

ected on a Büchner funnel, washed with two 25 ml. portions of benzene, and dried *in vacuo*. The product, which weighed 29.1 g. (72%), melted at 185–187°.

*Anal.* Calcd. for  $C_{36}H_{36}O_6Ti$ : C, 70.58; H, 5.92; Ti, 7.82. Found: C, 70.69; H, 6.01; Ti, 7.86, 7.91.

*Bis(1-oxy-1-propene-1,3-diphenyl-3-one)bis(triphenylsiloxy)titanium.* A solution of 4.45 g. (0.007 mole) of bis(1-oxy-1-propene-1,3-diphenyl-3-one)diisopropoxytitanium in 35 ml. of benzene was treated with 4.0 g. (0.014 mole) of triphenylsilanol over 30 min., while the mixture was stirred and refluxed. Heating was continued for 3 hr. and the benzene-isopropyl alcohol azeotrope was allowed to distill from the reaction flask. The solvents were removed *in vacuo* to yield 7.9 g. of the product melting at 210–216°. An analytical sample, which was prepared by recrystallization from benzene, melted at 233–238°.

*Anal.* Calcd. for  $C_{66}H_{82}O_8Si_2Ti$ : C, 75.86; H, 5.02; total oxides, 19.15. Found: C, 75.76; H, 5.26; total oxides, 18.84, 18.75.

*Bis(2-oxy-2-pentene-4-one)(bis(trimethylsiloxy)titanium.* From bis(2-oxy-2-pentene-4-one)titanium oxide and ethoxytrimethylsilane. Bis(2-oxy-2-pentene-4-one)diisopropoxytitanium was prepared by treating 145.6 g. (0.51 mole) titanium isopropylate with 102.6 g. (1.01 moles) acetylacetone in 100 ml. cyclohexane. The product, boiling 135–137° at 0.08 to 0.1 mm., was obtained in 79.2% yield after fractional distillation (reported b.p. 121–122° at 0.3 mm.).<sup>6</sup>

*Anal.* Calcd. for  $C_{16}H_{20}O_6Ti$ : C, 13.15. Found: Ti, 12.96, 12.91.

The diisopropylate was converted into bis(2-oxy-2-pentene-4-one)-titanium oxide according to the method of Yamamoto<sup>4</sup> in a yield of 79 per cent.

*Anal.* Calcd. for  $C_{16}H_{14}O_6Ti$ : Ti, 18.28. Found: Ti, 18.26, 18.41.

A mixture of 7.9 g. (0.03 mole) bis(2-oxy-2-pentene-4-one)-titanium oxide, 3.8 g. (0.03 mole) ethoxytrimethylsilane, and 20 ml. of *n*-hexane was refluxed for 20 hr. The volatiles were removed under reduced pressure and collected in a Dry Ice trap. The nonvolatile portion was mixed with anhydrous ether, filtered, and the filtrate was evaporated and dried under reduced pressure (final pressure at room temperature, 0.04 mm.). An attempt to distill the 3.6 g. of residue through a short path apparatus at 0.06 mm. gave

1.4 g. of a distillate boiling at 110° which solidified on cooling. This product, melting at 49–50°, was unaffected by atmospheric moisture and was identified as bis(2-oxy-2-pentene-4-one)bis(trimethylsiloxy)titanium (reported m.p. 56–57°).<sup>7</sup> The yield was 9%.

Repetition of the procedure using 10.0 g. (0.038 mole) bis(2-oxy-2-pentene-4-one)titanium oxide, 10.0 g. (0.085 mole) ethoxytrimethylsilane, and 40 ml. benzene gave 3.0 g. (19 per cent) of the same product boiling 113–116° at 0.1 mm.

*Anal.* Calcd. for  $C_{16}H_{20}O_6Si_2Ti$ : C, 45.27; H, 7.60; M.W., 425. Found: C, 45.57; H, 8.03; M.W. ( $K_f$ , benzene = 5.12), 367, 369).

Although the experimental molecular weights are low, they are low by about the same degree of magnitude as those reported by Yamamoto<sup>4</sup> for the corresponding titanium alkoxides. The infrared spectra of this compound and the titanium oxide contained bands at 1378, 1545, and 1600  $cm^{-1}$ , indicating the presence of the acetylacetone group in both compounds.<sup>4</sup> Absorption at 751, 844, and 1248  $cm^{-1}$  also established the trimethylsiloxy group<sup>16</sup> in the subject compound. In the region where Si—O—Ti absorption may be expected, 919 and 925  $cm^{-1}$ ,<sup>17</sup> no sharp bands were found, but rather a broad band extending from about 980–940  $cm^{-1}$ .

*Tetrakis(triphenylsilyl)titanate.* From bis(2-oxy-2-pentene-4-one)diisopropoxytitanium and triphenylsilanol. A solution of the title compounds, 7.26 g. (0.02 mole) and 11.0 g. (0.04 mole), respectively, in 50 ml. cyclohexane was heated at 70° for 24 hr. During the reflux period, 2 g. of tetrakis(triphenylsiloxy)titanium formed. This product, which was collected by filtration, decomposed at about 505° in a sealed tube. The compound has been reported to melt at 501–505°.<sup>8</sup> From the filtrate 5.6 g. of triphenylsilanol was recovered.

*Anal.* Calcd. for  $C_{72}H_{60}O_4Si_4Ti$ : C, 75.23; H, 5.25. Found: C, 75.53; H, 5.49.

KANSAS CITY, MO.

(16) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd ed., Wiley, New York, 1958.

(17) V. A. Zeitler and C. A. Brown, *J. Phys. Chem.*, **61**, 1174 (1957).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

## Preparation and Properties of Trialkylfluorosilanes<sup>1</sup>

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The preparation of symmetric and unsymmetric trialkylfluorosilanes, from  $C_6H_{17}$ — to  $C_{18}H_{17}$ —, by various methods is reported. Since the synthesis of unsymmetrical trialkylfluorosilanes involves preparing the alkylloxysilane and alkyltrifluorosilane as intermediates, the synthesis of those compounds is also described. The physical properties of all the newly synthesized compounds are reported.

Jaeger and Dykstra<sup>4</sup> reported the first synthesis of symmetric trialkylfluorosilanes ( $R_3SiF$ ) as a side

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(3) Abstracted from the M.S. thesis of G. W. Miller, Duquesne University, 1957, and the M.S. thesis of J. Makhlof, Duquesne University, 1958. Requests for reprints should be sent to: G. W. Miller, Harris Research Laboratories, 6220 Kansas Ave., Washington 11, D. C.

(4) A. O. Jaeger and H. B. Dykstra, *Z. Anorg. Chem.*, **143**, 233 (1935).

product in the reaction of silicon tetrafluoride with ethylmagnesium bromide. Gierut, Sowa, and Nieuwland<sup>5</sup> obtained yields of  $R_3SiF$  up to fifty per cent from the reaction of silicon tetrafluoride with propyl, butyl, and amyl Grignard reagents.

The symmetrical trialkylfluorosilanes in this study were prepared by the method of Gierut et al.<sup>5</sup>

As can be observed from Table I, the yield of

(5) J. A. Gierut, F. J. Sowa, and J. A. Nieuwland, *J. Am. Chem. Soc.*, **58**, 897 (1936).

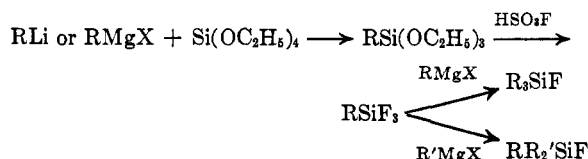
TABLE I

YIELD OF PRODUCTS IN THE PREPARATION OF TRIALKYLFLUOROSILANES

Bromide	Moles	R <sub>3</sub> SiF(%)	R-R(%)	Method
<i>n</i> -Amyl	1.00	44	8	A
<i>n</i> -Octyl	0.52	58	14	A
<i>n</i> -Decyl	0.45	59	18	A
<i>n</i> -Dodecyl	0.30	45	24	A
<i>n</i> -Dodecyl	1.00	68	20	B
<i>n</i> -Tetradecyl	0.09	30	29	A
<i>n</i> -Hexadecyl	0.33	19	40	A
<i>n</i> -Octadecyl	0.35	14	55	A
2-Ethylhexyl	1.00	39	9	A
3,5,5-Trimethylhexyl	1.00	42	13	A

R<sub>3</sub>SiF decreases with increase in chain length. When dioxane was substituted for ethyl ether as a solvent in the preparation of the dodecyl compound the yield of R<sub>3</sub>SiF increased sharply.

The following sequence can lead to either symmetrical or unsymmetrical trialkylfluorosilanes:



The first step in this sequence involves the preparation of the alkylalkoxysilane. Andrianov and Gribanova,<sup>6</sup> reacted the Grignard reagent prepared without solvent, with tetraethoxysilane with digestion for three hours on a water bath, obtaining yields ranging from twenty to sixty per

(6) A. Andrianov and G. Gribanova, *J. Am. Chem. Soc., U.S.S.R.*, **8**, 522 (1939); *Chem. Abstr.*, **32**, 7892 (1938). A. Andrianov and Y. Kamonskaya, *Chem. Abstr.*, **32**, 969 (1938); *Chem. Abstr.*, **33**, 1266 (1939).

cent. Post and Hofrichter<sup>7</sup> used the Grignard reagent in ethyl ether at room temperature, and in benzene or toluene at reflux temperature with tetraethoxysilane and obtained yields between twenty and thirty per cent for methyl, ethyl, and *n*-butyltriethoxysilane, accompanied by higher boiling side products.

Modifying the reaction of the Grignard reagent and tetraethoxysilane, it was found that the desired long chain alkyltriethoxysilane could be obtained in yields up to seventy-seven per cent by methods A and E (see experimental section). The effect of low temperature increases the yields over those already reported for small chain compounds; little or no stirring may also contribute to the increase in yields of the alkyltriethoxysilanes. The reactions which were hydrolyzed with saturated ammonium chloride solution after reaction was complete, gave poor yields of alkyltriethoxysilane and poor recovery of starting materials, probably due to the hydrolysis of the alkyltriethoxysilane to give silanol which polymerizes.

It can be seen from Table II that using dioxane as solvent and refluxing for several hours gave a large amount of tridodecylmonoethoxysilane and a low yield of dodecyltriethoxysilane, but in the case of the octyl compound at room temp., no trioctylmonoethoxysilane was isolated. Voronkov and his co-workers<sup>8</sup> found that alkyl lithium reagents reacted at low temperatures with excess tetraethoxysilane to yield forty to forty-five per cent of the alkyltriethoxysilane. However, extending this work to long chain alkyls, in one

(7) H. W. Post and H. Hofrichter, *J. Org. Chem.*, **5**, 572 (1940).

(8) M. G. Voronkov, B. N. Dolgov, and N. P. Zapevoleve, *Ser. Khim. Nauk*, **12**, 163, 161 (1953); *Chem. Abstr.*, **49**, 5277 (1955).

TABLE II

REACTIONS OF GRIGNARD AND ALKYL LITHIUM REAGENTS WITH TETRAETHOXYSILANE

Bromide	Moles	Metal	Moles Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub>	Method	Temp. of Addition	Moles of Isolated RSi(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	Compound R—R	Moles of Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> Recovered	Comments
Dodecyl	1.00	Mg	1.00	D	25	0.25	0.13	0.47	0.17 mole R <sub>3</sub> SiOC <sub>2</sub> H <sub>5</sub>
	1.50 <sup>b,c</sup>	Mg	3.50	D	25	0.49	<sup>a</sup>	1.90	
	0.50	Mg	1.00	B	25	0.11	<sup>a</sup>	0.53	Inverse addition
	0.50	Mg	0.60	E	0	0.23	<sup>a</sup>	0.35	
	0.25	Li	0.50	C	55	0.005	0.08	0.39	
Decyl	0.45	Mg	1.10	A	0	0.24	0.03	0.66	
Octyl	0.67 <sup>c</sup>	Li	1.30	C	-60	<sup>a</sup>	<sup>a</sup>	0.65	0.15 mole R <sub>3</sub> SiOC <sub>2</sub> H <sub>5</sub>
	0.67 <sup>c</sup>	Mg	5.00	A	0	0.51	0.02	2.77	0.01 mole R <sub>3</sub> SiOC <sub>2</sub> H <sub>5</sub>
	1.03 <sup>b</sup>	Mg	1.00	D	25	0.07	<sup>a</sup>	0.23	R <sub>3</sub> SiOC <sub>2</sub> H <sub>5</sub>
3,5,5-Tri-methyl-hexyl	0.50	Mg	0.70	E	0	0.38	<sup>a</sup>	0.15	0.10 mole R <sub>3</sub> Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>
	0.70 <sup>d</sup>	Mg	0.90	E	0	0.43	<sup>a</sup>	0.20	

<sup>a</sup> None obtained. <sup>b</sup> Replaced ether by dioxane. <sup>c</sup> Used the alkyl chloride. <sup>d</sup> Reaction mixture left at room temperature for 24 hr., instead of at 0°. <sup>e</sup> Stirred and refluxed for 14 hr.

preparation using *n*-octyl chloride, only trioctylmonoethoxysilane (sixty per cent yield) and unreacted tetraethoxysilane were obtained.

Another method for the preparation of the alkyltriethoxy compounds is the ethanolysis of the corresponding alkyltrichlorosilane. Several alkyltrichlorosilanes<sup>9</sup> have been prepared by the reaction of the Grignard with tetrachlorosilane. Reaction of dodecyl Grignard with silicon tetrachloride, followed directly by reaction with absolute methanol, without isolation of the dodecyltrichlorosilane, gave on distillation only a 20% yield of dodecyltrimethoxysilane.

The second step in the sequence outlined above is the conversion of the alkyltriethoxysilane to the corresponding trifluoro compound. This was accomplished with fluorosulfonic acid by modification of the method of Sowa.<sup>10</sup>

He reported the preparation of alkyltrifluorosilanes at room temperature or above for *n*-amyl, lauryl, 2-ethylhexyl; at 10° for cyclohexyl; ice bath temperatures for diethyl and dibutyl and at -30° for butyltrifluorosilane. Preparation of amyltrifluorosilane at room temperature produced only a very low yield of the product. Reduction of the reaction temperature to -25° gave an 82% yield of the desired alkyltrifluorosilane, but further lowering to -32° decreased the yield to sixty per cent, possibly due to incomplete reaction. Dodecyltrifluorosilane was prepared at -19° from dodecyltriethoxysilane in sixty-five per cent yield. It was not possible to reduce the temperature to -29° since the reaction mixture began to solidify. In order to be able to carry out the reaction at the lower temperature, dodecyltrimethoxysilane was prepared, as described above, but this compound gave only a forty per cent yield of the trifluoro compound. The reactions are summarized in Table III.

TABLE III

REACTIONS OF FLUOROSULFONIC ACID WITH ALKYLTRIETHOXYSILANES

RSi(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	Moles of		Temp.	% Yield	
	HSO <sub>3</sub> F	HSO <sub>3</sub> F		Crude RSiF <sub>3</sub>	HSO <sub>3</sub> F Recovered
<i>n</i> -Amyl	0.50	1.50	-30	60	0.09
	0.50	1.50	-25	82	0.12
<i>n</i> -Dodecyl	0.23	0.69	-19	65	0.11
3,5,5-Trimethylhexyl	0.30	0.90	-25	75	0.07

The final step in the sequence is the Grignard reaction with the alkyltrifluorosilane. Depending

(9) F. C. Whitmore, L. H. Sommer, P. A. DiGiorgio, R. E. van Strien, D. L. Bailey, H. K. Hall, W. A. Strong, E. W. Pietrusza, and G. T. Kerr, *J. Am. Chem. Soc.*, **68**, 475 (1946).

(10) F. J. Sowa, U.S. Pat. 2,477,704, *Chem. Abstr.*, **32**, 7892 (1938).

on the Grignard reagent used, symmetrical or unsymmetrical (RR'<sub>2</sub>SiF) trialkylfluorosilanes can be obtained. The latter type compounds have not been reported in the literature. The reactions are summarized in Table IV.

TABLE IV

REACTION OF ALKYLTRIFLUOROSILANES WITH GRIGNARD REAGENTS

RSiF <sub>3</sub>	Moles	R'MgBr	Moles	R'-R'	% Yield RR' <sub>2</sub> SiF
<i>n</i> -Amyl	0.41	<i>n</i> -dodecyl	0.85	0.03	55
<i>n</i> -Dodecyl	0.15	2-ethylhexyl	0.40	0.05	45
3,5,5-Trimethylhexyl	0.17	<i>n</i> -dodecyl	0.34	0.02	53
	0.20	2-ethylhexyl	0.40	0.04	48

The Si—F bond in the R<sub>3</sub>SiF compound is relatively chemically inert. This stability is probably due to double-bond character of the Si—F bond, and it is demonstrated by: (1) Medoks'<sup>11,12</sup> failure to cleave the Si—F bond with sodium in ammonia; (2) no reaction with a Grignard reagent to form the tetraalkylfluorosilane. But, the Si—F bond can be broken by alcoholysis with sodium ethoxide in absolute ethanol and with sodium methoxide in absolute methanol. Results of alcoholysis are in Table V.

TABLE V

REACTION OF SODIUM ALKOXIDES WITH SYMMETRICAL TRIALKYLFLUOROSILANES

R <sub>3</sub> SiF	Moles	Reagent in Excess	% Yield R <sub>3</sub> SiOC <sub>2</sub> H <sub>5</sub>
Methyl <sup>a</sup> (room temp.)	0.300	NaOCH <sub>3</sub>	95
Methyl <sup>a</sup> (room temp.)	0.300	NaOC <sub>2</sub> H <sub>5</sub>	95
<i>n</i> -Amyl (room temp.)	0.060	NaOCH <sub>3</sub>	90
<i>n</i> -Amyl (room temp.)	0.060	NaOC <sub>2</sub> H <sub>5</sub>	90
3,5,5-Trimethylhexyl (reflux one hour)	0.044	NaOC <sub>2</sub> H <sub>5</sub>	85

<sup>a</sup> Used R<sub>3</sub>SiCl instead of R<sub>3</sub>SiF.

EXPERIMENTAL<sup>13,14</sup>

**Materials.** All alkyl halides were of C. P. grade except 1-bromododecane, which was purified by distillation, b.p., 94–95°/0.6 mm, lit. 134–136°/5 mm.<sup>15</sup> Tetraethoxysilane was purified by distillation, b.p., 165–166°, lit. 165.5°.<sup>16</sup>

(11) J. Medoks and D. Kostolov, *J. Gen. Chem., U.S.S.R.*, **7**, 2007 (1937); *Chem. Abstr.*, **32**, 531 (1938).

(12) J. Medoks and D. Kostolov, *J. Gen. Chem., U.S.S.R.*, **8**, 291 (1938); *Chem. Abstr.*, **32**, 5392 (1938).

(13) All melting and boiling points are uncorrected.

(14) Elementary analyses reported herein were carried out by: Dr. A. Bernhardt, Mühlheim, Germany; Elek Micro-analytical Laboratories, Los Angeles, Calif.; or Drs. G. Weiler and G. Strauss, Oxford, England.

(15) E. E. Reed, J. R. Ruhoff, and R. E. Burnett, *Org. Syn., Coll. Vol. II*, 246 (1943).

(16) W. W. Dearing and E. E. Reed, *J. Am. Chem. Soc.*, **50**, 3058 (1938).

TABLE VI  
 PHYSICAL PROPERTIES

Alkyl Residue	M.P.	B.P.	$n_D^{25}$	$M_r$ (Exp.)	$M_r$ (Calcd.)	Density (G./ML.)		Viscosity (Millipoise)	
						25°	40°	25°	40°
SYMMETRICAL TRIALKYLFLUOROSILANES									
<i>n</i> -Butyl		224/745 <sup>a</sup>	1.4250 <sup>a</sup>	66.66	65.88	0.8327 <sup>a</sup>	0.8332	24.24	19.11
<i>n</i> -Amyl		265/745 <sup>a</sup>	1.4305 <sup>a</sup>	79.84	79.77	0.8389 <sup>a</sup>	0.8347	35.78	25.54
<i>n</i> -Octyl	-10	190/1.0	1.4454	120.24	121.44	0.8455	0.8409	73.15	54.41
<i>n</i> -Decyl	-6.0	240-5/1.0	1.4492	148.20	149.22	0.8504	0.8454	137.65	84.32
<i>n</i> -Dodecyl	-4.5	290-5/1.0	1.4548	175.53	177.00	0.8605	0.8475	263.63	124.80
<i>n</i> -Octadecyl	71-72	310/3.0							
2-Ethylhexyl		170-1/0.2	1.4443	119.52	121.44	0.8598	0.8547	68.13	48.27
3,5,5-Trimethylhexyl		150-2/0.6	1.4453	135.18	135.33	0.8432	0.8387	212.20	123.23
UNSYMMETRICAL TRIALKYLFLUOROSILANES									
<i>n</i> -Amyl-di( <i>n</i> -dodecyl)	19-20	201/0.5	1.4455	143.6	144.6	0.8530	0.8443	184.06	107.41
<i>n</i> -Dodecyl-di(2-ethylhexyl)	-12	182/0.7	1.4450	139.69	139.96	0.8520	0.8430	157.88	90.30
3,5,5-Trimethylhexyl-di(2-ethylhexyl)		150/0.65	1.4467	125.7	126.1	0.8530	0.8420	136.57	63.02
3,5,5-Trimethylhexyl-di( <i>n</i> -dodecyl)	14	240/1.2	1.4484	162.3	163.1	0.8462	0.8375	263.29	146.93
ALKYLTRIETHOXY-SILANES									
<i>n</i> -Octyl		84-5/0.5	1.4160	80.53	78.86	0.8575	0.8515	15.02	12.69
<i>n</i> -Decyl		100-1/0.6	1.4205	88.59	88.12	0.8699	0.8633	21.98	18.52
<i>n</i> -Dodecyl		127-9/0.7	1.4330	97.64	97.38	0.8844	0.8825	30.52	22.72
3,5,5-Trimethylhexyl		87/0.5	1.4135	83.95	83.46	0.8592	0.8546	25.04	23.24
ALKYLTRIMETHOXY-SILANE									
<i>n</i> -Dodecyl		117-8/1.25	1.4263	83.18	83.49	0.8943	0.8909	30.86	24.68
DIMETHYLDIETHOXY-SILANE									
3,5,5-Trimethylhexyl		110/0.25	1.4439	114.55	115.14	0.8540	0.8482	97.53	68.13
TRIALKYL-MONOETHOXY-SILANES									
<i>n</i> -Amyl		123/3.0	1.4400	90.57	91.23	0.8372	0.8294	33.52	15.58
<i>n</i> -Octyl		189/1.2	1.4533	134.82	132.99	0.8340			
<i>n</i> -Dodecyl	15	210/1.1	1.4575	174.80	175.82	0.9062			
3,5,5-Trimethylhexyl		135/0.5	1.4542	146.62	146.79	0.8384	0.8324	202.41	119.23

<sup>a</sup> E. G. Rochow, *Chemistry of the Silicones*, Wiley, New York, p. 40.

Lithium sand was prepared by heating lithium metal in mineral oil at 150° for 3 hr. and rapidly shaking the flask to give a fine dispersion of the lithium metal. The solution was then cooled, the lithium metal filtered on a Büchner funnel, washed three times with anhydrous ether, and immediately used. While Gilman<sup>17</sup> describes the use of lithium wire in his preparation of organolithium reagents, it was found that lithium sand reacts as rapidly as lithium wire and that it was much easier to prepare the sand.

*General Methods for the Preparation of Trialkylfluorosilanes.*

*Method A* (symmetric compounds only). Silicon tetrafluoride, prepared by the method of Gierut *et al.*,<sup>8</sup> was bubbled into a Grignard solution with rapid stirring for a period of 3 hours when the solution was completely saturated, evidenced by the formation of a clear ethereal layer and a heavy, turbid layer on the bottom. The solution was hydrolyzed with a saturated solution of ammonium chloride, filtered and the solid portion extracted three times with benzene. After combining the ethereal layer and the benzene extracts and distilling the ether-benzene mixture, the remaining solution was fractionated at reduced pressure through an electrically heated Vigreux column (19.5 in. in length).

*Method B* (symmetric compounds only). This method

differed from Method A only in the use of dioxane as solvent. After the formation of the Grignard, dioxane was added dropwise to the solution, the ether distilled, and the resulting mixture refluxed for 14 hr., prior to the use of silicon tetrafluoride. The remainder of the procedure was identical with Method A.

*Method C* (symmetric and unsymmetric compounds) To the stirred alkyltriethoxysilane in a three-neck flask, cooled in an acetone-Dry Ice bath to -25°, was added dropwise three moles of fluorosulfonic acid per mole of triethoxy compound. After the addition was completed, stirring was continued for 1 hr. at -25°. The mixture separated into two layers, the upper containing most of the alkylfluorosilane. This upper layer was distilled under reduced pressure (0.1 mm.) to remove any unreacted fluorosulfonic acid. The results are shown in Table III.

The alkyltrifluorosilane was added dropwise to the appropriate Grignard reagent, keeping the reflux rate as low as possible. After the addition was completed, the reaction mixture was refluxed for about 1 hr., hydrolyzed with saturated ammonium chloride solution and treated as in Method A. The yields are shown in Table IV.

*General Methods for the Preparation of Alkyltriethoxysilane.* *Method A.* The following procedure is a representative example of this synthetic method. A Grignard solution, prepared from 100 g. (0.45 moles) of decyl bromide and 18 g. (0.75 G. atoms) of magnesium metal, was added dropwise

(17) H. Gilman, *Org. Reactions*, Vol. VIII, Wiley, New York, 1953, p. 285.

TABLE VII  
ANALYSES

Compounds	Calcd., %			Found, %		
	C	H	F	C	H	F
( <i>n</i> -Octyl) <sub>3</sub> SiF	74.48	13.27		74.86	13.35	
( <i>n</i> -Decyl) <sub>3</sub> SiF	76.60	13.47		76.05	13.16	
( <i>n</i> -Dodecyl) <sub>3</sub> SiF	77.98	13.52		78.51	13.32	
(2-Ethylhexyl) <sub>3</sub> SiF	73.95	13.21		73.90	13.06	
(3,5,5-Trimethylhexyl) <sub>3</sub> SiF	75.70	13.31		75.63	13.15	
( <i>n</i> -Octadecyl) <sub>3</sub> SiF	80.31	13.85		80.21	13.67	
<i>n</i> -Amyl( <i>n</i> -dodecyl) <sub>2</sub> SiF	76.21	13.47		76.22	13.38	
<i>n</i> -Dodecyl(2-ethylhexyl) <sub>2</sub> SiF	75.91	13.43	4.73	76.60	13.35	4.67
3,5,5-Trimethylhexyl(2-ethylhexyl) <sub>2</sub> SiF	75.00	13.25	4.74	76.53	13.46	5.14
3,5,5-Trimethylhexyl( <i>n</i> -dodecyl) <sub>2</sub> SiF	77.25	13.58		77.05	13.69	
( <i>n</i> -Octyl)Si(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	60.84	11.63		61.38	11.88	
( <i>n</i> -Decyl)Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	63.10	11.91		63.14	11.85	
( <i>n</i> -Dodecyl)Si(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	66.26	12.09		66.19	12.13	
(3,5,5-Trimethylhexyl)Si(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	62.36	11.44		62.34	11.29	
( <i>n</i> -Amyl)Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	71.24	13.37		71.08	13.29	
( <i>n</i> -Amyl)Si(OCH <sub>3</sub> ) <sub>3</sub>	70.50	13.32		70.62	13.27	
( <i>n</i> -Dodecyl)Si(OCH <sub>3</sub> ) <sub>3</sub>	62.01	11.79		61.40	11.37	
(3,5,5-Trimethylhexyl) <sub>2</sub> Si(OC <sub>2</sub> H <sub>5</sub> )	70.88	12.97		71.01	12.73	
( <i>n</i> -Octyl) <sub>3</sub> SiOC <sub>2</sub> H <sub>5</sub>	75.65	13.67		75.58	13.20	
( <i>n</i> -Dodecyl) <sub>3</sub> SiOC <sub>2</sub> H <sub>5</sub>	77.22	13.87		76.92	13.23	
(3,5,5-Trimethylhexyl) <sub>3</sub> SiOC <sub>2</sub> H <sub>5</sub>	76.56	13.75		76.98	13.77	

to 230 g. (1.10 moles) of tetraethoxysilane at 0° with little or no stirring. The reaction mixture was left at 5° for 24 hr. The ether was then distilled, and the resulting mixture fractionated at reduced pressure through an electrically heated Vigreux column (19.5 in.).

*Anal.* Calcd. for C<sub>16</sub>H<sub>32</sub>SiO<sub>3</sub>: C, 63.10; H, 11.91. Found: C, 63.14; H, 11.85.

The distillation residue was then extracted with benzene, and on addition of acetone, a white solid, eicosane, precipitated from the solution. The eicosane was recrystallized several times from absolute methanol, m.p., 36°.

*Anal.* Calcd. for C<sub>20</sub>H<sub>42</sub>: C, 85.10; H, 14.90. Found: C, 85.23; H, 14.63.

*Method B.* A Grignard solution was slowly added to tetraethoxysilane at 25°, and the resulting mixture was stirred for 1 to 2 hr. The ether was then distilled, and final purification was accomplished as in Method A above.

*Method C.* Tetraethoxysilane was added rapidly to an alkyl lithium solution. The resulting mixture was stirred for several hours and then raised to room temperature. After distillation of the ether, the separation was accomplished as in Method A above.

*Method D.* This method is the same as Method B, but after the reaction of the Grignard reagent with tetraethoxysilane, the resulting mixture was hydrolyzed with a saturated solution of ammonium chloride and the solid portion extracted three times with benzene. After distilling the ether-benzene mixture, the remaining solution was fractionated as in Method A.

*Method E.* This method is like Method A, except that after standing for 24 hr at 5°, the reaction mixture is extracted three times with benzene, and the extracts are distilled under reduced pressure.

*Preparation of Dodecyltrimethoxysilane.* A Grignard solution, prepared from 124.5 g. (0.50 moles) of dodecyl bromide and 18 g. (0.75 G. atoms) of magnesium metal, was added dropwise to 2 moles of silicon tetrachloride at 0°, and upon completion of the addition, 2.5 hr, an excess of absolute

methanol was slowly added. After distillation of the ether and methanol, the separation was accomplished by fractionation at reduced pressure through an electrically heated Vigreux column.

The fraction, boiling at 117–118°/1.25 mm., was dodecyltrimethoxysilane, 30.0 g. (a 20% yield based on dodecyl bromide).

*Anal.* Calcd. for C<sub>18</sub>H<sub>38</sub>SiO<sub>3</sub>: C, 62.01; H, 11.79. Found: C, 61.40; H, 11.37. The carbon-hydrogen analyses for all compounds prepared in this study are given in Table VII.

*General Method for the Hydrolysis of Symmetrical Trialkylfluorosilanes.* Excess sodium ethoxide in absolute ethanol or excess sodium methoxide in absolute methanol were added dropwise to the trialkylfluorosilane. After addition was completed, the mixture was refluxed for 1 hr., filtered and distilled. A slight warming was necessary to start the hydrolysis in the case of the tri(3,5,5-trimethylhexyl)fluorosilane and tri-*n*-amylfluorosilane. Triphenylfluorosilane was not hydrolyzed even on refluxing for 2 hr. The yields are reported in Table V.

*Determination of Physical Properties.* The data obtained are collected in Table VI. Density measurements were made by the usual pycnometer method at 25° and 40°, and the refractive indices were measured with an Abbe refractometer at 25°. Utilizing the above data and the bond refractions of Denbigh<sup>18</sup> and Warrick,<sup>19</sup> the experimental molar refractivity was calculated using the Lorenz and Lorentz formula<sup>20</sup> and the theoretical molar refractivity was calculated by addition of the appropriate bond refractivities. The viscosities of the various liquids were measured at 25° and 40° in the usual manner, using an Ostwald viscometer.

#### PITTSBURGH, PA.

(18) K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

(19) E. L. Warrick, *J. Am. Chem. Soc.*, **68**, 2455 (1946).

(20) S. Glasstone, *Textbook of Physical Chemistry*, Van Nostrand, New York, 1946, p. 529.