ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Selective Reactions of the Silicon–Hydrogen Group with Grignard Reagents. The Preparation of Some Unsymmetrical Silane Derivatives

BY HENRY GILMAN AND ERNEST A. ZUECH

RECEIVED MAY 18, 1959

Grignard reagents react readily with phenyl- and diphenylsilane in THF to give good yields of the corresponding di- and trisubstituted silanes. Triphenylsilane was found to react with some Grignard reagents, but only after extended refluxing. Utilizing proper conditions, it was possible to join selectively the silicon–hydrogen groups of phenylsilane to synthesize a number of unsymmetrical organosilicon derivatives containing three or four unlike substituents.

In a preliminary communication[1] a series of reactions was reported in which organosilicon hydrides were alkylated and/or arylated with Grignard reagents, and we now have extended that work. It was possible to synthesize a wide variety of organosilicon compounds, particularly those of an unsymmetrical nature, without the usual mixture of compounds encountered in treating chlorosilanes with Grignard or organolithium reagents.[2] The synthesis is especially appropriate for the preparation of low-melting compounds of the type R_4Si where all of the R groups may be different. The compounds were prepared by treating phenylsilane with Grignard reagents in tetrahydrofuran (THF) yielding unsymmetrical disubstituted silicon hydrides. Subsequent treatment with other Grignard reagents led to the trisubstituted derivatives which were converted to tetrasubstituted compounds by organolithium reagents in diethyl ether. It may be noted from this series of reactions that R_4Si types having four unlike groups are prepared by reactions involving, first, a choice of solvents; second, a choice of two RM compounds.

$$\mathrm{PhSiH_3 + RMgX \xrightarrow{THF} PhRSiH_2}$$

$$\mathrm{PhRSiH_2 + R'MgX \xrightarrow{THF} PhRR'SiH}$$

$$\mathrm{PhRR'SiH + R''Li \xrightarrow{ether} PhRR'R''Si}$$

A number of workers have observed the reaction of silicon hydrides with the more reactive organometallic compounds. Triethylsilane has been reported to react with methyl-,[3] *n*-propyl-,[4] *n*-butyl-,[4] and phenyllithium[4] to give the respective tetrasubstituted organosilicon compounds. Reactions occur between triphenylsilane[5] and methyl-, *n*-butyl- and phenyllithium to give the corresponding tetrasubstituted derivatives in yields of 93, 63.5 and 90%, respectively.

Phenylsilane[6] in diethyl ether reacts with phenyllithium and ethyllithium to form tetraphenylsilane and phenyltriethylsilane in excellent yields. Peake, *et al.*,[7] have reported the reaction of silane (SiH_4) with organolithium compounds. When diethyl ether was employed as the reaction medium the main product was the tetrasubstituted derivative with smaller amounts of the di- and trisubstituted products; however, when low boiling petroleum ether was used as the solvent, trisubstituted derivatives were isolated.

The fact that the solvent plays an important role in such reactions had been noted previously. Meals[4] found that triethylsilane was unreactive toward organolithium compounds in petroleum ether, and Nebergall[6] obtained phenyldiethylsilane instead of phenyltriethylsilane from the reaction of phenylsilane with excess ethyllithium in the same solvent.

Silane[7] was found to react with phenylsodium to give tetraphenylsilane while Grignard reagents were unreactive. Attempts to alkylate silane with other organometallic compounds, such as phenylcalcium iodide, diphenylcalcium and diethylzinc, also were unsuccessful.

Earlier workers had shown that Grignard reagents were unreactive toward the silicon–hydrogen group, in the various solvents tried. Triphenylsilane[5] did not react with phenylmagnesium bromide in ether, refluxing xylene and a mixture of ether and dioxane. West and Rochow[8] found di-*n*-butylsilane to be unchanged by treatment with ethylmagnesium bromide in a toluene solution at 100°. Nebergall[6] states that no evidence of a reaction was observed when phenylsilane was treated with a large excess of phenylmagnesium bromide in diethyl ether.

Recently, Harvey, *et al.*,[9] reported the first alkylation of a silicon–hydrogen group by Grignard reagents. *sym*-Diphenyldisiloxane was found to react with ethereal solutions of methylmagnesium iodide and ethylmagnesium bromide to give *sym*-dimethyldiphenyldisiloxane and *sym*-diethyldiphenyldisiloxane, respectively.

Grignard reagents have now been found to react with a number of organosilicon hydrides. The solvent of choice appears to be tetrahydrofuran (THF), but with mono- and disubstituted organosilicon hydrides, diethyl ether may be used. As shown in Table I, triphenylsilane reacts with phenylmagnesium bromide in refluxing THF to give low yields of tetraphenylsilane. The same reaction carried out at room temperature gave only unre-

---

[1] H. Gilman and E. A. Zuech, THIS JOURNAL, **79**, 4560 (1957).

[2] E. G. Rochow, "Chemistry of Silicones," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1951, p. 35.

[3] H. Gilman and S. P. Massie, Jr., THIS JOURNAL, **68**, 1128 (1946).

[4] R. N. Meals, *ibid.*, **68**, 1880 (1946).

[5] H. Gilman and H. W. Melvin, Jr., *ibid.*, **71**, 4050 (1949)-

[6] W. H. Nebergall, *ibid.*, **72**, 4702 (1950).

[7] J. S. Peake, W. H. Nebergall and Yun Ti Chen, *ibid.*, **74**, 1526 (1952).

[8] R. West and E. G. Rochow, *J. Org. Chem.*, **18**, 303 (1953).

[9] M. C. Harvey, W. H. Nebergall and J. S. Peake, THIS JOURNAL, **79**, 1437 (1957).

acted triphenylsilane, indicating that temperature is a factor. However, it should be noted that previous work had shown that triphenylsilane did not react with phenylmagnesium bromide in refluxing xylene.[5] The more reactive allylmagnesium chloride and benzylmagnesium chloride gave good yields of the corresponding tetrasubstituted products. The extent of the reaction between triphenylsilane and *n*-butylmagnesium bromide appeared to be insignificant, for in two runs only triphenylsilane was recovered in high yields. β-Phenylethylmagnesium bromide was similarly unreactive.

Diphenylsilane was found to be more reactive than triphenylsilane toward Grignard reagents. The reactions were generally carried out in refluxing THF employing two moles of Grignard reagent to one of diphenylsilane yielding the corresponding trisubstituted silanes in fair to excellent yields. Refluxing an ethereal solution of diphenylsilane and phenylmagnesium bromide for 3 days afforded a 30.5% yield of triphenylsilane. The same reaction when carried out in refluxing THF for 2 days gave a 79% yield: a shorter reaction time of 2 hours gave triphenylsilane in 68% yield, indicating the superiority of THF as the reaction medium. Two equivalents of allylmagnesium chloride gave allyldiphenylsilane in 77% yield. However, the extended heating of a THF solution containing a large excess of allylmagnesium chloride and diphenylsilane produced diallyldiphenylsilane, showing that both of the silicon–hydrogen bonds will react under forced conditions.

Phenylsilane was found to react selectively with Grignard reagents at room temperature in THF giving high yields of the corresponding disubstituted silanes. For example, treatment with one equivalent of *n*-dodecylmagnesium bromide gave *n*-dodecylphenylsilane in 78% yield.

When an ethereal solution of phenylsilane and phenylmagnesium bromide was allowed to react at room temperature for 24 hours, there was obtained a 52% yield of diphenylsilane. However, the same reactants in THF at a shorter time of 6.5 hours gave a 66% yield of diphenylsilane, again demonstrating the advantage of using THF as the solvent. A large excess of phenylmagnesium bromide with phenylsilane was found to yield triphenylsilane.

In an effort to produce silicon derivatives that are either low-melting solids or liquids at room temperature, the selective reactions of Grignard reagents with silicon hydrides were utilized to obtain unsymmetrical compounds. Tetraarylsilanes were prepared which contain four unlike aryl groups, apparently for the first time. These were synthesized with relative ease, while the preparation of unsymmetrical tetraarylmethanes is much more difficult, indicative of the facile substitution at silicon as compared to carbon. The synthesis of phenyl-*m*-tolyl-*o*-tolyl-*p*-tolylsilane is a typical example of the preparation of these compounds. *o*-Tolylmagnesium bromide was treated with phenylsilane producing phenyl-*o*-tolylsilane which was subsequently treated with *m*-tolylmagnesium bromide. The tetrasubstituted compound was obtained by treatment of the PhRR′SiH compound with *p*-tolyllithium. Most of the unsymmetrical compounds were either low melting solids, viscous liquids or glass-like semi-solids.

Recently, a qualitative test[9a] for degree of substitution of organosilicon hydrides has been developed. Essentially, the test involves treatment of a basic solvent, such as pyridine, and two drops of an approximately 5% aqueous solution of copper(II) chloride with one drop of the silane. Monosubstituted silanes were found to be the most reactive, disubstituted silanes intermediate and trisubstituted silanes the least reactive. This same order of reactivity holds for the reactions of Grignard reagents with silicon hydrides. In general, the silicon hydrides appear to behave analogously to silicon halides, but they are of lower reactivity.

The pronounced solvent effects of THF have been demonstrated by Normant[9b] and by Ramsden, *et al.*,[10] in the preparation of Grignard reagents from normally unreactive halides. The effect of the more polar THF in the reactions of Grignard reagents with silicon hydrides must be to increase the reactivity of the Grignard reagents. However, the possibility that the THF might be increasing the reactivity of the silicon hydrides cannot be excluded, since THF with its greater coördinating power is known to retard certain Grignard reactions.[11] It was once thought that the silicon hydrides and the Grignard reagents were initially forming a complex, selectively stopping the reaction. However, this is probably untenable since it was found to be possible to replace more than one silicon–hydrogen group by employing forced conditions. The selectivity is believed to be due to considerable differences of reactivity in the various silicon–hydrides, thus allowing one to utilize different reaction conditions to obtain the degree of substitution desired.

In all of these reactions, the silicon hydrides contained at least one phenyl group. Other silicon hydrides containing only aralkyl[12] or alkyl[13] groups behave somewhat differently. The reaction of Grignard reagents with alkyl silanes is slow and the yields are low. For example, *n*-hexadecylphenylsilane[13] is formed in only 34% yield, after the extended refluxing of a THF solution of *n*-hexadecylsilane and phenylmagnesium bromide, and no tetrabenzylsilane[12] was obtained from the reaction of tribenzylsilane with benzylmagnesium chloride.

Experimental

All melting points and boiling points are uncorrected. The reactions were carried out under an atmosphere of dry, oxygen-free nitrogen. Tetrahydrofuran, boiling at 65–66°, was freed from peroxides and moisture before use by refluxing over sodium followed by distillation from lithium aluminum hydride. The triphenylsilane,[14] diphenylsilane[15] and phenylsilane[16] used in this investigation were prepared by

---

(9a) H. Gilman, H. G. Brooks, Jr., and M. B. Hughes, *J. Org. Chem.*, **23**, 1398 (1958).

(9b) H. Normant, *Compt. rend.*, **239**, 1510 (1954).

(10) H. E. Ramsden, A. E. Balint, W. R. Whitford, J. J. Walburn and R. Cserr, *J. Org. Chem.*, **22**, 1202 (1957); see also, C. S. Marvel and R. G. Woolford, *ibid.*, **23**, 1658 (1958).

(11) R. N. Lewis and J. R. Wright, THIS JOURNAL, **74**, 1253 (1952).

(12) H. Gilman and R. A. Tomasi, *ibid.*, **81**, 137 (1959).

(13) Unpublished studies, M. B. Hughes.

(14) H. Gilman and G. E. Dunn, THIS JOURNAL, **73**, 3404 (1951).

(15) R. A. Benkeser, H. Landesman and D. J. Foster, *ibid.*, **74**, 648 (1952).

(16) A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach and H. L. Schlesinger, *ibid.*, **69**, 2692 (1947).

TABLE I

Ph_3SiH WITH RMgX IN REFLUXING THF

RMgBr, R =	Mole of RMgBr	Mole of Ph_3SiH	Time	Yield of Ph_3SiR, %	M.p., °C.
C_6H_5—	0.063	0.07	20 hr.	14.7	236–238
C_6H_5—	.064	.07	11 days	25.6[a]	235–237
C_6H_5—[b]	.064	.07	2 days	...	.....
$CH_2=CHCH_2$—[c]	.07	.07	1 day	53	88–90
$CH_2=CHCH_2$—[c]	.064	.07	4 days	60	89–90
$C_6H_5CH_2$—[c]	.061	.07	4 days	53	97–99
$CH_3(CH_2)_3$—[d]	.064	.07	3 days	...	.....
$CH_3(CH_2)_9$—[e]	.068	.07	4 days	...	.....
$C_6H_5(CH_2)_2$—[f]	.06	.06	4 days	...	.....

[a] In addition, 57% of the Ph_3SiH was recovered. [b] Reaction carried out at room temperature; 96.4% recovery of Ph_3SiH. [c] RMgCl. [d] 91% recovery of Ph_3SiH. [e] 89% recovery of Ph_3SiH. [f] 92% recovery of Ph_3SiH.

TABLE II

Ph_2SiH_2 WITH RMgX IN REFLUXING THF

RMgBr. R =	Mole of RMgBr	Mole of Ph_2SiH_2	Time	Yield of Ph_2SiHR, %	B.p., °C.	B.p., Mm.	$n^{20}D$	d^{20}_{20}	Silicon, % Calcd.	Silicon, % Found
C_6H_5—	0.097	0.05	2 hr.	68	[a]		....	....	...	....
C_6H_5—	.095	.05	48 hr.	79	.....	...	....	....	...	....
C_6H_5—[b]	.089	.05	72 hr.	30.5	.....	...	....	....	...	....
$CH_2=CHCH_2$—[c]	.10	.05	48 hr.	77	112–116	1.5	1.5743	0.9940	[d]	....
$CH_2=CHCH_2$—[c]	.217	.05	120 hr.	77[e]	117–120	0.1	1.5745	....	...	....
$CH_3(CH_2)_3$—	.09	.05	48 hr.	72	110–112	1.0	1.5541	0.9604	11.68	11.53, 11.52
$CH_3(CH_2)_9$—	.072	.05	24 hr.	70	164–168	1.5	1.5253	0.9262	8.65	8.51, 8.54
$C_6H_5CH_2$—[c]	.05	.05	24 hr.	70	140–143	0.1	1.6073	1.0494	10.24	10.10, 10.23
—$(CH_2)_5$—[f]	.038	.077	14 hr.	43	217–220	.008	1.5946	1.0390	12.86	12.83, 12.68

[a] M.p. 44–45.5°. [b] In refluxing diethyl ether; 45.5% recovery of Ph_2SiH_2. [c] RMgCl. [d] Calcd.: C, 80.29; H, 7.19. Found: C, 80.30; H, 7.08. [e] $Ph_2Si(CH_2CH=CH_2)_2$. [f] $BrMg(CH_2)_5MgBr$.

TABLE III

$PhSiH_3$ WITH RMgX IN THF AT ROOM TEMPERATURE

RMgBr, R =	Mole of RMgBr	Mole of $PhSiH_3$	Time	Yield of $PhSiH_2R$, %	B.p., °C.	B.p., Mm.	$n^{20}D$	d^{20}_{20}	Silicon, % Calcd.	Silicon, % Found
C_6H_5—	0.049	0.05	6.5 hr.	66	71–73	0.5	1.5797	....	...	....
C_6H_5—	.18	.05	48 hr.	67[a]	.....	..	....	....	...	....
C_6H_5—[b]	.05	.05	24 hr.	52	69–71	0.5	1.5792	....	...	....
$CH_3(CH_2)_9$—	.06	.06	18 hr.	62	108–111	.6	1.4906	0.8648	11.31	11.29, 11.37
$CH_3(CH_2)_{11}$—	.01	.01	18 hr.[c]	78	130–131	.6	1.4884	0.8629	10.16	10.13, 9.99
$C_6H_5CH_2$—[d]	.07	.07	20 hr.	67	97–98	.9	1.5738	....	...	....
4-$CH_3OC_6H_4$—	.19	.20	17 hr.	75	118–121	.15[e]	....	....	13.11	13.16, 13.22
2-$CH_3C_6H_4$—	.16	.15	24 hr.	87	85–89	.1	1.5808	1.0015	14.17	14.35, 14.47
4-$C_6H_5OC_6H_4$—	.10	.11	17 hr.	74	145–147	.02	1.6093	....	10.17	10.45, 10.29

[a] Ph_3SiH, m.p. 44–45.5°. [b] In diethyl ether. [c] Also refluxed for 1 hr. [d] RMgCl. [e] M.p. 45–47°, recrystallized from a mixture of methanol and petroleum ether (b.p. 60–70°).

the reduction of the corresponding chlorosilanes. The preparation of diphenylsilane was carried out in THF, affording a higher yield.[17] Silicon analyses were carried out by a published method.[18] Illustrative examples of the reactions of the various silicon hydrides are given below.

Triphenylsilane and Allylmagnesium Chloride (Table I).—A solution of 6.12 g. (0.08 mole) of allyl chloride in 60 ml. of tetrahydrofuran (THF) was added to a suspension of 9.72 g. (0.4 g. at.) of magnesium turnings in 20 ml. of THF at such a rate as to maintain a moderate reflux. After the addition was complete, the Grignard reagent was filtered and titrated, indicating a yield of 0.0635 mole (79%). This reagent was added to a solution of 18.2 g. (0.07 mole) of triphenylsilane in 50 ml. of THF and the mixture refluxed for 4 days. After hydrolyzing with 100 ml. of saturated ammonium chloride solution, the organic layer was separated, the aqueous layer extracted with two portions of ether, and the combined organic layer dried with anhydrous sodium sulfate. The solvents were distilled and the residue crystallized from absolute ethanol to give 12.1 g. (60%) of allyltriphenylsilane, m.p. 88.5–90° (mixed m.p.).

Diphenylsilane and Phenylmagnesium Bromide in Diethyl Ether (Table II).—An ethereal solution (100 ml.) of 0.089 mole of phenylmagnesium bromide was added to 9.2 g. (0.05 mole) of diphenylsilane in 50 ml. of ether and the mixture refluxed for 3 days. After hydrolysis the reaction was worked up as usual and the residue distilled at reduced pressure. There was obtained 4.3 g. (46%) of diphenylsilane, b.p. 76–81° (1 mm.), $n^{20}D$ 1.5782. The distillation residue was taken up in methanol giving 3.95 g. (30.5%) of triphenylsilane, m.p. 43–45° (mixed m.p.).

Diphenylsilane and Phenylmagnesium Bromide in THF (Table II).—Phenylmagnesium bromide (0.095 mole) in 100 ml. of THF was added to 9.2 g. (0.05 mole) of diphenylsilane in 50 ml. of THF. After refluxing for 2 days, the reaction was hydrolyzed. The aqueous layer was separated, extracted with ether and discarded. The organic layer was distilled and the remaining material crystallized from methanol to give 10.4 g. (79%) of triphenylsilane, m.p. 43–45° (mixed m.p.).

Phenylsilane and *n*-Dodecylmagnesium Bromide (Table III).—A solution of 0.1 mole of *n*-dodecylmagnesium bromide in 130 ml. of THF was added to 10.8 g. (0.1 mole) of phenylsilane in 35 ml. of THF. The reaction mixture was stirred for 18 hr., refluxed for 1 hr. and then hydrolyzed with 100 ml. of 5% hydrochloric acid. The THF layer was separated, the water layer extracted with portions of ether, and the combined organic layer dried over anhydrous calcium sulfate. The solvents were removed by distillation and the residue was distilled under reduced pressure to give 21.75 g. (78%) of *n*-dodecylphenylsilane, b.p. 130–131° (0.6 mm.), $n^{20}D$ 1.4880, d^{20}_{20} 0.8629.

Anal. Calcd. for $C_{18}H_{32}Si$: Si, 10.16; *MR*D, 92.29. Found: Si, 10.13, 9.99; *MR*D, 92.41.

Phenylsilane and *o*-Tolylmagnesium Bromide (Table III).—A solution of 16.2 g. (0.15 mole) in 25 ml. of THF was treated with 0.16 mole of *o*-tolylmagnesium bromide in 180 ml. of THF. After stirring at room temperature for 24 hr.,

---

[17] Unpublished studies, R. D. Gorsich.

[18] H. Gilman, B. Hofferth, H. W. Melvin, Jr., and G. E. Dunn, THIS JOURNAL, **72**, 5767 (1950).

TABLE IV

$RPhSiH_2$ WITH $R'MgBr$ (1:1 RATIO) IN REFLUXING THF

$RPhSiH_2$ R =	$R'MgBr$, R' =	Time, hr.	Yield of $RPhSi\cdot HR'$, %	B.p., °C.	B.p., Mm.	$n^{20}D$	d^{20}_{20}	Silicon, % Calcd.	Silicon, % Found
$CH_3(CH_2)_{11}$–	$C_6H_5CH_2$–	18	63	176–186	0.3	1.5233	0.9209	7.66	7.59, 7.62
4-$CH_3OC_6H_4$–	2-$CH_3C_6H_4$–	20	32	171–173	.02	1.6115	1.0854	9.23	9.37, 9.43
2-$CH_3C_6H_4$–	4-$C_6H_5OC_6H_4$–	18	55.5	205–207	.004	....	....	7.66	7.76, 7.61
4-$CH_3OC_6H_4$–	4-$C_6H_5OC_6H_4$–	18	60	227–230	.005	....	....	7.34	7.63, 7.52
2-$CH_3C_6H_4$–	3-$CH_3C_6H_4$–	24	73	145–148	.006	....	....	9.74	9.75, 9.81
4-$C_6H_5OC_6H_4$–	2-$C_6H_5OC_6H_4$–	30	43	234–236	.003	....	....	6.32	6.28, 6.49

TABLE V

$RR'PhSiH$ WITH EXCESS $R''Li$ IN REFLUXING DIETHYL ETHER

RR'PhSiH R =	RR'PhSiH R' =	R''Li, R' =	Yield of RR'PhSiR'', %	B.p., °C.	B.p., Mm.	Silicon, % Calcd.	Silicon, % Found
4-$CH_3OC_6H_4$–	2-$CH_3C_6H_4$–	4-$CH_3C_6H_4$–	72	204–212	0.008	7.12	7.30, 7.15
4-$CH_3OC_6H_4$–	4-$C_6H_5OC_6H_4$–	CH_3–	79	225–228	.003	7.08	7.09, 7.14
2-$CH_3C_6H_4$–	4-$C_6H_5OC_6H_4$–	CH_3–	69	210–213	.004[a]	7.38	7.35, 7.48
2-$CH_3C_6H_4$–	3-$CH_3C_6H_4$–	4-$CH_3C_6H_4$–	85	196–200	.003	7.42	7.56, 7.61
4-$CH_3OC_6H_4$–	4-$C_6H_5OC_6H_4$–	4-$CH_3C_6H_4$-	60	260–264	.003	5.94	6.17, 6.06
2-$CH_3C_6H_4$–	4-$C_6H_5OC_6H_4$–	4-$CH_3C_6H_4$–	68	249–251	.004	6.15	6.33, 6.18
2-$CH_3C_6H_4$–	3-$CH_3C_6H_4$–	CH_3–	63	143–144	.005	9.27	9.41, 9.33
4-$C_6H_5OC_6H_4$–	2-$C_6H_5OC_6H_4$–	CH_3–	52	225–227	.004	6.13	6.11, 6.21

[a] Solidified upon standing to a white solid, m.p. 72–75°.

the reaction mixture was hydrolyzed with 150 ml. of 5% hydrochloric acid. The aqueous layer was separated, extracted twice with ether and discarded. The combined organic layer was dried over anhydrous calcium sulfate and the solvents removed by distillation. The remaining liquid was distilled to give 25.8 g. (87%) of phenyl-*o*-tolylsilane, b.p. 85–89° (0.1 mm.), $n^{20}D$ 1.5808, d^{20}_{20} 1.0015.

Anal. Calcd. for $C_{13}H_{14}Si$: Si, 14.17; *MR*D, 65.81. Found: Si, 14.35, 14.47; *MR*D, 65.98.

Phenyl-*o*-tolylsilane and *m*-Tolylmagnesium Bromide (Table IV).—A solution of 0.051 mole of *m*-tolylmagnesium bromide in 70 ml. of THF was added to 10.1 g. (0.051 mole) of phenyl-*o*-tolylsilane in 25 ml. of THF. After refluxing for 24 hr., the reaction mixture was hydrolyzed with 100 ml. of 5% hydrochloric acid. The water layer was separated, extracted twice with ether and discarded. The combined THF–ether solution was dried and the solvents removed by distillation. Reduced pressure distillation of the remaining material gave 10.72 g. (73%) of phenyl-*m*-tolyl-*o*-tolysilane as a rather thick, colorless liquid, b.p. 145–148° (0.006 mm.).

Anal. Calcd. for $C_{20}H_{20}Si$: Si, 9.74. Found: Si, 9.75, 9.81.

Phenyl-*m*-tolyl-*o*-tolylsilane and *p*-Tolyllithium (Table V).—An ethereal solution (40 ml.) of 0.029 mole of *p*-tolyllithium was added to 4.45 g. (0.015 mole) of phenyl-*m*-tolyl-*o*-tolylsilane in 25 ml. of ether and the reaction mixture refluxed for 18 hr. The reaction was hydrolyzed with 100 ml. of 5% hydrochloric acid and worked up in the usual manner. Attempts to crystallize the material were unsuccessful; so, it was distilled at reduced pressure to give 4.85 g. (85%) of phenyl-*m*-tolyl-*o*-tolyl-*p*-tolysilane as a colorless glass-like material, b.p. 196–200° (0.003 mm.).

Anal. Calcd. for $C_{27}H_{26}Si$: Si, 7.42. Found: Si, 7.56, 7.61.

Infrared Absorption Spectra.—All of the infrared spectra of the silicon hydrides in carbon tetrachloride or as liquids showed a characteristic absorption band between 2155 and 2125 cm.$^{-1}$ with the trisubstituted derivatives absorbing at the longer wave lengths.[19]

Acknowledgment.—This research was supported in part by the United States Air Force under Contract AF 33(616)-3510 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright–Patterson AFB, Ohio. Infrared analyses were obtained through the courtesy of the Institute for Atomic Research, Iowa State College, and special acknowledgment is made to Dr. V. A. Fassel and Mr. R. Kniseley for the spectra.

AMES, IOWA

---

(19) Unpublished studies correlating the position of the infrared absorption with the number of hydrogens attached to a silicon atom in organosilanes; M. B. Hughes.