Tables I and II. A variation was used for hexadecyltrifluorosilane, the mixture being heated at 90° for two hours before back-titration with hydrochloric acid.

Method B (Gravimetric).—A weighed sample of *ca.* 0.4 g. of alkylfluorosilane was added to 150 ml. of methanol and a 100% excess of 0.1–0.2 *N* NaOH in a 500-cc. erlenmeyer flask. The mixture was shaken for five minutes and then the methanol was evaporated on a steam-bath. The remainder of the procedure is that for the gravimetric determination of fluoride ion as lead chlorofluoride.[18] Results are presented in Table II.

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[18] N. H. Furman, "Scott's Standard Methods of Chemical Analysis," Vol. I, 5th Ed., D. Van Nostrand Co., New York, N. Y., 1925, p. 406.

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[CONTRIBUTION FROM THE WHITMORE LABORATORY, THE PENNSYLVANIA STATE COLLEGE]

The Polar Effects of Organosilicon Substituents in Aliphatic Amines[1,2]

BY LEO H. SOMMER AND JACK ROCKETT

The synthesis of four silicon-containing aliphatic amines, which comprise the first examples of compounds of this type, has been achieved. These are trimethylsilylmethylamine, β-trimethylsilylethylamine, γ-trimethylsilylpropylamine and di-(trimethylsilylmethyl)-amine. Base-strengths in dilute aqueous solution and other properties of these compounds have been determined. Also reported are the syntheses of a number of compounds used as intermediates for the amines. These include N-trimethylsilylmethylphthalimide, β-trimethylsilylpropionamide, methyl N-(β-trimethylsilylethyl)-carbamate, N,N'-di-(β-trimethylsilylethyl)-urea and β-trimethylsilylpropionitrile. From the fact that the amines are strong bases, it is concluded that expansion of the silicon valence shell beyond a covalency of four is not a general phenomenon for organosilicon compounds.

Because silicon is found in the second short period of the periodic table, and in harmony with the existence of the $SiF_6^=$ ion, Sidgwick assigned to silicon a maximum covalency of six.[3] Based upon this principle, he proposed[3] a general mechanism for the hydrolysis and alcoholysis of chlorosilanes, in which silicon first expands its valence shell to coördinate one or more molecules of the attacking reagent. Thereafter it is presumed to lose some small molecule of condensation and return to the normal valency of four.

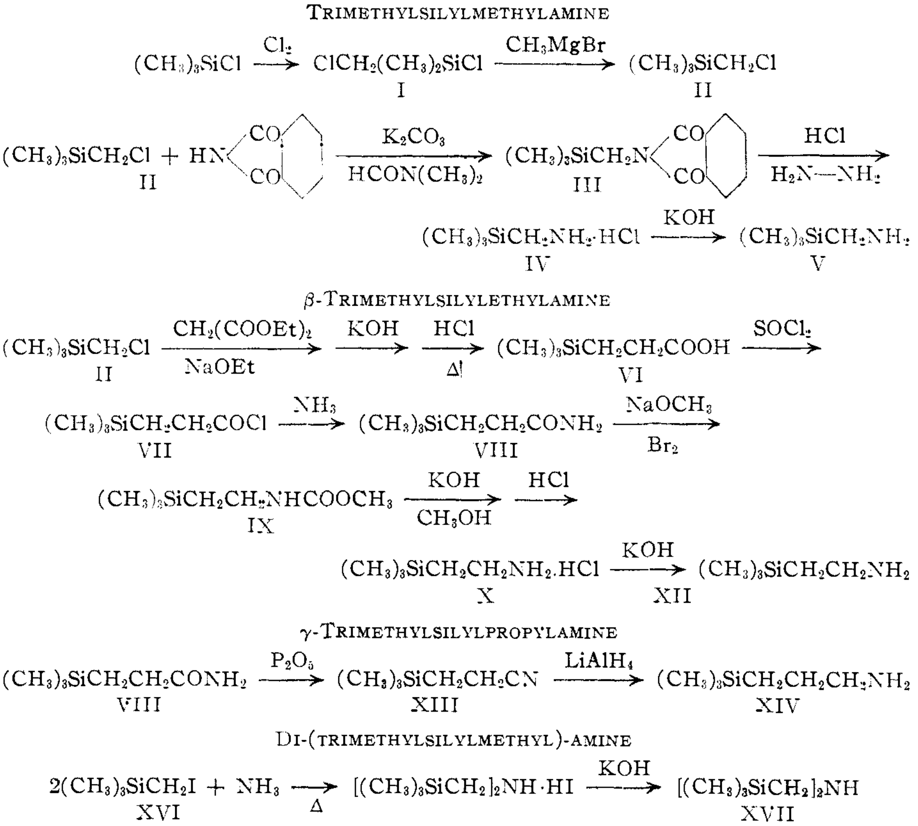

Fig. 1.—The synthesis of aliphatic amines containing organosilicon substituents.

Acid strengths of silicon-containing carboxylic acids taken in this Laboratory[4] first indicated to us the possibility that the expanded shell theory might not be applicable to organosilicon compounds. A further study with organosilicon aliphatic amines was undertaken to shed light upon the general validity of the theory. Another stimulus lay in the fact that no true aliphatic amines, *i.e.*, those in which nitrogen is bound to carbon, had heretofore been reported in the organosilicon literature. The compounds trimethylsilylmethylamine, β-trimethylsilylethylamine, γ-trimethylsilylpropylamine and di-(trimethylsilylmethyl)-amine were accordingly synthesized by the procedures schematically outlined in Fig. 1.

The base strengths of the amines were deter-

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[1] Paper XXIX on organosilicon chemistry. For XXVIII see THIS JOURNAL, **73**, 5127 (1951).

[2] Presented in part before the Organic Division at the 117th Meeting of the American Chemical Society.

[3] N. V. Sidgwick, "The Electronic Theory of Valency," Oxford University Press, 1932, pp. 155–160; N. V. Sidgwick, *J. Chem. Soc.*, **125**, 2672 (1924).

[4] L. H. Sommer, J. R. Gold, G. Goldberg and N. Marans, THIS JOURNAL, **71**, 1509 (1949).

mined potentiometrically, the pH's of the aqueous solution being taken with the Beckman Type G pH meter. The blue (lithium) glass electrode especially designed for pH readings above 9.5 were used throughout this work. The results are given in Table I.

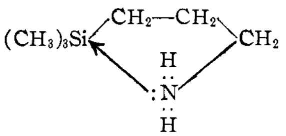
TABLE I

	Amine	$K_b \times 10^4$ (25°)	pK_a (25°)
1	*n*-Propyl-	4.9	10.69
2	Trimethylsilylmethyl-	9.1	10.96
3	β-Trimethylsilylethyl-	9.7	10.99
4	γ-Trimethylsilylpropyl-	5.6	10.75
5	Di-(trimethylsilylmethyl)-	25.0	11.40
6	Neopentyl-	1.6	10.21

The value for *n*-propylamine was determined, both to check our method against those previously used in the literature, and for its own significance in this study. The value obtained is in good agreement with that of Bredig.[5] Neopentylamine was also determined for comparative purposes, apparently for the first time.

Discussion

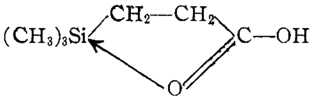
If silicon showed any tendency to expand its valence shell in these compounds, then it would logically be expected to coördinate the extra electron pair on the nitrogen of γ-trimethylsilylpropylamine, in the manner shown.



If it did so to any considerable extent in dilute aqueous solution, then the base strength of this amine would be markedly less than that of *n*-propylamine. However, the silicon substituted amine is stronger than *n*-propylamine. Thus, there is no apparent tendency for silicon to coordinate the extra electron pair on the nitrogen.

The order of magnitude of the decrease in base strength which can be expected from such coordination can be estimated by a consideration of the compounds trimethylamine ($K_b = 7.4 \times 10^{-5}$) and trimethylamine oxide ($K_b = 10^{-10}$).[6] The effect upon base strength is obviously huge.

Corroboration for these data lies in the acid strength of β-trimethylsilylpropionic acid[4] as compared with that of propionic acid. Coördination of the extra electron pair on the silicon substituted acid would lead to a significant increase in the acid strength, as shown.



The values actually found are 1.34×10^{-5} for propionic acid and 1.24×10^{-5} for β-trimethylsilylpropionic acid. It may be concluded, therefore, that in the acids and bases which we have studied silicon shows no tendency to expand its valence shell beyond the normal covalency of four.[7] Other recent physical-chemical studies from the field of dipole moments[8] and thermal analysis[9] give significant substantiation to this conclusion.

The effect of the silicon atom upon the base strength of the amines is to appreciably increase it. Thus trimethylsilylmethylamine is 5.69 times as strong as neopentylamine, its exact carbon analog. Silicon being electropositive relative to carbon, a permanent dipole exists at the Si–C bond, partial positive on silicon and partial negative on carbon. The net polar (inductive) effect diminishes rapidly through the chain. Thus, the ratio of base strengths of the silicon amine to the unsubstituted aliphatic amine is

Amine No.1	Amine No. 2	$Kb_{(1)}/Kb_{(2)}$
Trimethylsilylmethylamine	Methylamine	1.82
β-Trimethylsilylethylamine	Ethylamine	1.73
γ-Trimethylsilylpropylamine	Propylamine	1.14

The physical properties of the amines have been summarized in Table II. An interesting comparison lies in the physical properties of trimethylsilylmethylamine and neopentylamine. The increase in boiling point, density and molar volume of the silicon compound can all be attributed to the increased weight and size of the silicon atom. The most striking change in property, however, is the decrease in solubility of the silicon compound. The carbon compound is at least 19.5 times as soluble in water, on a molar basis, as its silicon counterpart. If the only factor influencing solubility is the formation of hydrogen bonds, then the results should have been in the opposite direction, since the silicon amine is more than five times as strong as the carbon compound. It might also be mentioned that if silicon expanded its valence shell and coördinated one or two molecules of water, then this solvation should certainly have made it more soluble in water than the carbon compound. At present, the lesser solubility of the silicon compound has no adequate explanation.

Experimental

N-Trimethylsilylmethylphthalimide (III).—In a 1-liter, three-necked flask equipped with a mercury-sealed stirrer, a thermometer, and a condenser closed by a Gilman sulfuric acid trap were placed 73.6 g., 0.5 mole, of phthalimide, 73.6 g., 0.6 mole, of chloromethyltrimethylsilane,[10,11] 36.8 g.,

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[5] G. Bredig, *Z. physik. Chem.*, **13**, 191 (1895). "International Critical Tables" has applied a correction to all of Bredig's values. However, A. Marckinkow and E. Plazek, *C. A.*, **31**, 1776 (1937), have obtained values in close agreement with Bredig's original values.

[6] N. V. Sidgwick, "The Organic Chemistry of Nitrogen," Oxford University Press, 1937, p. 168.

[7] C. G. Swain, R. M. Esteve, Jr., and R. H. Jones, THIS JOURNAL, **71**, 965 (1949), have interpreted kinetic data obtained in a study of the hydrolysis of organofluorosilanes in aqueous acetone to indicate that a pentacovalent silicon intermediate is involved in these reactions. In our view, this interpretation is at least open to some question on the basis that the primary products of these hydrolyses may not be the conjugate acids of the silanols. Thus, if the silanols themselves are the primary products, the data would be equally consistent with a simple S_N2 mechanism. On the other hand, it is not impossible that silicon in triorganofluorosilanes can expand its violence shell beyond four, whereas in tetraorganosilanes and in some other type silicon compounds this situation does not obtain.

[8] T. V. Lane, P. A. McCusker and B. C. Curran, *ibid.*, **64**, 2076 (1942); Kennard and McCusker, *ibid.*, **70**, 1039 (1948).

[9] H. H. Sisler and co-workers, *ibid.*, **70**, 3818 (1948); **70**, 3821 (1948); **70**, 3825 (1948); **70**, 3826 (1948).

[10] R. H. Krieble and J. R. Elliot, *ibid.*, **67**, 1810 (1945).

[11] F. C. Whitmore, L. H. Sommer and J. R. Gold, *ibid.*, **69**, 1976 (1947).

TABLE II

	Amine	B.p., °C.	B.p., Mm.	n^{20}_D	d^{20}_4	MR_D (found)	MR_D (calcd.)	Solubility, moles/l.	M_V cc./mole
1	Trimethylsilylmethyl-	94	729	1.4168	0.7697	33.70	33.75	0.0173	134.1
2	β-Trimethylsilylethyl-	121	735	1.4241	.7807	38.33	38.38	.0156	150.2
3	γ-Trimethylsilylpropyl-	145.5	732	1.4295	.7866	43.07	43.01	.0112	174.2
4	Di-(trimethylsilylmethyl)-	90	57	1.4267	.7864	61.79	62.07	.00116	240.8
5	Neopentyl-	80.5	729	1.4023	.7455	28.49	28.75	.337[a]	116.9

[a] This figure probably does not represent maximum solubility. No undissolved amine could be observed.

0.266 mole, of anhydrous potassium carbonate, and 300 cc. of dimethylformamide. The flask was heated by mantle as the contents were stirred. When the temperature reached approximately 105°, a moderate evolution of gas commenced, which, when passed into a clear aqueous solution of barium hydroxide gave a heavy white precipitate. The evolution of gas continued for about one hour, after which time the temperature climbed to 142°. The color of the reaction mixture had meanwhile deepened to a cherry red. Heating was continued for another hour, after which time the flask contents were permitted to cool.

The reaction mixture was filtered into a 500-cc. fractionating flask. The solid residue was washed several times with anhydrous ether and the ether was added to the fractionating flask. Fractionation through a column of about thirteen theoretical plates gave (1) ether, (2) an azeotrope of excess chloromethyltrimethylsilane and water, b.p. 84° (109 mm.), and (3) dimethylformamide, b.p. 93° (110 mm.), 273 cc., a 91.0% recovery.

The residue, a clear red oil containing some solid salt was washed with water and separated. The water washings were ether extracted and the ether was added to the organic material. After drying for 12 hours over anhydrous sodium sulfate it was filtered into a Claisen flask and distilled. After removal of the ether there was obtained 104.4 g., 0.448 mole, of a clear, water-white oil, N-(trimethylsilylmethyl)-phthalimide, b.p. 117° (2 mm.), f.p. 23°, n^{20}_D 1.5427 (refractive index taken before crystallization was induced), an 89.8% yield.

Anal. Calcd. for $C_{12}H_{15}NO_2Si$: Si, 12.01. Found: Si, 11.71.

The conventional method of Gabriel synthesis with potassium phthalimide and no solvent did not work for this halide at all. The use of dimethylformamide as a solvent was attempted and gave an excellent yield of the desired product. It may be that this highly polar solvent may prove of general value for the Gabriel synthesis.

Trimethylsilylmethylamine Hydrochloride (IV).—In a 1-liter three-necked flask equipped with a mercury-sealed Hershberg stirrer (nichrome wire), a dropping funnel, and a condenser, the entire system closed off by a Gilman sulfuric acid trap, were placed 103.0 g., 0.442 mole, of N-(trimethylsilylmethyl)-phthalimide and 250 cc. of absolute alcohol. While stirring smoothly, 22.1 g., 0.442 mole, of 100% hydrazine hydrate was added dropwise, in the cold. When nearly all of the hydrazine had been added, solid particles began to form and, within a few seconds, the entire flask contents were transformed into a thick white paste. Heat was applied and the contents were stirred at reflux temperature for three hours.

Concentrated hydrochloric acid, 50.0 cc., 0.582 mole, was now added dropwise while stirring at reflux temperature. When it had all been added, stirring and heating were continued for another six hours. The flask contents were cooled and filtered into a 3-liter beaker. The residue was washed many times with dilute hydrochloric acid. Finally, the residue was boiled with 200 cc. of 1:1 hydrochloric acid and suction filtered. All filtrates were combined and evaporated to dryness. The solid material was collected, dissolved in water, made strongly alkaline with aqueous potassium hydroxide, and steam distilled. Acidification of the distillate with hydrochloric acid and evaporation to dryness gave 58.2 g., 0.417 mole, 94.5%, of trimethylsilylmethylamine hydrochloride. Recrystallization from isopropyl alcohol plus anhydrous ether gave beautiful long rectangular plates, m.p. 242–243°.

Anal. Calcd. for $C_4H_{14}ClNSi$: Cl, 25.34. Found: Cl, 25.45.

Trimethylsilylmethylamine (V).—In a 1-liter erlenmeyer flask was placed 264 g., 4.10 moles, of potassium hydroxide pellets. The flask was fitted with a dropping funnel and a T tube connected to a nitrogen cylinder to keep the system free from carbon dioxide. The erlenmeyer flask was immersed in an ice–water-bath as a saturated, aqueous solution, of 92.8 g., 0.665 mole, of trimethylsilylmethylamine hydrochloride was added, dropwise, through the dropping funnel. A clear organic layer formed over the saturated aqueous potassium hydroxide. When the addition was complete, the organic layer was separated and the aqueous material was extracted with 3 × 50 cc. portions of ether. The ether extract was combined with the amine layer and dried over a mixture of potassium hydroxide pellets and anhydrous potassium carbonate. It was filtered and fractionated through a column of about thirteen theoretical plates to give 45.9 g., 0.446 mole, of trimethylsilylmethylamine, b.p. 94° (729 mm.), n^{20}_D 1.4168, a 67.1% conversion.

Anal. Calcd. for $C_4H_{13}NSi$: Si, 27.19; *MR*D, 33.75. Found: Si, 26.68; *MR*D, 33.70.

β-Trimethylsilylpropionic Acid (VI).—The method was a conventional malonic ester synthesis[4] by which 857.5 g., 7.0 moles, of chloromethyltrimethylsilane was converted to 80.1 g., 0.46 mole, of ethyl β-trimethylsilylpropionate, b.p. 90° (35 mm.), n^{20}_D 1.4197, a 6.6% yield,[12] and 706.3 g., 4.83 moles, of β-trimethylsilylpropionic acid, b.p. 131° (34 mm.), n^{20}_D 1.4282, a 69.1% yield.

β-Trimethylsilylpropionyl Chloride (VII).—In a 1-liter three-necked flask were placed 150.4 g., 1.27 moles, of thionyl chloride. β-Trimethylsilylpropionic acid, 120.0 g., 0.822 mole, was added dropwise with stirring. The contents of the flask were heated in an 80° bath for three hours and in a 95° bath for another three hours. Some excess thionyl chloride was then removed by placing the flask under a stripping column and distilling at room temperature. The remaining material was fractionated through a column of about thirteen theoretical plates to give 130.6 g., 0.794 mole, of β-trimethylsilylpropionyl chloride, b.p. 92° (65 mm.), a 96.6% yield.

Anal. Calcd. for $C_6H_{13}SiOCl$: Si, 17.03. Found: Si, 16.84.

β-Trimethylsilylpropionamide (VIII).—A 1-liter three-necked flask equipped with a water condenser, a rubber sealed mechanical stirrer, and a dropping funnel was immersed in a Dry Ice–acetone-bath in a large dewar flask. When the system was cooled, 300 cc. of anhydrous ether was placed in the flask. To it was added 190 g., 11.2 moles, of liquid ammonia. β-Trimethylsilylpropionyl chloride, 166.4 g., 1.01 moles, was diluted with 150 cc. of ether and added dropwise through the dropping funnel while stirring vigorously. A solid precipitate formed with each drop and the flask contents thickened considerably as the reaction proceeded. When it had all been added, the flask was left immersed to warm gradually during the next 12 hours. It was then raised about the bath level and allowed to warm to room temperature. The flask contents were extracted with successive portions of ether and filtered into a 3-liter beaker. Approximately 1.5 liters of ether filtrate was obtained. The solid residue was now dissolved in the smallest quantity of water needed to dissolve it and extracted with three 50-cc. portions of ether. The combined ether extracts were evaporated to dryness. A pale yellow crystalline product was obtained, 146.0 g., 1.008 moles, a 99.7% yield. It was recrystallized from 900 cc. of heptane to give 137.5 g., 94.3%, of gleaming white flakes, m.p. 95–96°.

Anal. Calcd. for $C_6H_{15}SiON$: Si, 19.32. Found: Si, 19.02.

Methyl N-(β-Trimethylsilylethyl)-carbamate (IX).—In a 2-liter three-necked flask equipped with a mercury-sealed

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[12] L. H. Sommer and N. S. Marans, THIS JOURNAL, **72**, 1935 (1950).

stirrer, a reflux condenser, and a dropping funnel were placed 540 cc. of dry methanol. The contents of the flask were protected from moisture by means of a Gilman sulfuric acid trap. Sodium metal, 40.5 g., 1.76 moles, was added in small pieces, and, when the reaction was complete, a solution of 136.9 g., 0.881 mole, of β-trimethylsilylpropionamide dissolved in 500 cc. of dry methanol was added rapidly. Liquid bromine was dried by vigorous stirring with concentrated sulfuric acid and 46.0 cc., 0.893 mole, was placed in the dropping funnel of the apparatus. The bromine was added dropwise, with good stirring, over a period of two hours. The flask warmed considerably during the addition and an ice-bath was applied to keep the temperature down. The last two drops of bromine turned the solution light orange in color.

The flask was now heated to reflux temperature and maintained at this temperature for one and one-quarter hours. After cooling, the solution was found to be practically neutral and only 0.5 cc. of glacial acetic acid was needed to make the solution slightly acid. The methanol was fractionated out of the filtered solution by means of a column of about thirteen theoretical plates. The remaining mixture of oil and solid was extracted with a total of 300 cc. of ether, which was then dried over anhydrous sodium sulfate and fractionated. Fractionation gave 127.5 g., 0.729 mole, of the urethan, methyl N-(β-trimethylsilylethyl)-carbamate, a clear water-white liquid, b.p. 108° (12 mm.), n^{20}_{D} 1.4410, an 82.7% yield.

Anal. Calcd. for $C_7H_{17}NSiO_2$: Si, 16.01. Found: Si, 15.78.

The residue from the fractionation was extracted with 95% alcohol to give 20.5 g., 0.1415 mole, of the starting amide, a 16.1% recovery.

β-Trimethylsilylethylamine Hydrochloride (X).—In a 1-liter round-bottomed flask equipped with a reflux condenser closed at the top by a T-tube were placed 450 cc. of methanol and 278 g., 4.31 moles, of potassium hydroxide. Nitrogen was passed through the T-tube, the other end of which was closed by a soda-lime tube. The urethan, methyl N-(β-trimethylsilylethyl)-carbamate, 139.6 g., 0.798 mole, was added, plus 75 cc. more of methanol and the solution was refluxed on the steam-bath for 11 hours.

The methanol was distilled out of the reaction flask by means of a short stripping column and the remainder of the solution was steam distilled, using live steam. A total of 850 cc. of liquid was distilled. The combined steam distillate and methanol distillate was acidified with concd. hydrochloric acid and evaporated to dryness on the steam-bath. There was obtained 114.9 g., 0.748 mole, 93.8%, of the amine hydrochloride.

An excellent recrystallization solvent was found in absolute alcohol which had been treated with sodium and distilled. Anhydrous ether was added in 10-cc. portions until the solution remained cloudy while still quite warm. The compound then crystallized out slowly in beautiful white needles, m.p. 300°. A total of 36.1 g. was obtained, a 90.3% yield.

Anal. Calcd. for $C_5H_{16}ClNSi$: Cl, 23.10. Found: Cl, 23.41.

N,N′-Di-(β-trimethylsilylethyl)-urea (XI).—During the steam distillation of the urethan hydrolysate, it was observed that a yellow oil appeared on the surface of the liquid in the flask. It was extracted with ether and washed free of excess base. The ether was evaporated and the resulting oil, after standing for several days, crystallized. It was recrystallized from acetone plus water to give small, fluffy white needles, m.p. 77–78°. Qualitative analysis showed the presence of nitrogen and silicon, and the absence of halogen.

The solid material, upon refluxing for 12 hours with alcoholic potassium hydroxide and being distilled gave an amine whose hydrochloride was identical with X. More than one mole of amine hydrochloride was obtained per mole of compound, calculated as urea.

Anal. Calcd. for $C_{11}H_{28}N_2OSi_2$: Si, 21.54. Found: Si, 21.57.

This is apparently the first time a urea has been obtained as the result of the hydrolysis of a urethan.

β-Trimethylsilylethylamine (XII).—In a 1-liter erlenmeyer flask equipped with a dropping funnel and a T-tube was placed 260 g., 4.04 moles of potassium hydroxide pellets. The T-tube was connected to the top of the dropping funnel and a nitrogen atmosphere was maintained throughout the system. The amine hydrochloride, 114.9 g., 0.748 mole was dissolved in 250 cc. of water and added through the dropping funnel dropwise. When all of the amine hydrochloride had been added, a clear yellow layer was present above the aqueous layer. This layer was separated and placed in a flask over solid potassium hydroxide plus anhydrous potassium carbonate. The aqueous residue was extracted two times with 50-cc. portions of ether and added to the amine. After drying overnight, it was fractionated. Fractionation gave 73.0 g., 0.624 mole, of β-trimethylsilylethylamine, b.p. 121° (735 mm.), n^{20}_{D} 1.4244, an 83.5% yield.

Anal. Calcd. for $C_5H_{15}NSi$: Si, 23.93; *MR*D, 38.38. Found: Si, 24.06; *MR*D, 38.33.

β-Trimethylsilylpropionitrile (XIII).—In a 2-liter round-bottomed flask fitted to a Claisen head by means of a ground glass joint, were placed 72.5 g., 0.5 mole, of finely powdered β-trimethylsilylpropionamide and 88.7 g., 0.625 mole, of finely powdered phosphorus pentoxide. The flask was stoppered immediately and shaken well to obtain a homogeneous mixture. A magnetic stirrer was placed in the flask and the Claisen head was adjusted to the flask. A fraction cutter was connected to the Claisen head and the pressure was reduced to 47 mm. The temperature was slowly raised as the mixture was stirred. As the mixture melted, distillation took place. When the distillation stopped the pressure was reduced, gradually, to 25 mm. When nothing further distilled, the flask was permitted to cool. There was obtained 42.9 g. of the crude nitrile. Decomposition of the solid residue with ice and extraction with ether gave another 2.5 g. of nitrile upon distillation. The total is 45.4 g., 0.358 mole, a 71.6% yield.

The combined product of several runs, 89.4 g., was fractionated through a column of about thirteen theoretical plates to give 76.8 g. of β-trimethylsilylpropionitrile, b.p. 94° (49 mm.), n^{20}_{D} 1.4240, d^{20}_{4} 0.8270, and 86.0% yield. It is a clear colorless liquid of a very pleasant minty odor.

Anal. Calcd. for $C_6H_{13}NSi$: Si, 22.05; *MR*D, 39.42. Found: Si, 21.97; *MR*D, 39.26.

γ-Trimethylsilylpropylamine (XIV).—In a 5-liter round bottomed flask, 2 liters of anhydrous ether was further dried by refluxing for two hours with calcium hydride. It was then distilled directly into a 2-liter three-necked flask equipped with a mercury-sealed stirrer, a condenser, and dropping funnel, the entire system kept moisture-free by means of a Gilman sulfuric acid trap. When about 1.1 liters of ether had been distilled, 28.5 g., 0.75 mole, of lithium aluminum hydride was added to the ether. The system was quickly closed and heated at reflux temperature for 18 hours. There was still a small amount of undissolved solid.

β-Trimethylsilylpropionitrile, 63.5 g., 0.50 mole, was dissolved in 500 cc. of ether and placed in the dropping funnel. The system was flushed through with nitrogen and a pyrogallol Gilman trap was placed in series with the sulfuric trap. The nitrile solution was added dropwise, with good stirring, during a period of about three hours. A white solid formed during the addition and a slight warming of the reaction flask was observed. When addition was complete, the flask was heated at reflux temperature for 20 hours. It was then cooled.

Methanol, 25.5 cc., 1.0 mole, was now added dropwise at a very slow rate. Addition took one hour, after which time the flask contents were stirred for another hour. Now 200 cc. of 20% sodium potassium tartrate was added dropwise. The upper, ether layer was siphoned into a 2-liter separatory funnel, and after separation from the water layer, was filtered into a 1-liter erlenmeyer flask. The aqueous material was extracted two times with 200 cc. of ether. The combined ether extracts were dried over potassium hydroxide pellets and anhydrous potassium carbonate. Fractionation gave 53.7 g., 0.410 mole, of γ-trimethylsilylpropylamine, b.p. 145° (726 mm.), n^{20}_{D} 1.4301, d^{20}_{4} 0.7866, an 82.0% yield.

Anal. Calcd. for $C_6H_{17}NSi$: Si, 21.37; *MR*D, 43.01. Found: Si, 21.08; *MR*D, 43.07.

γ-Trimethylsilylpropylamine Hydrochloride (XV).—The aqueous layer was made strongly basic with potassium hydroxide solution and steam distilled. The distillate was acidified with concentrated hydrochloric acid and evaporated to dryness. There was obtained 4.1 g., 0.0246 mole, of γ-trimethylsilylpropylamine hydrochloride, a 4.9% yield. It was recrystallized from acetone to give fine, silky needles, m.p. 183–184°.

Anal. Calcd. for $C_6H_{18}ClNSi$: Cl, 21.19. Found: Cl, 21.08.

Di-(trimethylsilylmethyl)-amine (XVII).—In the liner of a hydrogenation bomb (American Instrument Co.), cooled in a Dry Ice–acetone-bath, were placed 107.0 g., 0.50 mole, of iodomethyltrimethylsilane (XVI)[13] and 102 g., 6.0 moles, of liquid ammonia. The liner was capped and it was placed in the bomb which was immediately closed for operation. The bomb was adjusted on the rocker with the gas inlet attached to the pressure gage. Gentle heat was applied. The rocker was not started until the temperature reached 95° and the pressure read 510 lb. The rocker was then started and continued for 10 hours during which time the temperature was kept at about 100°.

At the end of this time the rocker was stopped and the bomb was allowed to cool overnight. The bomb contents were extracted with many washings of hot water, and, finally with three washings of dilute hydrochloric acid. The extract was evaporated to dryness, and the solid material was dissolved in 2 liters of water, made alkaline with potassium hydroxide, and steam distilled. The distillate was now acidified with hydrochloric acid and evaporated to dryness. The white solid was dissolved in the smallest amount of water needed to dissolve it, made alkaline with potassium hydroxide, and extracted by ether for 40 hours in a continuous extractor. Fractionation through a column of about thirteen theoretical plates gave 11.3 g., 0.0592 mole, of di-(trimethylsilylmethyl)-amine, b.p. 90° (57 mm.), $n^{20}D$ 1.4267, d^{20}_4 0.7864, a 23.7% yield.

Anal. Calcd. for $C_8H_{23}NSi$: Si, 29.63; *MR*D, 62.07. Found: Si, 30.06; *MR*D, 61.79.

Only about 5.1 g. of the primary amine was obtained in this run. The limitations of our bomb capacity made it impossible to use a greater excess of liquid ammonia.

Di-(trimethylsilylmethyl)-amine Hydrochloride (XVIII).—In a 500-cc. erlenmeyer flask were placed 350 cc. of anhydrous ether and 3 cc. of the free amine. Gaseous hydrogen chloride was passed into the solution for approximately 20 minutes. The flask contents were then warmed to the boiling point of ether and then allowed to cool slowly. The fine crystalline material was filtered and dried under the infrared lamp. There was obtained 2.9 g., m.p. 158°.

Anal. Calcd. for $C_8H_{24}ClNSi$: Cl, 15.74. Found: Cl, 15.41.

The Base Strength of the Amines.—The determinations were made by the potentiometric technique. Approximately 700 cc. of distilled water which had been freshly boiled for 15 minutes to remove carbon dioxide, was placed in a 1-liter separatory funnel. An atmosphere of nitrogen was kept over the water, and it was stoppered by a soda-lime tube. When it had cooled to room temperature, 2 cc. of the amine was added to the separatory funnel, again under a nitrogen atmosphere. The separatory funnel was shaken well, using a glass stopper, and then, substituting the soda-lime stopper, was allowed to stand for a minimum of six hours.

By means of a 50-cc. buret, five successive portions of 50 cc., or a total of 250 ± 0.20 cc. was drawn from the separatory funnel into a special 500-cc. four-necked round bottomed flask. The flask was fitted with the two electrodes of the Beckman Type G *p*H meter, using the blue, lithium glass electrode for high *p*H readings. In the third side neck was placed a mechanical stirrer and a nitrogen gas inlet. The middle neck was fitted to a buret containing standardized acid. The titration was thus made, with constant stirring, in a nitrogen atmosphere. The normality of the solution was thus obtained.

Now three solutions of the amine were made up, each in a 200-cc. three-necked flask. Each contained 100.00 ± 0.10 cc. of the amine solution and a definite volume of standardized acid. The solutions were stirred and stoppered. An atmosphere of nitrogen was kept in each flask as the solutions were made up. Each flask was then placed in a 25° bath for 30 minutes. While still in the thermostat it was fitted with a stopper in the center neck containing a thermometer and a nitrogen inlet tube. The side necks were then fitted with the electrodes and a *p*H reading was made.

In all cases the *p*H meter was freshly standardized against *p*H 10.00 buffer immediately before taking a set of readings. The buffer (Eimer and Amend) had been standardized against Bureau of Standards buffer and found to be low by 0.03 *p*H unit. Thus, instead of setting the machine at *p*H 10.00 at 25°, the machine was set at 9.97, using this buffer.

The equation derived for the calculation of the base strength is[14]

$$pK_{1} = pK_{\mathrm{w}} - p\mathrm{H} - \log \frac{[\mathrm{RNH_3^+}]}{[\mathrm{RNH_2}]}$$

$[RNH_3^+]$ and $[RNH_2]$ must be corrected for neutralization and hydrolysis. Thus

$[RNH_3^+]$ = concn. acid added to the solution plus $[OH^-]$
$[RNH_2]$ = concn. amine added to the solution minus (concentration of acid added to the solution plus $[OH^-]$)

Solubility Studies.—The titration of the saturated solution of amine as described above gave, immediately, the solubility in moles per liter.

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