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^{25}_{D} 1.3934. By adjustment of the known constants of *n*-butyltrimethoxysilane,[11] the constants of isobutyltrimethoxysilane were estimated to be n^{25}_{D} 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 addition, 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.

Acknowledgment. The authors wish to express their appreciation for the interest and help of the following Ethyl Corp. personnel: Dr. W. E. Foster, who administered the project; Dr. G. E. Schroll for his synthesis work; and Dr. R. P. Curry for the infrared spectroscopic analyses.

KANSAS CITY 10, MO.

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

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE UNIVERSITY]

Relative Reactivities of Some Functional Groups with Triphenylsilyllithium

HENRY GILMAN AND WILLIAM J. TREPKA[1]

Received June 1, 1961

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 organolithium 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

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(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).

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

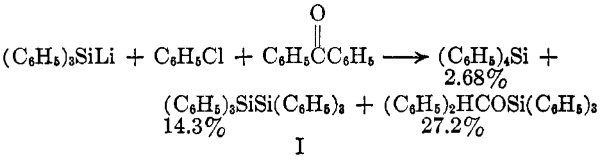
of several Grignard reagents with a miscellany of reactants was reported.[7] These studies culminated in the splendid studies of Entemann and Johnson.[8] These investigators carried out a series of competitive reactions in which one equivalent of phenylmagnesium bromide was added to a solution containing one equivalent of each of two reactants. An examination of the products revealed the extent of each reaction. On this basis, the relative reactivities of some functional groups are:

$$\text{—CHO} > \text{—COCH}_3 > \text{—NCO} > \text{—COF} > \text{—COC}_6\text{H}_5,\ \text{—COCl},\ \text{—COBr} > \text{—CO}_2\text{C}_2\text{H}_5 > \text{—C}\equiv\text{N}$$

Organolithium compounds undergo all of the reactions typical of Grignard reagents and, due to their higher reactivitity, several others as well such as metalation.[9,10]

The reaction of triphenylsilyllithium with RX compounds produces hexaphenyldisilane (I) in a secondary coupling reaction.[11] Since hexaphenyldisilane is insoluble in most organic solvents and, as a result, is very easy to isolate with excellent reproducibility of yield, the extent of its formation from a competitive reaction involving triphenylsilyllithium with a functional compound and an organic halide could be used as an indication of the relative reactivity of that functional grouping. The particular halide chosen as the standard for this study was chlorobenzene,[12] which reacts with triphenylsilyllithium at a moderate rate to give a reproducible yield (51–53%) of hexaphenyldisilane. Chlorobenzene is not known to react with the functional groups under study, and would not be expected to catalyze their reaction with triphenylsilyllithium.

A typical example of such a competitive reaction involving chlorobenzene is shown below:



$$(\text{C}_6\text{H}_5)_3\text{SiLi} + \text{C}_6\text{H}_5\text{Cl} + \text{C}_6\text{H}_5\overset{\text{O}}{\overset{\|}{\text{C}}}\text{C}_6\text{H}_5 \longrightarrow \underset{2.68\%}{(\text{C}_6\text{H}_5)_4\text{Si}} + \underset{\substack{14.3\% \\ \text{I}}}{(\text{C}_6\text{H}_5)_3\text{SiSi}(\text{C}_6\text{H}_5)_3} + \underset{27.2\%}{(\text{C}_6\text{H}_5)_2\text{HCOSi}(\text{C}_6\text{H}_5)_3}$$

As can be seen, a yield of only 14.3% of hexaphenyldisilane was obtained as compared to 51% when chlorobenzene is allowed to react alone with triphenylsilyllithium. This shows clearly that the ketone grouping is appreciably more reactive than the halobenzene.

The amount of phenyllithium, formed by the halogen-metal interconversion reaction of triphenylsilyllithium with chlorobenzene, should not be sufficiently large to interfere significantly with evaluation of the results. This is so because phenyllithium, giving rise to tetraphenylsilane through reaction with chlorotriphenylsilane, is produced slowly and in only a 12.0% total yield from triphenylsilyllithium and chlorobenzene. In the competitive reactions the ratio of chlorobenzene, functional group containing compound, and triphenylsilyllithium is 1:1:1. Accordingly, at any one time the concentration of functional group containing compound should be much greater than the phenyllithium, and the concentration of the former compound would not be changed significantly owing to reaction with the organometallic reagent. With the more reactive functional groups, there would be less reaction of triphenylsilyllithium with chlorobenzene and a corresponding decrease in the formation of phenyllithium.

A second assumption considers that there will not be a shift in the point of an equilibrium as the result of the insolubility of hexaphenyldisilane. It seems unlikely that these are equilibria reactions since most go rapidly to completion; there is always an insufficient amount of triphenylsilyllithium; and the reactions are usually interrupted as soon as the silylmetallic compound is used up as evidenced by a negative Color Test I.[13] Furthermore, it should be noted that hexaphenyldisilane is not isolated from the competitive reactions involving the more reactive functional groups.

Unfortunately, the Entemann and Johnson series could not be studied in its entirety. A requirement of the functional group under study was that it must not give hexaphenyldisilane through its own reaction with triphenylsilyllithium. This eliminated the aldehyde grouping which gives some hexaphenyldisilane following reaction with triphenylsilyllithium.[14] It would have been possible to include reactions in which low reproducible yields of hexaphenyldisilane are obtained if the constant value was subtracted from the total amount of disilane obtained. Such reactions were not included to avoid further complications.

The particular compounds brought into competition with chlorobenzene for triphenylsilyllithium were benzonitrile,[15] ethyl benzoate,[16] anisole,[17] *n*-octyl fluoride,[12] benzophenone,[4] styrene oxide,[18] and

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[7] H. Gilman, L. L. Heck, and N. B. St. John, *Rec. trav. chim.*, **49**, 212 (1930).

[8] C. E. Entemann and J. R. Johnson, *J. Am. Chem. Soc.*, **55**, 2900 (1933).

[9] G. E. Coates, "Organo-Metallic Compounds," Methuen and Co., Ltd., London, 1956, p. 8.

[10] E. G. Rochow, D. T. Hurd, and R. N. Lewis, "The Chemistry of Organometallic Compounds," John Wiley and Sons, Inc., New York, 1957, p. 71.

[11] H. Gilman and D. Aoki, *J. Org. Chem.*, **24**, 426 (1959).

[12] Unpublished studies by Glen Dappen.

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

[14] D. Wittenberg, T. C. Wu, and H. Gilman, *J. Org. Chem.*, **24**, 1349 (1959).

[15] H. Gilman and D. J. Peterson, *J. Org. Chem.*, **23**, 1895 (1958).

[16] W. J. Trepka, unpublished studies.

[17] H. Gilman and W. J. Trepka, *J. Org. Chem.*, **27**, 1418 (1962).

[18] H. Gilman, D. Aoki, and D. Wittenberg, *J. Am. Chem. Soc.*, **81**, 1107 (1959).

TABLE I

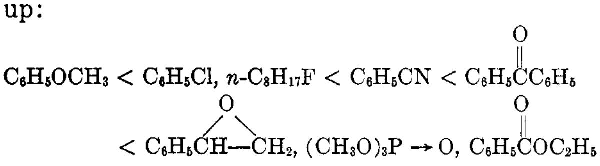
YIELDS OF HEXAPHENYLDISILANE FROM COMPETITIVE REACTIONS OF TRIPHENYLSILYLLITHIUM WITH CHLOROBENZENE AND VARIOUS FUNCTIONAL GROUPS

Compounds	% Hexaphenyldisilane
Chlorobenzene[a]	53.0
Anisole	51.0
n-Octyl fluoride	25.0
Benzonitrile	23.0
Benzophenone	14.3
Styrene oxide	0
Trimethyl phosphate	0
Ethyl benzoate	0

[a] Yield of hexaphenyldisilane when only chlorobenzene is reacted with triphenylsilyllithium.

trimethyl phosphate.[19] The yields of hexaphenyldisilane from these competitive reactions are presented in Table I.

From the results shown in Table I, the following tentative series of relative reactivities was set up:

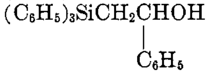


$$C_6H_5OCH_3 < C_6H_5Cl,\ n\text{-}C_8H_{17}F < C_6H_5CN < C_6H_5\overset{O}{\overset{\|}{C}}C_6H_5 < C_6H_5\overset{O}{CH}\text{—}CH_2,\ (CH_3O)_3P \rightarrow O,\ C_6H_5\overset{O}{\overset{\|}{C}}OC_2H_5$$

As can be seen, a differentiation between chlorobenzene–*n*-octyl fluoride and styrene oxide–trimethyl phosphate–ethyl benzoate can not be easily made. Therefore, careful product analyses, at times inherently difficult, were carried out on the competitive reactions involving mixtures of those functional groups not yet clearly placed. The results are presented in Table II.

TABLE II

PRODUCTS ISOLATED FROM COMPETITIVE REACTIONS

	Products					
Competing species	Product	% obtained	% in previous reaction[a]	Product	% obtained	% in previous reaction
Chlorobenzene/*n*-octyl fluoride	$(C_6H_5)_4Si$	11.0	12.0	$(C_6H_5)_3Si\text{—}C_8H_{17}\text{-}n$	33.5	86.5
Trimethyl phosphate/styrene oxide	$(C_6H_5)_3SiCH_3$	46.0[b]	71.1[b]	 $(C_6H_5)_3SiCH_2\underset{C_6H_5}{\underset{\mid}{C}}HOH$	15.8	43.3
Trimethyl phosphate/ethyl benzoate	$(C_6H_5)_3SiCH_3$	40.1[b]	71.1[b]	no definite product	—	—

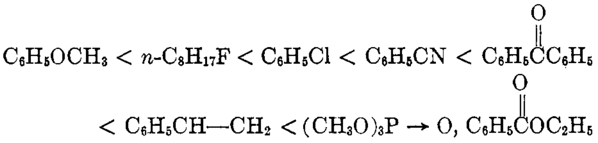
[a] The per cent reported here is based upon the yield of product obtained when the compound containing the functional group was reacted with triphenylsilyllithium. [b] Crude yields are reported for methyltriphenylsilane because of its high solubility in the recrystallization solvent. This does not alter the basic conclusions since the yields are compared only with their own previous yields of similar purity.

When triphenylsilyllithium reacted with a mixture of chlorobenzene and *n*-octyl fluoride, less than 50% of the yield of *n*-octyltriphenylsilane, compared to the yield obtained when *n*-octyl fluoride alone reacted with triphenylsilyllithium, was obtained (33.5 *vs.* 86.5%). This result indicated that *n*-octyl fluoride was reacting at a slower rate than was chlorobenzene.

From the competitive reaction involving trimethyl phosphate and styrene oxide, the products indicated that trimethyl phosphate had reacted approximately 60% as much as previously, and that styrene oxide had reacted only to an extent of 31.5%. Thus, trimethyl phosphate reacted more rapidly than styrene oxide.

No definite products have been isolated thus far from the reaction of triphenylsilyllithium with ethyl benzoate.[16] The conclusions are based upon a decrease in the yield of products obtained from trimethyl phosphate. However, the amount of methyltriphenylsilane obtained was 57.8% of the amount obtained when the reaction appeared to be exclusive with the phosphate ester. Since conclusions are based on the decrease in yield of methyltriphenylsilane, a difference of only 7.8% of a product which is rather soluble in its recrystallization solvent would not be large enough to warrant a definite statement as to a difference in reactivity.

In summary, the results obtained in the competitive reactions indicate the following series of reactivities:



$$C_6H_5OCH_3 < n\text{-}C_8H_{17}F < C_6H_5Cl < C_6H_5CN < C_6H_5\overset{O}{\overset{\|}{C}}C_6H_5 < C_6H_5CH\text{—}CH_2 < (CH_3O)_3P \rightarrow O,\ C_6H_5\overset{O}{\overset{\|}{C}}OC_2H_5$$

The only functional group included in the Entemann-Johnson series which appears to react at a different rate is ethyl benzoate. With triphenylsilyllithium it appears to be among the most reactive. It would, indeed, be somewhat surprising if there were a complete correlation between the two series. The organosilylmetallic compounds may be considered as pseudo-organometallic compounds and significant differences might be expected in the intermediate complexes. Steric factors also indicate that comparisons with triphenylmethyllithium may prove interesting.

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(19) B. J. Gaj, doctoral dissertation, Iowa State University of Science and Technology, 1960.

EXPERIMENTAL[20]

Chlorobenzene and anisole with triphenylsilyllithium. To a stirred solution of 5.63 g. (0.05 mole) of chlorobenzene, 5.41 g. (0.05 mole) of anisole and 50 ml. of tetrahydrofuran was added 0.05 mole of triphenylsilyllithium[2] in tetrahydrofuran solution over a period of 10 min. The reaction mixture became warm during the addition, and a small amount of white solid appeared suspended in the dark solution. Color Test I[13] was positive. The reaction mixture was warmed at 50° for 1.5 hr., at which time Color Test I was negative. After the reaction mixture was hydrolyzed with concd. ammonium chloride solution, the suspended white solid was filtered off, washed, and dried to give 6.60 g. (51.0%) of hexaphenyldisilane, m.p. 358–366°. The melting point of a mixture with an authentic sample was not depressed.

The original organic layer was separated, dried over anhydrous sodium sulfate, and then evaporated to leave a yellow oily solid. This was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave 1.75 g. (30.6%) of recovered anisole, n^{20}_{D} 1.5181. The infrared spectrum was identical with that of an authentic sample. Elution of the column with benzene gave a white solid melting over the range 205–228°. Several recrystallizations from ethyl acetate gave 1.95 g. (11.6%) of tetraphenylsilane, m.p. 230–232.5° (mixture melting point, infrared spectra comparison). Elution of the column with ethyl acetate gave a white solid melting over the range 140–150°. Recrystallization from petroleum ether (b.p. 60–70°) gave 0.20 g. (1.45%) of triphenylsilanol, m.p. 155–156° (mixture melting point). Further elution of the column with ethyl acetate and with ethanol gave an orange tarry residue which was not investigated further.

Chlorobenzene and n-octyl fluoride with triphenylsilyllithium. A tetrahydrofuran solution of 0.05 mole of triphenylsilyllithium was added to a solution of 6.61 g. (0.05 mole) of *n*-octyl fluoride, 5.63 g. (0.05 mole) of chlorobenzene, and 50 ml. of tetrahydrofuran over a 50-min. period. A white solid appeared suspended in the flask. Color Test I was positive at the completion of addition but was negative after the reaction mixture had been stirred at room temperature overnight. Hydrolysis was carried out with concd. ammonium chloride solution, and the resulting mixture was filtered and subjected to the chromatographic work-up described in the previous reaction. The insoluble material was 3.25 g. (25.0%) of hexaphenyldisilane, m.p. 365–369° (mixture melting point).

The chromatography yielded *n*-octyltriphenylsilane[12] (33.5% crude, 27.4% pure), m.p. 72–73°; and tetraphenylsilane (17.9% crude, 11.0% pure). The products were identified by mixture melting points and infrared spectra comparisons.

Benzonitrile and chlorobenzene with triphenylsilyllithium. A tetrahydrofuran solution of 0.05 mole of triphenylsilyllithium was added slowly over a 45-min. period to a solution of 5.16 g. (0.05 mole) of benzonitrile, 5.63 g. (0.05 mole) of chlorobenzene and 50 ml. of tetrahydrofuran. Slight warming occurred during the addition. The dark solution gave a positive Color Test I, and some white solid appeared to be suspended in it. After stirring at room temperature for 24 hr., Color Test I was slightly positive, but was negative after 36 hr. of stirring. After hydrolysis of the reaction mixture with concd. ammonium chloride solution, the white solid was filtered, washed with ether, and dried to give 3.00 g. (23.0%) of hexaphenyldisilane. The filtrate was worked up in the usual manner to give tetraphenylsilane (2.68%) and a considerable amount of yellow tar. Nothing, however, was extracted from the tar.

Chlorobenzene and benzophenone with triphenylsilyllithium. To a solution of 9.11 g. (0.05 mole) of benzophenone, 5.63 g. (0.05 mole) of chlorobenzene, and 50 ml. of tetrahydrofuran was added slowly 0.05 mole of triphenylsilyllithium in tetrahydrofuran solution. As the addition proceeded the color of the solution changed from yellow to green to dark brown. No white solid was observed suspended in the solution. The addition was completed in 20 min. Color Test I was positive, but, after the reaction mixture had been stirred at room temperature for 1 hr., the color test was negative. A small amount of white solid was then observable. Hydrolysis was effected with dilute ammonium chloride solution, and the work-up was carried out as described previously.

The suspended white solid was 1.85 g. (14.3%) of hexaphenyldisilane, m.p. 363–366° (mixture melting point). The colorless oil obtained from evaporation of the organic layer was chromatographed on alumina as described previously. There was obtained 6.00 g. (27.2%) of benzhydryloxytriphenylsilane,[4] m.p. 83–84.5°; 0.45 g. (2.68%) of tetraphenylsilane, melting range 227–234°; and 0.30 g. (2.17%) of triphenylsilanol. The products were identified by the method of mixture melting points.

Chlorobenzene and styrene oxide with triphenylsilyllithium. To a solution of 5.63 g. (0.05 mole) of chlorobenzene, 6.01 g. (0.05 mole) of styrene oxide, and 50 ml. of tetrahydrofuran chilled to ice bath temperature was added slowly a tetrahydrofuran solution of 0.05 mole of triphenylsillylithium. Addition was completed in 30 min., at which time Color Test I was slightly positive. The ice bath was removed, and after the reaction mixture had stirred at room temperature for 1 hr., Color Test I was negative. No suspended solid was noted. Hydrolysis was effected with concd. ammonium chloride solution, and the work-up with subsequent chromatography was carried out as described previously.

The product isolated was 8.25 g. (43.3%) of 2-triphenylsilyl-1-phenylethanol,[18] m.p. 135–137° (mixture melting point, infrared spectrum). The only other material present was some dark brown tar which was not investigated further.

Chlorobenzene and trimethyl phosphate with triphenylsilyllithium. A tetrahydrofuran solution of 0.05 mole of triphenylsilyllithium was added to a solution of 7.00 g. (0.05 mole) of trimethyl phosphate, 5.63 g. (0.05 mole) of chlorobenzene, and 50 ml. of tetrahydrofuran over a period of 1 hr. Warming of the solution occurred and Color Test I was negative upon completion of the addition. Hydrolysis and chromatographic work-up were effected as described previously.

The product isolated was methyltriphenylsilane (71.1% crude, 65.3% pure), m.p. 67–69° (mixture melting point).

Chlorobenzene and ethyl benzoate with triphenylsilyllithium. A tetrahydrofuran solution of 0.05 mole of triphenylsilyllithium was added slowly to a solution of 7.50 g. (0.05 mole) of ethyl benzoate, 5.63 g. (0.05 mole) of chlorobenzene, and 50 ml. of tetrahydrofuran. The addition was completed in 1 hr., at which time Color Test I was negative. There was no suspended solid in the solution. Ammonium chloride solution hydrolysis and the usual chromatographic work-up were effected.

Elution of the column with petroleum ether (b.p. 60–70°) gave 1.15 g. (7.56%) of crude ethoxytriphenylsilane (infrared spectra comparison); however, this could not be purified, probably due to instability of the compound. Further elution with petroleum ether (b.p. 60–70°) gave an intractable yellow tar. Elution with benzene also gave a yellow tarry residue. However, when this was slurried with ethanol, 0.20 g. (3.77%) of benzoin, m.p. 133–135° (mixture melting point, infrared spectrum), was obtained. Evaporation of the ethanol extract gave 0.90 g. (6.52%) of crude triphenylsilanol melting over the range 131–148°. Recrystallization from petroleum ether (b.p. 80–110°) raised the melting point to 152–153° (mixture melting point).

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(20) All melting points are uncorrected. 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 and then distilling from lithium aluminum hydride.

Trimethyl phosphate and styrene oxide with triphenylsilyllithium. To a solution of 7.00 g. (0.05 mole) of trimethyl phosphate, 6.01 g. (0.05 mole) of styrene oxide and 50 ml. of tetrahydrofuran was added slowly 0.05 mole of triphenylsilyllithium in tetrahydrofuran solution. The solution turned yellow, then orange, and became warm during the addition, which was completed in 1 hr. Color Test I was negative. The reaction mixture was hydrolyzed with concd. ammonium chloride solution and the usual chromatographic work-up was employed.

The products isolated were methyltriphenylsilane (46.0% crude, 38.3% pure) and 2-triphenylsilyl-1-phenylethanol (15.8% crude, 13.7% pure), both identified by mixture melting points.

Trimethyl phosphate and ethyl benzoate with triphenylsilyllithium. To a solution of 7.00 g. (0.05 mole) of trimethyl phosphate, 7.50 g. (0.05 mole) of ethyl benzoate, and 50 ml. of tetrahydrofuran was added slowly 0.05 mole of triphenylsilyllithium in tetrahydrofuran solution. The solution became warm during the addition, which was completed in 1.25 hr. Color Test I was negative. Aqueous hydrolysis followed by the usual chromatographic work-up gave methyltriphenylsilane (crude 40.1%, pure 28.8%); 0.30 g. of an unidentified solid, m.p. 183–185°; and triphenylsilanol (2.17%).

The infrared spectrum of the unknown solid showed bands to be expected for the addition-rearrangement product, phenyl(triphenylsilyl)triphenylsiloxymethane (C_6H_5)-$[(C_6H_5)_3Si][(C_6H_5)_3SiO]CH$. The silicon analysis also agrees with the structure.

Anal. Calcd. for $C_{43}H_{36}OSi_2$: Si, 8.99. Found: Si, 9.04, 8.83.

However, additional supporting evidence for the structure has not been obtained.

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY]

Preparation and Reactions of Some Unsymmetrical Phenoxasilin Compounds

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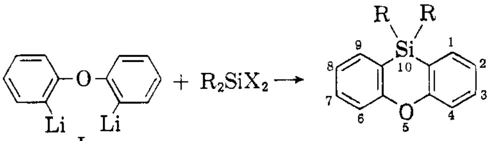
A number of unsymmetrical phenoxasilin compounds were prepared. The procedure involved the synthesis of the functional Si-H compound, 10-phenylphenoxasilin, from 2,2′-dilithiodiphenyl ether and phenylsilane. Reaction of the Si-H compound with a number of RLi reagents produced the desired unsymmetrical phenoxasilin compounds. The chemistry of the phenoxasilin system was explored briefly.

The first reported phenoxasilin compounds (II) were prepared by reaction of 2,2′-dilithiodiphenyl ether (I) with R_2SiX_2 or SiX_4 reagents.[1–3] Later reports have described the preparation of phenoxasilin compounds by a Wurtz coupling of an *o,o′*-dibromodiphenyl ether with R_2SiX_2[4] and by extended reaction of diphenylsilane with phenoxathiin.[5]



I

II

All of the compounds prepared previously contained like R groups on the silicon atom. Attempts had not been made to prepare unsymmetrically substituted phenoxasilin compounds, and it was toward this goal that the present investigation was directed. The inaccessibility of unsymmetrical diorganosilicon halides negated the aforementioned routes to these compounds. An alternative approach was to prepare a phenoxasilin ring system containing either Si-X or Si-H at the bridge-position which could then be coupled with an RLi reagent.

Such an approach was not new. 2,2′-Dilithiobiphenyl had been coupled with several monorganosilicon halides, such as methyltrichlorosilane, to produce 5 - chloro - 5 - organodibenzosilole compounds.[6] The reaction of these halides with organolithium reagents gave the appropriate unsymmetrical molecules. Since many difficulties were experienced in the handling and storing of the halo-silicon compounds, $RSiH_3$, reagents were substituted for $RSiX_3$ in reaction with *N*-ethyl-2,2′-dilithiodiphenylamine.[7] The resulting cyclic Si-H compound could be handled with little risk of atmospheric hydrolysis, but still coupled readily with RLi reagents to give unsymmetrical phenazasiline compounds. The latter reaction was chosen as the method for preparing the proposed unsymmetrical phenoxasilin compounds.

The dilithium intermediate employed for the phenazasilin compounds had been prepared through the use of a halogen-metal interconversion reaction and was known to be of relatively high quality.

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