move residual hydrogen chloride. The resulting phosphonic acids were dried to constant weight at 100°, under vacuum when necessary. The one crystalline solid acid was recrystallized three times from cyclohexane and appeared to contain one molecule of water of hydration.

Hydrolysis with alkali. A typical example of an alkaline hydrolysis follows: $(n\text{-}C_4H_9O)(CH_3)_2SiCH_2CH_2P(O)(OC_4H_9\text{-}n)_2$, 10.56 g., 0.03 mole, was refluxed for 24 hr. with a 0.9*N* NaOH solution. The acidified hydrolysis mixture was extracted with benzene from which the product was isolated on evaporation of the benzene. The product weighed 5.0 g. and an electrometric titration gave neutral equivalents of 279 and 211 for one hydrogen and both hydrogens, respectively. Assuming no cleavage, the titration values would be satisfied by an overall structural formula of:

$$[(n\text{-}C_4H_9O)_{0.93}(HO)_{1.67}P(O)CH_2CH_2(CH_3)_2Si]_2O \qquad (A)$$

with 24 mole % of the phosphorus present with 2(—OH), 59 mole % with 1($—OC_4H_9\text{-}n$) and 1(—OH), and 17 mole % with 2($—OC_4H_9\text{-}n$). The 5.0 g. of product isolated represents a 73% yield based on formula A. A second structural formula in agreement with the titration data, but in which cleavage to yield dimethylsiloxy-units is assumed, would be:

$$[(n\text{-}C_4H_9O)_{0.70}(HO)_{1.30}P(O)CH_2CH_2(CH_3)_2SiO_{1/2}]_{1.00}\cdot(CH_3)_2SiO_{0.80} \qquad (B)$$

with 30 mole % of the phosphorus present with 2(—OH), 70 mole % with 1($—OC_4H_9\text{-}n$), and 1(—OH), and none with 2($—OC_4H_9\text{-}n$). The 5.0 g. of product would then represent a 120% yield; this was the first evidence against formula B. The H^1 NMR spectra were obtained on the product diluted to 50% in carbon tetrachloride and on the product diluted to 25% by addition of benzene to the carbon tetrachloride solution. Only one methyl-silicon peak was found in each spectrum. The benzene solvent was chosen because a single peak is often split into two peaks by benzene if two different groups are present but give superimposed resonances. Only one methyl-silicone peak is consistent with formula A, but two peaks would be expected for formula B. Also, from these spectra, the ratio of $—CH_2O—$ to —OH groups estimated from the area under the respective peaks to be 0.85. The ratio calculated for formula A is 0.87 and for formula B 0.54. Thus, all of the evidence available is in agreement with the product having structural formula A rather than B.

Analyses. The phosphorus bond refraction values used in this work were calculated from organophosphorus compounds found in the literature, and agreed favorably with values recently reported by Gillis *et al.*[10] Their data included only one value for the P=O bond refraction in either phosphate or phosphonate structures, whereas our data indicated that two different values were necessary as listed in Table III.

TABLE III

BOND REFRACTION (CC.$^{-1}$)

Bond	Gillis	Our Values
P—O	3.18	3.14
P=O in phosphates	−1.22	−1.07
P=O in phosphonates		−1.42
P—C	3.60	3.66

Both silicon and phosphorus were determined gravimetrically following a sodium peroxide fusion in a Parr peroxide bomb. Considerable difficulty was encountered in this procedure by both analytical laboratories.

A Beckman *p*H meter, model H 2, was used for the electrometric titrations.

Acknowledgment. The NMR spectra and interpretations thereof were performed by Mr. P. C. Lauterbur of this laboratory.

PITTSBURGH 13, PA.

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[10] R. G. Gillis, J. T. Horwood, and G. L. White, *J. Am. Chem. Soc.*, **80**, 2999 (1958).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE UNIVERSITY]

Some Derivatives of Tribenzylsilane

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A series of compounds containing the tribenzylsilyl group has been prepared from tribenzylsilane and the appropriate organolithium reagent. One of these compounds, tetrakis(*p*-tribenzylsilylphenyl)silane, is apparently the highest molecular weight compound containing only carbon, hydrogen, and silicon. Compounds containing the tribenzylsilyl group are characteristically low-melting solids or liquids and are thermally stable.

The unusual stability of tetrabenzylsilane[1] and tribenzylsilane[2] prompted the preparation of a series of tetrasubstituted silanes containing the tribenzylsilyl group.

The tribenzylsilyl derivatives were prepared by treatment of tribenzylsilane with the appropriate aryllithium reagent, a method which has been used for the synthesis of tetrasubstituted silanes.[3]

$$(C_6H_5CH_2)_3SiH + ArLi \longrightarrow (C_6H_5CH_2)_3SiAr + LiH$$

The aryllithium reagents were obtained by reaction of the organic halide with lithium metal, by halogen-metal interconversion reactions, and by metalation reactions. The new tribenzylsilyl derivatives and their physical properties are listed in Table I.

In the preparation of *p*-bromophenyltribenzylsilane from *p*-bromophenyllithium[4] and tribenzyl-

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[1] A. Polis, *Ber.*, **19**, 1012 (1886).

[2] H. Gilman, R. A. Tomasi, and D. Wittenberg, *J. Org. Chem.*, **24**, 821 (1959).

[3] H. Gilman and S. P. Massie, Jr., *J. Am. Chem. Soc.*, **68**, 1128 (1946); R. N. Meals, *J. Am. Chem. Soc.*, **68**, 1880 (1946); H. Gilman and H. W. Melvin, *J. Am. Chem. Soc.*, **71**, 4050 (1949); H. Gilman and E. A. Zuech, *J. Am. Chem. Soc.*, **81**, 5925 (1959).

TABLE I

$(C_6H_5CH_2)_3SiR$ COMPOUNDS

R	Product	S[a]	M.P.°	Yield, %	Silicon, % Calcd.	Silicon, % Found	Volatilization Temperature[b]
o-Tolyl	$C_{28}H_{28}Si$	A	70–72	48	7.15	7.19, 7.15	465
m-Tolyl	$C_{28}H_{28}Si$		[d]	30.8	7.15	7.27, 7.16	440
p-Tolyl	$C_{28}H_{28}Si$[c]		41–43	68	7.15	7.13, 7.22	460
o-Biphenylyl	$C_{33}H_{30}Si$	A	124–125	15.8	6.18	6.17, 6.18	480
m-Biphenylyl[e]	$C_{33}H_{30}Si$	A	133–134	8.1	6.18	6.10, 6.22	
p-Biphenylyl	$C_{33}H_{30}Si$	A	121–123	51.6	6.18	6.14, 6.25	490
o-Phenoxyphenyl	$C_{33}H_{30}OSi$	A	81–82.5	13.6	5.97	5.85, 5.84	450
m-Phenoxyphenyl	$C_{33}H_{30}OSi$		[f]	68.6	5.97	6.06, 5.79	490
p-Phenoxyphenyl	$C_{33}H_{30}OSi$	A	105–107	56.8	5.97	6.00	490
p-Trimethylsilylphenyl[g]	$C_{30}H_{34}Si_2$		[g]	28.3			440
p-Bromophenyl[h]	$C_{27}H_{25}BrSi$	A	72–74	32.8	6.14	6.19, 6.23	465[i]
p-Bromobiphenylyl	$C_{33}H_{29}BrSi$	B	114.5–115.8	25.9	5.26	5.23, 5.20	
p-Terphenyl-4-yl[j]	$C_{39}H_{34}Si$	C	125–127	24.6	5.29	5.28, 5.20	510

[a] Solvent for recrystallization. A = petroleum ether (b.p. 60–70°), B = pentane-benzene mixture, and C = petroleum ether (b.p. 60–70°)–toluene mixture. [b] See Ref. 6. [c] B.p. 198–200°/0.007 mm. [d] B.p. 187–191°/0.005 mm., n_D^{20} 1.6163, d_{20}^{20} 1.0692, MR_D 128.36 (Calcd. MR_D 128.0). [e] Prepared by W. J. Trepka of these laboratories. [f] B.p. 240–243°/0.003 mm. [g] Prepared by E. A. Zuech of these laboratories, b.p. 200–202°/0.005 mm., n_D^{20} 1.5952, d_{20}^{20} 1.0362, *Anal.* Calcd. for $C_{30}H_{34}Si_2$: C, 79.93; H, 7.60; MR_D 149.09. Found: C, 79.91, 79.90; H, 7.41, 7.30; MR_D 146.85. [h] *p*-Phenylenebis(tribenzylsilane) was also isolated. See Table II. [i] Turns amber color at this temperature. [j] Prepared by E. A. Zuech of these laboratories.

TABLE II

COMPOUNDS PREPARED FROM *p*-TRIBENZYLSILYLPHENYLLITHIUM

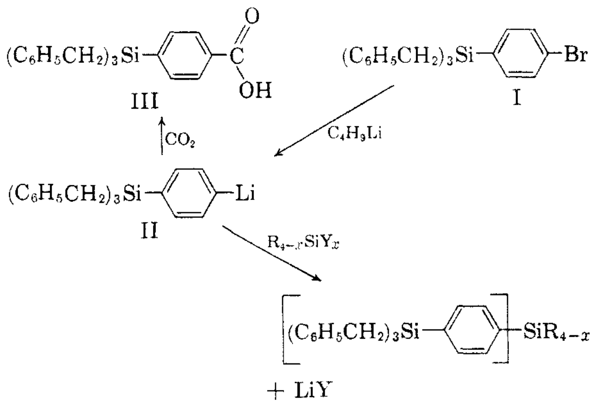
Reagent	Product	Formula	S[a]	M.P.°	Yield, %	Silicon, % Calcd.	Silicon, % Found	Volatilization Temperature[b]
Carbon Dioxide	*p*-Tribenzylsilylbenzoic Acid	$C_{28}H_{26}O_2Si$	A	150–152	36.5	6.65	6.57, 6.58	440[c]
Tribenzylsilane	*p*-Phenylenebis(tribenzylsilane)	$C_{48}H_{46}Si_2$	B	155–157	15	8.27	8.28, 8.28	520[d]
Diphenyldichlorosilane	Bis(*p*-tribenzylsilylphenyl)-diphenylsilane	$C_{66}H_{60}Si_3$	B	142–143.5	43.4	8.99	8.82, 8.90	540[e]
Methylphenyl-*p*-tolylsilane	Methylphenyl-*p*-tolyl(*p*-tribenzylsilylphenyl)silane	$C_{41}H_{40}Si_2$	[f]	[f]	56.1	9.54	9.34, 9.43	475
Silicon tetrachloride	Tetrakis(*p*-tribenzylsilylphenyl)silane	$C_{108}H_{100}Si_5$	A	159–161	51	9.13	9.07, 9.22	510

[a] Solvent for recrystallization. A = petroleum ether (b.p. 60–70°) and B = benzene–petroleum ether (b.p. 60–70°) mixture. [b] See Ref. 6. [c] Turns an amber color at 425°. [d] Condensate was light amber. [e] Turns yellow to amber 525–535°. [f] Viscous oil, b.p. 290–291°/0.003 mm., which slowly forms a soft waxy product.

silane, *p*-phenylenebis(tribenzylsilane)[5] was isolated as a side-product. The compound was identical with that formed by the interaction of *p*-tribenzylsilylphenyllithium and tribenzylsilane. Evidently some 1,4-dilithiobenzene was formed in the halogen-metal interconversion reaction for the preparation of *p*-bromophenyllithium.

The compounds of Table II were obtained by the reaction of *p*-tribenzylsilylphenyllithium (II) with the appropriate reagent. The organolithium compound II, formed also *via* a halogen-metal interconversion reaction, was partially characterized by carbonation to the benzoic acid derivative III.

The monomeric tribenzylsilanes (Table I) were all crystalline low melting solids with the exception of *m*-tolyl- and *p*-trimethylsilylphenyltribenzyl-



+ LiY

R = Aryl and/or alkyl

Y = H or Cl

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(4) H. Gilman, W. Langham, and F. W. Moore, *J. Am. Chem. Soc.*, **62**, 2327 (1940).

(5) The names used herein are those preferred by *Chemical Abstracts*.

silane which were liquids. The tribenzylsilyl derivatives of both Tables I and II are also noteworthy for their good thermal stability properties, volatilizing above 440°.[6]

Tribenzylsilyl compounds previously prepared are also low-melting solids or liquids and, in those cases studied, possess rather high volatilization temperatures. These compounds with their physical properties are shown in Table III.

TABLE III

PHYSICAL PROPERTIES OF TRIBENZYLSILYL COMPOUNDS

	M.P.°	B.P.°/ mm.	Volatilization Temperature	Reference
Tribenzylsilane	91			*a*
Tribenzyldodecylsilane		216/0.06	430	
Tribenzylcyclohexylsilane		198/0.25	420	*b*
Tribenzylphenylsilane	59		450	*b*
Tribenzyl-*p*-anisylsilane	83			*c*
Tribenzyl-1-naphthylsilane		314/26		*d*
Tribenzylvinylsilane	76.5			*e*
Tetrabenzylsilane	127.5	550		*f*
Tetra(*m*-fluorobenzyl)silane	62			*g*
(Oxydi-*p*-phenylene)bis(tribenzylsilane)		320/0.001	540	*h*

[a] W. E. Evison and F. S. Kipping, *J. Chem. Soc.*, 2830 (1931). See also Ref. 2. [b] H. Gilman and D. Miles, *J. Org. Chem.*, **21**, 254 (1956). [c] H. Gilman and F. G. Marshall, *J. Am. Chem. Soc.*, **71**, 2066 (1949). [d] V. S. Chugunov and A. D. Petrov, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 713 (1953), [*Chem. Abstr.*, **48**, 12716 (1954)]. [e] R. Nagel and H. W. Post, *J. Org. Chem.*, **17**, 1379 (1952). [f] See Ref. 1. [g] H. Gilman and R. K. Ingham, *J. Am. Chem. Soc.*, **77**, 1680 (1955). [h] H. Gilman and D. Miles, *J. Org. Chem.*, **23**, 1363 (1958).

The compounds of Table II were also rather low-melting solids, except for methylphenyl-*p*-tolyl-(*p*-tribenzylsilylphenyl)silane, which was a very viscous oil slowly solidifying to a waxy solid. The low melting points of these compounds can be contrasted with the high melting points of the perphenylated analogs (Table IV).

The most interesting compound of Table II is tetrakis(*p*-tribenzylsilylphenyl)silane obtained from the reaction of the organolithium compound II with silicon tetrachloride. This low-melting solid has a molecular weight of 1537 and can be crystallized from petroleum ether (b.p. 60–70°). Only a few compounds containing only carbon, hydrogen, and silicon and having a molecular weight of this order, are known: 1,2-ethylenebis(tri-*n*-hexadecylsilane) ($C_{98}H_{202}Si_2$)[7a]; *m*-phenylenebis(tri-*n*-hexadecylsilane) ($C_{102}H_{202}Si_2$),[7b] and *p*-biphenylenebis(tri-*n*-hexadecylsilane) ($C_{102}H_{206}Si_2$, isolated as a slightly impure liquid).[8] Apparently, tetrakis(*p*-tribenzylsilylphenyl)silane is the first known example of a pure nonpolymeric organosilicon compound containing only carbon, hydrogen, and silicon with a molecular weight greater than 1500. However, compounds containing other elements in addition to the above with known molecular weights equal to or greater than 1500 have been reported.[9]

EXPERIMENTAL[10]

Starting materials. Except for *m*-bromophenyl phenyl ether and *p*-bromophenyltrimethylsilane, the aryl halides were commercially available. *m*-Bromophenyl phenyl ether was prepared, in a manner similar to the preparation of *p*-bromophenyl phenyl ether,[11] by heating *m*-dibromobenzene and potassium phenoxide in the presence of copper catalyst at 205° for 20 hr.: 39.4%, b.p. 168–171°/15 mm., n_D^{20} 1.6075, d_{20}^{20} 1.3944.

Anal. Calcd. for $C_{12}H_9BrO$: C, 57.82; H, 3.64; Br, 32.08. Found: C, 58.50, 58.75; H, 3.74, 3.80; Br, 31.18, 31.40.

p-Bromophenyltrimethylsilane was prepared as described previously from *p*-bromophenyllithium[4] and trimethylchlorosilane.[12]

o-Tolyltribenzylsilane. o-Tolyllithium (0.047 mole) in 40 ml. of dry ether was added to 9.07 g. (0.03 mole) of tribenzylsilane dissolved in 50 ml. of ether. After refluxing 68 hr., Color Test I[13] was negative. The reaction mixture was hydrolyzed with dilute acid and the layers separated. The organic layer was washed free of acid, dried, and distilled. The residual oil was distilled under reduced pressure to give 5.85 g. of material boiling over the range 172–192° at 0.018 mm. After standing, the distillate crystallized, and upon recrystallization from petroleum ether (b.p. 60–70°), there was obtained 5.65 g. (48%) of pure product melting at 70–72°.

Anal.[14] Calcd. for $C_{28}H_{28}Si$: Si, 7.15. Found: 7.19, 7.15.

The same general procedure was used to prepare *m*- and *p*-tolyl-, *o*-, *m*-, and *p*-biphenylyl-, and *p*-trimethylsilylphenyltribenzylsilane (Table I).

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[6] Volatilization points were determined by heating the compounds in an unsealed capillary tube mounted in a flame-heated copper block. All the compounds produced clear or pale yellow condensates unless otherwise noted.

(7) (a) R. D. Gorsich, Ph.D. thesis, Iowa State University, 1957; (b) R. D. Gorsich, unpublished studies.

(8) D. Miles, Ph.D. thesis, Iowa State University, 1957.

(9) See, for example, Pharmazeutische Industrie G.m.b.H. and R. Hauschka, Austrian Patent 86,131, *Chem. Abstr.*, **17**, 1865 (1923); G. Klein and H. Nienberg, *Ber.*, **69B**, 2066 (1936); V. Morrill, Jr., U.S. Patent 2,416,531, *Chem. Abstr.*, **41**, 3819 (1947); H. Staudinger and W. Hahn, *Makromol. Chem.*, **11**, 24 (1953); V. A. Zeitler and C. A. Brown, *J. Am. Chem. Soc.*, **79**, 4616 (1957).

(10) All reactions were carried out under a dry, nitrogen atmosphere using oven-dried glass ware. All melting points are uncorrected. The infrared spectrum of each of the compounds was compatible with the assigned structure.

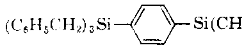
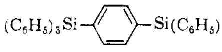
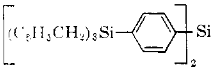
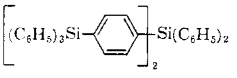
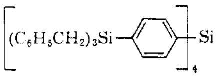
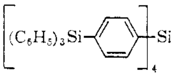
(11) E. Krause and K. Weinberg, *Ber.*, **62**, 2235 (1929).

(12) C. A. Burkhard, *J. Am. Chem. Soc.*, **68**, 2103 (1946); H. Gilman, H. W. Melvin, and J. J. Goodman, *J. Am. Chem. Soc.*, **76**, 3219 (1954).

(13) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

(14) The silicon content was determined by the method of H. Gilman, B. Hofferth, H. W. Melvin, and G. E. Dunn, *J. Am. Chem. Soc.*, **72**, 5767 (1950).

TABLE IV

Tribenzylsilyl	M.P.°	Perphenylated	M.P.°
	155		360[a]
	142		419[b]
	159		385[b]

[a] K. Oita, Ph.D. thesis, Iowa State University, 1955, and J. J. Goodman, Ph.D. thesis, Iowa State University, 1955. [b] L. Spialter and C. W. Harris, Aeronautical Research Laboratory, Wright Air Development Center Technical Report 58-276 Wright-Patterson Air Force Base, Ohio, January 1959.

o-Phenoxyphenyltribenzylsilane. *o*-Phenoxyphenyllithium[15] was added to 8.57 g. (0.028 mole) of tribenzylsilane in 100 ml. of ether. After refluxing 14 hr., Color Test I was negative. The reaction mixture was cooled and hydrolyzed with dilute sulfuric acid. The organic layer was separated, dried, and distilled to remove the solvent. The oily residue was distilled under reduced pressure to give a viscous fraction which crystallized on standing. The material was recrystallized from petroleum ether (b.p. 60–70°) to yield 1.79 g. (13.6%) of pure *o*-phenoxyphenyltribenzylsilane, m.p. 81–82.5°.

Anal. Calcd. for $C_{33}H_{30}OSi$: Si, 5.97. Found: Si, 5.85, 5.84.

From lower boiling fractions collected during the distillation, tribenzylsilane, amounting to 5.75 g. (67.9%), was recovered.

m-Phenoxyphenyltribenzylsilane. *m*-Phenoxyphenyllithium was prepared by adding 0.02 mole of an ethereal solution of *n*-butyllithium[16] to 4.98 g. (0.02 mole) of *m*-bromophenyl phenyl ether at −15°. When the addition was complete, Color Test II[17] was negative. Tribenzylsilane (5.44 g., 0.018 mole) dissolved in 60 ml. of ether was added to the *m*-phenoxyphenyllithium while maintaining the temperature near −15°. The reaction mixture was warmed to room temperature and then refluxed 20 hr. at which time Color Test I was negative. Careful hydrolysis with a saturated solution of ammonium chloride, followed by the usual separation, drying, and distillation procedures gave an oily product which was distilled to give 5.81 g. (68.6%) of *m*-phenoxyphenyltribenzylsilane, b.p. 240–243°/0.003 mm.

Anal. Calcd. for $C_{33}H_{30}OSi$: Si, 5.97. Found: Si, 6.06, 5.79.

Similarly, *p*-phenoxyphenyl-,[18] *p*-bromobiphenylyl-,[4] and *p*-terphenyl-4-yllithium[19] were prepared as described and reacted with tribenzylsilane (Table I).

p-Bromophenyltribenzylsilane. *p*-Bromophenyllithium[4] was prepared as previously described from 81.6 g. (0.35 mole) of *p*-dibromobenzene and 0.35 mole of *n*-butyllithium in 250 ml. of ether. The temperature was maintained between −15° and −20°, and after 5 hr. of stirring at this temperature, Color Test II was negative. Tribenzylsilane (107 g., 0.35 mole), dissolved in 950 ml. of ether, was added to the organolithium reagent. The solution was allowed to warm to room temperature and then refluxed for 34 hr. Although Color Test I was positive at the end of this period, the reaction mixture was hydrolyzed with dilute hydrochloric acid and filtered to remove the white solid which had formed at the interface. The aqueous layer was separated, extracted with ether, and discarded. The organic layer was washed with water and dried over anhydrous calcium sulfate. The insoluble solid was crystallized from a benzene–petroleum ether (b.p. 60–70°) mixture to give 16.96 g. (14.3%, based on tribenzylsilane) of a crystalline solid melting at 155–157°, and identified as *p*-phenylenebis(tribenzylsilane) by its silicon analysis, synthesis from *p*-tribenzylsilylphenyllithium and tribenzylsilane, and by comparison of the infrared spectra.

Anal. Calcd. for $C_{48}H_{46}Si_2$: Si, 8.27. Found: Si, 8.28, 8.09, 8.28.

The dried organic layer was concentrated, and ethanol added to the residue. The solid that formed was removed by filtration and recrystallized twice from petroleum ether (b.p. 60–70°) to give 52.5 g. (32.8%) of pure *p*-bromophenyltribenzylsilane melting at 72–74°.

Anal. Calcd. for $C_{27}H_{25}BrSi$: Si, 6.14. Found: Si, 6.19, 6.23.

p-Tribenzylsilylbenzoic acid. *p*-Tribenzylsilylphenyllithium was prepared by adding 0.005 mole of *n*-butyllithium to 2.33 g. (0.005 mole) of *p*-bromophenyltribenzylsilane dissolved in 50 ml. of ether. After stirring 2 hr. at room temperature, Color Test I was positive and Color Test II was negative. The mixture was poured onto a slurry of Dry Ice and ether and warmed to room temperature. Subsequent to hydrolysis, the organic layer was separated from the basic aqueous layer. The aqueous layer was acidified and the crude acid removed by filtration. Recrystallization of the acid from petroleum ether (b.p. 60–70°) gave 0.77 g. (36.5%) of pure product, m.p. 150–152°.

Anal. Calcd. for $C_{28}H_{26}O_2Si$, 6.65. Found: Si, 6.57, 6.58.

Methylphenyl-p-tolyl(p-tribenzylsilylphenyl)silane. *p*-Tribenzylsilylphenyllithium was prepared as described above from 10.06 g. (0.022 mole) of *p*-bromophenyltribenzylsilane and 0.022 mole of *n*-butyllithium in 75 ml. of ether. To this solution there was added 4.67 g. (0.022 mole) of methylphenyl-*p*-tolysilane[20] in 25 ml. of ether. After stirring 3 hr. at room temperature, hydrolysis was effected with dilute acid and the reaction worked up in the usual manner. Distillation of the residue gave 6.71 g. (56.1%) of a viscous oil, b.p. 290–291°/0.003 mm.

Anal. Calcd. for $C_{41}H_{40}Si_2$: Si, 9.54. Found: Si, 9.34, 9.43.

Tetrakis(p-tribenzylsilylphenyl)silane. Silicon tetrachloride (1.19 g., 0.007 mole) in 15 ml. of ether was added dropwise to 0.028 mole of *p*-tribenzylsilylphenyllithium prepared as described above. The solution was allowed to stir for 18 hr.

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(15) K. Oita and H. Gilman, *J. Org. Chem.*, 21, 1009 (1956).

(16) H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, *J. Am. Chem. Soc.*, 71, 1499 (1949).

(17) H. Gilman and J. Swiss, *J. Am. Chem. Soc.*, 62, 1847 (1940).

(18) H. Gilman and J. J. Goodman, *J. Org. Chem.*, 22, 25 (1957).

(19) H. Gilman and E. A. Weipert, *J. Org. Chem.*, 22, 446 (1957).

(20) H. G. Brooks, Jr., unpublished studies.

after which Color Test I was negative. The reaction mixture was hydrolyzed with dilute acid and treated as previously described. There was obtained from the organic layer, a white solid which was recrystallized from petroleum ether (b.p. 60–70°) to give 5.1 g. (51%) of crystalline product melting at 159–161°.

Anal. Calcd. for $C_{108}H_{100}Si_5$: C, 84.31; H, 6.55; Si, 9.13. Found: C, 84.41, 84.43; H, 6.53, 6.43; Si, 9.07, 9.22.

The reactions of *p*-tribenzylsilylphenyllithium with tribenzylsilane and diphenyldichlorosilane were carried out in an analogous manner (Table II).

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[CONTRIBUTION FROM THE MIDWEST RESEARCH INSTITUTE]

Synthesis of Bis(diethoxymethylsilyl) Derivatives of 4,4′-Dibromobiphenyl, 4-Bromophenyl Ether, α,*p*-Dibromotoluene, and 1,6-Dibromohexane[1]

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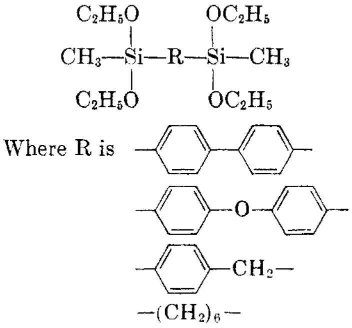
The syntheses of bis-*p*-(diethoxymethylsilyl)phenyl ether, 4,4′-bis(diethoxymethylsilyl)biphenyl, 1,6-bis(diethoxymethylsilyl)hexane, and α,*p*-bis(diethoxymethylsilyl)toluene are described.

As a part of our continued interest in novel silane monomers for use in the preparation of cross-linked siloxane polymers, we have prepared a series of compounds with the following structure:



$$CH_3-\overset{C_2H_5O}{\underset{C_2H_5O}{Si}}-R-\overset{OC_2H_5}{\underset{OC_2H_5}{Si}}-CH_3$$

Although the synthesis of *p*-phenylenedisilanes was investigated earlier,[2] procedures for their preparation could not be extended to this series. For each of the new compounds it was necessary to find a method that would give pure materials in satisfactory quantities for evaluation studies.

Derivatives of 4,4′-dibromobiphenyl and p-bromophenyl ether. According to the literature, lithium and sodium reactions give 4,4′-disilyl derivatives of 4,4′-dibromobiphenyl and *p*-bromophenyl ether, but only the lithium derivatives have been used to prepare silane derivatives with hydrolyzable functionality. With dilithium intermediates Baum obtained 4,4′-bis(chlorodimethylsilyl)biphenyl and bis-*p*-(chlorodimethylsilyl)phenyl ether[3]; however, others have reported difficulty in repeating his procedure.[4] Various totally alkylated and arylated derivatives, also prepared *via* the dilithium intermediates, have been reported by Gilman.

By means of condensations in the presence of sodium, Clark prepared 4,4′-bis(trimethylsilyl)biphenyl, 4,4′-bis(dimethylphenylsilyl)biphenyl, and bis-*p*-(dimethylphenylsilyl)phenyl ether from the dibromides and the appropriate chlorosilanes, but reported no yields.[5]

Polymeric materials were the chief products when dilithium reagents were treated with polyfunctional silanes in our laboratory. Polyfunctionality of both reactants required inverse addition, but the dilithium derivative could not be transferred and added satisfactorily to the silane because it was a solid.

Although the bis-*p*-(diethoxymethylsilyl)phenyl ether was conveniently prepared by a condensation in ethyl ether in the presence of sodium, the corresponding derivative of 4,4′-dibromobiphenyl could not be prepared by the same method. The limiting factor was apparently the solubility of the dibromide whose concentration in solution was too low to permit the reaction to proceed at a satisfactory rate. Arylsodium intermediates were apparently formed in tetrahydrofuran, but were destroyed by the solvent. Only *p*-bromophenyl ether in ethyl ether provided adequate dibromide concentration to promote an exothermic reaction; the same reactants in toluene did not produce the con-

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[1] (1) This research was supported in whole or in part by the United States Air Force under Contract AF 33(616)-3675, monitored by the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

[2] (2) L. W. Breed, W. J. Haggerty, Jr., and F. Baiocchi, *J. Org. Chem.*, in press.

[3] (3) G. Baum, *J. Org. Chem.*, **23**, 480 (1958).

[4] (4) R. L. Schaaf, P. T. Kan, and K. L. Rinehart, Jr., WADC Technical Report 58-187, Part II (1959); ASTIA Document No. 216451.

[5] (5) H. A. Clark, U. S. Patent **2,628,242** (1953); Brit. Patent **671,553** (1952).