2,2'-Bis-(trifluoromethyl)-4,4'-dinitrodiphenyl Sulfone from (IV).[6]—Two and one-tenths gram of (IV), m.p. 136–137°, was dissolved in a mixture of equal parts by volume of glacial acetic acid and acetic anhydride (18 ml.). The solution was cooled in an ice-bath and maintained at approximately 0° while 2 ml. of 30% hydrogen peroxide was added slowly. The mixture was allowed to come slowly to room temperature as the ice melted and to stand for four days while the 2,2'-bis-(trifluoromethyl)-4,4'-dinitrodiphenyl sulfone precipitated as long needles. The product was already essentially pure, m.p. 171–172°; yield almost quantitative. A sample, recrystallized from acetone, melted at 172–173°. A mixed melting point of this product with (VI) showed no depression.

2,2'-Bis-(trifluoromethyl)-4,4'-diaminodiphenyl Sulfone (VII).—Twenty-two and two-tenths grams (0.05 mole) of (VI) was added to 300 ml. of 50% acetic acid and heated on a steam-bath at 70–80° while 18.7 g. of iron powder was added with constant stirring. After heating and stirring for three hours the mixture was filtered while still hot and the filtrate diluted with 800 ml. of water. This threw out the 2,2'-bis-(trifluoromethyl)-4,4'-diaminodiphenyl sulfone as a white precipitate which was purified by dissolving in 10% hydrochloric acid solution, treating the solution with charcoal, filtering and neutralizing with 20% sodium carbonate. The yield of 2,2'-bis-(trifluoromethyl)-4,4'-diaminodiphenyl sulfone 17.5 g. or 91%. A sample recrystallized from alcohol–water gave white needles, m.p. 211–212°.

Anal. Calcd. for $C_{14}H_{10}O_2N_2SF_6$: S, 8.34. Found: S, 8.39.

Sodium 2-Trifluoromethyl-4-nitrobenzenesulfonate (VIII).—The filtrate, after separation of (VI), was evaporated to half its volume. About 100 ml. of distilled water was then added and the solution was evaporated again. This operation was repeated four or five times to remove nitric acid. The free 2-trifluoromethyl-4-nitrobenzenesulfonic acid (V) may be isolated from the mother liquor by evaporating to incipient crystallization as light yellow, very hygroscopic needles. The sodium salt was prepared by neutralizing the acidic solution with 15% sodium hydroxide solution. Evaporation of the mother liquor to a small volume precipitated the sodium salt of (V) as yellow crystals. This precipitate was filtered off and washed with a little cold alcohol and dried at 120°. It was practically pure, and used for conversion to the sulfonyl chloride without further crystallization. A yield of 30 g. of sodium 2-trifluoromethyl-4-nitrobenzenesulfonate (VIII) was obtained. The corresponding *p*-toluidine[14] salt after recrystallization from water melted at 237–238°, forming white, brilliant crystals.

2-Trifluoromethyl-4-nitrobenzenesulfonyl Chloride (IX).—Twenty-nine and three-tenths grams (0.1 mole) of (VIII) which had previously been dried for two hours at 120° was mixed with 50 g. (0.25 mole) of phosphorus pentachloride. The mixture was heated in an oil-bath at 160–170° for ten hours. From the resulting pasty mass, the phosphorus oxychloride formed was removed by distillation at 105–110°. The residue was cooled and drowned in 300 ml. of ice-water. The crude 2-trifluoromethyl-4-nitrobenzenesulfonyl chloride (IX) precipitated as a red-brown solid which was filtered, washed with cold water, sucked as dry as possible and dried *in vacuo* over concentrated sulfuric acid; yield 22 g., or 76%. This product was recrystallized from ethylene trichloride, m.p. 80–81°.

Anal. Calcd. for $C_7H_3O_4NSClF_3$: Cl, 12.24. Found: Cl, 12.24.

2-Trifluoromethyl-4-nitrobenzenesulfonamide (X).—Five grams of pure (IX), m.p. 80–81°, was added in small portions to 20 g. of 28% ammonia solution at room temperature. The mixture was stirred after each addition and allowed to stand for 90 minutes. After evaporating at 40–45° on a water-bath to dryness, the residue was dissolved in 200 ml. of hot water, treated with charcoal and the solution filtered. Upon cooling, 2-trifluoromethyl-4-nitrobenzenesulfonamide (X) separated which, after recrystallizing from water, melted at 160–161°; yield 3 g., or 64%.

2-Trifluoromethyl-4-aminobenzenesulfonamide (XI).—To a mixture of 3 g. of iron powder in 80 ml. of water and 2 ml. of glacial acetic acid, heated at 70–80° on a steam-bath, 2 g. of (X) was added in portions with continuous stirring. Stirring and heating at 70–80° was continued for three hours whereupon about 60 ml. of ethyl alcohol was added and the mixture boiled, filtered, and the hot filtrate neutralized with 20% solution of sodium carbonate. The solution was treated with charcoal, boiled, and filtered. Upon cooling, 2-trifluoromethyl-4-aminobenzenesulfonamide precipitated as white crystals; yield 1.4 g., m.p. 196–197° from aqueous alcohol.

Anal. Calcd. for $C_7H_7O_2N_2SF_3$: N, 11.66. Found: N, 11.68.

Attempts to condense 2-aminopyrimidine with 2-trifluoromethyl-4-nitrobenzenesulfonyl chloride were unsuccessful.

(14) L. F. Fieser, *Org. Syntheses*, **16**, 65 (1936); THIS JOURNAL, **51**, 2460 (1929).

PHILADELPHIA 22, PENNA. RECEIVED MAY 21, 1951

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

Preparation of Organofluorosilanes Using Aqueous Hydrofluoric Acid[1]

BY N. S. MARANS,[2] L. H. SOMMER AND F. C. WHITMORE[3]

A series of organofluorosilanes has been prepared by reaction of the corresponding organoalkoxysilanes and trialkylchlorosilanes with aqueous hydrofluoric acid.

Organofluorosilanes have been prepared by the following reactions: (1) alkylmagnesium halides and silicon tetrafluoride,[4] (2) hexaalkyldisiloxane and ammonium fluoride–sulfuric acid,[5] (3) dialkyldichlorosilanes and trialkylchlorosilanes with anhydrous hydrogen fluoride,[6] and (4) organochlorosilanes with zinc fluoride or antimony trifluoride.[7–10]

This investigation reports the preparation of organofluorosilanes from organoalkoxysilanes and trialkylchlorosilanes using aqueous hydrofluoric acid. For the most part these reactions were carried out at 0°.

By this method tri-*n*-propylethoxysilane, di-*n*-propyldiethoxysilane, tri-*n*-butylethoxysilane, di-*n*-butyldiethoxysilane, trimethylethoxysilane, diphenyldiethoxysilane, phenylmethyldiethoxysilane, hexadecyltriethoxysilane, triethylchlorosilane and tri-*n*-propylchlorosilane have been converted to

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(1) Paper XXVIII in a series on organosilicon chemistry. For paper XXVII, see THIS JOURNAL, **73**, 882 (1951).

(2) Taken in part from a thesis submitted by N. S. Marans in partial fulfillment of the requirements for the M.S. degree, February, 1947.

(3) Deceased.

(4) J. A. Gierut, F. J. Sowa and J. A. Nieuwland, THIS JOURNAL, **58**, 897 (1936); *cf.* also H. V. Meddoks and N. Z. Kotelkov, *J. Gen. Chem.* (*U. S. S. R.*), **7**, 2007 (1937) or *C. A.*, **32**, 531 ((1938) and H. V. Meddoks and N. Z. Kotelkov, *ibid.*, **8**, 291 (1938) or *C. A.*, **32**, 5392 (1938).

(5) E. A. Flood, THIS JOURNAL, **55**, 1735 (1933).

(6) W. H. Pearlson, T. J. Brice and J. H. Simons, *ibid.*, **67**, 1769 (1945).

(7) A. E. Newkirk, *ibid.*, **68**, 2736 (1946).

(8) P. A. McCusker and C. E. Green, *ibid.*, **70**, 2807 (1948).

(9) H. S. Booth and P. H. Carnell, *ibid.*, **68**, 2650 (1946).

(10) H. S. Booth and R. L. Jarry, *ibid.*, **71**, 971 (1949).

the corresponding organofluorosilanes in 60–95% yields.

In an extension of this method, it was found that the mixtures of dialkyldiethoxysilane and trialkylethoxysilane from the reaction of an alkylmagnesium bromide and ethyl orthosilicate may be treated with four times the stoichiometric quantity of aqueous 48% hydrofluoric acid to give the readily separable dialkyldifluorosilane and trialkylfluorosilane in nearly quantitative yields. However, trialkylsilane, R_3SiH, formed in the reaction of alkylmagnesium bromide and ethyl orthosilicate did not react quantitatively with 48% hydrofluoric acid and remained as a contaminant in the trialkylfluorosilane. Since this impurity could not readily be removed by fractionation, it was removed by treatment with bromine water which gave silanol and disiloxane.

Variation of the amount of 48% hydrofluoric acid in excess of the theoretical for conversion of the alkoxyl radicals to fluoro radicals and variation of the concentration of hydrofluoric acid (from 48 to 6%) were noted to have very little effect on the preparation of diethyldifluorosilane, triethylfluorosilane and di-*n*-propyldifluorosilane. However, in the cases of tri-*n*-propylfluorosilane and tri-*n*-butylfluorosilane, variations in the concentration and mole excess of hydrofluoric acid had a marked effect on the yield.

Experimental

I. Starting Materials.—The following organoalkoxysilanes were obtained from Dow–Corning Corporation and were used without further purification: Diphenyldiethoxysilane,[11] b.p. 106° (0.015 mm.), calcd. for $C_{16}H_{20}SiO_2$: Si, 10.3. Found: Si, 10.4. Hexadecyltriethoxysilane, calcd. for $C_{22}H_{48}SiO_3$: Si, 7.3. Found: Si, 7.4. Phenylmethyldiethoxysilane, calcd. for $C_{11}H_{18}SiO_2$: Si, 13.4. Found: Si, 13.2. Trimethylethoxysilane[12] obtained from Dow-Corning Corporation was fractionally distilled, b.p. 75° (730 mm.), $n^{20}D$ 1.3774.

Preparation of Mixtures of Dialkyldiethoxysilanes and Trialkylethoxysilanes[13] (1) **Diethyldiethoxysilane and Triethylethoxysilane.**—A mixture of diethyldiethoxysilane and triethylethoxysilane containing traces of triethylsilanol and triethylsilane[14] was prepared as follows: In a 22-liter copper reactor[15] there was prepared ethylmagnesium bromide from 384 g., 25.0 g. atoms, of magnesium turnings, 8 liters of ether and 3000 g., 27.6 moles, of ethyl bromide. In one hour with stirring 1240 g., 5.9 moles, of ethyl orthosilicate was added. The mixture was heated under reflux for 12 hours, the ether was distilled, and then the solid mass was heated for 12 hours. Hydrolysis (no acid used), steam distillation and subsequent distillation gave 815 g. of a mixture of diethyldiethoxysilane and triethylethoxysilane. This was a yield of 82% as calculated from the proportion of triethylethoxysilane to diethyldiethoxysilane; assumed to be the same as the proportion of fluorosilanes later obtained by treatment with hydrofluoric acid.

(2) **Di-*n*-propyldiethoxysilane and Tri-*n*-propylethoxysilane.**—The reaction was run in the same manner as above. The quantities used were 437 g., 18.0 g. atoms of magnesium turnings, 2524 g., 18.4 moles, of *n*-propyl bromide, 6 liters of dry ether and 1180 g., 5.67 moles, of ethyl orthosilicate. The final mixture after steam distillation and drying was 938 g. of alkylethoxysilanes, representing an 83% yield.

(3) **Di-*n*-butyldiethoxysilane and Tri-*n*-butylethoxysilane.**—The procedure used was essentially the same as that above. The quantities used were 425 g., 17.5 g. atoms, of magnesium turnings, 5.5 liters of anhydrous ether, 2355 g., 17.6 moles, of *n*-butyl bromide, and 1100 g., 5.28 moles, of ethyl orthosilicate. The preparation differed from the previous two runs in that the organic layer of the product of hydrolysis was separated without steam distillation. The final product of 1120 g. represented a 92% yield.

Separation of the Mixtures of Dialkyldiethoxysilanes and Trialkylethoxysilanes (1) **Di-*n*-propyldiethoxysilane and Tri-*n*-propylethoxysilane.**—Careful fractionation of a mixture of di-*n*-propyldiethoxysilane and tri-*n*-propylethoxysilane (obtained from the reaction of *n*-propylmagnesium bromide and ethyl orthosilicate) gave di-*n*-propyldiethoxysilane, b.p. 184° (730 mm.), $n^{20}D$ 1.4098, d^{20}_4 0.8508, molar refraction, calcd. 59.58, found 59.44. *Anal.* Calcd. for $C_{10}H_{24}SiO_2$: Si, 13.7. Found: Si, 13.6. The material remaining after the fractionation of the di-*n*-propyldiethoxysilane was distilled from sodium and then fractionally distilled to give tri-*n*-propylethoxysilane, b.p. 109° (40 mm.), $n^{20}D$ 1.4245, d^{20} 0.8155, molar refraction, calcd. 63.45, found 63.35. *Anal.* Calcd. for $C_{11}H_{26}SiO$: Si, 13.9. Found: Si, 13.9. These compounds were also characterized by conversion to the corresponding organofluorosilanes.

(2) **Di-*n*-butyldiethoxysilane and Tri-*n*-butylethoxysilane.**—Purification of these compounds from their mixture was accomplished in the same manner as above. Fractionation gave di-*n*-butyldiethoxysilane, b.p. 125° (38 mm.), $n^{20}D$ 1.4190, d^{20}_4 0.8500, molar refraction calcd. 68.84, found 68.98, and tri-*n*-butylethoxysilane, b.p. 145° (34 mm.), $n^{20}D$ 1.4341, d^{20}_4 0.8246; molar refraction calcd. 77.34, found 77.17.

Anal. Calcd. for $C_{12}H_{28}SiO_2$: Si, 12.1. Found: Si, 12.0. Calcd. for $C_{14}H_{32}SiO$: Si, 11.5. Found: Si, 11.5.

Triethylchlorosilane and Tri-*n*-propylchlorosilane.—Hexaethyldisiloxane was obtained from the reaction of ethylmagnesium bromide and ethyl orthosilicate. By treatment of hexaethyldisiloxane with ammonium chloride and sulfuric acid and subsequent fractionation triethylchlorosilane was obtained. Tri-*n*-propylchlorosilane was prepared in a similar manner substituting *n*-propylmagnesium bromide for ethylmagnesium bromide.

II. Preparation of Organofluorosilanes from Purified Organoalkoxysilanes.—A typical preparation of an organofluorosilane taken from those in Table I is given below. In a 1250-cc. copper flask, fitted with a stirrer and cooled in an ice-bath to 0°, there were placed 100 g., 2.4 moles, of 48% hydrofluoric acid, and 52 g., 0.258 mole, of di-*n*-propyldiethoxysilane. The mixture was stirred for three hours and then the upper organic layer separated. Fractionation of the organic layer gave 37.0 g., 0.243 mole, of di-*n*-propyldifluorosilane, 95.5% yield.

Preparation of Dialkyldifluorosilanes and Trialkylfluorosilanes from Mixtures of Dialkyldiethoxysilane and Trialkylethoxysilane (1) **Triethylfluorosilane and Diethyldifluorosilane.**—Analyses for the compounds prepared in the following runs are given in Table II. In a 1250-cc. copper flask in an ice-bath and equipped with a stirrer, there were placed 390 g., 9.5 moles, of 48% hydrofluoric acid and 290 g., (*ca.* 1.75 moles) of a mixture of diethyldiethoxysilane and triethylethoxysilane. The above mixture with the temperature maintained at 0° was stirred for three hours. Fractionation of the organic layer, 216 g., gave 107.8 g., 0.95 mole, of diethyldifluorosilane, 45% yield based on starting ethyl orthosilicate. The remaining material, 95 g. was treated with 300 cc. of saturated bromine water,[16] and after drying over magnesium carbonate, fractionation gave 57 g., 0.43 mole, of triethylfluorosilane, 21% yield based on ethyl orthosilicate. The total yield based on ethyl orthosilicate was 66%.

(2) **Di-*n*-propyldifluorosilane and Tri-*n*-propylfluorosilane.**—The same procedure was used as above with the following materials: 360 g., 8.5 moles, of 48% hydrofluoric acid and 305 g. (*ca.* 1.5 moles) of a mixture of di-*n*-propyldiethoxysilane and tri-*n*-propylethoxysilane. Final fractionation gave 145.0 g., 0.95 mole, of di-*n*-propyldifluorosilane, 52% yield based on ethyl orthosilicate, and 45.0 g., 0.256 mole, of tri-*n*-propylfluorosilane, 14% yield based on

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[11] F. S. Kipping and A. G. Murray, *J. Chem. Soc.*, 2734 (1927).

[12] R. Sauer, This Journal, **66**, 1707 (1944).

[13] P. A. DiGiorgio, W. A. Strong, L. H. Sommer and F. C. Whitmore, *ibid.*, **68**, 1380 (1946).

[14] This is formed in small quantities in the reaction of an alkylmagnesium bromide and ethyl orthosilicate.

[15] This copper reactor was designed especially for large scale Grignard preparations by Dr. N. C. Cook of this Laboratory.

[16] Bromine water was not used on the entire organofluorosilane mixture as bromination on the alkyl side chain in the dialkyldifluorosilanes is extensive.

TABLE I

PREPARATION OF ORGANOFLUOROSILANES

Compound[a]		Organoalkoxysilane, mole	Hydrofluoric acid (48%), moles	B.p., °C.	P, mm.	Yield, %	Fluorine,[b] % Calcd.	Found
Di-*n*-propyldifluorosilane	I	0.255	2.4	111	733	95.5	25.00	25.04
Di-*n*-butyldifluorosilane	II	.172	2.4	156	733	93.6	21.03	20.88
Tri-*n*-propylfluorosilane	III	.185	2.25	170	733	91.3	10.78	10.92
Tri-*n*-butylfluorosilane	IV	.129	1.9	222	730	89.2	8.70	8.84
Trimethylfluorosilane	V	.33	2.1	19	730	70.3	20.63	20.75
Hexadecyltrifluorosilane[c,d]	VI	.103	3.0	171	45	55.8	18.36	18.00
Diphenyldifluorosilane	VII	.147	2.0	157	50	71.5	17.09	17.34
Phenylmethyldifluorosilane[e]	VIII	.276	3.2	141	730	69.5	24.02	23.90

[a] References describing previous preparations of the compounds listed in Table I and II are as follows: compound V is included in reference 5, compounds III, IV and IX, in reference 4, compounds II and IV in reference 6, and compounds V and VIII in reference 17. [b] The volumetric method of analysis was used for fluorine. [c] This preparation was stirred at 25° for 12 hours. Shorter times and lower temperatures gave incomplete conversion. [d] The $d^{20}{}_4$ of hexadecyltrifluorosilane is 0.9221. [e] The $d^{20}{}_4$ of phenylmethyldifluorosilane is 1.0993.

ethyl orthosilicate. The total yield based on ethyl orthosilicate was 66%.

(3) **Di-*n*-butyldifluorosilane and Tri-*n*-butylfluorosilane.**—The same procedure was used as above, employing 338 g., 8.3 moles, of 48% hydrofluoric acid and 400 g. (*ca.* 1.9 moles) of a mixture of di-*n*-butyldiethoxysilane and tri-*n*-butylethoxysilane. Final fractionation gave 120 g., 0.67 mole, of di-*n*-butyldifluorosilane, a 36% yield based on ethyl orthosilicate, and 154 g., 0.71 mole, of tri-*n*-butylfluorosilane, 38% yield based on ethyl orthosilicate. The total yield based on ethyl orthosilicate was 74%.

TABLE II

ANALYSES AND PHYSICAL PROPERTIES OF ORGANOFLUOROSILANES PREPARED FROM MIXTURES

Compound[a]	$d^{20}{}_4$	Fluorine, % Calcd.	Found[b]	Found[c]
Triethylfluorosilane (IX)	0.8361	14.15	14.14 14.16	14.12 14.18
Tri-*n*-propylfluorosilane (III)	.8383	10.77	10.79 10.78	10.80 10.83
Tri-*n*-butylfluorosilane (IV)	.8402	8.70	8.70 8.72	8.72 8.73
Diethyldifluorosilane[d] (X)	.9348	30.64	31.10 30.40	30.9 30.8
Di-*n*-propyldifluorosilane (I)	.9113	25.00	25.18 25.13	25.5 25.3
Di-*n*-butyldifluorosilane (II)	.8999	21.09	20.99 21.09	21.6 21.7

[a] Literature values for $d^{25}{}_4$, Compound II 0.9408, Compound III 0.8339, Compound IV 0.8372, Compound IX 0.8345. [b] Fluorine was determined by the lead chlorofluoride method (Method B). [c] Fluorine was determined by the volumetric method (Method A). [d] Reference 6 describes a previous preparation of this compound.

Effect of Concentration and Excess of Hydrofluoric Acid on the Conversion of Organoalkoxysilanes to Organofluorosilanes.—A mixture of 48% hydrofluoric acid and a mixture composed of dialkyldiethoxysilane and trialkylethoxysilane was stirred at 0° for three hours and the organic layer was then fractionally distilled. Both the mole equivalents of 48% hydrofluoric acid and the concentration of the hydrofluoric acid were varied to study the effect on the yields of organofluorosilanes. The results of the runs are tabulated in Table III. Significant variations are those for tri-*n*-propylfluorosilane and tri-*n*-butylfluorosilane.

III. **Preparation of Trialkylfluorosilanes from Trialkylchlorosilanes** (1) **Triethylfluorosilane.**—To a 500-cc. copper flask in an ice-bath there were added 120 g., 2.9 moles, of 48% hydrofluoric acid and 45 g., 0.30 mole, of triethylchlorosilane. The mixture was stirred at 0° for five hours and then the upper organic layer was separated and dried over sodium sulfate. Fractionation gave 32.5 g., 0.243 mole, of triethylfluorosilane, b.p. 109° (730 mm.), 81% yield. Reduction of the time of the reaction or the reduction of the mole equivalents of hydrofluoric acid used reduced the yields.

TABLE III

EFFECT OF CONCENTRATION OF HYDROFLUORIC ACID AND MOLE EXCESS ON YIELDS OF DIALKYLDIFLUOROSILANES AND TRIALKYLFLUOROSILANES FROM THE CORRESPONDING ALKOXYSILANES

Run	Wt. of mono- and di- ethoxy compounds,[a] g.	Concentration of hydrofluoric acid, %	Mole equivalents of hydrofluoric acid[b]	R_2SiF_2 yield, %[c,d]	R_3SiF yield, %[c,d]
		Ethylfluorosilanes			
1	150	48	4	40	46
2	105	48	2	33	43
3	150	48	1.5	37	46
4	150	24	2	40	43
5	150	12	2	41	47
6	150	6	2	38	43
		n-Propylfluorosilanes			
1	150	48	4	21	63
2	150	48	2	23	68
3	150	48	1.5	21	47
4	150	24	2	24	47
5	150	12	2	24	36
6	150	6	2	22	20
		n-Butylfluorosilanes			
1	150	48	4	5	76
2	150	48	2	5	40

[a] These mixtures are unreported preparations of dialkyldiethoxysilanes and trialkylethoxysilanes. The same preparation was used for the entire series. [b] The amount of 48% hydrofluoric acid required to react stoichiometrically with all alkoxyl groups present in the mixture of dialkyldiethoxysilane and trialkylethoxysilane is one mole equivalent of hydrofluoric acid. [c] The yields are based on ethyl orthosilicate and the summation of the yields of R_2SiF_2 and R_3SiF represents the total yield. [d] The trialkylsilane, R_3SiH, was not removed in these reactions.

(2) **Tri-*n*-propylfluorosilane.**—The same procedure was used as above, employing 70 g., 1.7 moles, of 48% hydrofluoric acid and 28 g., 0.145 mole, of tri-*n*-propylchlorosilane. Fractionation gave 15 g., 0.085 mole, of tri-*n*-propylfluorosilane, b.p. 170–172° (730 mm.), 58% yield. Reduction of the time or of the mole equivalents of hydrofluoric acid used reduced the yield.

IV. **Analytical Methods for Fluorine. Method A (Volumetric).**—A weighed sample *ca.* 0.4 g., of the alkylfluorosilane was shaken for five minutes in the presence of a measured excess of standard 0.1 *N* NaOH (100% excess), and 150 ml. of methanol. The excess of sodium hydroxide was back-titrated with standard 0.1 *N* HCl using phenolphthalein as an indicator. In all cases a blank run was made using the same amount of sodium hydroxide solution in methanol. Results for the organofluorosilanes are given in

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(17) H. J. Emeleus and C. G. Wilkins, *J. Chem. Soc.*, 454 (1944).

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.

STATE COLLEGE, PA.

RECEIVED MARCH 4, 1950

[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.

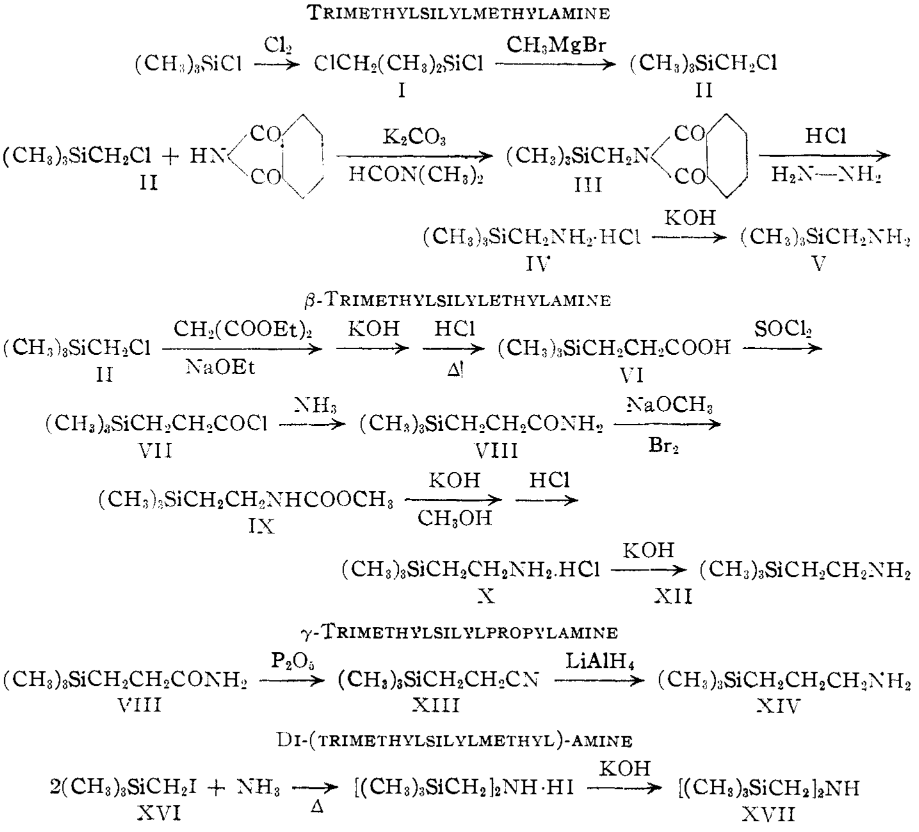

Fig. 1.—The synthesis of aliphatic amines containing organosilicon substituents.

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).