Anal. Calcd. for $C_{18}H_{19}OCl$: C, 75.38; H, 6.68; Cl, 12.36. Found: C, 75.70; H, 6.83; Cl, 12.70.

A broad absorption band at 288 mμ indicates the presence of a carbonyl group (log *E* 2.67, 95% ethanol).

When methanol was used as the recrystallizing medium only the starting material was isolated.

The product obtained from the treatment of 2-ethylidene-3,3-diphenyl-5-methyl-tetrahydrofuran with concentrated hydrochloric acid and ethanol was not obtained in a pure state. It apparently reverted to the starting material on attempted purification.

Reaction of Hydroxylamine with IIa.—A mixture of 2 g. of the ethylidenetetrahydrofuran (IIa), 2 g. of hydroxylamine hydrochloride and 1 g. of pyridine in ethanol was refluxed for two hours and then allowed to stand overnight. A precipitate appeared which, after recrystallization from ethanol and then several times from methanol, melted at 190–192°.

Anal. Calcd. for $C_{19}H_{23}NO_2$: C, 76.76; H, 7.79; N, 4.71. Found: C, 76.43; H, 7.78; N, 4.65, 4.74.

Reaction of Hydroxylamine with IIb.—The reaction was run as above but since no crystals appeared, the mixture was diluted with water and an oil separated, which soon crystallized, m.p. 160–161° (from methanol).

Anal. Calcd. for $C_{18}H_{21}NO_2$: C, 76.30; H, 7.47; N, 4.84. Found: C, 76.60; H, 7.66; N, 4.94.

The Reaction of 2-Ethylidene-3,3-diphenyltetrahydrofuran with 2,4-Dinitrophenylhydrazine.—A solution of 0.5 g. of IIb and 0.275 g. of 2,4-dinitrophenylhydrazine in 30 ml. of ethanol was acidified with 3 drops of concentrated hydrochloric acid and refluxed 1.5 hours. The resulting solution was concentrated to 20 ml., and 8 ml. of water was added. An oil separated which was redissolved and crystallized on cooling slowly, m.p. 163–165°.

Anal. Calcd. for $C_{24}H_{23}O_5N_4$: N, 12.52. Found: N, 12.45, 12.43.

Ozonization of 3,3-Diphenyl-5-methyl-2-ethylidenetetrahydrofuran.—A chloroform solution of the ethylidenetetrahydrofuran (IIa) was treated with ozone and the ozonide was decomposed on standing overnight with water. The lactone[13] was isolated and identified by melting point and mixed melting points. Acetaldehyde was identified as the 2,4-dinitrophenylhydrazone (m.p. and mixed m.p. with authentic sample).

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BETHLEHEM, PA.

[CONTRIBUTION FROM THE LEWIS FLIGHT PROPULSION LABORATORY OF THE NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS]

Synthesis and Properties of Some Alkylsilanes

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Twelve alkylsilanes have been synthesized and the following physical properties were measured: boiling point, freezing point, index of refraction, molecular weight and density. Vinylsilane and isobutylsilane are reported for the first time. Vapor pressures were measured using a static system, and the heats of vaporization were calculated from the data. By the use of a special sample filling technique, it was possible to measure the heats of combustion in an oxygen bomb calorimeter and then to calculate the heats of formation.

Introduction

As a part of a program at this Laboratory involving the investigation of organometallic compounds, a number of alkylsilanes have been prepared and their physical properties determined. These compounds are methyl-, dimethyl-, trimethyl-, tetramethyl-, ethyl-, diethyl-, triethyl-, tetraethyl-, butyl-, isobutyl-, vinyl- and dimethyldipropylsilane. Isobutylsilane and vinylsilane are reported here for the first time.

Several procedures for the synthesis of alkylsilanes are available.[1–4] One of the most common methods is the Grignard reaction, which involves the interaction of a suitable alkylmagnesium halide with a halosilane in anhydrous ether. The reaction is illustrated by the equation for the preparation of trimethylsilane.[5] This method was used by the authors in the present work to prepare dimethyldipropylsilane and tetraethylsilane.

$$3CH_3MgBr + SiHCl_3 \xrightarrow[\text{ether}]{\text{ethyl}} Si(CH_3)_3H + 3MgBrCl$$

An excellent method for the preparation of a series of alkylsilanes was reported recently.[6] By reduction of the proper alkylchlorosilane with lithium aluminum hydride in anhydrous ethyl ether or dioxane, the alkylsilane can be obtained in high yield and free of side products. This type of reaction is illustrated by the following equation for the synthesis of ethylsilane

$$4Si(C_2H_5)Cl_3 + 3LiAlH_4 \xrightarrow{\text{dioxane}} 4Si(C_2H_5)H_3 + 3LiCl + 3AlCl_3$$

The reaction is rapid, and yields exceeding 80% are not uncommon. This method was chosen to prepare the following compounds: methyl-, dimethyl-, trimethyl-, ethyl-, diethyl-, triethyl-, vinyl-, butyl- and isobutylsilane. In addition, tetramethylsilane was purified from a commercially available product.

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[1] A. Ladenburg, *Ann.*, **164**, 302, 327 (1872).

[2] A. Stock and C. Somieski, *Ber.*, **52**, 695 (1919).

[3] F. C. Whitmore, E. W. Pietrusza and L. H. Sommer, THIS JOURNAL, **69**, 2108 (1947).

[4] E. G. Rochow, "The Chemistry of the Silicones," John Wiley and Sons, Inc., New York, N. Y., 1946, p. 32.

[5] A. G. Taylor and B. V. de G. Walden, THIS JOURNAL, **66**, 842 (1944).

[6] A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach and H. I. Schlesinger, *ibid.*, **69**, 2692 (1947).

The physical properties in the literature are incomplete for compounds containing Si–H bonds, and few thermodynamic data are available.[3,4,6,7] Consequently, the following properties were determined in this research where possible: freezing point, boiling point, density, index of refraction, vapor pressure, heat of vaporization, molecular weight and heat of combustion. The heats of formation for both the liquid and gaseous phases have been calculated using the experimental values for heat of combustion and heat of vaporization. Infrared spectra also were obtained.

Experimental

Synthesis

The alkylsilanes were prepared by the reduction of the proper alkychlorosilane with excess lithium aluminum hydride in anhydrous dioxane. In general, 80–90% yields were obtained, based on the alkylchlorosilane. Approximately 500 ml. of each compound was prepared to provide sufficient material for the determination of properties.

Ethylsilane.—To illustrate the general procedure for the preparation of alkylsilanes, the synthesis of ethylsilane will be described. The apparatus consisted of a 5-liter, 3-necked flask fitted with a mineral oil sealed stirrer. The side necks were provided with openings for a flow of dry nitrogen gas, a dropping funnel, a thermometer and a water condenser. A still head cooled with a Dry Ice–acetone slush was mounted atop the condenser and was fitted with a receiver packed in Dry Ice. All openings exposed to air were protected with calcium chloride drying tubes and a nitrogen atmosphere was maintained in the reactor at all times. About 1200 ml. of freshly distilled dioxane was placed in a flask together with 85 g. (2.23 moles) of lithium aluminum hydride which had been pulverized in a dry box and suspended in 500 ml. of dioxane. A 20–25% excess of lithium aluminum hydride was used. The mixture was stirred and brought to reflux at 100–105°. After $^1/_2$ hour, 328 g. (2.0 moles) of ethyltrichlorosilane was added at a rate sufficient to maintain steady reflux. As the product was formed, it distilled from the reaction mixture. A total of 115.5 g. of crude ethylsilane was collected and distilled in a 3-ft. vacuum-jacketed column packed with $^1/_8$-inch glass helices. The material boiling in the range −12.5 to −10.5° was collected and amounted to 105.6 g. or 88% based on ethyltrichlorosilane. This material was repurified by careful distillation prior to determining the physical properties.

The same general method was employed for the other alkylsilanes with the exception of dimethyldipropylsilane and tetraethylsilane, which were prepared by the Grignard method.

Dimethyldipropylsilane.—In a typical preparation of dimethyldipropylsilane, 92 g. (3.78 g. atoms) of magnesium turnings was placed in a dried 5-liter 3-necked flask equipped with a stirrer, condenser, funnel and an inlet for a supply of dry nitrogen. The turnings were covered with 1 liter of dry ether, and 41.0 g. of *n*-propyl bromide was added to start the reaction. The remainder of the halide (total 433 g., 3.52 moles) was added in 500 ml. of ether at such a rate that reflux was maintained.

The Grignard mixture was refluxed for $^1/_2$ hour after the addition was completed. The addition of dimethyldichlorosilane (226 g., 1.74 moles) was started dropwise, then continued in a slow stream for 2 to 3 hours. At the completion of the addition, a hot water-bath was placed around the flask, and after 10–15 minutes crystals of magnesium halide began to form on the sides of the flask. The reaction was completed by refluxing with stirring overnight.

The organic layer was then decanted from the salts which subsequently were hydrated and dissolved in very dilute hydrochloric acid. This solution was extracted with ether and the ether extract combined with the organic layer. After the ether had been removed, the crude product was distilled on a 3-ft. column packed with $^3/_{16}$-inch glass helices, and the compound was given a final purification by fractionation through a Podbielniak column rated at over 100 theoretical plates.

Physical Properties

Density.—Densities of those alkylsilanes boiling above room temperature were measured at 20.0 ± 0.1° with a fine capillary Sprengel-type pycnometer.[8] Several determinations were made for each compound and the average deviation was 0.0002 g./ml.

For the very low boiling alkylsilanes a straight tube pycnometer was used consisting of a 14-inch piece of 0.500 mm. precision bore capillary tubing with a bulb formed on one end and an expansion bulb with a capillary outlet on the other end. A scale calibrated in 0.5 mm. divisions was affixed to the precision tubing and the entire unit was attached by a 10/30 $\overline{\text{T}}$ joint to the vacuum system for filling. The pycnometer was calibrated with purified ethyl alcohol. Densities were determined from −80° to the boiling point in roughly 10° steps. Temperature was measured with a fine wire copper–constantan thermocouple recording on a portable Rubicon potentiometer. Both methods were checked with benzene to an accuracy of ±0.0002 g./ml.

Index of Refraction.—Indices of refraction were measured with a Bausch and Lomb Abbé 56 refractometer at 20.0 ± 0.1°. Measurements were made rapidly in order to minimize oxidation and hydrolysis.

Molecular Weights. (1).—For those alkylsilanes boiling above room temperature, the molecular weight was determined by the freezing point depression of solutions in benzene. At least two different concentrations of alkylsilane in benzene were studied. Temperatures were measured with a Beckmann thermometer.

(2).—For alkylsilanes boiling below room temperature and others with high volatility, the vapor density method was applied. Measurements were made at two pressures, and a tared flask was used to minimize weighing errors. The volume of the calibrated flask was 322 ml. In most cases agreement was within ±0.5% of the calculated value.

Boiling Point.—Two methods were employed: (1) Extrapolation of vapor pressure *vs.* temperature curves to a pressure of 760 mm. afforded the boiling points of the more volatile alkylsilanes. The accuracy of these values is ±0.5°. (2) An ebulliometer[9] equipped with a platinum resistance thermometer was used to determine the remaining boiling points. The measurements were made in a nitrogen atmosphere with an accuracy of ±0.1°.

Freezing Point.—The standard technique[10] was employed for compounds boiling above room temperature. The procedure was modified for low boiling compounds by adapting the apparatus described by Glasgow, *et al.*,[11] replacing the Sylphon bellows used in the original apparatus with a tall mercury seal fabricated of metal. This adaptation was necessary because of the extremely short life of the bellows.

Infrared Spectra.—The spectra were obtained with a Baird double-beam recording spectrophotometer. The precision of the instrument is ±1% of the transmission value and ±0.02 μ for the wave length. Liquid samples were examined in a 0.1-mm. cell and gaseous samples were studied in a 5-cm. cell.

Vapor Pressure.—A static system was used which was very similar to that described by Sanderson.[12] The manometer differed only in that it had a 6-inch center section of 25-mm. tubing to reduce meniscus errors in the low pressure region. Pressures were read with a cathetometer to ±0.1 mm. A calibrated fine wire copper–constantan thermocouple connected to a portable Rubicon potentiometer gave temperatures accurate to ±0.5°.

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[7] (a) H. W. Post, "Silicones and Other Organic Silicon Compounds," Reinhold Publ. Corp., New York, N. Y., 1949; (b) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933; (c) A. Bygden, *C. A.*, **14**, 1974 (1920); (d) H. H. Anderson, This Journal, **69**, 3049 (1947); (e) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," Circular No. 500, Natl. Bur. Standards, Feb. 1, 1952.

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[10] A. R. Glasgow, Jr., N. C. Krouskop, J. Beadle, G. D. Axilrod and F. D. Rossini, *Anal. Chem.*, **20**, 410 (1948).

[11] A. R. Glasgow, N. C. Krouskop and F. D. Rossini, *ibid.*, **22**, 1521 (1950).

[12] R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 82.

At least 15 readings were taken at approximately 10° intervals from a temperature at which the vapor pressure was about 10 mm. up to the boiling point or room temperature, whichever was lower.

Thermodynamic Properties

Heat of Combustion.—The apparatus was a Parr Adiabatic Calorimeter with an Illium constant volume bomb[13] and a mercury thermometer (calibrated by the Natl. Bur. Standards) which could be read to ±0.005°F. The bomb was calibrated using standard benzoic acid supplied by the Parr Instrument Co. Because of their volatility and oxidizability, most of the samples were introduced into the bomb in glass bulbs somewhat sturdier than those described by Richards and Barry.[14] A bulb was filled so that at about room temperature the liquid occupied the entire volume. It was then suspended by an iron ignition wire in a perforated nickel crucible and placed in the bomb, which was subsequently charged with 25 to 30 atmospheres of oxygen. Combustion was initiated by passing current through the iron wire held tightly to the bulb with a small piece of cellulose tape. The heat generated by the burning of the wire and tape caused the liquid to rupture the glass bulb and burn. In several experiments the bulbs burst prior to the ignition of the wire but combustion still occurred, indicating that the compounds are spontaneously inflammable under the existing conditions.

The most satisfactory sample size was 0.35 to 0.60 g. of alkylsilane. Corrections were made for the heat supplied from the combustion of the cellulose tape.

Methylsilane was not investigated because it was too difficult to handle this low boiling compound by the procedure described. The method was also inapplicable to dimethyldipropylsilane and tetraethylsilane because of their high boiling points. The values for the latter two compounds were obtained by combustion of these materials in a gelatin capsule, with a known heat of combustion, supported on a series of perforated monel baffle plates.

The completeness of combustion was determined by a visual inspection of the bomb contents for traces of black or yellow materials.[15] This evidence was supplemented in several cases by an analysis of the combustion gases. The carbon dioxide gas formed was absorbed in Ascarite after drying by passage through Anhydrone. To provide accurate analyses every precautionary measure was taken to prevent leaks, but tiny leaks might still have been present during some of the experiments. The visual inspection as well as the gas analyses shown below indicate that essentially complete combustion was achieved in all cases.

Compound	Carbon, % Theor.	Carbon, % Exptl.	$\frac{C_{\text{exptl.}}}{C_{\text{theor.}}}$ %
$(C_2H_5)_3SiH$	61.99	61.49	99.2
i-$C_4H_9SiH_3$	54.47	54.17	99.4
n-$C_4H_9SiH_3$	54.47	54.25	99.6
$CH_2{=\!=}CHSiH_3$	41.32	41.02	99.2
$(CH_3)_2Si(C_3H_7)_2$	66.58	66.35	99.7
$(C_2H_5)_4Si$	66.58	66.35	99.7

It frequently was necessary to perform 10 or more experiments before three consistent values were obtained which met the visual criteria and for which the gas analyses were also satisfactory. Great difficulty was experienced in attempting to measure the heat of combustion of vinylsilane. Twenty-five determinations were made and only two satisfied the criteria for complete combustion. In all other cases, black and yellow materials were observed at the end of the experiments and gas analyses indicated incomplete combustion to the extent of 1.5 to 2.5%. The value reported is the average of the two good results.

Analyses

In addition to carbon analyses obtained during the measurement of heats of combustion, the following analytical data are reported.

Elemental Analysis.—Elemental analyses were obtained for dimethyldipropylsilane and tetraethylsilane. For dimethyldipropylsilane: Calcd. for $C_8H_{20}Si$: C, 66.57; H, 13.98; Si, 19.45. Found: C, 66.57; H, 14.06; Si, 19.38. For tetraethylsilane: Calcd. for $C_8H_{20}Si$: C, 66.57; H, 13.98; Si, 19.45. Found: C, 66.65; H, 14.08; Si, 19.40.

Hydrolysis.—The number of Si–H groups was determined by hydrolysis with 30% aq. NaOH or alcoholic KOH. The values obtained were

Compound	Theor. no. of Si–H bonds	Exptl. no. of Si–H bonds
CH_3SiH_3	3.00	2.91
$(CH_3)_2SiH_2$	2.00	1.99
$(CH_3)_3SiH$	1.00	0.98
$C_2H_5SiH_3$	3.00	2.97
$(C_2H_5)_2SiH_2$	2.00	1.88
$(C_2H_5)_3SiH$	1.00	0.95
n-$C_4H_9SiH_3$	3.00	2.97
i-$C_4H_9SiH_3$	3.00	2.98
$CH_2{=\!=}CHSiH_3$	3.00	2.99

When vinylsilane was hydrolyzed in aqueous sodium hydroxide, 3 moles of hydrogen was obtained. If the residual liquid was then heated to 170°, ethylene was evolved. In two experiments, heating for 15 hours resulted in 92 and 95% of the theoretical quantity of ethylene, which was identified by carbon–hydrogen analysis, measurements of the molecular weight and infrared spectra. It is interesting to note that when ethylsilane was heated at 170° for 40 hours and at 225° for 6 hours, nothing but hydrogen could be detected.

Results and Discussion

Physical Properties.—Table I presents the boiling points, freezing points, refractive indices, molecular weights and densities obtained for the alkylsilanes. The densities of those compounds which are gases at room temperature obey a straight-line relationship over the temperature range from −80° to the boiling point and are given in terms of constants A and B of the equation $D = -At + B$ (t = °C.). The average deviation between experiment and the least-squares equation for any compound was never greater than ±0.05%.

The Rankin equation[16] for the vapor pressure–temperature relations was found to give a good rep-

$$\log P = -(A/T) - B \log T + D$$

resentation of the experimental data as shown in Table II. The average deviations are also listed. Dimethyldipropyl-, tetraethyl- and triethylsilane were not studied since their vapor pressures are too low at room temperature. The heats of vaporization calculated from the vapor pressure data are included in Table II. The value at the boiling point only is reported, this being obtained by extrapolation of a least-squares line, for the five highest temperatures investigated, up to 760 mm.

The infrared spectra show a band at 4.7 μ which corresponds to the absorption band of the Si–H bond. The Si–alkyl band lies in the range 7.8–8.5 μ for methyl, ethyl, propyl and butyl radicals.

Thermodynamic Properties. Heat of Combustion.—The values given in Table III represent the average of the three best values obtained for each compound.

The experiments were subject to several errors. Temperatures could be read to ±0.005°F. and the maximum error in both readings would then be ±0.01°F. Since the temperature rise was about

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(13) "Oxygen Bomb Calorimetry and Oxygen Bomb Combustion Methods," Parr Manual No. 120, Parr Instrument Co., Moline, Ill.

(14) T. W. Richards and F. Barry, THIS JOURNAL, **37**, 993 (1915).

(15) L. H. Long and R. G. W. Norrish, *Trans. Roy. Soc.* (*London*), **A241**, 587 (1949).

(16) A. Weissberger, "Physical Methods of Organic Chemistry—Part I," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1949. p. 205.

TABLE I

PHYSICAL PROPERTIES OF ALKYLSILANES

Compound	B.p., °C. (760 mm.)	F.p., °C.	$n^{20}D$	Mol. wt. Δ F.p. method	Mol. wt. Vapor density method	Mol. wt. Calcd.	d^{20}, g./ml.	Density of low boiling compounds[b] A	Density of low boiling compounds[b] B	Density[c]
$(CH_3)SiH_3$	−57.5[a]	−156.81	....	...	45.9	46.12	....	0.001282	0.5540	0.6277
$(CH_3)_2SiH_2$	−19.6[a]	−150.22	....	...	60.2	60.14	....	.001143	.6149	.6377
$(CH_3)_3SiH$	6.7[a]	−135.89	....	...	74.8	74.17	....	.001085	.6448	.6375
$(CH_3)_4Si$	26.2[a]	α = −101.7 β = − 99.5	1.3582	...	88.2	88.20	....	.001042	.6634	.6361
$(C_2H_5)SiH_3$	−13.7[a]	−179.7	....	...	59.7	60.14	....	.001112	.6243	.6396
$(C_2H_5)_2SiH_2$	55.99	−134.39	1.3920	...	89.4	88.20	0.6832	......	....	....
$(C_2H_5)_3SiH$	108.77	−156.90	1.4119	115.7	..	116.25	.7318	......	....	....
$(C_2H_5)_4Si$	153.70	− 82.54	1.4267	142.0	..	144.30	.7662	......	....	....
$(CH_2{=}CH)SiH_3$	−22.8[a]	α = −179.08 β = −171.61	....	...	58.3	58.13	....	.001187	.6393	.6664
$(i\text{-}C_4H_9)SiH_3$	48.60	Glass	1.3905	87.6	89.1	88.20	.6753	......	....	....
$(n\text{-}C_4H_9)SiH_3$	56.42	−138.24	1.3922	87.7	89.2	88.20	.6786	......	....	....
$(CH_3)_2Si(C_3H_7)_2$	141.69	Glass	1.4146	139.8	..	144.30	.7399	......	....	....

[a] Determined by extrapolation of vapor pressure data. [b] Constants for equation $D = -At + B$. [c] Density at boiling point.

TABLE II

VAPOR PRESSURES AND HEATS OF VAPORIZATION OF ALKYLSILANES

Compound	Vapor pressure constants[a] A	B	D	Temp. range, °C.	Average dev., %	ΔH_{vap} at b.p., kcal./mole
$(CH_3)SiH_3$	1329.5	4.1741	18.7871	−117 to −58	1.02	4.39
$(CH_3)_2SiH_2$	1889.2	7.5510	28.4812	−86 to −22	0.49	5.10
$(CH_3)_3SiH$	1628.3	2.9574	15.9404	−68 to 0	.90	5.82
$(CH_3)_4Si$	1845.8	3.6664	18.1309	−55 to 22	.64	6.25
$(C_2H_5)SiH_3$	1784.3	6.0372	24.3222	−75 to −16	.57	5.33
$(C_2H_5)_2SiH_2$	2564.5	7.9119	30.5841	−32 to 22	.41	7.18
$(CH_2{=}CH)SiH_3$	1893.9	7.7159	28.9480	−87 to −23	.76	5.12
$(i\text{-}C_4H_9)SiH_3$	2398.1	7.0214	27.9253	−40 to 20	.54	7.05
$(n\text{-}C_4H_9)SiH_3$	2896.8	10.5930	38.3121	−33 to 11	.56	7.37

[a] Constants for the equation $\log P = -(A/T) - B \log T + D$.

TABLE III

THERMODYNAMIC PROPERTIES OF ALKYLSILANES

Compound	ΔH_{comb}, kcal./mole	ΔH_{form}, kcal./mole, (l)	ΔH_{form}, kcal./mole, (g)
$(CH_3)_2SiH_2$	− 624	−41	−36
$(CH_3)_3SiH$	− 766	−60	−54
$(CH_3)_4Si$	− 920	−69	−63
$(C_2H_5)SiH_3$	− 644	−20	−15
$(C_2H_5)_2SiH_2$	− 951	−37	−30
$(C_2H_5)_3SiH$	−1272	−41	[a]
$(C_2H_5)_4Si$	−1597	−41	−31[b]
$(CH_2{=}CH)SiH_3$	− 603	+ 7	+12
$(i\text{-}C_4H_9)SiH_3$	− 964	−25	−18
$(n\text{-}C_4H_9)SiH_3$	− 962	−26	−18
$(CH_3)_2Si(C_3H_7)_2$	−1594	−44	[a]

[a] No heat of vaporization data available. [b] $\Delta H_{vap} = 9.5$. Whitmore, *et al.*, THIS JOURNAL, **68**, 475 (1946).

4°F., this represents an error of ±0.25%. Another source of error is in the correction for heat supplied by the combustion of the cellulose tape and iron ignition wire. It was sometimes difficult to ascertain how much wire and tape were burned, and this source of error is believed to have a maximum magnitude of ±0.2% based on the bomb calibration. The total error due to the above causes can therefore be estimated at ±0.5%.

The largest uncertainty was due to the difficulty of assessing the completeness of combustion. The gas analyses reported in the experimental section indicate that the combustion efficiency was at least 99.2%, giving an error of 0.8%. The maximum error can therefore be estimated as −1.3% to +0.5% but can be as low as ±0.5%. Since minute traces of incompletely burned material were noticed even in the best runs, the authors feel that the values listed are on the low side. In general, experiences in applying the criteria for completeness of combustion indicate that a +0.5% correction to the heats of combustion would yield a result more nearly coinciding with the true value but the data were not treated in this manner.

Considering the magnitude of the errors outlined above, the corrections described by Washburn[17] for converting the process to constant temperature and 1 atmosphere pressure are negligible and have not been applied. Table III lists the values for the constant pressure process, and these values may be regarded as those for the reaction at 25°.

Heat of Formation.—The values listed in Table III were calculated from the heats of combustion for the reaction

$$\text{Alkylsilane(l)} + O_2(g) \longrightarrow SiO_2(s) + CO_2(g) + H_2O(l)$$

The heats of formation for SiO_2(s), CO_2(g) and H_2O(l) were taken from ref. (7e). Several values were given for SiO_2(s) depending on the crystal form. An X-ray analysis revealed that the SiO_2 formed in the

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[17] E. W. Washburn, *J. Research Natl. Bur. Standards*, **10**, 525 (1933).

bomb is amorphous and therefore the value for SiO_2(vitreous) = −202.5 kcal./mole was used. Where the heat of vaporization of the alkylsilane was available, the heat of formation for the gaseous phase also was calculated.

In spite of the large uncertainty attached to the determination of the heats of combustion, it is ininteresting to note the correlation between the thermodynamic stability of these compounds, as measured by their heats of formation (assuming a fairly constant entropy of formation), and the number of Si–H bonds they contain. For example, ethylsilane with three Si–H bonds and a ΔH_f of −20 kcal./mole has a lower heat of formation than its isomer dimethylsilane with two Si–H bonds and a ΔH_f of −41 kcal./mole. Inspection of Table III will confirm this relation for the isomers butyl-, diethyl- and tetramethylsilane; for the homologous series dimethyl-, trimethyl- and tetramethylsilane; and for the homologous series ethyl-, diethyl-, triethyl- and tetraethylsilane.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Tetra-substituted Aryl Silanes

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A number of tetra-substituted triphenylsilanes have been prepared by the reaction of triphenylchlorosilane with the appropriate alkyl- or aryllithium compound. Other miscellaneous preparations include the synthesis of trimethyl-(triphenylmethyl)-silane, bis-(*p*-triphenylsilylphenyl)-phenylmethane, 1,3-dimethyl-1,1,3,3-tetrakis-(*p*-chlorophenyl)-disiloxane and triphenyl-*t*-butoxysilane.

We wish to report the synthesis and physical properties of a number of previously unreported tetra-substituted silanes, prepared recently in this Laboratory in connection with studies of the cleavage of silanes by alkaline reagents.

The general method of synthesis of the simpler silanes follows that used previously in the preparation of these compounds, namely, treatment of triphenylchlorosilane with the appropriate alkyl- or aryllithium derivative.

$$(C_6H_5)_3SiCl + RLi \longrightarrow (C_6H_5)_3SiR + LiCl$$

The organolithium derivatives were prepared by treatment of the organohalide, where available, with lithium, according to published procedures.[1] In cases where the organohalide was not available, the hydrocarbon was metalated using either *n*-propyl- or *n*-butyllithium, and after metalation was complete, as indicated by the absence of a positive Color Test IIa, the metalated hydrocarbon was treated with triphenylchlorosilane. Using these

TABLE I

TETRA-SUBSTITUTED TRIPHENYLSILANES $(C_6H_5)_3SiR$

Reagent	Metalating agent	Yield, of RLi, %	Reaction (hr.) with chlorosilane	Product	M.p., °C.	Yield, %	Formula	Si analyses Calcd.	Si analyses Found
n-Propyl bromide	Li	78	24[a]	*n*-Propyltriphenylsilane	84[e]	89	$C_{21}H_{22}Si$	9.29	9.48
n-Amyl bromide	Li	81	24[b]	*n*-Amyltriphenylsilane	47[f]	42	$C_{23}H_{26}Si$	8.49	8.52
n-Hexyl bromide	Li	77	24[a]	*n*-Hexyltriphenylsilane	78[f]	99	$C_{24}H_{28}Si$	8.15	8.00
Fluorene	*n*-PrLi	..	16[b,c]	Triphenyl-9-fluorenylsilane	183[g]–184	70	$C_{31}H_{24}Si$	6.61	6.49
Diphenylmethane	*n*-PrLi	..	24[b,d]	Benzhydryltriphenylsilane	159[g]	66	$C_{31}H_{26}Si$	6.59	6.60
β-Bromoethylbenzene	Li	86	2[b]	Triphenyl-β-phenylethylsilane	147[h]	95	$C_{26}H_{24}Si$	7.70	7.69
Phenylacetylene	*n*-BuLi	..	12[a]	Triphenylphenylethynylsilane[k]	100–101	72	$C_{26}H_{20}Si$	7.77	7.55
Indene	*n*-PrLi	..	14[a]	Triphenyl-1-indenylsilane	136[i]	13	$C_{27}H_{22}Si$	7.50	7.55
				(1,1)-Bis-triphenylsilylindene[l]	206[g]	8	$C_{45}H_{36}Si_2$	8.88	8.97
m-Bromobenzotrifluoride	*n*-BuLi	..	17[a]	Triphenyl-*m*-(trifluoromethylphenyl)-silane	101[e]	72	$C_{25}H_{19}F_3Si$	[m]	..

[a] Reaction carried out at room temperature. [b] Reaction carried out at reflux temperature. [c] Solvent was benzene–ether (1.7:1). [d] Solvent was benzene–ether (1:1). [e] Recrystallized from methanol. [f] Recrystallized from ethanol. [g] Recrystallized from ethyl acetate. [h] Recrystallized from ethanol–ethyl acetate (1:1). [i] Recrystallized from ethyl acetate–methanol (5:1). [k] Prepared first by Mary Alys Plunkett in this Laboratory. [l] Cleavage with aqueous alkali yielded 85% triphenylsilanol. The position of the two triphenylsilyl groups has not been definitely established. [m] Silicon analyses were erratically low due to loss of Si possibly as SiF_4. *Anal.* Calcd. for $C_{25}H_{19}F_3Si$: C, 74.3; H, 4.74. Found: C, 75.8; H, 4.62. Cleavage with alkali yielded triphenylsilanol and benzotrifluoride, b.p. 100–101°, $n^{18.6}D$ 1.4155.

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(1) H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, THIS JOURNAL, **71**, 1499 (1949).