aminobutyric acid, additional hydrogen fluoride did not raise the low yield.

In the absence of hydrogen fluoride, sulfur tetrafluoride converts nicotinic acid to nicotinyl fluoride. Nicotinic acid (20 g. 0.16 mole), sulfur tetrafluoride (40 g. 0.37 mole), and 0.2 g. of water were heated for 4 hr. at 100° and 6 hr. at 120°. Distillation of the product gave a 50% yield of nicotinyl fluoride, b.p. 50–52°/6 mm.[11] The compound is quickly hydrolyzed by water.

Isolation procedures. Except for the picolines, the reaction products were poured into a polyethylene dish and heated on a steam bath to expel hydrogen fluoride. From this point the procedure may vary. The residue, especially if tarry, may be transferred to a steam-distillation apparatus, made strongly alkaline with sodium hydroxide solution, and steam distilled. The higher, sparingly soluble amines may be collected from the distillate with ether and dried and distilled in the usual manner. For the lower, water-soluble amines it is best to make the steam distillate acid with hydrochloric acid and evaporate the solution to dryness to obtain the amine hydrochloride which may, however, contain ammonium chloride as a contaminant. The amine may then be liberated from the hydrochloride with 40% potassium hydroxide solution, separated, dried over sodium hydroxide, and distilled.

In the case of the products from simple, aliphatic amino acids, the residue remaining after the evaporation of hydro-

(11) Results supplied through the courtesy of Dr. R. J. Harder.

gen fluoride may be stirred with water and filtered to separate insoluble materials from the amine hydrofluoride. The filtrate may then be evaporated to obtain the solid amine hydrofluoride from which tarry contaminants can be removed by washing with acetone. The amine can then be liberated with 40% potassium hydroxide and collected. However, precipitated heavy metal hydroxides formed from salts produced by attack on the stainless-steel reaction tube may cause minor difficulties here.

The trifluoromethylpicolines are volatile and such weak bases that evaporation of the reaction mixture, unless carefully done, will result in loss of the free picoline. Hence, the reaction mixture was diluted with 75 ml. of water and made basic with 33% sodium hydroxide while being cooled with ice. The mixture was then steam distilled. The oil was separated and the aqueous layer was extracted once with ether. The combined oil and ether extract were dried and distilled.

The product obtained from quinaldic acid was warmed to expel most of the hydrogen fluoride, and the residue was stirred with water. The crystalline 2-(trifluoromethyl)quinoline was filtered off, washed with water, air-dried, and recrystallized from hexane. The product from 4,5-imidazoledicarboxylic acid was treated similarly. The air-dried 4,5-bis(trifluoromethyl)imidazole was dissolved in ether and decolorized. Benzene was added and the ether was boiled away until the product crystallized out. The compound is soluble in aqueous sodium hydroxide.

WILMINGTON, DEL.

Synthesis of *t*-Butylsilicon Compounds by the Wurtz-Fittig Reaction[1]

C. C. CHAPPELOW, JR., R. L. ELLIOTT, AND J. T. GOODWIN, JR.[2]

The Wurtz-Fittig reaction of *t*-butyl chloride with tetramethoxysilane, tetraethoxysilane, tetraisopropoxysilane, and phenyltrimethoxysilane gave *t*-butyltrimethoxysilane, *t*-butyltriethoxysilane, *t*-butyltriisopropoxysilane, and *t*-butyldimethoxyphenylsilane in average yields of 40, 40, 13, and 35%, respectively. Reactions of chlorodiethoxysilane and triethoxysilane with *t*-butyl chloride and molten sodium gave *t*-butyltriethoxysilane instead of *t*-butyldiethoxysilane. Reactions attempted with methyltrichlorosilane, chlorodiethoxymethylsilane, chlorodiisopropoxymethylsilane, and silicon tetrachloride did not yield any *t*-butylated products. During all the reactions, some of the *t*-butyl chloride was converted to volatile off-gases. In nearly all cases these off-gases were composed mainly of an equal molar mixture of isobutane and isobutylene. The infrared spectra of *t*-butyltrimethoxysilane and *i*-butyltrimethoxysilane were determined. It was found that the number and intensity of the absorption bands in these compounds which are due to the *t*-butyl group and the *i*-butyl group are exactly opposite to the spectral correlations for ordinary aliphatic hydrocarbons which contain these groups.

t-Butylsilicon compounds have been prepared by treating various chlorosilanes with *t*-butyllithium[3] and *t*-butylmagnesium chloride.[4] During a study of the Wurtz-Fittig reaction in the preparation of organosubstituted silanes, Emblem and co-workers[5,6] were unable to obtain a *t*-butylsilicon

product from the reaction of *t*-butyl bromide, silicon tetrachloride, and sodium.

This paper reports the preparation of several *t*-butylsilicon compounds by the Wurtz-Fittig reaction of certain silicon compounds with *t*-butyl chloride and sodium. The results of the study are summarized in Table I.

Production of t-butylsilicon compounds by the Wurtz-Fittig reaction. The reaction of tetraethoxysilane and *t*-butyl chloride with molten sodium gave *t*-butyltriethoxysilane. A vapor phase chromatogram and an infrared spectrum of the reaction product were identical with those of an authentic sample of *t*-butyltriethoxysilane. The *t*-butyltri-

(1) This research was sponsored by the Research and Development Department of the Ethyl Corp., Baton Rouge, La.

(2) Present address: Corn Industries Research Foundation, Washington, D. C.

(3) L. J. Tyler, L. H. Sommer, and F. C. Whitmore, *J. Am. Chem. Soc.*, **70**, 2876 (1948).

(4) M. C. Harvey, W. H. Nebergall, and J. S. Peake, *J. Am. Chem. Soc.*, **79**, 2762 (1957).

(5) E. A. Bassett, H. G. Emblem, M. Frankel, and D. Ridge, *J. Soc. Chem. Ind.*, **67**, 177 (1948).

(6) H. G. Emblem, D. Ridge, and M. Todd, *Chem. and Ind.* (London), 905 (1955).

TABLE I
THE PREPARATION OF t-BUTYLSILICON COMPOUNDS BY THE WURTZ-FITTIG REACTION

| Run No.	Starting Material Compound	Moles	t-C4H9Cl (moles)	Na (moles)	"Catalyst"	Solvent	Temp.	% t-C4H9Cl Converted to Off-Gases	t-Butyl Silicon Product	Yield, %
1	Si(OCH3)4	0.70	0.35	0.85	Cu–Hg^c	None	110	31	t-C4H9Si(OCH3)3	13
2^a	Si(OCH3)4	1.40	0.35	0.85	Cu–Hg^c	None	110	28	t-C4H9Si(OCH3)3	40
3	Si(OCH3)4	0.60	0.30	0.75	None	C9H20^d	110	28	t-C4H9Si(OCH3)3	31
4	Si(OCH3)4	1.25	1.00	2.20	None	C9H20^d	110	33	t-C4H9Si(OCH3)3	20
5	Si(OCH3)4	3.68	1.00	2.20	None	None	110	28	t-C4H9Si(OCH3)3	54
6	Si(OC2H5)4	0.70	0.35	0.85	Cu–Hg^c	None	110	20	t-C4H9Si(OC2H5)3	34
7	Si(OC2H5)4	0.70	0.35	0.85	None	None	110	16	t-C4H9Si(OC2H5)3	44
8	Si(OC2H5)4	0.70	0.35	0.85^b	Cu–Hg^c	None	110	19	t-C4H9Si(OC2H5)3	52
9	Si(OC2H5)4	1.05	0.35	0.85	Cu–Hg^c	None	60	22	t-C4H9Si(OC2H5)3	40
10	Si(O-i-C3H7)4	1.05	0.35	0.85	Cu–Hg^c	None	110	16	t-C4H9Si(O-i-C3H7)3	12
11	Si(O-i-C3H7)4	1.05	0.35	0.85	None	None	110	23	t-C4H9Si(O-i-C3H7)3	14
12^a	SiCl4	0.15	0.15	0.40^b	None	C9H20^d	40	4	None	—
13	SiCl4	0.15	0.15	0.40	None	C9H20^d	110	21	None	—
14	C6H5Si(OCH3)3	1.05	0.35	0.85	None	C9H20^d	110	3	t-C4H9SiC6H5(OCH3)2	40
15	C6H5Si(OCH3)3	1.40	0.35	0.85	None	C9H20^d	110	14	t-C4H9SiC6H5(OCH3)2	29
16^a	CH3Si(OC2H5)2Cl	0.70	0.35	0.85	None	None	110	56	None	—
17	CH3Si(O-i-C3H7)2Cl	1.44	0.70	1.54	None	None	115	50	None	—
18	CH3Si(O-i-C3H7)2Cl	0.72	0.35	0.85^b	None	Toluene	65	22	None	—
19	CH3SiCl3	0.35	0.35	0.85	None	Toluene	105	40	None	—
20^a	CH3SiCl3	0.70	0.35	1.70^b	None	M-2-M^e	35	47	None	—
21^a	CH3SiCl3	0.70	0.35	1.70^b	None	E-1-E^f	35	25	None	—
22	HSi(OC2H5)3	1.05	0.35	0.85	None	None	110	0	t-C4H9Si(OC2H5)3	53
23	HSi(OC2H5)3	1.05	0.35	0.85	None	None	110	0	t-C4H9Si(OC2H5)3	35
24	HSi(OC2H5)3	0.15	0.15	0.40	None	C9H20^d	110	35	t-C4H9Si(OC2H5)3	22
25	HSi(OC2H5)2Cl	0.15	0.15	0.40	None	C9H20^d	110	24	t-C4H9Si(OC2H5)3	27

^a Duplicate run gave similar results. ^b As a dispersion. ^c One to three grams of a liquid copper amalgam (1–15 wt. % copper). ^d 2,2,5-Trimethylhexane. ^e Dimethyl ether of diethylene glycol. ^f Diethyl ether of ethylene glycol.

methoxysilane and *t*-butyltriisopropoxysilane were prepared in a similar way.

$$t\text{-}C_4H_9Cl + Si(OR)_4 + 2Na \longrightarrow$$
$$t\text{-}C_4H_9Si(OR)_3 + NaCl + NaOR$$
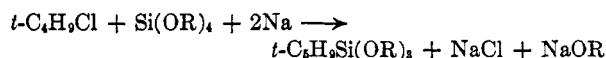
The proximity of the boiling points of the silane starting material and the *t*-butylated product made separations difficult, so yields were obtained by vapor phase chromatography of the reaction mixtures. The presence of a copper amalgam did not show any catalytic effect[7] upon the yield of *t*-butylated product. In the *t*-butylation of tetraethoxysilane, a slightly lower yield was obtained by the use of a sodium dispersion than the yields obtained by using sodium in the molten form. Excess tetramethoxysilane as solvent gave higher yields of *t*-butyltrimethoxysilane, than did the use of 2,2,5-trimethylhexane as a solvent. Tetramethoxysilane and tetraethoxysilane gave comparable yields (*ca.* 40%), but the runs using tetraisopropoxysilane gave much lower yields (*ca.* 13%).

The *t*-butylation of phenyltrimethoxysilane gave an average yield of 35% *t*-butylphenyldimethoxysilane.

$$t\text{-}C_4H_9Cl + C_6H_5Si(OCH_3)_3 + 2Na \longrightarrow$$
$$t\text{-}C_4H_9SiC_6H_5(OCH_3)_2 + NaCl + NaOR$$
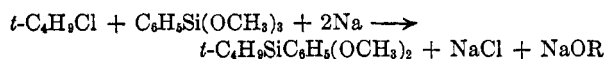
The product was isolated and identified by vapor phase chromatography. A chromatogram of the distilled reaction mixture revealed two major components. The component with the shorter retention time was identical with an authentic sample of phenyltrimethoxysilane. Infrared spectra of the distilled reaction mixtures contained absorption bands in the 7.2-μ region. Phenyltrimethoxysilane and phenyltrichlorosilane (used as a filtration aid) do not have this type of absorption in this region.
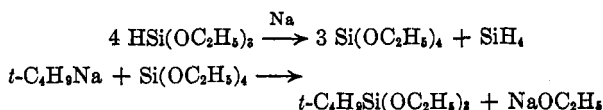
During all the reactions, varying amounts of off-gases were produced. The attempted *t*-butylation of chlorodiisopropoxymethylsilane resulted in the conversion of approximately 70% of the *t*-butyl chloride to volatile off-gases which were condensed in a $-80°$ trap. Vapor phase chromatography of the off-gas mixture revealed the presence of seven components: largely isobutane and isobutene in equal molar amounts, and smaller amounts of methane, propane, propene, *t*-butyl chloride, and an unidentified material.

We speculate that the isobutane and isobutene were produced by the disproportionation of *t*-butyl radicals. This type of reaction which involves the dehydrogenation of one radical by another, is characteristic of the usual mode of attack by a free radical.
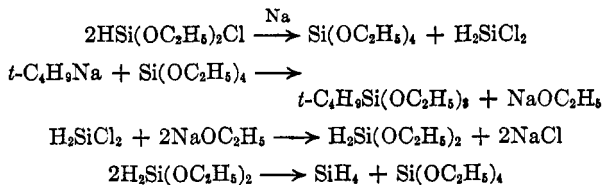
Diethoxychloromethylsilane, diisopropoxychloromethylsilane, methyltrichlorosilane, and tetrachlorosilane gave no evidence of *t*-butylation

(7) L. Tagnik, U. S. Patent 2,521,267 (September 5, 1950).

occurring. Sodium dispersions were no more effective than molten sodium. A reaction between methyltrichlorosilane and *t*-butyl chloride using sodium dispersions in dimethoxydiethyleneglycol or diethoxyethyleneglycol at lower temperatures could not be initiated. The presence of isobutane as the principal off-gas component suggests hydrogen extraction from the solvent media.

The reaction of triethoxysilane with molten sodium and *t*-butyl chloride gave *t*-butyltriethoxysilane, tetraethoxysilane, and silane (SiH_4) instead of the expected product, *t*-butyldiethoxysilane. Apparently, the presence of the metallic sodium-catalyzed[8] the disproportionation of the triethoxysilane to yield silane and tetraethoxysilane which subsequently reacted with the organosodium intermediate to yield *t*-butyltriethoxysilane.

$$4\ HSi(OC_2H_5)_3 \xrightarrow{\text{Na}} 3\ Si(OC_2H_5)_4 + SiH_4$$
$$t\text{-}C_4H_9Na + Si(OC_2H_5)_4 \longrightarrow$$
$$t\text{-}C_4H_9Si(OC_2H_5)_3 + NaOC_2H_5$$

Similarly, the *t*-butylation of chlorodiethoxysilane gave tetraethoxysilane and *t*-butyltriethoxysilane instead of the expected product, *t*-butyldiethoxysilane. The reactions involved may possibly be represented by the following series of equations:

$$2HSi(OC_2H_5)_2Cl \xrightarrow{\text{Na}} Si(OC_2H_5)_4 + H_2SiCl_2$$
$$t\text{-}C_4H_9Na + Si(OC_2H_5)_4 \longrightarrow$$
$$t\text{-}C_4H_9Si(OC_2H_5)_3 + NaOC_2H_5$$
$$H_2SiCl_2 + 2NaOC_2H_5 \longrightarrow H_2Si(OC_2H_5)_2 + 2NaCl$$
$$2H_2Si(OC_2H_5)_2 \longrightarrow SiH_4 + Si(OC_2H_5)_4$$

Infrared spectra of t-butyltrimethoxysilane and i-butyltrimethoxysilane. In order to determine whether isomerization of the *t*-butyl radical to the *i*-butyl radical had occurred during the sodium condensation reactions, the infrared spectra of a *t*-butylsilane and a *i*-butylsilane were determined and analyzed. For these purposes, a sample of *t*-butyltrimethoxysilane was prepared by the Wurtz-Fittig reaction and a sample of *i*-butyltrimethoxysilane was prepared by the Grignard method. The infrared bands in these compounds which are independent of the methoxy silicon portions of the molecules, are listed in Table II.

TABLE II

INFRARED SPECTRA OF *i*-BUTYLTRIMETHOXYSILANE AND *t*-BUTYLTRIMETHOXYSILANE

i-C$_4$H$_9$Si(OCH$_3$)$_3$	*t*-C$_4$H$_9$Si(OCH$_3$)$_3$
7.16 μ (m)	7.19 μ (ms)
7.24 μ (*m*)	7.35 μ (m)
7.32 μ (ms)	8.15 μ (m)
7.53 μ (ms)	9.90 μ (m)
8.16 μ (m)	10.64 μ (m)
10.45 μ (m)	13.82 μ (s)
13.05 μ (s)	

(8) C. Friedel and A. Ladenburg, *Ann.*, **143**, 124 (1867).

In ordinary aliphatic hydrocarbons, a general correlation[9] exists which makes a distinction between the *t*-butyl group (or more generally a 2,2-dimethyl compound) and an isobutyl group (or a 2-methyl compound) on the basis of number, position, and relative intensities of infrared bands in the 7.1–7.4-μ region. The bands in this region arise from the symmetrical CH₃ deformations in the molecule. The basis of this correlation is that molecules possessing the 2,2-dimethyl group or groups have either two or three bands between 7.15 and 7.35 μ and the long wave length band is always the most intense, whereas a molecule containing a 2-methyl group has only two bands in this region (unless an isolated methyl group exists elsewhere in the molecule) and the short wave length band is always the more intense.

The spectra observed for the silicon compounds containing these groups do not conform with this correlation. In *t*-butyltrimethoxysilane there are two bands in this region and the short wave length band is the more intense. In the *i*-butyltrimethoxysilane there are three bands in the CH₃ deformation region and the long wave length band is the most intense. In these compounds, there is no complication from the methoxy CH₃ as the —O—CH₃ group shows no CH₃ deformation in any compounds known. Since the observed spectra are diametrically opposed to the structures which were synthesized, one must rely on the method of preparation of the isobutyl compound for a basis of assignment. The isobutyl compound was made by the reaction of an isobutylmagnesium bromide and this is regarded as an unequivocal route to the isobutyl compound. Having accepted one of the structures as isobutyl, one must then regard the other as a *t*-butyl containing compound.

EXPERIMENTAL[10]

Vapor phase chromatography. Analyses were carried out with a Perkin-Elmer Model 154B Vapor Fractometer using a 2-m. column packed with column material "A" and helium as a carrier gas at a pressure of 20 p.s.i.g. The column was operated at a temperature of: 25° for analyses of the off-gases; 115° for analyses of *t*-C₄H₉Si(OCH₃)₃ reaction mixtures; 150° for analyses of *t*-C₄H₉Si(OC₂H₅)₃ and *t*-C₄H₉Si-(O-*i*-C₃H₇)₃ reaction mixtures; and at 165° for analyses of *t*-C₄H₉SiC₆H₅(OCH₃)₂ reaction mixtures.

t-Butyltriethoxysilane. To 19.5 g. (0.85 g.-atom) of molten sodium and 1.0 g. of copper amalgam (15 wt. % copper) in 145 g. (0.70 mole) of tetraethoxysilane was added slowly 32.4 g. (0.35 mole) of *t*-butyl chloride. The alkyl chloride was added to the rapidly stirred mixture (5000 r.p.m.) at a rate that would maintain a temperature of 115° in the reaction mixture. The reaction was initiated immediately, as indicated by a temperature increase and a purple color development. After the addition was complete, the reaction mixture was maintained at 115° for 15 min. The reaction mixture

(9) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, 1958.

(10) Molar refractions were calculated from the values of E. L. Warrick, *J. Am. Chem. Soc.*, **68**, 2455 (1946).

was cooled to 80° and 28.8 g. (0.17 mole) of silicon tetrachloride was added dropwise to facilitate filtration. The filtered reaction mixture was subjected to an atmospheric pressure distillation through a 10-plate, 1 in. i.d. Oldershaw column in which all the material distilling below 165° was removed. The residue was distilled through a Claisen head and 104 g. of material, b.p. 165–185°, were collected. Vapor phase chromatographic analysis (62.1 mole% tetraethoxysilane, 37.9 mole % *t*-butyltriethoxysilane) gave 40.8 g. (53.0% yield) of *t*-butyltriethoxysilane. Comparison of gas phase chromatograms of the product fraction with a 2:1 mixture of tetraethoxysilane and authentic *t*-butyltriethoxysilane and a 1:1 mixture of authentic *t*-butyltriethoxysilane with the product fraction gave indistinguishable chromatograms. The infrared spectrum of this product fraction was indistinguishable from a mixture of authentic tetraethoxysilane and *t*-butyltriethoxysilane.

Two similar runs, one with and one without the copper amalgam, gave 26.5 g. (34.4% yield) and 33.5 g. (43.6% yield) of *t*-butyltriethoxysilane, respectively.

A similar run carried out with a sodium dispersion at a temperature of 60° gave 30.7 g. (40.0% yield) of *t*-butyltriethoxysilane.

t-Butyltrimethoxysilane. To 50.6 g. (2.2 g.-atoms) of molten sodium in 559.4 g. (3.68 moles) of tetramethoxysilane was added slowly 92.5 g. (1.0 mole) of *t*-butyl chloride. The alkyl chloride was added to the rapidly stirred mixture (5000 r.p.m.) at a rate that would maintain a temperature of 110° in the reaction mixture. The reaction initiated immediately, as indicated by a temperature increase and a purple color development. After the addition was complete, the reaction mixture was maintained at 110° for 0.5 hr. Filtration and collection of the distillate range, b.p. 119–148°, gave 96.8 g. (54.3% yield) of *t*-butyltrimethoxysilane by an analytical procedure similar to that of the *t*-butyltriethoxysilane.

A similar run was carried out with 19.5 g. (0.85 g.-atom) of sodium, 1.0 g. of copper amalgam (15 wt.% copper) 212.8 g. (1.40 moles) of tetramethoxysilane, and 32.3 g. (0.35 mole) of *t*-butyl chloride gave 24.9 g. (40.0% yield) of product by vapor phase chromatographic analysis.

t-Butyltriisopropoxysilane. To 19.5 g. (0.85 g.-atom) of molten sodium in 277.2 g. (1.05 moles) of tetraisopropoxysilane was added slowly 32.3 g. (0.35 mole) of *t*-butyl chloride in a manner similar to that of the *t*-butyltriethoxysilane. The reaction temperature was maintained at 110° for 0.5 hr. after the addition was complete. After filtration and collection of the distillate range, b.p. 184–202°, the yield of *t*-butyltriisopropoxysilane was 13.1 g. (14.3% yield) as determined by vapor phase chromatographic analysis.

A similar run using 1.0 g. of copper amalgam (15 wt. % copper) gave 11.3 g. (12.3% yield) of *t*-butyltriisopropoxysilane.

t-Butylphenyldimethoxysilane. To 19.5 g. (0.85 g.-atom) of molten sodium and 207.9 g. (1.05 moles) of phenyltrimethoxysilane in 200 ml. of 2,2,5-trimethylhexane was added slowly 32.3 g. (0.35 mole) of *t*-butyl chloride. The reaction mixture was stirred rapidly (5000 r.p.m.), and the *t*-butyl chloride was added at a rate that would maintain a temperature of 110° in the reaction mixture. After the addition was complete, the reaction mixture was maintained at 115° for 0.5 hr. It was necessary to add 74.0 g. (0.35 mole) of phenyltrichlorosilane and heat the reaction mixture at a temperature of 85° for 1 hr. before filtration. Filtration then distillation of the reaction mixture through a Claisen head gave 162 g. of material distilling between 110–124° at 20 mm. Redistillation of this fraction through a 90 cm. high temperature spiral wire column, 7 mm. i.d., gave a small amount of material, b.p. 220–224°, 0.6% Cl. Analysis of this distillate by gas chromatography gave 20 mole % phenyltrimethoxysilane (identified by an authentic sample) and 80 mole % of *t*-butylphenyldimethoxysilane (identified by its infrared spectrum which contained the tertiary methyl group doublet absorption bands in the 7.2-μ region). The

TABLE III
Compounds Prepared and Characterized during This Study

Compound	B.P./Mm.	n^tD	d^t_4	MRD Calcd.	MRD Found
t-C₄H₉Si(OCH₃)₃[a]	143/740	1.3969[29]	0.9043[29]	46.45	47.34
i-C₄H₉Si(OCH₃)₃[a]	154–157/760	1.3934[25]	—	—	—
Si(OCH₃)₄[b]	120–123/740	1.3844[25]	0.8744[25]	70.36	70.76
C₆H₅Si(OCH₃)₃[c]	110/20	1.4708[25]	1.0620[25]	51.38	52.10
t-C₄H₉Si(OC₂H₅)₃[a]	173/743	1.3952[25]	0.8645[25]	60.30	61.03
CH₃Si(OC₂H₅)₂Cl[d]	129/760	1.3881[25]	0.9755[25]	49.36	49.36
HSi(OC₂H₅)₂Cl[e]	110/743	1.3853[23]	0.9815[23]	36.32	36.96
HSi(OC₂H₅)₃[f]	131/740	1.3751[23]	0.8894[23]	42.08	42.29
t-C₄H₉Si(O-i-C₃H₇)₃[a]	198/736	1.3970[31]	0.8379[31]	74.23	75.30
Si(O-i-C₃H₇)₄[g]	184–186/745	1.3844[25]	0.8744[25]	70.36	70.76
CH₃Si(O-i-C₃H₇)₂Cl[a]	145/736	1.3899[26]	0.9398[26]	49.95	49.55

[a] New compound. [b] B.p. 121–122/759, n^{20}D 1.3681, d^{20}_4 1.0523[12]. [c] B.p. 108/20, n^{25}D 1.4701, d^{20}_{25} 1.067[13]. [d] B.p. 126.5–127.5/760, n^{25}D 1.393, d^{20}_4 1.010.[14] [e] B.p. 107–110/743, n^{25}D 1.3845, d^{25}_4 0.9806.[15] [f] B.p. 131.5/760, n^{25}D 1.3744, d^{25}_4 0.8903.[16] [g] B.p. 186/760, n^{20}D 1.3852, d^{20}_4 0.8754[17].

starting materials, phenyltrimethoxysilane and phenyltrichlorosilane, do not have this type of absorption in this region.

The yield of t-butylphenyldimethoxysilane was 39.5% (31.0 g.), as calculated from gas chromatography analysis.

A similar run was carried out using 19.5 g. (0.85 g.-atom) of sodium, 249.2 g. (1.4 moles) of phenyltrimethoxysilane, 32.3 g. (0.35 mole) of t-butyl chloride, and 24.9 g. (0.118 mole) of phenyltrichlorosilane, added with the t-butyl chloride to maintain a liquid reaction mixture. Distillation through a Claisen head gave 140 g. of material distilling between 108–117° at 20 mm. The yield of product was 29.4% (26.0 g.), as calculated from gas chromatography analysis.

The attempted t-butylation of methyldialkoxychlorosilanes. To 19.5 g. (0.85 g.-atom) of molten sodium in 200 ml. of toluene at a temperature of 105° and with rapid stirring (6000 r.p.m.) was added a mixture of 32.3 g. (0.35 mole) of t-butyl chloride and 118 g. (0.7 mole) of methyldiethoxychlorosilane. The temperature was maintained at 105° by controlling the rate of addition of the reactants. During the course of the reaction, a gas evolved steadily; it was condensed completely in a Dry Ice–acetone trap. After the addition of the reactants was complete, the reaction temperature was maintained at 105° for 15 min., then the reaction mixture was filtered. The lower boiling materials were removed by distillation through a 10-plate, 1-in. i.d. Oldershaw column at 748 mm. The remaining material was fractionated through a 10-in. glass helices packed Claisen head at 80 mm. The expected product, t-butyldiethoxymethylsilane, could not be identified or isolated. About 60% of the chlorosilane starting material has been converted to methyltriethoxysilane, b.p. 142° at 746 mm., n^{25}D 1.3825, d^{25}_4 0.8856; MRD calcd. 46.5, found 46.9.

A similar run with double the molar amounts was carried out using methyldiisopropoxychlorosilane. A total of 47 ml. of condensate was collected in a Dry Ice–acetone trap. A small amount of methyltriisopropoxysilane,[3] b.p. 159° at 745 mm., n^{25}D 1.3878, d^{25}_4 0.8532; MRD calcd. 60.34, found 60.3, was collected. The expected product, t-butyldiisopropoxymethylsilane, could not be identified or isolated. The 47 ml. of condensate collected in this run was found to contain seven components: (compound, composition in mole %) isobutane, 34.0; isobutylene, 32.5; t-butyl chloride, 9.5; air-methane, 5.3; A, 06; and B, 14.6 by gas chromatography. The identity of the components was established with identical chromatograms of authentic compounds.

A series of similar runs were carried out in an attempt to t-butylate methyltrimethoxysilane, methyltriethoxysilane, methyltriisopropoxysilane, tetrachlorosilane (molten sodium at 110° and sodium in dispersion form at 40°), and methyltrichlorosilane (sodium dispersion at 30° and 0–5°), but no t-butylated product was identified.

The t-butylation reaction of triethoxysilane and diethoxychlorosilane. To 19.5 g. (0.85 g.-atom) of molten sodium in 172.2 g. (1.05 moles) of triethoxysilane was added 32.3 g. (0.35 mole) of t-butyl chloride. Rapid stirring (5000 r.p.m.) was employed, and the temperature of the reaction mixture was maintained at 110° by the rate of addition. After the addition was complete, the reaction mixture was heated at 110° 0.5 hr. and filtered. There was no condensate in the Dry Ice–acetone trap. Distillation through a 10-plate, 1-in. i.d. Oldershaw column gave no distillate boiling in the triethoxysilane range, b.p. 134°. The boiling point range of the material collected was 160–169°. Gas chromatography revealed two major components that gave identical chromatograms with authentic samples of t-butyltriethoxysilane and tetraethoxysilane, and a minor component identical with triethoxysilane. Instead of the expected product, t-butyldiethoxysilane, 41.0 g. (53.3% yield) of t-butyltriethoxysilane was obtained, as calculated by gas chromatography analysis.

A similar run was carried out using 9.2 g. (0.4 g.-atom) of sodium, 23.2 g. (0.15 mole) of chlorodiethoxysilane, 13.9 g. (0.15 mole) of t-butyl chloride, and 60 ml. of 2,2,5-trimethylhexane. Tetraethoxysilane (23.5% yield) and t-butyltriethoxysilane (26.5% yield) were obtained instead of the expected product, t-butyldiethoxysilane, as determined by vapor phase chromatographic analysis.

Authentic t-butyltrimethoxysilane. t-Butyltrichlorosilane was prepared by the t-butyllithium method.[3] To 63.0 g. (2.0 moles) of anhydrous methanol was added 30.0 g. (0.157 mole) of t-butyltrichlorosilane during a 1-hr. period while the temperature was maintained at 0°. Then the reaction mixture was warmed to 35° and 7.2 g. (0.32 g.-atom) of sodium was added in small pieces during a 1-hr. period. The reaction mixture became basic upon the addition of the last small portion of sodium; then it was refluxed for 1 hr. and filtered. Distillation through a semimicro distillation apparatus gave a center fraction of t-butyltrimethoxysilane, b.p. 143° at 740 mm., n^{29}D 1.3969, d^{29}_4 0.9043; MRD calcd. 46.45, found 47.34.

Authentic t-butyltriethoxysilane. A similar run using ethyl alcohol gave t-butyltriethoxysilane, b.p. 173° at 743 mm., n^{25}D 1.3952, d^{25}_4 0.8645; MRD calcd. 60.30, found 61.03.

Anal. Calcd. for C₁₀H₂₄O₃Si: C, 55.27; H, 10.97. Found: C, 55.27, 54.99; H, 10.98, 10.95.

Authentic t-butyltriisopropoxysilane. In a similar manner, t-butyltriisopropoxysilane was prepared, b.p. 198° at 736 mm., n^{31}D 1.3970, d^{31}_4 0.8379; MRD calcd. 74.23, found 75.30.

Preparation of a sample of i-butyltrimethoxysilane. Isobutylmagnesium bromide was prepared by addition of a mixture of 68.5 g. (0.5 mole) of isobutylbromide and 70 g. of ethyl ether to a stirred mixture of 17 g. (0.7 g.-atom) of oven-dried magnesium and 47 g. of ethyl ether. The addition

was carried out over a period of 2 hr. so as to maintain a gentle reflux temperature. The mixture was stirred for 30 min. after addition. The isobutylmagnesium bromide was filtered through a glass-wool plug in a Tygon tube into a dropping funnel and was subsequently added over 45 min. to a stirred mixture of 122 g. (0.8 mole) of tetramethoxysilane and 122 g. of ethyl ether. A white precipitate formed almost immediately without liberation of much heat. The mixture was then heated under reflux conditions for 2 hr. The cooled mixture was filtered through Celite, dried over Drierite, and concentrated by distillation. The concentrate was distilled through a 6-in., bead-packed column to give three fractions: (A) b.p. 80–130°; (B) b.p. 130–154°; and (C) b.p. 154–157° n_D^{25} 1.3934. By adjustment of the known constants of n-butyltrimethoxysilane,[11] the constants of isobutyltrimethoxysilane were estimated to be n_D^{25} 1.3959 and b.p. 155° at 760 mm.

The preparation of certain alkoxychlorosilanes and alkoxysilanes. Certain methoxy, ethoxy, and isopropoxy derivatives of tetrachlorosilane, methyltrichlorosilane, phenyltrichlorosilane, and trichlorosilane, which were not commercially available, were prepared by the following general procedure.

A calculated amount of the anhydrous alcohol was added slowly to a calculated amount of the chlorosilane which was dissolved in an equal amount of benzene. During the addi-

tion, the reaction mixture was stirred vigorously while the temperature was maintained at 0°. After the addition was complete, the reaction mixture was slowly purged with nitrogen until most of the dissolved hydrogen chloride was expelled. The degassed reaction mixture was distilled through a 10-plate, 3/4-in. i.d. Oldershaw column and the product collected in a desiccant vented receiver.

The physical properties of the known[12–17] silicon compounds and the new silanes which were prepared during this study, are listed in Table III.

(11) M. G. Voronkov, and A. Y. Yakubovskaya, *Zhur. Obshchei Khim.,* **25,** 1124 (1955); *Chem. Abstr.,* **50,** 3217i (1956), report b.p. 164.8° at 760 mm., d_4^{20} 0.9312, n_D^{20} 1.3979.

(12) D. Peppard, D. Brown, and W. Johnson, *J. Am. Chem. Soc.,* **68,** 76 (1946).

(13) L. J. Tyler, *J. Am. Chem. Soc.,* **77,** 770 (1950).

(14) K. A. Andrianov, S. A. Golubtsov, and N. P. Lobusevich, *Zhur. Obshchei Khim.,* **26,** 197 (1956); *Chem. Abstr.,* **50,** 13730 (1956).

(15) A. F. Reilly, and H. W. Post, *J. Org. Chem.,* **16,** 387 (1951).

(16) C. A. MacKenzie, A. P. Mills, and J. M. Scott, *J. Am. Chem. Soc.,* **72,** 2032 (1950).

(17) B. E. F. Smith, *Svensk. Kem. Tid.,* **61,** 213 (1949); *Chem. Abstr.,* **44,** 883 (1950).

Relative Reactivities of Some Functional Groups with Triphenylsilyllithium

HENRY GILMAN AND WILLIAM J. TREPKA[1]

By combining several methods involving competitive reactions, a relative reactivity series of some functional groups with triphenylsilyllithium has been established. The ester function was found to react very rapidly with triphenylsilyllithium; this is in contrast to its relatively slow reaction with organometallic reagents.

With the easy and efficient preparation of triphenylsilyllithium by the cleavage of hexaphenyldisilane in tetrahydrofuran by lithium,[2] another synthetic tool has been added to the field of versatile organometallic types. However, some of the reactions of triphenylsilyllithium with various functional groups do not follow their counterparts, *i.e.,* Grignard reagents and organolithium reagents.[3] An outstanding example is that triphenylsilyllithium adds to benzophenone in a normal manner, but apparently rearranges immediately to give benzhydryloxytriphenylsilane, rather than the expected diphenyltriphenylsilylmethanol.[4] Also, in contrast to the relatively clean-cut reaction of Grignard reagents or organo-

lithium reagents with derivatives of carboxylic acids, the reaction of triphenylsilyllithium with these compounds gave low yields of products and involved difficult work-up conditions.[5] A question arose as to whether the reactivities of the various functional groups with triphenylsilyllithium are in the same order as that observed with organometallic reagents.

The relative reactivity of a number of ketones toward methylmagnesium iodide was determined by Hibbert[6] in 1912. Later, the relative reactivity

(1) Shell Companies Fellow, 1959–1960.

(2) H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.,* **80,** 608 (1958).

(3) For a comprehensive review see, D. Wittenberg and H. Gilman, *Quart. Revs.* (London), **13,** 116 (1959).

(4)(a) H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.,* **80,** 607 (1958). See also, (b) H. Gilman and T. C. Wu, *J. Am. Chem. Soc.,* **75,** 2935 (1953). (c) A. G. Brook, *J. Am. Chem. Soc.,* **80,** 1886 (1958). (d) A. G. Brook, C. M. Warner, and M. E. McGriskin, *J. Am. Chem. Soc.,* **81,** 781 (1959). (e) A. G. Brook and N. V. Schwartz, *J. Am. Chem. Soc.,* **82,** 2435 and 2439 (1960).

(5) D. Wittenberg and H. Gilman, *J. Am. Chem., Soc.,* **80,** 4529 (1958).

(6) H. Hibbert, *J. Chem. Soc.,* **101,** 341 (1912).