tures employed in plasma fractionation have not exceeded mole fraction 0.163 and rarely 0.091, and the temperature has been maintained between 0° and the freezing point of the solution.

The balance between (1) the precipitating action of ethanol and (2) the interaction with salt permits attainment of a variety of conditions under which the protein to be separated may be brought to any desired solubility. This balance is different at constant ethanol and salt concentration for each *p*H and temperature, and for each protein component.

The *p*H has been controlled by buffering the ethanol–water mixtures with acetates or other buffers of known ionic strength, and adjusted so as to take advantage of the differences in the isoelectric points and the directions of the interactions with salts of the protein components to be separated.

Crystallization of a separated component has also been effected in an ethanol–water mixture of low ionic strength and low temperature.

Removal of salts and other organic molecules by trituration, reprecipitation, or recrystallization in an ethanol–water mixture at low temperature replaces dialysis of protein solutions in this system.

Removal of the organic precipitant without raising the temperature has generally been accomplished by drying the separated proteins from the frozen state yielding stable, salt-poor, dried protein products of any desired degree of purity.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE

Organo-silicon Compounds. I. Synthesis and Properties of *n*-Alkyltrimethyl- and *n*-Alkyltriethyl-silanes

BY F. C. WHITMORE, L. H. SOMMER, P. A. DI GIORGIO, W. A. STRONG, R. E. VAN STRIEN, D. L. BAILEY, H. K. HALL, E. W. PIETRUSZA AND G. T. KERR

In 1863 Friedel and Crafts[1] synthesized tetraethylsilane, the first tetraalkylsilane, by heating diethyl zinc with silicon tetrachloride in a sealed tube; tetramethylsilane was synthesized by the same method.[2] Twenty years later Polis[3] utilized the reaction of sodium with a mixture of aryl halide and silicon tetrachloride for the synthesis of arylsilicon compounds, a method applied later by Kipping[4] to the synthesis of alkylsilicon compounds. In 1904 Kipping[5] reported that Grignard reagents could be used in the synthesis of organo-silicon compounds. Chemists were quick to adopt this method, since it was far superior to those previously used, and the synthesis of organosilicon compounds went forward at a rapid pace. In 1916 Bygden[6] reported the preparation and physical properties of sixteen tetraalkylsilanes. Among these were five *n*-alkyltrimethylsilanes and three *n*-alkyltriethylsilanes.

As a starting point for our program of research on organo-silicon compounds, we chose to extend the series of *n*-alkyltrimethylsilanes and *n*-alkyltriethylsilanes into a higher molecular weight range; a study of the physical properties of such compounds seemed of considerable interest. It should be noted that only six carbon analogs of the nineteen tetraalkylsilanes herein reported are known. The difficulties encountered in the synthesis of neo hydrocarbons are well known[7] whereas the synthesis of tetraalkylsilanes, which contain a neo silicon atom (silicon attached to four carbons), is a relatively simple procedure and may be achieved in high yield, due to the ease with which silicon–halogen bonds couple with primary Grignard reagents. The higher *n*-alkyltrimethyl- and *n*-alkyltriethyl-silanes may possibly supply indications regarding the physical properties of neo hydrocarbons which have yet to be prepared.

We have synthesized and here reported seven new *n*-alkyltrimethylsilanes and six new *n*-alkyltriethylsilanes, and, in addition, we have prepared again three known *n*-alkyltrimethylsilanes and three known *n*-alkyltriethylsilanes to insure a comparable purity for determination of physical properties including viscosities. Incidental to the synthesis of new *n*-alkyltrimethylsilanes, we have synthesized five new *n*-alkyltrichlorosilanes.

Preparation of the Tetraalkylsilanes

In the preparation of *n*-alkyltrimethylsilanes two methods were used. Method I involved preparation of an *n*-alkyltrichlorosilane from a Grignard reagent and silicon tetrachloride in yields of about 50%. The *n*-alkyltrichlorosilane, after purification by fractional distillation, was added to an ether solution of methylmagnesium bromide to give the *n*-alkyltrimethylsilane in about 70% yield. This was the method used by Bygden[6] for the preparation of *n*-alkyltrimethylsilanes

$$\mathrm{RMgBr + SiCl_4 \longrightarrow RSiCl_3}$$
$$\mathrm{RSiCl_3 + 3CH_3MgBr \longrightarrow RSi(CH_3)_3}$$

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[1] Friedel and Crafts, *Ann.*, **127**, 31 (1863).

[2] Friedel and Crafts, *ibid.*, **136**, 203 (1865).

[3] Polis, *Ber.*, **18**, 1540 (1885).

[4] Kipping and Lloyd, *J. Chem. Soc.*, **79**, 449 (1901).

[5] Kipping, *Proc. Chem. Soc.*, **20**, 15 (1904).

[6] See Krause and Grosse "Die Chemie der metall-organischen Verbindungen," Gebrüder Borntraeger, Berlin, 1937, p. 263.

[7] *Cf.* Whitmore and Fleming, THIS JOURNAL, **55**, 4161 (1933).

TABLE I

PHYSICAL PROPERTIES OF THE TETRAALKYLSILANES

No.	Name	Calcd. molecular weight	Boiling point, °C.		Calcd. heat of vapn., cal./mole	Ref. index $n^{20}{}_D$	Density in g./ml.			Mol. refr. M_D	Atomic ref. of silicon SiR$_D$	Absolute viscosity, centipoises		
			200 mm.	760 mm.			d^0	d^{20}	d^{60}			0°C.	20°C.	60°C.
1	Ethyltrimethylsilane	102.2	25	62	7,200	1.3820	0.7040	0.6849		34.73	7.23	0.422	0.334	
2	Propyltrimethylsilane	116.2	49	90	7,500	1.3929	.7197	.7020	0.6653	39.49	7.37	.479	.380	
3	Butyltrimethylsilane	130.3	74	115	8,000	1.4030	.7352	.7181	.6835	44.28	7.54	.658	.504	
4	Amyltrimethylsilane	144.3	95	139	9,200	1.4096	.7477	.7313	.6979	48.85	7.49	.870	.644	
5	Hexyltrimethylsilane	158.3	117	163	9,800	1.4154	.7578	.7422	.7100	53.46	7.48	1.186	0.847	0.502
6	Heptyltrimethylsilane	172.4	137	184	10,600	1.4201	.7659	.7506	.7196	58.14	7.54	1.618	1.105	0.621
7	Octyltrimethylsilane	186.4	156	202	11,700	1.4242	.7729	.7581	.7277	62.77	7.55	2.149	1.412	0.758
8	Decyltrimethylsilane	214.4	191	240	12,800	1.4310	.7848	.7705	.7413	72.04	7.58	3.718	2.261	1.096
9	Lauryltrimethylsilane	242.4	222	273	14,100	1.4358	.7938	.7800	.7515	81.22	7.52	6.190	3.469	1.535
10	Myristyltrimethylsilane	270.5	250	300	15,600	1.4410	Solid	.7911	.7634	90.30	7.36	Solid	5.106	2.083
11	Methyltriethylsilane	130.3	84	127	8,600	1.4160	.7600	.7437	.7107	43.98	7.24	0.679	0.524	
12	Tetraethylsilane	144.3	108	153	9,500	1.4268	.7810	.7662	.7352	48.34	6.98	.855	.649	
13	Propyltriethylsilane	158.3	127	173	9,400	1.4308	.7868	.7724	.7423	53.03	7.05	.998	.738	
14	Butyltriethylsilane	172.4	144	192	11,000	1.4348	.7931	.7786	.7489	57.78	7.18	1.351	0.954	
15	Amyltriethysilane	186.4	162	211	11,500	1.4377	.7977	.7835	.7545	62.43	7.21	1.740	1.185	0.667
16	Hexyltriethylsilane	200.4	179	230	11,700	1.4400	.8018	.7880	.7595	67.06	7.22	2.314	1.515	0.813
17	Heptyltriethylsilane	214.4	196	247	11,700	1.4422	.8045	.7907	.7627	71.79	7.23	3.054	1.918	0.980
18	Octyltriethylsilane	228.4	208	262	12,900	1.4438	.8108	.7971	.7696	76.09	7.01	3.865	2.343	1.144
19	Decyltriethylsilane	256.5	241	293	14,800	1.4472	.8175	.8036	.7771	85.31	6.99	6.541	3.705	1.648

Method II, which was used for the synthesis of lauryltrimethylsilane and heptyltrimethylsilane, involved the reaction of trimethylchlorosilane with the appropriate Grignard reagent

$$(CH_3)_3SiCl + RMgBr \longrightarrow RSi(CH_3)_3$$

In our opinion this latter method of synthesis is better for the following reasons: (a) It is, in essence, a one-step process, since a stock of trimethylchlorosilane can be prepared and used as starting material for the synthesis of a large number of *n*-alkyltrimethylsilanes. (b) It avoids the preparation and purification of high-boiling alkyltrichlorosilanes which are unpleasant to work with due to their ease of hydrolysis to solid siliconic acids, and (c) it is more economical of the expensive long chain alkyl bromides.

Extensive use of Method II was not possible at the beginning of this work because we did not have a good laboratory method for the preparation of large amounts of trimethylchlorosilane. Later, we prepared pure trimethylchlorosilane in good yield by the reaction of ammonium chloride with a concentrated sulfuric acid solution of hexamethyldisiloxane; details will be published shortly.[8]

The *n*-alkyltriethylsilanes have also been prepared by two methods. Method I, which was only used for the synthesis of three out of the eight compounds prepared, involved the reaction of an *n*-alkyltrichlorosilane with excess ethylmagnesium bromide. Method II utilized the reaction of a Grignard reagent with triethylchlorosilane as follows

$$RMgBr + (C_2H_5)_3SiCl \longrightarrow RSi(C_2H_5)_3$$

Triethylchlorosilane was prepared in high purity and good yield from ethyl orthosilicate through the disiloxane.[9] Here, as in the case of the *n*-alkyltrimethylsilanes, Method II is the better one.

All tetraalkylsilanes reported were purified by careful fractionation in columns of 20 or more theoretical plates. Only constant boiling material having a refractive index range of 0.0002 units or less was used for determination of physical properties.

Physical Constants

In Table I are listed the nineteen tetraalkylsilanes prepared and some of their physical properties. Boiling points at 760 mm. are extrapolated from vapor-pressure curves drawn from six or more points covering the range 20–735 mm.; 200 mm. values are taken from the curves. Heats of vaporization were calculated by use of the Clausius–Clapeyron equation for the range 200 to 730 mm. Refractive indices are accurate to 0.0002 unit. Densities were determined by the use of pycnometers of about 5-cc. capacity and are corrected to the vacuum values. Molecular refraction was calculated by use of the Lorentz–Lorenz equation. Atomic refraction of silicon was calculated by difference from the molecular refraction, using 2.42 for carbon and 1.10 for hydrogen. Viscosities were determined by the use of Cannon–Fenske viscometers with a precision of ±0.2%.

Discussion of the Physical Properties

Boiling Point.—The change in boiling point with molecular weight is about the same for the trimethyl and triethyl compounds as for hydrocarbons of similar molecular-weight range. The increase in boiling point per methylene group for the silicon compounds varies from 28 to 10° on ascending the series; normal alkanes in the same molecular-weight range have a variation of 27

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(8) (a) Unpublished work of Pray, Sommer, Goldberg and Whitmore; (b) *cf.* Flood, THIS JOURNAL, **55**, 1735 (1933); (c) the preparation of trimethylchlorosilane by other methods has been reported. See Taylor and Walden, *ibid.*, **66**, 842 (1944); Gilliam and Sauer, *ibid.*, **66**, 1793 (1944).

(9) Unpublished work of Di Giorgio, Strong, Sommer and Whitmore.

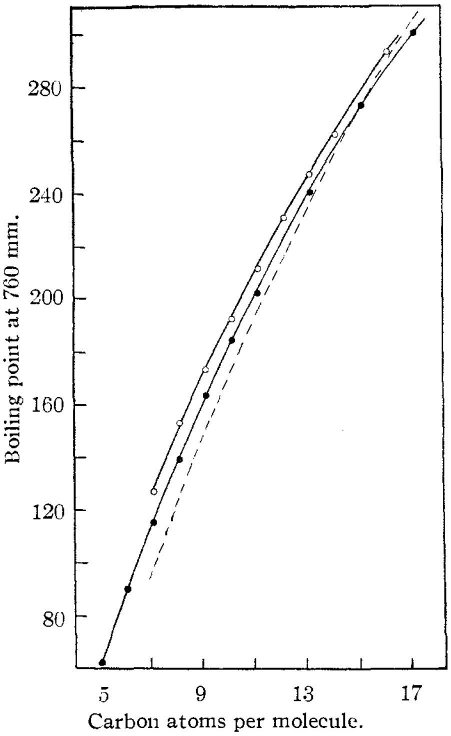

Fig. 1.—Change of boiling point with molecular weight: ●, alkyltrimethylsilanes; O, alkyltriethylsilanes; ———, *n*-alkanes.

to 10°. Figure 1 shows the variation of boiling point with molecular weight for the two series of compounds and for the normal alkanes of about the same molecular weight.[10] When trimethyl and triethyl compounds of the same molecular weight are compared, *i. e.*, compounds 3–8 with 11–15 and 17 (Table I) it is found that the trimethyl compounds have lower boiling points. When carbon analogs of trimethyl compounds 3-5 are compared with those of triethyl compounds 11–13, it is found that the trimethyl carbon compounds also have lower boiling points. This is shown in Table II, which compares the boiling points of eight of the tetraalkylsilanes with those of their carbon analogs. The higher boiling points of the silicon compounds may be attributed to the fact that their molecular weights are greater by 16 units.

TABLE II

BOILING POINTS OF SILICON AND CARBON ANALOGS

Type formula	Boiling points, °C.	
	T = Si	T = C
(1) EtTMe$_3$	62	50
(2) PrTMe$_3$	90	79
(3) BuTMe$_3$	115	107
(4) AmTMe$_3$	139	130
(5) HexTMe$_3$	163	155
(11) MeTEt$_3$	127	118
(12) EtTEt$_3$	153	139
(13) PrTEt$_3$	173	161

The data of Table II may also be used to compare the boiling points of tetraalkylsilanes with those of carbon compounds having about the same molecular weight and molecular symmetry. For this purpose, compare silicon compounds 1, 2, 3, 4, 11 and 12 with carbon compounds 2, 3, 4, 5, 12 and 13, respectively, *i. e.*, EtSiMe$_3$ with PrCMe$_3$. Such a comparison shows that the silicon compounds have boiling points which are from 17–18° lower, despite the fact that their molecular weights are 2 units higher than the carbon compounds. This is probably caused by the greater compactness of the tetraalkylsilane molecules.

Density and Refractive Index.—The increase of density and refractive index with molecular weight is about the same for the tetraalkylsilanes as for hydrocarbons of similar molecular-weight range. The increase in density per methylene

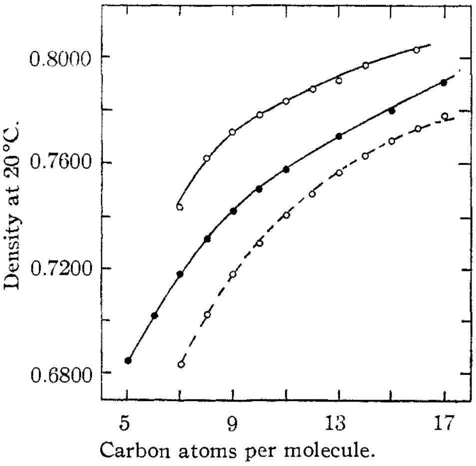

Fig. 2.—Change of density with molecular weight: ●, alkyltrimethylsilanes; O—O, alkyltriethylsilanes; O- - -O, *n*-alkanes.

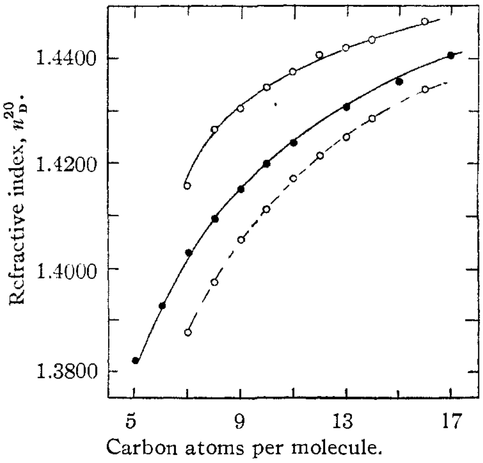

Fig. 3.—Change of refractive index with molecular weight: ●, alkyltrimethylsilanes; O—O, alkyltriethylsilanes; O- - -O, *n*-alkanes.

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[10] Physical property data for hydrocarbons are taken from Doss, "Physical Constants of the Principal Hydrocarbons," The Texas Company, 1943.

group varies from 0.018 to 0.005 unit on ascending the series of silicon compounds. Refractive index increases from 0.0109 to 0.0025 unit per additional methylene group. Figs. 2 and 3 give the variation of density and refractive index with molecular weight for the tetraalkylsilanes; included for comparison are similar plots for the normal alkanes. When trimethyl and triethyl compounds of the same molecular weight are compared (Table I), it is found that the trimethyl compounds have lower densities and refractive indices. Similarly, carbon analogs of trimethyl compounds 3–5 have lower densities and refractive indices than carbon analogs of triethyl compounds 11–13. This is shown in Table III which compares the densities and refractive indices of eight of the tetraalkylsilanes with those of their carbon analogs. The higher densities and refractive indices of the silicon compounds are doubtless due to their greater molecular weights.

TABLE III

COMPARISON OF DENSITIES AND REFRACTIVE INDICES FOR SILICON AND CARBON ANALOGS

Type formula	d^{20}		n^{20}D	
	T = Si	T = C	T = Si	T = C
(1) EtTMe$_3$	0.6849	0.6492	1.3820	1.3688
(2) PrTMe$_3$	.7020	.6739	1.3929	1.3822
(3) BuTMe$_3$	.7181	.6953	1.4030	1.3931
(4) AmTMe$_3$	.7313	.7105	1.4096	1.4023
(5) HexTMe$_3$	.7422	.7233	1.4154	1.4084
(11) MeTEt$_3$	.7437	.7274	1.4160	1.4078
(12) EtTEt$_3$	.7662	.7522	1.4268	1.4197
(13) PrTEt$_3$	.7724	.7613	1.4308	1.4258

Table III may be used to compare densities and refractive indices of tetraalkylsilanes with those of carbon compounds having about the same molecular weight and molecular symmetry (*cf.* above). This shows that, although their boiling points are lower, the silicon compounds, with the exception of methyltriethylsilane, have higher densities than the carbon compounds. With the exception of methyltriethylsilane, the silicon compounds have refractive indices which are higher or about the same as those of the carbon compounds; the difference in indices for the first two pairs of compounds is too small to be significant. Greater density and refractive index of the silicon compounds compared to carbon compounds of about the same molecular weight may be attributed to the greater compactness of the tetraalkylsilane molecules; in alkanes refractive index and density are generally higher the more compact the molecule. An interesting point is that the high symmetry of the tetraethylmethane molecule reverses the usual order so that this substance has a higher density and refractive index than methyltriethylsilane.

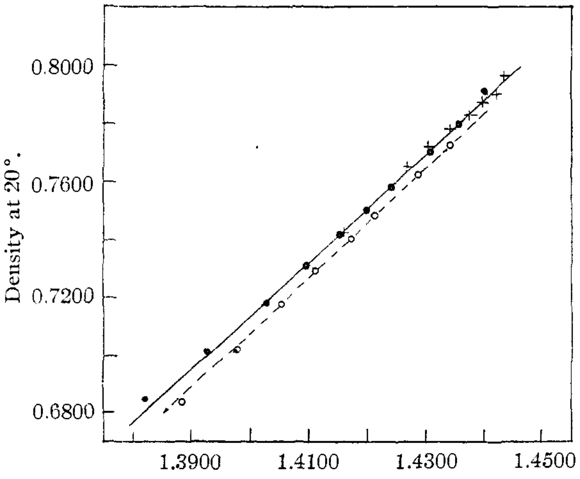

Fig. 4.—Change of refractive index with density: ●, alkyltrimethylsilanes; +, alkyltriethylsilanes; O, *n*-alkanes.

The temperature coefficients of density for the tetraalkylsilanes are about the same as for normal alkanes of corresponding molecular weights.

In view of the variation in the atomic refraction of silicon, to be discussed below, it was of interest to compare the change of refractive index with density in the trimethyl and triethyl compounds with that in the normal alkanes. Figure 4 shows the similarity in this relationship for the silicon and carbon compounds.

Atomic Refraction of Silicon.—As can be seen from Table I the atomic refraction values for silicon in the trimethylsilanes, with the exception of ethyltrimethylsilane, are all higher than for the triethylsilanes. In the trimethylsilanes the average value for the atomic refraction of silicon is 7.47 with a mean deviation of 0.09 unit; for the triethylsilanes the average value is 7.12 with a mean deviation of 0.09 unit. While it may be argued that the differences in SiRD among the trimethylsilanes or triethylsilanes themselves are small enough to warrant an assumption of constancy of atomic refraction of silicon—the differences being due to small amounts of impurities in the compounds—the relatively large difference in the average values of SiRD for the two series of compounds can only be attributed to a real variation in the atomic refraction of silicon. The fact that SiRD is different, even in two such similar series of compounds, is not too surprising. For example, the atomic refraction of silicon in trimethylchlorosilane is 6.72; in hexamethyldisilane it is 8.45. These data indicate the greater polarizability or deformability of the electronic sheaths in the silicon atom as compared to carbon. We are studying the relationship between SiRD and chemical reactivity of various groups attached to silicon. As yet, no definite conclusions are possible.

Viscosity.—Since we were unable to find any viscosity data for silanes, it was of interest to study the viscosities and temperature–viscosity coefficients of the compounds herein reported. The increase in viscosity with molecular weight

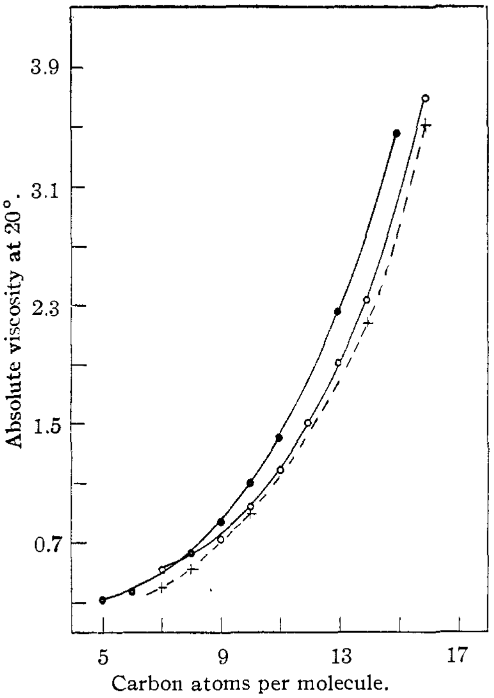

Fig. 5.—Change of absolute viscosity with molecular weight: ●, alkyltrimethylsilanes; ○, alkyltriethylsilanes; +, n-alkanes.

is about the same for the tetraalkylsilanes as for normal alkanes in the same molecular-weight range; Fig. 5 shows this relationship. As far as could be determined from available viscosity data for alkanes, it was found that on comparing a tetraalkylsilane with all the known alkanes of about the same molecular weight (alkanes having a molecular weight 2 units less than the silicon compound), the viscosity of the tetraalkylsilane, at a corresponding temperature, is lower; *i. e.*, ethyltrimethylsilane has a lower viscosity than any of the heptanes. Table IV, which compares absolute viscosities of tetraalkylsilanes and alkanes at 20°, shows that the silicon compounds have viscosities which are about 25% lower than those of the carbon compounds.

TABLE IV

ABSOLUTE VISCOSITIES OF SILICON AND CARBON COMPOUNDS OF ABOUT THE SAME MOLECULAR WEIGHT

Si cpd.	C cpd.	Viscosity at 20°, centipoises Si cpd.	C cpd.
$EtSiMe_3$	$PrCMe_3$	0.33	0.39
$PrSiMe_3$	$BuCMe_3$	.38	.53
$AmSiMe_3$	n-$C_{10}H_{22}$	.64	.91
Et_4Si	n-$C_{10}H_{22}$	.65	.91
$HexSiMe_3$	n-$C_{11}H_{24}$	.85	1.17
$HexSiEt_3$	n-$C_{14}H_{30}$	1.52	2.18
$OctSiEt_3$	n-$C_{16}H_{34}$	2.34	3.52

The change of viscosity with temperature is about the same for the tetraalkylsilanes as for normal alkanes. Figure 6 shows this for representative tetraalkylsilanes.

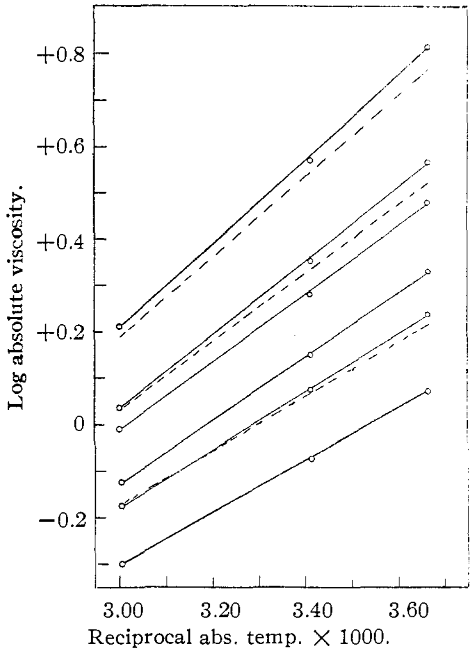

Fig. 6.—Change of absolute viscosity with temperature: tetraalkylsilanes, ○—○, bottom to top, compounds 5, 15, 7, 17, 8, 19; n-alkanes, - - -, bottom to top, undecane, tetradecane, hexadecane.

Previous Work.—To E. A. Bygden[6] must go the credit for the first intensive study of the physical properties of tetraalkylsilanes. Among the compounds which he studied were 1, 2, 3, 12, 13 and 14 in Table I. In general, this data for these compounds and those of the present work are in good agreement. For example, Bygden's average value for SiRD in compounds 1, 2 and 3 is 7.50 with a mean deviation of 0.06 unit; for compounds 12, 13 and 14 his average value is 7.13 with a mean deviation of 0.06 unit. His values for *M*D agree with ours to within 0.5%. Boiling points agree to within 1°.

Experimental

Starting Materials.—Silicon tetrachloride (Stauffer Chemical Co., Niagara Falls, N. Y.) was used directly without purification; fractional distillation of a large batch of this material showed it to be better than 95% silicon tetrachloride. Methyl and ethyl bromides (Dow Chemical Co., Midland, Mich.) were used without purification. n-Propyl and n-butyl bromides were prepared from good grade commercial alcohols by the hydrobromic–sulfuric acid method. n-Amyl, n-hexyl, n-heptyl, n-octyl, lauryl and myristyl bromides were prepared in yields of 70–80% by reaction of the respective alcohols maintained at 110° with hydrogen bromide gas which was generated from hydrogen and bromine vapor in a quartz tube at 330°. All of the bromides were carefully fractionated in columns of 20 or more theoretical plates and only the purest material was used in the preparation of the Grignard reagents.

The n-Alkyltrichlorosilanes.—The synthesis of n-hexyltrichlorosilane will be described as representative of the method used. A 3-liter three-necked, round-bottomed flask was equipped with a mercury-sealed mechanical stirrer, reflux condenser and dropping funnel. In the flask there was placed 255 g. (1.5 moles) of silicon tetrachloride dissolved in 500 cc. of dry ether and the system was protected from moisture by a concentrated sulfuric acid trap. *n*-Hexylmagnesium bromide, 1.5 equivalents by titration, in 600 cc. of ether was filtered into the dropping funnel through glass wool and added to the silicon tetrachloride over a period of three hours. Addition was accompanied by the formation of magnesium salts which precipitated, and by moderate refluxing of the ether. After four hours of heating on the steam-bath, the reaction product was filtered by suction and the magnesium salts extracted with dry ether. Upon removal of the ether by distillation, the crude product was purified by fractional distillation in a 20-plate glass-helix packed column. The trichlorosilanes were analyzed for chlorine content as follows: weighed samples, 0.5–1 g., were dissolved in 25 cc. of methanol and titrated with standard alkali using phenolphthalein; this method is made possible by the easy hydrolysis of silicon–chlorine bonds. Table V gives the pertinent data for the new trichlorosilanes.

TABLE V

NEW TRICHLOROSILANES, $RSiCl_3$

R—	B. p.[a]		Yield,[b]	Chlorine, %	
	°C.	Mm.	%	Calcd.	Found
C_5H_{11}	107	120	52	51.8	50.8
C_6H_{13}	127	98	50	48.2	48.0
C_8H_{17}	119	28	46	43.0	43.1
$C_{10}H_{21}$	183	84	54	38.6	38.3
$C_{12}H_{25}$	120	3	29	35.1	34.8
$C_{14}H_{29}$	156	3	48	32.1	31.7

[a] Boiling points are uncorrected. [b] Yields are based on the quantity of Grignard reagent.

Preparation of *n*-Alkyltrimethylsilanes by Method I.—The synthesis of *n*-hexyltrimethylsilane will be described as typical. In the usual apparatus (see above) there was prepared methylmagnesium bromide, 1.7 equivalents by titration, in 800 cc. of ether. The flask was surrounded with an ice-bath, and 107 g. (0.5 mole) of *n*-hexyltrichlorosilane was added during three hours; precipitation of magnesium halide etherate started after one hour. After completion of the addition, the cooling bath was removed and stirring was continued for ten hours at room temperature. This was followed by refluxing for five hours, after which the ether was distilled and the residue heated on the steam-bath for five hours. The distilled ether was then returned to the flask, the solid material broken up, and the contents of the flask worked up with water and acid. The ether layer was separated and the water layer extracted with 100 cc. of ether. After distillation of the ether, the residue was washed with two 20-cc. portions of concentrated sulfuric acid in order to remove silicon–oxygen compounds, followed by washing with water and carbonate solution. The crude product was then dried with calcium chloride and fractionated.

Method II.—Trimethylchlorosilane, 40 g. (0.37 mole), was dissolved in 50 cc. of dry ether and added all at once to a solution of 0.6 equivalent of laurylmagnesium bromide in 300 cc. of ether. From here on the procedure used was the same as above (Method I).

Preparation of *n*-Alkyltriethylsilanes.—The procedures used for the preparation of these compounds by Methods I and II were essentially the same as for the trimethyl compounds. However, cooling during the addition of the trichlorosilane to ethylmagnesium bromide (Method I), and refluxing after addition of triethylchlorosilane to the Grignard reagent (Method II) were found to be unnecessary.

Analyses.—The tetraalkylsilanes were analyzed for silicon content in the following manner: Small samples, about 0.5–1 g., were fused with 15 g. of sodium peroxide and 1 g. of sucrose in a Parr bomb. The fusion was dissolved in 100 cc. of distilled water, filtered to remove a small amount of iron hydroxide, and the filtrate evaporated twice with hydrochloric acid to dehydrate the silica. Preparations and analyses of the tetraalkylsilanes are summarized in Table VI.

TABLE VI

THE TETRAALKYLSILANES

Cpd. No.	Method of prepn.	Yield,[a] %	Silicon, %	
			Calcd.	Found
1	I	32	27.5	27.3
2	I	54	24.1	24.1
3	I	64	21.5	21.3
4	I	50	19.5	19.6
5	I	79	17.7	17.5
6	II	46	16.3	16.3
7	I	89	15.1	15.0
8	I	80	13.1	13.0
9	II	56	11.6	11.2
10	I	50	10.4	10.4
11	II	60	21.5	21.2
12	*b*	68	19.5	19.6
13	I	71	17.7	17.8
14	II	50	16.3	16.1
15	II	75	15.1	15.0
16	II	60	14.0	14.2
17	II	68	13.1	12.8
18	I	77	12.3	12.0
19	I	78	10.9	10.7

[a] Yields are based on the trichlorosilane for Method I, and on the monochlorosilane for Method II. [b] Prepared from silicon tetrachloride.

Physical Properties.—Boiling points were determined in a modified Cottrell apparatus.[11] Determinations were made at six pressures covering the range 20–735 mm. Temperatures were read on high precision thermometers graduated in 0.2° (Double Diamond, H. B. Instrument Co.) and pressures were corrected.

Refractive indices were determined with an Abbe type refractometer.

Densities were measured with pycnometers of about 5-cc. capacity. All determinations were checked by running each compound in two different pycnometers. The instruments were calibrated at the three temperatures using triple-distilled water. All densities are corrected to the vacuum values.

Viscosities were determined in Cannon–Fenske viscometers.[12] All determinations were checked by running each compound in two different instruments.

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Summary

1. Ten *n*-alkyltrimethylsilanes and nine *n*-alkyltriethylsilanes have been prepared. The best method of preparation involves reaction of trimethylchlorosilane or triethylchlorosilane with a Grignard reagent.

2. Physical properties of these compounds have been determined and discussed.

3. Boiling points, refractive indices and densities are higher in the tetraalkylsilanes than in their carbon analogs. This is attributed to the fact that molecular weights in the silicon compounds are greater by sixteen units.

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[11] Quiggle, Tongberg and Fenske, *Ind. Eng. Chem., Anal. Ed.*, **6**, 466 (1934).

[12] Cannon and Fenske, *ibid.*, **10**, 297 (1938).

4. The silicon compounds have lower viscosities than alkanes of corresponding molecular weight.

5. Comparison of trimethyl and triethyl silicon compounds with trimethyl and triethyl alkanes of corresponding molecular weight, *i. e.*, Me_3SiEt with Me_3CPr, reveals that the silicon compounds have lower boiling points, higher densities and higher refractive indices than the carbon compounds. This is attributed to the greater compactness of the tetraalkylsilanes.

6. The change of viscosity and density with temperature is about the same in tetraalkylsilanes and in alkanes.

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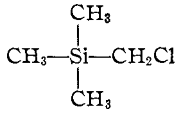
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Organo-silicon Compounds. II.[1] Silicon Analogs of Neopentyl Chloride and Neopentyl Iodide. The Alpha Silicon Effect[1]

BY FRANK C. WHITMORE AND LEO H. SOMMER

The rapidly growing importance of organosilicon chemistry suggested a thorough study of haloalkyl silicon compounds as of practical as well as theoretical interest. Only a few of these compounds have been reported.[2] Among these are the monochlorinated derivatives of tetraethylsilane.[2a] The lower boiling of these two isomers was assigned the α-chloroethyltriethylsilane structure. Since we wished first to investigate the properties of a simple α-haloalkyltrialkylsilane, we synthesized Compound I, chloromethyltrimethylsilane (silico-neopentyl chloride).[3]



$$CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-CH_2Cl \qquad (I)$$

We are interested in this compound because of the importance of the analogous neopentyl grouping.[4]

We have compared the properties of chloromethyltrimethylsilane with those of its carbon analog; neopentyl chloride. Such studies give information on the "silicon effect," the effect of a silicon atom on the reactivity of a functional group in an attached carbon chain.

Tetramethylsilane was prepared from silicon tetrachloride and methylmagnesium bromide.[5]

The liquid phase, photochemical chlorination of tetramethylsilane goes about as readily as that of neopentane.[4] It gives Compound I in fair yield.

$$(CH_3)_4Si + Cl_2 \longrightarrow \underset{(I)}{(CH_3)_3SiCH_2Cl} + HCl$$

Silico-neopentyl chloride (I) is a colorless stable liquid which can be distilled at atmospheric pressure without decomposition. It readily forms a Grignard reagent, the first aliphatic example of such a compound containing silicon. The synthetic possibilities of this reagent are being developed.

Reaction with mercuric chloride gave siliconeopentylmercuric chloride (chloromercurimethyltrimethylsilane, trimethylsilylmethylmercuric chloride).

Silico-neopentyl chloride (I) is less reactive than *n*-hexyl chloride, but far more reactive than the very inert neopentyl chloride.[4a] Results with nine reaction mixtures justify these important conclusions. Unless otherwise indicated each reaction was carried out at the boiling point of the solvent for four hours. Whereas *n*-hexyl chloride reacted completely with sodium ethylate in absolute ethanol, (I) reacted only about 40% under the same conditions. The activity of the two compounds with the following four reagents was approximately the same. The figures in parentheses indicate the percentage reaction, the first figure in each case corresponding to chloromethyltrimethylsilane (I) and the second to *n*-hexyl chloride: potassium acetate in absolute ethanol (23–29); potassium acetate in glacial acetic acid (26–32); potassium hydroxide in absolute ethanol (52–69); potassium hydroxide in 70:30 aqueous ethanol (16–22). It will be noted that (I) appears slightly less active in each case. Aqueous potassium hydroxide gave no reaction with (I) but gave about 1% conversion with the alkyl halide. Refluxing for eight hours with aqueous ethanol (1:1) gave no reaction with (I) and less than 1% change with the other chloride. Boiling (I) for five minutes with ethanolic silver nitrate gave no action, whereas similar treatment of

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[1] Presented before the Division of Organic Chemistry at the Pittsburgh Meeting of the American Chemical Society, September 6, 1943. Paper I, Whitmore, *et al.*, THIS JOURNAL, **68**, 475 (1946).

[2] (a) Ushakov and Itenberg, *J. Gen. Chem. U. S. S. R.*, **7**, 2495 (1937); (b) Krieble and Elliot, THIS JOURNAL, **67**, 1810 (1945).

[3] We use the silico-neopentyl naming as well as that suggested by Sauer, *J. Chem. Ed.*, **21**, 303 (1944), and the unpublished Dow Committee Report of July 1, 1944.

[4] (a) Whitmore and co-workers, *ibid.*, **55**, 4161 (1933); **61**, 1585, 1586 (1939); **63**, 124 (1941); **64**, 1783 (1942); (b) Skell and Hauser, *ibid.*, **64**, 2633 (1942); (c) Aston and co-workers, *J. Chem. Phys.*, **12**, 336 (1944); (d) Kharasch and Fineman, THIS JOURNAL, **63**, 2776 (1941); (e) van Wijk and others, *Physica*, **7**, 45 (1940); (f) Halford, *J. Chem. Phys.*, **8**, 496 (1940); (g) Kincaid and Henriques, Jr., THIS JOURNAL, **62**, 1474 (1940); (h) Silver, *J. Chem. Phys.*, **7**, 1113 (1939); (i) Frey, *C. A.*, **37**, 5079 (1943).

[5] (a) Krause and von Grosse, "Die Chemie der metall-organischen Verbindungen," Berlin, 1937, p. 260; (b) Bygden, *Ber.*, **44**, 2640 (1911).