

30 mg/kg of body weight caused only 3% inhibition, but the tumor growth could be inhibited to 85% by increasing the dose to 120 mg/kg.

Discussion

The Structure of Picrates.—The elemental analyses of the picrates prepared from 4'-aminobutyrophenone hydrochlorides indicate that the products have been dehydrated. Perhaps dehydration occurred during the process of converting the hydrochlorides into the picrates. Since all the picrates were subjected to prolonged heating in absolute alcohol during recrystallization, it seemed reasonable to suspect that the heating caused dehydration. In order to test this premise, the attempted picrate of 4'-chloro-4-aminobutyrophenone was also prepared by adding an aqueous solution of picric acid to the aqueous solution of 4'-chloro-4-aminobutyrophenone hydrochloride. The precipitate was thoroughly washed with water and dried at 40°. The infrared spectrum and the melting point of this product proved that the compound was identical with a sample of 2-(4-chlorophenyl)- Δ^1 -pyrroline picrate. This experiment indicated that dehydration and cyclization took place at room temperature and was not due to the influence of heat during recrystallization. The detailed structures of these pyrroline picrates will be discussed in a subsequent paper.

Structure-Activity Relationships.—The *in vivo* antitumor screening of 4-aminobutyrophenone hydrochloride indicated that this compound possessed a weak carcinostatic activity, but the effect was not significant from a practical view point. The *in vitro* cytotoxicity tests against protozoa, bacteria, and mammalian cells disclosed three interesting generalities for structure-activity relationships. In general the growth-inhibitory activity of the pyrimidinylhydrazones of 4-aminobutyrophenone hydrochlorides are twice as great as that of the parent 4-aminobutyrophenone hydrochlorides.

The second generality points out that the growth-inhibitory activities are greater for the hydrochlorides with an electronegative halogen atom at the *para* position of the benzene nucleus than for those carrying an electropositive moiety such as hydrogen, methyl, or methoxyl at the same position of the phenyl ring. The third generality indicates that the growth-inhibitory activities of the 4'-halogeno-4-aminobutyrophenone hydrochlorides and their pyrimidinylhydrazones vary with the sizes of the halogen atoms. Thus the activity of the bromo derivative is greater than that of the chloro derivative, which, in turn, is greater than that of the fluoro derivative (Tables IV and VII). Consequently, it seems that both inductive and mesomeric effects play a role in determining the magnitudes of the growth-inhibitory activities of the compounds being tested.

TABLE VII
RELATIVE GROWTH-INHIBITORY ACTIVITIES OF
4-AMINOBUTYROPHENONE HYDROCHLORIDES AND
2-AMINOACETOPHENONE HYDROCHLORIDES

Organism	Order of activity ^a
<i>E. coli</i>	13 > 10 > 11 > 14 > 15 > 8 > 17 > 12 > 16 > 7 > 9
<i>K. pneu.</i> <i>moniae</i>	16 > 13 > 17 > 10 > 14 > 11 > 15 > 12 > 8 > 9 > 7
<i>P. vulgaris</i>	13 > 16 > 17 > 10 > 14 > 11 > 9 > 12 > 8 > 15 > 7
<i>P. aeru.</i> <i>ginosa</i>	15 > 13 > 8 > 16 > 17 > 12 > 14 > 10 > 7 > 9 > 11
<i>S. aureus</i>	16 > 17 > 13 > 10 > 11 > 14 > 15 > 8 > 9 > 12 > 7
<i>T. pyri-</i> <i>formis</i>	13 > 10 > 11 > 14 > 8 > 16 > 15 > 9 > 17 > 12 > 7
KB cell culture	17 > 10 > 16 > 9 > 11
L cell culture	17 > 16 > 10 > 11 > 9

^a The numbers correspond to the compounds listed in Tables II-III.

Among five species of bacteria and one species of protozoa tested, the *P. aeruginosa* test system seemed to show more irregularities in adhering to the above generalities than other test systems.

Some Herbicidal Silicon Compounds

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A large number of organofunctional silicon compounds were examined for biological activity. A small, closely related group of (haloalkyl)silicon compounds was found to have strong herbicidal activity in both pre-emergence and postemergence screening tests, and to act in some cases as defoliant. The active compounds are leachable in moist soil but seem to become fixed upon drying. These compounds seem to be the first organo-silicon compounds that have been found to have herbicidal activity.

A program of screening silicon compounds for biological activity revealed a small group of closely related structures that have strong herbicidal activity. Although there exists extensive literature concerned with the herbicidal properties of thousands of chemical compounds, no reference could be found for such activity in an organosilicon compound. Therefore, these results were especially interesting as the first of their kind.

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Active compounds had RCHXSiMeY₂ for their structure with R = H or CH₃; X = Cl, Br, or I; and Y being Cl, F, or an alkoxy group. Variations of this structure such as RCX₂SiMeY₂ or RCHXSiMeY or RCHXSiY₃ showed no activity. (Trichloromethyl)methylidimethoxysilane [Cl₃CMeSi(OMe)₂] was active and an exception to the above generalizations.

Hydrolysis of Y and the formation of siloxane polymers would be expected during the testing of all of the active compounds. Therefore the corresponding polymer [ClCH₂MeSiO]_x was prepared. It had very little

TABLE I
 TEST RESULTS^a

Compd	Preemergence				Postemergence			
	5.6 g of compd/m ²		2.24 g of compd/m ²		Spray concn, 4000 ppm		Spray concn, 10,000 ppm	
	Japanese millet	Radish	Japanese millet	Beans	Corn	Tomato	Japanese millet	Beans
ClCH ₂ MeSi(OMe) ₂	100	95	100	100	30	100	40	100
ClCH ₂ MeSi(OEt) ₂	100	100	100	100	30	60	40	100
ClCH ₂ MeSi(O- <i>i</i> -Pr) ₂	100	85	91	100	0	98	30	100
ClCH ₂ MeSiCl ₂	90	40	98	100	0	40	30	100
ClCH ₂ MeSiF ₂	100	100	100	100	20	50	100	90
BrCH ₂ MeSi(OMe) ₂	99	60	70	95	0	70	30	100
ICH ₂ MeSi(OEt) ₂	100	50	98	100	0	20	30	70
CH ₃ CHClMeSi(OMe) ₂	100	70	90	98	0	30	60	95
ClCH ₂ CH ₂ MeSi(OMe) ₂	0	0	0	0	0	0	0	0
ClCH ₂ CHClMeSi(OMe) ₂	0	0	0	0	0	0	0	0
ClCH ₂ CHClSi(OMe) ₃	0	0	0	0	0	0	0	0
ClCH ₂ Me ₂ SiOEt	0	0	0	0	0	0	0	0
Cl ₂ CHMeSi(OMe) ₂	0	0	0	0	0	0	0	0
Cl ₂ CHMeSiCl ₂	0	0	0	0	0	0	0	0
Cl ₂ CHMe ₂ SiOMe	0	0	0	0	0	0	0	0
Cl ₂ CHMe ₃ Si	0	0	0	0	0	0	0	0
Cl ₃ CMeSi(OMe) ₂	95	40	85	100	0	0	20	95
MeOCH ₂ MeSi(OMe) ₂	0	0	0	0	0	0	0	0
(ClCH ₂ Me ₂ Si) ₂ O	0	0	0	0	0	0	0	0
Me ₂ SiCl ₂	0	0	0	0	0	0	0	0
MeSiCl ₃	0	0	0	0	0	0	0	0
MeSi(OMe) ₃	0	0	0	0	0	0	0	0
<i>n</i> -PrSi(OMe) ₃	0	0	0	0	0	0	0	0
ClCH ₂ CH ₂ CH ₂ Si(OMe) ₃	0	0	0	0	0	0	0	0
ClCH ₂ CH ₂ CH ₂ Me ₂ SiOEt	0	0	0	0	0	0	0	0
ClCH ₂ CHClCH ₂ Si(OMe) ₃	0	0	0	0	0	0	0	0
(ClCH ₂ MeSiO) _n polymer	40	40	0	0	0	0

^a Ratings are on a scale of 100 = kill, 0 = no effect.

activity. This suggests that the biologically active species in these tests may have been silanols or water-soluble low polymers of the formula HO[ClCH₂MeSiO]_{*x*}H in which *x* had low values, perhaps 1, 2, or 3.

The compounds listed in Table I were applied to the surface of the soil for the effect upon preemergent seeds and applied as a spray upon healthy foliage. None of these compounds showed an effect upon aquatic plants or upon algae.

The data in Table I indicate that silicon compounds of the type XCSi(Y)₂C were most active as herbicides when X was chlorine, and slightly less active when X was bromine or iodine. As long as Y remained any of the groups commonly known to be subject to easy hydrolysis from silicon, changes in Y had only minor effects upon the activity of the compound. Changing the number of Y groups on silicon to 0, 1, or 3, or the number of X groups on carbon to 0 or 2, destroyed the activity.

Trichloromethylmethyldimethoxysilane [Cl₃CMeSi(OMe)₂] is active, but 1,2-dichloroethylmethyldimethoxysilane [ClCH₂CHClMeSi(OMe)₂] which seems to meet the requirements of the above generalized formula proved to be inactive.

Chloromethylmethyldiethoxysilane was selected for more extensive tests in a greenhouse as a preemergent herbicide. The results of these tests are shown in Table II.

The response plants showed to chloromethylmethyldiethoxysilane was unusual. The broadleaved species of plants emerged as seedlings and the first leaves opened normally. The leaves then wrinkled, browned at the edges, became malformed, and in some cases

 TABLE II
 PREEMERGENCE TESTS^a WITH ClCH₂MeSi(OEt)₂

Test plants	g of ClCH ₂ MeSi(OEt) ₂ /m ²				
	2.24	1.12	0.56	0.22	0.11
Soybeans	100	100	100	100	100
Sugar beets	100	100	100	100	100
Cotton	100	100	100	100	60
Cranberry beans	100	100	100	90	60
Sudan grass	100	99	99	60	40
Wheat	100	100	100	40	40
Barley	100	100	100	40	40
Crabgrass	100	106	95	0	0
Meadow fescue	100	90	90	20	0
Japanese millet	100	98	80	40	0
Wild oats	98	80	60	50	0
Johnson grass	95	90	60	0	0

^a Ratings are on a scale of 100 = kill, 0 = no effect.

dropped from the plant. The growing tips burned and in severe cases the plants died. Grass seedlings usually did not emerge at the higher rates of application. At lower rates, the grass seedlings emerged, turned a pale, yellowish green and died back from the tips.

Chloromethylmethyldiethoxysilane was dispersed in water and sprayed onto plants at the concentrations shown in Table III. The plants were sprayed to wetness.

The response of broadleaved plants showed three effects to varying degrees. First, the plants were stunted; second, the foliage became yellow and necrosis started at the tips and edges of the leaves; and third, the plants were defoliated. The typical response of grass was that of stunting with yellowing of the foliage.

TABLE III
POSTEMERGENCE TESTS^a OF $\text{ClCH}_2\text{MeSi}(\text{OEt})_2$

Test plants	Concn of spray, ppm		
	10,000	5000	2000
Pigweed	100	100	80
Pinto bean	100	90	90
Marigold	100	100	50
Cucumber	98	80	60
German millet	98	40	20
Large crabgrass	95	80	30
Japanese millet	40	20	20
Wild oats	40	30	0
Radish	40	20	10
Corn	30	20	0
Sudan grass	30	20	20
Meadow fescue	20	20	0

^a Ratings are on a scale of 100 = kill, 0 = no effect.

The ease with which chloromethylmethyldiethoxysilane was leached through soil was measured in columns 45.7 cm deep and 7.6 cm in diameter. The compound was applied to the top of the column at a rate of 2.24 g/m² and leached with water. In one series of tests the water was applied immediately. In a second series, the soil was permitted to stand dry for 1 week before the leaching.

In the first series, the active chemical was detected at a depth of 20.3 cm in the column when water to a depth of 15–30 cm was used for leaching. In the second series, the penetration was only 5 cm. The distribution of the chemical in the soil was measured by comparing the growth of seeds planted in soil taken from different levels in each column. The data indicate that the silicon compound is fairly mobile in wet soil, but that once it dries on the particles of soil, it becomes resistant to the leaching effects of water.

In order to determine persistence, the herbicide was applied at 2.24 g/m² as a preemergent treatment to soil in 20.3-cm glazed crocks. The soil was watered as required for good growth of plants but not enough to cause leaching through the bottom of the pots. Plant growth was observed during 4 weeks, after which the plants were carefully removed from the soil. A second planting was made in the same soil and the cycle was repeated with no further application of the chemical until herbicidal effects were no longer observed. Results of these tests shown in Table IV indicate that the effect of the chemical disappears during the fourth month.

TABLE IV
MONTHLY PLANTINGS IN SOIL TREATED ONCE
WITH $\text{ClCH}_2\text{MeSi}(\text{OEt})_2$ ^a

Planting no.	Japanese millet	Radish	Wild oats	Cranberry bean
1	95	40	90	100
2	90	0	20	70
3	70	0	0	30
4	0	0	0	0

^a Rating on a scale of 100 = kill, 0 = no effect.

Experimental Section

Reagents.—Methyltrichlorosilane, dimethyldichlorosilane, methyltrimethoxysilane, and *n*-propyltrimethoxysilane were redistilled commercial materials sold by Dow Corning Corp.

Chlorination of trimethylchlorosilane was carried out as described by Speier.² The chlorinated products were separated by distillation. Chloromethylmethyldichlorosilane, bp 115° (734 mm), and dichloromethylmethyldichlorosilane, bp 148° (734 mm), were isolated. Dimethyldichlorosilane was similarly chlorinated. Distillation then gave the compounds previously described: chloromethylmethyldichlorosilane,³ bp 122°; dichloromethylmethyldichlorosilane, bp 149°;⁴ and trichloromethylmethyldichlorosilane, mp 99–97°.⁵

Chloromethylmethylethoxysilane was prepared from the corresponding chlorosilane as previously described,⁵ bp 132°.

Dichloromethylmethyldimethoxysilane was prepared by adding anhydrous methanol (3.8 moles) to a solution of dichloromethylmethyldichlorosilane (3.4 moles) in 500 ml of petroleum ether (Skelly F). The mixture was heated to reflux briefly to drive out most of the HCl that formed. The solution was then cooled to room temperature, saturated with anhydrous NH₃, filtered free of NH₄Cl, and distilled to give 470 g (79% yield), bp 66° (35 mm), *n*_D²⁵ 1.4392, *d*₄²⁵ 1.1260, *R*_D 0.2333, calcd *R*_D 0.2336.⁶

Chloromethylmethyldimethoxysilane was prepared in the preceding manner from chloromethylmethyldichlorosilane, bp 138°, *n*_D²⁵ 1.4094, *d*₄²⁵ 1.058, *R*_D 0.2343, calcd *R*_D 0.2368.

Chloromethylmethylethoxysilane was prepared from chloromethylmethyldichlorosilane (481 g, 3 moles) and ethyl orthoformate (1,000 g, 7 moles) by the procedure of Shorr⁷ in 85% yield, bp 74° (30 mm), *n*_D²⁵ 1.4123, *d*₄²⁵ 0.9952, *R*_D 0.2502, calcd *R*_D 0.2515.

Anal. Calcd for C₆H₁₃ClO₂Si: Si, 15.39. Found: Si, 15.43, 15.44.

Chloromethylmethyldiisopropoxysilane was prepared from chloromethylmethyldichlorosilane and isopropyl alcohol in petroleum ether, bp 91° (40 mm), *n*_D²⁵ 1.4114, *d*₄²⁵ 0.951, *R*_D 0.2613, calcd *R*_D 0.2617.

Dichloromethylmethyldimethoxysilane was prepared from dichloromethylmethyldichlorosilane (3.6 moles) and anhydrous methanol (7.5 moles) in 500 ml of petroleum ether. Distillation gave 588 g (87% yield), bp 88° (50 mm), *n*_D²⁵ 1.4332, *d*₄²⁵ 1.1917, *R*_D 0.2181, calcd *R*_D 0.2118.

Trichloromethylmethyldimethoxysilane was prepared in the same manner from trichloromethylmethyldichlorosilane (465 g) in unusually low yield (137 g), bp 80° (25 mm), *n*_D²⁵ 1.441, *d*₄²⁵ 1.2521, *R*_D 0.2122, calcd *R*_D 0.2118.

Iodomethylmethylethoxysilane.—Chloromethylmethyldiethoxysilane (320 g, 1.75 moles) and NaI (300 g, 2 moles) in acetone (750 ml) were stirred and refluxed intermittently for 6 days. At the end of this time, a vapor phase chromatogram (vpc) indicated that the metathesis was greater than 99% complete. The mixture was then filtered and distilled to give 374 g (1.37 moles, 78% yield) of purity greater than 99% by vpc, bp 101° (30 mm), *n*_D²⁵ 1.4660, *d*₄²⁵ 1.414, *R*_D 0.1959, calcd *R*_D 0.1972.

Anal. Calcd for C₆H₁₃IO₂Si: Si, 10.23. Found: Si, 10.37, 10.31.

Bromomethylmethyldimethoxysilane was prepared from the corresponding dichlorosilane, which was made by brominating dimethyldichlorosilane with BrCl by the method of Speier.⁸ The bromomethylmethyldichlorosilane had bp 50° (25 mm), *n*_D²⁵ 1.4758.

Anal. Calcd for BrCH₂MeSiCl₂: neut equiv, 103.9. Found: neut equiv, 104.1, 104.7.

This product was heated to reflux 3 hr with a slight excess of methyl orthoformate and stripped free of volatiles under vacuum to give bromomethylmethyldimethoxysilane, *n*_D²⁵ 1.4352, *d*₄²⁵ 1.324, *R*_D 0.197, calcd *R*_D 0.197.

Chlorination of ethylmethyldichlorosilane (3375 g, 25 moles) was performed by the photocatalyzed reaction with chlorine in an apparatus designed to favor the formation of monochlorinated

(2) J. L. Speier, *J. Am. Chem. Soc.*, **73**, 824 (1951).

(3) R. H. Kriebel and I. R. Elliott, *ibid.*, **67**, 1810 (1945).

(4) A. D. Petrov, V. F. Mironov, and N. A. Pogankina, *Dokl. Akad. Nauk. SSSR*, **81**, 100 (1955).

(5) H. Freiser, M. V. Eagle, and J. L. Speier, *J. Am. Chem. Soc.*, **75**, 2824 (1953).

(6) Specific refractions, *R*_D, were calculated using the values for bond refractions published by E. L. Warrick, *ibid.*, **68**, 2455 (1946), and revised by the use of C–C and C–H values of A. I. Vogel, W. T. Creswell, and J. Leicester, *J. Phys. Chem.*, **58**, 174 (1954).

(7) L. M. Shorr, *J. Am. Chem. Soc.*, **76**, 1300 (1954).

(8) J. L. Speier, *ibid.*, **73**, 826 (1951).

products.⁹ The products were carefully fractionated. The first product was 1-chloroethylmethyldichlorosilane (1645 g, 9.3 moles, 37% yield), bp 136.7°, n_D^{20} 1.4477, d_4^{25} 1.219, R_D 0.2196, calcd R_D 0.2185.

Anal. Calcd for MeCHClSiMeCl₂: neut equiv, 88.8. Found: neut equiv, 88.9.¹⁰

This fraction was followed by a rather large intermediate fraction which by vpc analysis was a mixture of four compounds including the above, two which were not identified, and 2-chloroethylmethyldichlorosilane, the highest boiling of the four. Distillation at 100 mm gave a large fraction of the last of these, essentially pure by vpc (1527 g, 8.6 moles, 34% yield), bp 95° (100 mm), n_D^{20} 1.4561, d_4^{25} 1.241, R_D 0.2191, calcd R_D 0.2185.¹¹

Anal. Calcd for ClCH₂CH₂SiMeCl₂:¹² neut equiv, 59.2. Found: neut equiv, 60.1.

1-Chloroethylmethyldimethoxysilane was prepared by adding methyl orthoformate (232 g, 2.2 moles) dropwise to 1-chloroethylmethyldichlorosilane (177 g, 1 mole) and by heating the solution to reflux overnight. Methanol (12 ml) was then added, and the solution was permitted to stand until the next day before it was distilled to give 157 g (92%), bp 60° (25 mm), n_D^{20} 1.4149, d_4^{25} 1.028, R_D 0.2435, calcd R_D 0.2448. The sample was essentially neutral with a neutralization equivalent greater than 21,000.

2-Chloroethylmethyldimethoxysilane was prepared from 2-chloroethylmethyldichlorosilane (177 g, 1 mole) in the same manner; yield 153 g (91%), bp 68–70° (23–25 mm), n_D^{20} 1.4218, d_4^{25} 1.040, R_D 0.2443, calcd R_D 0.2448.

Anal. Calcd¹² for ClCH₂CH₂MeSi(OMe)₂: neut equiv, 168.7. Found: neut equiv, 168.3, 169.3.

3-Chloropropylmethylethoxysilane was a portion of the sample described by Saam and Speier.¹³

3-Chloropropyltrimethoxysilane was a portion of the sample previously described.¹⁴

sym-**Bis(chloromethyl)tetramethyldisiloxane** was prepared by hydrolysis of chloromethylmethyldichlorosilane and had the properties described.^{4,15}

Methoxymethylmethyldimethoxysilane was prepared in anhydrous methanol from chloromethylmethyldimethoxysilane and an excess of sodium methoxide at room temperature. The progress of the reaction was followed by vpc analyses. In about 8 days, about 10% of the chloride remained. Most of it had been converted to a mixture made up of about 90% of the methyl ether and 10% methyltrimethoxysilane. The methanol was then removed under vacuum. The residue was shaken with petroleum ether and filtered free of solids. The filtrate was

distilled. Each fraction was contaminated by amounts of chloromethylmethyldimethoxysilane detectable by vpc analyses. The best fractions were combined and redistilled. Three fractions were obtained (34.6% yield) which contained no chloride and which appeared to be better than 99% pure by vpc, bp 47° (30 mm), n_D^{20} 1.3917, d_4^{25} 0.9389, R_D 0.2534, calcd R_D 0.2594.

Anal. Calcd for C₅H₁₄O₃Si: C, 40.0; H, 9.42; Si, 18.72. Found: C, 40.2; H, 9.8; Si, 18.66.

Chloromethylmethyldifluorosilane was prepared by adding chloromethylmethyldichlorosilane slowly to a stirred solution (200 ml) of 50% HF in a polyethylene bottle. The stream of HCl and fluorosilane that was generated was condensed into a Dry Ice cooled trap. The trap was then permitted to warm very slowly to room temperature so that most of the HCl evaporated. The residue was distilled to give 46% yield of product, bp 64° (744 mm), n_D^{20} 1.3526, d_4^{25} 1.207, R_D 0.179, calcd R_D 0.179.

Anal. Calcd for C₂H₅ClF₂Si: F, 29.1. Found: F, 28.6, 28.7.

The nmr H¹ spectrum of this compound shows a triplet at τ 9.49 for the CH₂SiF₂ protons, and a triplet at 7.18 for the ClCH₂SiF₂ protons.

1,2-Dichloroethyltrimethoxysilane.—Vinyltrichlorosilane (168 g, 1.04 moles) was chlorinated with chlorine (63.4 g, 0.89 mole) at 40–50° with strong illumination and the product was distilled. 1,2-Dichloroethyltrichlorosilane (191 g, 0.82 mole) was obtained; bp 86° (30 mm), n_D^{20} 1.4852.¹⁶

Anal. Calcd for ClCH₂CHClSiCl₂: neut equiv, 58.1. Found: neut equiv, 58.5.

An excess of methyl orthoformate was cautiously added to a portion of the above product (56.8 g, 0.25 mole). A very vigorous reaction took place. When it subsided, the product was distilled to give 1,2-dichloroethyltrimethoxysilane (45.5 g, 0.24 mole), bp 69–71° (89–93 mm), n_D^{20} 1.4369, d_4^{25} 1.227, R_D 0.2143, calcd R_D 0.2136.

Anal. Calcd for ClCH₂CHClSi(OMe)₃: neut equiv, 219. Found: neut equiv, 214.

1,2-Dichloroethylmethyldimethoxysilane was prepared by the preceding method from vinylmethyldichlorosilane. The crude product was not purified. Vapor phase chromatography indicated that it was at least 95% pure. It was used as such.

Anal. Calcd for ClCH₂CHClSiMe(OMe)₂: neut equiv, 203. Found: neut equiv, 190.

2,3-Dichloropropyltrimethoxysilane was prepared from allyltrichlorosilane in the manner described to form 2,3-dichloropropyltrichlorosilane, bp 105° (30 mm), n_D^{20} 1.4872.¹⁷ Methyl orthoformate converted this to 2,3-dichloropropyltrimethoxysilane in 88% yield, bp 206°, n_D^{20} 1.4412, d_4^{25} 1.203, R_D 0.2194, calcd R_D 0.2217.

Acknowledgment.—Most of the syntheses reported here were done by M. C. Musolf and Marilyn Stober in the Organic Research Laboratory, Dow Corning Corp.

(16) This synthesis is essentially that of C. L. Agre and W. Billing, *ibid.*, **74**, 3895 (1952), who report bp 63–65° (13 mm), n_D^{20} 1.4876.

(17) A. D. Petrov, V. F. Mironov, V. G. Chukhovtsev, and Yu. P. Egorov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1091 (1957), reported bp 208.5° (717 mm), n_D^{20} 1.4884.

(9) J. L. Speier, U. S. Patent 2,510,149 (June 6, 1950).

(10) V. A. Ponomarenko, B. A. Sokolov, and A. D. Petrov, *Bull. Acad. Sci. USSR*, 633 (1956), describe this compound as having bp 134° (7.1 mm), n_D^{20} 1.4490, d_4^{25} 1.2170.

(11) V. F. Mironov and V. V. Meppomina, *ibid.*, 1231 (1959), describe this compound as having bp 157° (7.4 mm), n_D^{20} 1.4339, d_4^{25} 1.2608, R_D 0.209.

(12) L. H. Sommer, D. L. Bailey, W. A. Strong, and F. C. Whitmore, *J. Am. Chem. Soc.*, **70**, 2869 (1948), showed that the chlorine β to silicon was titratable as a strong acid. Therefore the neutral equivalent is the molecular weight divided by 3 for this compound.

(13) J. C. Saam and J. L. Speier, *J. Org. Chem.*, **24**, 119 (1959).

(14) J. W. Ryan, G. K. Menzie, and J. L. Speier, *J. Am. Chem. Soc.*, **82**, 3601 (1960).

(15) J. L. Speier, *ibid.*, **71**, 273 (1949).