogen chloride gas and yielded N,N′-dicyclohexyl-(tetramethyldisiloxane)-1,3-bismethylamine dihydrochloride (12.5 g., 89%).

This dihydrochloride (9 g.) was shaken with 25 ml. of 10% sodium hydroxide solution and extracted with ether. Evaporation of the ether solution after drying over sodium carbonate yielded N,N′-dicyclohexyl-(tetramethyldisiloxane)-1,3-bismethylamine (6.4 g., 80% yield). N-Cyclohexyl-(ethoxydimethylsilylmethyl)-amine in aqueous alcohol yielded a product of the same properties.

Bis-(trimethylsilylmethyl)-amine and Sulfuric Acid.—Bis-(trimethylsilylmethyl)-amine (5.55 g., 0.0293 mole) was dissolved in 26 ml. of concentrated sulfuric acid to which 1.5 ml. of 30% fuming sulfuric acid had been added. The mixture was heated to 100°. Reaction was quite rapid, in this case being 80% complete in one hour. The volume of methane corrected to standard conditions corresponded to 0.0600 mole after six hours. No more was produced on further heating. The close agreement between the moles of methane produced and the equivalents of Me_3SiCH_2-groups, indicates that this reaction might well be adapted for the quantitative estimation of Me_3SiCH_2-groups in various compounds.

The same process was applied to 67.5 g. of bis-(trimethylsilylmethyl)-amine at 95–105° for nine hours. The sulfuric acid solution was then poured upon chipped ice. It formed a solid white mass of crystals. The mass was sucked as dry as possible on a suction filter, washed twice with water and finally twice with boiling methanol. After drying at 100° in an oven, the crystals weighed 100 g., 102% of theory for the bisulfate salt. *Anal.* Calcd. for $[(\text{–}OSiMe_2CH_2NHCH_2SiMe_2\text{–})H_2SO_4]_x$: neut. equiv., 273.3; $SO_4^{=}$, 35.2. Found: neut. equiv., 274.3; $SO_4^{=}$, 35.8.

This acid sulfate salt (95 g.) was made into a slurry with 200 ml. of water and neutralized with 30 g. of sodium hy-

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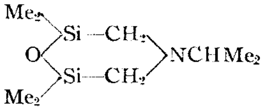
(4) L. H. Sommer, *et al.*, *ibid.*, **73**, 882 (1951).

(5) E. L. Warrick, *ibid.*, **68**, 2455 (1946).

(6) F. C. Whitmore and L. H. Sommer, *ibid.*, **68**, 481 (1946).

TABLE II

REACTION PRODUCTS OF HALOMETHYLSILANES AND AMINES

	Name of compound	Formula	Yield, %	B.p., °C.	B.p., Mm.	$n^{25}\mathrm{D}$	d^{25}_{4}	Sp. ref. Found	Sp. ref. Calcd.[3]	Element	Analyses, % Found	Analyses, % Calcd.
1	N-Methyl-(trimethylsilylmethyl)-amine	Me_3SiCH_2NHMe	50	101.6	735	1.4094	0.754	0.3283	0.3288	NE	121.1, 121.9	117.2
	Water azeotrope			83	735	1.4132				NE	128.4, 130.8	
	Hydrochloride			M.p. 198–199						Cl	23.04, 23.19	23.07
2	N,N-Dimethyl-(trimethylsilylmethyl)-amine	$Me_3SiCH_2NMe_2$	64	110.1	746	1.4102	.746	.3321	0.3302	Si	20.8, 20.9	21.4
										NE	131.5, 131.4	131.3
	Hydrochloride			M.p. 185–186						Cl	21.06, 21.13	21.4
3	N,N,N-Trimethyl-(trimethylsilyl)-methyl-ammonium											
	Bromide	$Me_3SiCH_2NMe_3Br$		M.p. 260–262						Br	35.56, 35.83	35.33
	Iodide[a]	$Me_3SiCH_2NMe_3I$	96	M.p. 241.5–242.5						I	46.0, 46.1	46.5
4	N-Isopropyl-(trimethylsilylmethyl)-amine	$Me_3SiCH_2NHCHMe_2$	83	129.5	736.5	1.4141	.758	.3299	.3290	NE	149, 149	145
	Hydrochloride			M.p. 136–137						Cl	19.47	19.51
5	N,N′-Diisopropyltetramethyldisiloxane-1,3-bismethylamine[b]	$O[SiMe_2CH_2NHCHMe_2]_2$		245	736.8	1.4278	.850	.3025	.3037	Si	20.51, 20.56	20.30
										NE	142.1, 141.5	138.2
	Dihydrochloride			M.p. 179–180						Cl	20.28, 20.30	20.30
6	2,2,6,6-Tetramethyl-4-isopropyl-1-oxa-2,6-sila-4-azacyclohexane		47	187.5	736.8	1.4328	.875	.2965	.2966	Si	26.05	25.82
										NE	219.8, 220.0	217.4
7	N-Cyclohexyl-(trimethylsilylmethyl)-amine[c]	$Me_3SiCH_2NHC_6H_{11}$	88	211	736.5	1.4519	.839	.3216	.3214	Si	15.28, 15.28	15.14
										NE	185.1, 185.2	185.3
	Hydrochloride			M.p. 235–239						Cl	16.18, 16.03	15.98
	Phenylthiourea			M.p. 136.5–137						Si	8.74, 8.76	8.75
8	N-Cyclohexyl-(ethoxydimethylsilylmethyl)-amine	$EtOSiMe_2CH_2NHC_6H_{11}$	64	162	99	1.4488	.889	.3014	.3016	Si	13.7, 13.8	13.0
										NE	219.4	215.4
9	N,N′-Dicyclohexyltetramethyldisiloxane-1,3-bismethylamine[d]	$O[SiMe_2CH_2NHC_6H_{11}]_2$	80			1.4679	.922	.3015	.3014	Si	16.0, 16.2	15.7
	Dihydrochloride			M.p. 228–232						Cl	16.51, 16.48	16.50
10	N-(Trimethylsilylmethyl)-octadecylamine	$Me_3SiCH_2NHC_{18}H_{37}\text{-}n$	67.5	193–194	2	1.4507(26°)	.815(26°)	.3294	.3297	Si	7.33, 7.47	7.88
				M.p. 26–32						NE[e]	352, 365	355
	Hydrochloride			M.p. 101–102						Cl	8.77	9.05
11	N-Trimethylsilylmethylaniline	$Me_3SiCH_2NHC_6H_5$		242	740.8	1.5213	.918	.3318	.3252	Si	15.4	15.6

[a] Prepared by reaction of 2 with MeI. [b] Prepared also by reaction of 4 with sulfuric acid. [c] Prepared also by hydrogenation of 11 over Raney nickel catalyst. [d] Prepared by reaction of 7 with sulfuric acid and by hydrolysis of 8. [e] The neutral equivalent was determined with a Beckman model H-2 *p*H meter in 50–50 alcohol and water.

droxide in 150 ml. of water. When one-half of the alkali was added, the solids quickly dissolved. This indicates that the normal sulfate salt is more soluble than the bisulfate. An oil separated after all the alkali was added. The oil smelled like burned fish. It was taken up in ether and dried. The ether was evaporated to leave 60 g. of a mixture of viscous liquid and pasty crystals. *Anal.* Calcd. for $(OSiMe_2CH_2NHCH_2SiMe_2-)_x$: neut. equiv., 175.3. Found: neut. equiv., 175.7.

This product was distilled at 23 mm. and yielded 18 g. of cyclic dimer, b.p. 152° at 23 mm., m.p. 45–49. See Table I, compound 9. The residue was heated to 330° at less than 1 mm. but could not be distilled. The residue was apparently a linear polymer of the same composition. It seems quite remarkable that the cyclic six-membered monomer was not produced in preference to the cyclic twelve-membered dimer.

Reaction of Chloromethyltrimethylsilane and Sodium Amide in Liquid Ammonia.—Chloromethyltrimethylsilane (122.5 g., 1 mole) and sodium amide (39 g., 1 mole) were sealed in an autoclave at 10° and liquid anhydrous ammonia was added. The temperature of the autoclave (80 lb. of iron) rose immediately to about 40° indicating a most vigorous reaction. The autoclave was heated to 120° for about $1^1/_2$ hours and cooled to room temperature. The excess ammonia was released and the non-volatile content of the bomb was washed out with ether. The solids (wt. 54 g., calculated 58.5 g. NaCl) were filtered off and the filtrate distilled in a still of about ten plates. During the distillation a gas was evolved ($MeNH_2$) and the boiling behavior of the material was erratic. The product was redistilled without difficulty and found to be essentially pure N-methylhexamethyldisilazane[7] (68 g., 78%), b.p. 148° at 740 mm., n^{25}_{D} 1.4190, d^{25}_{4} 0.794; sp. ref. 0.3181, calcd.[5] sp. ref. 0.3168. *Anal.* Calcd. for $C_7H_{21}NSi$: Si, 31.9; neut. equiv., 175.4. Found: Si, 31.2; neut. equiv., 176.6, 177.6.

To more firmly establish the identity of the product, it was shaken with benzoyl chloride in aqueous alkali and yielded N-methylbenzamide, m.p. 77.5–78.5°, which showed no depression of m.p. when mixed with authentic N-methylbenzamide, m.p. 80°.

Another sample was shaken with dilute acid. Hexamethyldisiloxane separated, b.p. 100.4° at 742 mm., n^{25}_{D} 1.3752, d^{25}_{4} 0.759. Sauer[8] reported for this compound a b.p. of 100.4° at 741 mm., n^{20}_{D} 1.3772, d^{20}_{4} 0.7638. Methylamine hydrochloride was obtained by evaporating the aqueous acid to dryness. Recrystallized once from acetone the hydrochloride melted at 223.5–224.5° and showed no depression when mixed with authentic hydrochloride, m.p. 225–226°.

The reaction that occurred probably can be represented by the equations

$$Me_3SiCH_2Cl + NaNH_2 \longrightarrow Me_3SiNHCH_3 + NaCl$$
$$2Me_3SiNHCH_3 \longrightarrow (Me_3Si)_2NMe + MeNH_2$$

The mechanism whereby the first reaction occurred in liquid ammonia solution is most obscure.

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(7) R. O. Sauer and R. H. Hasek, *ibid.*, **68**, 241 (1946), report a b.p. of 145°.

(8) R. O. Sauer, *ibid.*, **66**, 1707 (1944).

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[CONTRIBUTION FROM THE MULTIPLE FELLOWSHIP OF TECHNICAL GLASSWARE MAINTAINED AT MELLON INSTITUTE BY THE CORNING GLASS WORKS, IN COÖPERATION WITH THE DOW CORNING CORPORATION, AND FROM THE UNIVERSITY OF PITTSBURGH]

Effect of Organosilicon Substituents on the Basic Strength of Amines

BY JOHN E. NOLL,[1a] B. F. DAUBERT AND JOHN L. SPEIER[1b]

The basic dissociation constants of thirteen (silylmethyl)-amines and one β-aminoethylsilicon compound have been determined. Some effects of structure and of various substituents upon both the silicon and nitrogen atoms are described.

The basic dissociation constants of a series of silicon substituted amines[2] were determined to find the effects of organosilicon substituents on the basic strength of amines.

Two methods were used for determining the basic dissociation constants. One method gave dissociation constants at a relatively high ionic strength. In this method a purified sample of amine hydrochloride, analyzed for chlorine to determine its purity, was dissolved in a volume of water to which a known amount of standard hydrochloric acid had been added. The resulting solution was titrated with standard sodium hydroxide. The progress of the titration was followed by means of a Beckman model H-2 *p*H meter. From the curve of *p*H *versus* ml. of base added and the calculated ratio of amine to amine salt, the dissociation constant, *K*, was calculated using the formula

$$pK = \log \frac{[RNH_2]}{[RNH_3{}^+]} + pOH$$

As long as the ratio of amine to amine salt was small (less than 1:15) *pK* was constant and the value in this range was used. Another method, we will call the extrapolation method, for determining basic dissociation constants, was used to obtain dissociation constants at infinite dilution. This method was particularly suitable for those amines whose salts could not readily be prepared. The amines used in the determinations were carefully purified by distillation under nitrogen. Small quantities of amine were dissolved in known amounts of water and the *p*H of the resulting solution was determined. Standard hydrochloric acid was added in some cases so that a known ratio of amine to amine salt was present. From the *p*H and concentrations at each point, the *pK* was calculated and plotted against the ionic strength. Extrapolation of the curve to infinite dilution gave pK_B.

The two methods gave only slightly different results for the more water-soluble amines. The less soluble amines gave a much lower result by the second method. The *p*H could be determined to a precision of only about ±0.02 *p*H unit. A variation of this magnitude caused a variability of any single value of *K* of about 10%. Each value listed in Table I is the average of from five to eight separate values of *K* taken from a smooth curve of the plot of *pK versus* ionic strength (extrapolation method). The value of *pK* seldom varied by more than 0.2 of a unit over the concentration range used in the determination. The values obtained by

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(2) J. E. Noll, B. F. Daubert and J. L. Speier, THIS JOURNAL, **73**, 3867 (1951).