[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF IOWA STATE COLLEGE AND MUHLENBERG COLLEGE]

STERIC HINDRANCE IN HIGHLY-SUBSTITUTED ORGANOSILICON COMPOUNDS. I. THE REACTION OF ARYLLITHIUM COMPOUNDS WITH SOME CHLOROSILANES, ETHOXYSILANES, AND RELATED COMPOUNDS

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Received October 3, 1949

From time to time reference has been made to the effects of steric hindrance in connection with the preparation and reactions of certain organosilicon compounds. Cusa and Kipping (1) were unable to prepare *sym*-tetracyclohexyldiphenyldisiloxane from dicyclohexylphenylsilanol and they attributed this failure to steric factors. Schumb and Saffer (2) showed that in the reaction of silicon tetrachloride with *p*-, *m*-, and *o*-tolylmagnesium bromides, the yields of the corresponding tetratolylsilanes were 35%, 8%, and 0%, respectively. They were also unsuccessful in their attempts to prepare tetra-*o*-tolylsilane by a Wurtz reaction involving silicon tetrachloride, *o*-bromotoluene, and sodium. The negative results here were also attributed to steric factors. Gilman and Clark (3) have shown that when silicon tetrachloride (or ethyl silicate) is treated with excess isopropyllithium at moderate temperatures only three chlorine atoms are replaced by isopropyl groups. Again, while triisopropylphenylsilane could be prepared, triisopropyl-*o*-tolylsilane could not. Tyler, Sommer, and Whitmore (4) were able to prepare *tert*-butyltrichlorosilane by treating silicon tetrachloride with *tert*-butyllithium at the boiling point of *n*-pentane. A second *tert*-butyl group was readily attached to the silicon by the use of somewhat higher temperatures but neither tri-*tert*-butylchlorosilane nor tetra-*tert*-butylsilane could be prepared. These data may be interpreted in terms of steric hindrance.

The experiments reported in this paper indicate that steric factors are of prime importance in the case of *o*-tolyl- and mesityl-silanes. In *o*-methoxyphenylsilanes these factors appear to be less important. These conclusions are in accord with the findings of Adams and co-workers (5) who have demonstrated that the steric effect of the methoxyl group is much less than that of the methyl group. These investigators found, for example, that active β-chloro-β-(2-*methoxy*-4,6-dimethyl-5-chlorophenyl)acrylic acid could be easily racemized, the half-life being nine minutes in butanol at 20°; active β-chloro-β-(2-*methyl*-4,6-dimethyl-5-bromophenyl)acrylic acid had a half-life of 200 minutes in boiling butanol.

As might be predicted on the basis of atomic volume and position in the Periodic Table, steric factors are of greater importance in organosilicon compounds than in the corresponding derivatives of germanium, tin, and lead. Johnson and Nebergall encountered steric factors while preparing highly substituted germanes from germanium tetrachloride and organolithium compounds (6) but tetra-*o*-tolylgermane (7), tetra-*o*-tolyltin (8), and tetraisopropyllead (9) have all been prepared using less drastic conditions than appear necessary for the preparation of tetraisopropyl- and tetra-*o*-tolyl-silanes. On the other hand, steric factors appear to be less important in organosilicon compounds than in the corresponding methane derivatives. Tetraisopropylmethane, tetra-*o*-tolylmethane, and similar compounds have not been reported although both tri-*o*-tolylmethane (10) and triisopropylmethane (11) are known. The preparation of tris-2,5-dimethylphenylboron (12) is noteworthy. Here, however, the boron to carbon bonds may well be all in one plane [as they are in trimethylboron (13)] so that steric hindrance would be diminished as compared with the tetrahedral fourth-group elements.

Our attempts to prepare tetra-*o*-tolylsilane by the action of excess *o*-tolyllithium on silicon tetrachloride, silicochloroform, or ethyl silicate at the temperature of refluxing diethyl ether were without success, the tri-*o*-tolyl derivative being formed in each case:[1]

$$3\ \mathrm{RLi} + \mathrm{SiCl_4} \xrightarrow{35^\circ} \mathrm{R_3SiCl} + 3\ \mathrm{LiCl} \qquad 1.$$

$$3\ \mathrm{RLi} + \mathrm{HSiCl_3} \xrightarrow{35^\circ} \mathrm{R_3SiH} + 3\ \mathrm{LiCl} \qquad 2.$$

$$3\ \mathrm{RLi} + \mathrm{Si(OC_2H_5)_4} \xrightarrow{35^\circ} \mathrm{R_3SiOC_2H_5} + 3\ \mathrm{LiOC_2H_5} \qquad 3.$$

where $\mathrm{R} = o\text{-}\mathrm{CH_3C_6H_4}$—.

Tri-*o*-tolylchlorosilane, the most reactive of these derivatives (see Table II), did not react with *o*-tolyllithium or with *o*-methoxyphenyllithium at 35°, but with phenyllithium and *p*-methoxyphenyllithium the corresponding tetraarylsilanes formed readily:

$$\mathrm{R_3SiCl} + \mathrm{R'Li} \xrightarrow{35^\circ} \mathrm{R_3SiR'} + \mathrm{LiCl} \qquad 4.$$

where $\mathrm{R} = o\text{-}\mathrm{CH_3C_6H_4}$- and $\mathrm{R'} = \mathrm{C_6H_5}$- or $p\text{-}\mathrm{CH_3OC_6H_4}$—.

Di-*o*-tolyldichlorosilane did not react with mesityllithium even at elevated temperatures, but with phenyllithium in refluxing ether di-*o*-tolyldiphenylsilane was produced in excellent yield:

$$\mathrm{R_2SiCl_2} + 2\ \mathrm{R'Li} \xrightarrow{35^\circ} \mathrm{R_2SiR'_2} + 2\ \mathrm{LiCl} \qquad 5.$$

where $\mathrm{R} = o\text{-}\mathrm{CH_3C_6H_4}$—, $\mathrm{R'} = \mathrm{C_6H_5}$—.

When hexachlorodisilane was treated with excess *o*-tolyllithium, *sym*-tetra-*o*-tolyldihydroxydisilane (I) was isolated after hydrolysis instead of the expected hexa-*o*-tolyldisilane:

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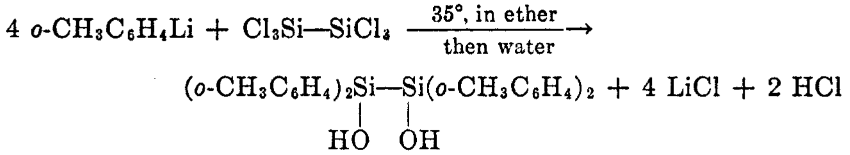
[1] We subsequently isolated tetra-*o*-tolylsilane (m.p. 230°) following reaction of *o*-tolyllithium with tri-*o*-tolylchlorosilane at 170°. Furthermore, when ethyl silicate or tri-*o*-tolylethoxysilane is refluxed with a large excess of *o*-tolyllithium in ether for a prolonged period of time a trace of highly insoluble material separates out (m.p. *ca.* 340°). Preliminary examination and analysis indicate that this may also be tetra-*o*-tolylsilane. We are considering the possibility that these two substances are geometrical isomers. This work and its extension will be described in a later report.



$$4\ o\text{-}CH_3C_6H_4Li + Cl_3Si\text{—}SiCl_3 \xrightarrow[\text{then water}]{35°,\ \text{in ether}} (o\text{-}CH_3C_6H_4)_2\underset{HO}{Si}\text{—}\underset{OH}{Si}(o\text{-}CH_3C_6H_4)_2 + 4\ LiCl + 2\ HCl \qquad 6.$$

I

The reaction of excess mesityllithium with ethyl silicate at 35° gave dimesityldiethoxysilane in fair yield:

$$2\ RLi + Si(OC_2H_5)_4 \xrightarrow{35°} R_2Si(OC_2H_5)_2 + 2\ LiOC_2H_5 \qquad 7.$$

where $R = 2,4,6\text{-}(CH_3)_3C_6H_2\text{—}$.

This compound resisted the further replacement of ethoxy groups with mesityls and did not react with phenyllithium at 35°. With silicochloroform excess mesitylmagnesium bromide apparently gave mono- and di-substituted mesitylsilanes at 35°, but at elevated temperatures three mesityl groups may have been introduced. Tetra-*o*-methoxyphenylsilane may be readily prepared at 35° by the action of *o*-methoxyphenyllithium on silicon tetrachloride (equation 8, $R = o\text{-}CH_3OC_6H_4\text{—}$) or tri-*o*-methoxyphenylchlorosilane (equation 4, $R = R' = o\text{-}CH_3OC_6H_4\text{—}$).

$$4\ RLi + SiCl_4 \xrightarrow{35°} R_4Si + 4\ LiCl \qquad 8.$$

When tri-*o*-methoxyphenylethoxysilane was treated with *o*-tolyllithium at 35°, tri-*o*-methoxyphenyl-*o*-tolylsilane was produced in excellent yield:

$$R_3SiOC_2H_5 + R'Li \xrightarrow{35°} R_3SiR' + LiOC_2H_5 \qquad 9.$$

where $R = o\text{-}CH_3OC_6H_4\text{—}$ and $R' = o\text{-}CH_3C_6H_4\text{—}$.

It is an important commentary on the nature and magnitude of steric hindrance in these compounds that tri-*o*-methoxyphenyl-*o*-tolylsilane formed so readily, while tri-*o*-tolyl-*o*-methoxyphenylsilane could not be prepared although more drastic conditions were used.

We had been concerned about the structure of those compounds designated as *o*-methoxyphenylsilanes. The ease of formation of tetra-*o*-methoxyphenylsilane was disturbing when contrasted with the non-formation of tetra-*o*-tolylsilane under similar conditions, even when allowance was made for the difference in steric effects of the methoxy and methyl groups. Furthermore, some *o*-methoxyphenylsilane derivatives were stable to a warm solution containing equal volumes of glacial acetic and concentrated sulfuric acids. This acetic-sulfuric reagent apparently attacks all phenyl-, *o*-tolyl-, *m*-tolyl-, *p*-tolyl-, and mesityl-silanes with the production of colloidal silica (about 20 compounds were tested). And again, tri-*o*-methoxyphenylchlorosilane[2] is abnormally insoluble and has a very high melting point when compared with the corresponding triphenyl, tri-*o*-tolyl, and tri-*p*-tolyl compounds. The abnormality in melting point is shown in Table I.

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[2] This compound was prepared by Mr. H. Melvin.

Several hypotheses were advanced to account for the anomalous behaviors, but these could not be supported by experiment. One explanation supposed that the so-called tetra-*o*-methoxyphenylsilane was actually tri-*o*-methoxyphenyl-*p*-methoxyphenylsilane. Gilman and Edwards (19) showed by carbonation experiments that *p*-methoxyphenyllithium can metalate itself in the *ortho* position, giving appreciable quantities of *o*-methoxyphenyllithium after prolonged periods of time. If *o*-methoxyphenyllithium can undergo an opposite [though unlikely (20)] rearrangement, then *p*-methoxyphenyllithium would be formed. This substance would then be expected to react with tri-*o*-methoxyphenylchlorosilane (formed early in the reaction from *o*-methoxyphenyllithium and silicon tetrachloride) to give tri-*o*-methoxyphenyl-*p*-methoxyphenylsilane. This could account for the ease of formation of the tetraarylsilane which was actually isolated. However, tri-*o*-methoxyphenyl-*p*-methoxyphenylsilane was made from pure tri-*o*-methoxyphenylethoxysilane and freshly prepared *p*-methoxyphenyllithium (equation 9, R = *o*-$CH_3CC_6H_4$— and R′ = *p*-$CH_3OC_6H_4$—) and was found to be different from the so-called tetra-*o*-methoxyphenylsilane. A second hypothesis entertained the possibility that *o*-methoxyphenyllithium can metalate itself on the methyl carbon giving phenoxymethyllithium. With silicon tetrachloride this reagent would give tetraphenoxymethylsilane or, more probably, mixed phenoxymethyl-*o*-methoxyphenylsilanes. This hypothesis would account for the ease of formation of the tetraarylsilane and, since alkylsilanes resist the action of hot acetic acid-sulfuric acid solution, might account for the stability to this reagent. However, when the mixture resulting from reaction of *o*-bromoanisole with lithium in diethyl ether was aged and subsequently carbonated, *o*-methoxybenzoic acid (m.p. 99–100°) was produced but neither phenoxyacetic acid (m.p. 99–100°) nor anisic acid (m.p. 184°) was isolated.

TABLE I

THE MELTING POINTS OF SOME TETRAARYLSILANES AND TRIARYLCHLOROSILANES

R	R_4Si M.P., °C.	R_3SiCl M.P., °C.
C_6H_5—	233 (14)	111 (15)
o-$CH_3C_6H_4$—	230 (16)	116 (16)
p-$CH_3C_6H_4$—	228 (14)	116 (17)
o-$CH_3OC_6H_4$—	224.5 (16)	203 (18)

On the basis of this work, then, it appears that the various *o*-methoxyphenylsilane structures postulated for our reaction products are correct and that an explanation for the abnormal properties must be sought elsewhere. Further reference is made to the acid stability of these materials in the experimental section dealing with qualitative tests for silicon.

Incidental to the main studies evidence has been obtained to indicate that, in the tri-*o*-tolylsilyl series at least, a chlorosilane is more reactive than a silicon hydride which in turn is more reactive than an ethoxysilane in the reaction of such compounds with phenyllithium and *p*-methoxyphenyllithium. Table II summarizes the results of experiments in which the tri-*o*-tolylsilyl derivatives were separately treated with an RLi compound under controlled conditions. The reactions are represented by equations 4, 9, and 10, where R = *o*-$CH_3C_6H_4$— and R′ = C_6H_5— or *p*-$CH_3OC_6H_4$—.

$$R_3SiH + R'Li \xrightarrow{35^\circ} R_3SiR' + LiH \qquad 10.$$

The results are in general agreement with others derived from simple rate studies: Color Test I (21) indicated that in a given run silicon tetrachloride reacted completely with 2.4 moles of *o*-tolyllithium (per mole of silicon tetrachloride) in less than ten minutes, while under identical conditions ethyl silicate consumed this amount only in about 30 minutes.[3] Further supporting evidence was obtained from reactions leading to the formation of triphenylsilyl and tri-*o*-tolylsilyl ethers and sulfides. This latter work will be discussed in a later report.

EXPERIMENTAL[4]

Preparation and purification of reagents. The organolithium compounds and Grignard reagents used in these researches were prepared for immediate use according to standard directions (23). These preparations were at all times protected by an atmosphere of dry nitrogen. Starting materials were carefully dried before use. The yield of organometallic compound was determined by direct titration (24), unless otherwise noted, and in every case this approximated the yield reported earlier.

Ethyl orthosilicate[5] was purified by distillation and the fraction boiling at 164.8–165.2°/752 mm. was used. Silicon tetrachloride was always distilled immediately before use; the fraction boiling at 55.5–56.5°/750 mm. was used. Hexachlorodisilane[6] and silicochloroform[7] were used without purification. Diethyl ether was thoroughly dried over fresh sodium. Bromobenzene, the bromotoluenes, and the bromoanisoles were Eastman Kodak White Label products; these were dried over phosphoric anhydride and distilled before use. Bromomesitylene was prepared[8] according to the directions of Smith (25). *p*-Bromodimethylaniline was dried and purified by distillation, and the *o*- and *p*-bromophenols by distilling in the presence of a little benzene (water removed as a low-boiling azeotrope).

Silicon analysis. About 0.25 g. of sample was weighed into a tared platinum crucible and treated with 1 ml. of concentrated sulfuric acid. The mixture in the covered crucible

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[3] A curious inversion was observed when more than three moles of *o*-tolyllithium was added. Although there is no evidence that appreciable reaction takes place between *o*-tolyllithium and tri-*o*-tolylchlorosilane or tri-*o*-tolylethoxysilane at the temperature of refluxing ether, nevertheless, the organolithium compound is slowly consumed (presumably in a side reaction). The rate of disappearance of the "excess" *o*-tolyllithium was markedly greater when ethyl silicate rather than silicon tetrachloride was used as the starting substance. We suggest that the by-product lithium ethoxide (equation 3) catalyses the ether cleavage reaction of the organolithium compound (see Ref. 22).

[4] Melting points were determined by use of a flame-heated copper block. Values are uncorrected.

[5] We acknowledge the generous gift of this compound from the Carbide and Carbon Chemicals Corporation.

[6] The authors are grateful to Dr. Walter C. Schumb, Massachusetts Institute of Technology, for this compound.

[7] We acknowledge the generous gift of this compound from the Dow Chemical Company.

[8] This material was prepared by Mr. R. C. Wiley.

was heated with a small ring burner at a level about 2 cm. above the sulfuric acid. The acid is best evaporated and the carbon burned off using a low flame. The white residue was then heated briefly with the full force of a Fisher burner. The silica residue was weighed and calculated as percent silicon.

Silicon tests. The decomposition of organosilicon compounds on heating with acetic acid-sulfuric acid solution was first observed during an attempt to hydrolyze tri-*o*-tolylethoxysilane. Finely divided silica (or some closely related substance) was produced. Similar results were obtained when we attempted to rearrange *sym*-tetra-*o*-tolyldihydroxydisilane (I) to the unsymmetrical isomer using this reagent. These preliminary observations were extended, and treatment with the acetic-sulfuric solution was found to constitute a useful test for the presence of silicon in organic compounds or mixtures.[9,10]

A small crystal or microdrop of the test compound in a 75-mm. test tube was dissolved in a minimum amount of glacial acetic acid (2–5 drops in most cases). The mixture was heated to achieve complete solution in the case of sparingly soluble substances. An equal volume of concentrated sulfuric acid was carefully added. If silicon was present a white cloud appeared at the interface between the two acids. Heat was generated at the interface and additional heating was not required. An alternate procedure involved complete mixing of the acetic acid solution with the sulfuric acid. Here the liquid became turbid within 10–30 seconds; heating was not necessary, although it did accelerate the reaction. The two procedures were used interchangeably and are together designated as Silicon Test I.

TABLE II

THE REACTION OF TRI-*o*-TOLYSILYL DERIVATIVES ($R_3Si—$) WITH ORGANOLITHIUM COMPOUNDS (R'Li)

ORGANOSILICON COMPOUND ($R = o\text{-}CH_3C_6H_4—$)	R'Li	MOLES R'Li / G.-ATOM Si	REACTION TIME, HOURS	PRODUCT R_3SiR' MOLE-%	RECOVERED $R_3Si—$ MOLE-%
R_3SiCl	C_6H_5Li	2.5	50	80	0
R_3SiH	C_6H_5Li	2.1	50	80	0
$R_3SiOC_2H_5$	C_6H_5Li	2.5	50	<20[a]	>20[a]
R_3SiCl	*p*-$CH_3OC_6H_4Li$	5.0	36	65	0
R_3SiH	*p*-$CH_3OC_6H_4Li$	2.2	15	0	70

[a] The separation of tri-*o*-tolylphenylsilane and tri-*o*-tolylethoxysilane is difficult in view of similar solubility characteristics; only a partial separation of the crude mixture was achieved.

Positive results were obtained with the following compounds: triphenylsilane, tetraphenylsilane, triphenylsilanol, di-*o*-tolyldiphenylsilane, tri-*o*-tolylsilane, tri-*o*-tolylphenylsilane, tri-*o*-tolylsilanol,[11] tri-*o*-tolylethoxysilane, tri-*o*-tolylchlorosilane, tri-*o*-tolyldi-*n*-butylaminosilane,[11] *sym*-tetra-*o*-tolyldihydroxydisilane, tetra-*m*-tolylsilane, tetra-*p*-tolylsilane, and tri-*o*-tolyl-*p*-methoxyphenylsilane. Dimesityldiethoxysilane gave the precipitate when sulfuric was added but, in addition, a beautiful cyclamen color was produced. This color faded on dilution with water but was restored by the addition of concentrated sulfuric or strong phosphoric acid (but not strong nitric acid or acetic anhydride). Alkali had the same effect as dilution. A crude syrup believed to be largely trimesitylsilane gave an orange-brown color along with the precipitate in Silicon Test I.

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[9] The authors are grateful to Mr. B. Hofferth for assistance.

[10] The ignition of silicon-containing organic compounds generally gives an ash but this test may be unsatisfactory if the sample volatilizes on heating.

[11] The preparation of these compounds will be described in a later report.

Tetra-*o*-methoxyphenylsilane and tri-*o*-methoxyphenylethoxysilane did not give a precipitate under the above conditions. On long standing a pink color was produced in each case. When the acetic-sulfuric solution was heated to the boiling point for a few minutes a gel deposited on the wall of the test tube. Negative results under the standard conditions of the test may be attributable, in part, to the low solubility of the test substances; when a larger amount of the *o*-methoxyphenylsilane was held in solution by the use of benzene along with the other reagents, silica deposited more readily although the character of the deposit differed from that obtained in the standard test. Crude materials thought to contain hexa-*o*-tolyldisiloxane and di-*o*-tolyl "Silicones" responded to Test I. But other crudes formed in the reaction of *p*-dimethylaminophenyllithium with silicon tetrachloride gave negative results even though the test material was readily soluble in acetic acid and unquestionably had *p*-dimethylaminophenyl groups in direct combination with silicon.

We have considered the possibility that sulfuric acid merely acts as a precipitant for the organosilicon compound in Test I and that the suspended solid was the starting material rather than silica. This hypothesis finds support in the fact that *o*-methoxyphenylsilanes and *p*-dimethylaminophenylsilanes (sulfuric-soluble materials) apparently do not respond to the standard test. However, one gram of tetraphenylsilane was treated with acetic and sulfuric acids under conditions approximating those of the standard test, the precipitate was separated in 80% yield (as SiO_2) and was found to be non-organic in character. It was insoluble in the common organic solvents at the boiling point and in water, dilute acid, and dilute alkali. It was unaffected by concentrated sulfuric acid at 200° but it dissolved readily in hydrofluoric acid and in hot 30% alkali. The material powdered on a spatula, but did not char, burn or melt. While the precipitate seems to be silica, the possibility should not be overlooked that in certain cases only partial degradation occurs with the formation of insoluble siliconic acid polymers. Since sulfuric-soluble substances do not appear to give silica it may be supposed that these (or intermediate degradation products) are stabilized by salt formation.

A method was devised for testing compounds which did not respond to Silicon Test I. Here the test sample was dissolved in a few drops of concentrated sulfuric acid in a 75-mm. test tube. A drop of 70% nitric acid was added and the solution heated until nitrous fumes were no longer evolved because of the exhaustion of either the nitric acid or the organic material. If the nitric acid was used up first, another drop was added to the cooled mixture and heating was resumed until the oxidation was complete. The clear solution was then poured off and the test tube washed with water. If silicon was present in the test sample the inside of the test tube was coated with a gel. This procedure (Silicon Test II) gave positive results with all of the test materials mentioned earlier, including those which did not give a positive reaction in Silicon Test I.

Arylation of silicon compounds (General procedure). Silicon tetrachloride, ethyl orthosilicate, trichlorosilane, hexachlorodisilane, a triarylchlorosilane, a triarylethoxysilane, a triarylsilane, or a diaryldichlorosilane was measured into a 3-necked flask equipped with a sealed stirrer, graduated funnel, and reflux condenser. The sample was diluted with 5–10 volumes of anhydrous ether and a calculated amount of an aryllithium or an arylmagnesium bromide in 1–2-molar ether solution was added. In general the reaction mixture was cooled during the addition period and, without exception, the reactions were carried out under a positive pressure of dry nitrogen.[12] The mixture was then stirred for a certain period at room temperature (20°), at the temperature of refluxing ether, or at a more elevated temperature.

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[12] Good quality nitrogen was used and was further purified by passage through a train consisting of alkaline pyrogallol, sulfuric acid, and soda lime. Although every reasonable precaution was observed it must be pointed out that "absolute" protection was not afforded. When reactions were carried out over a period of many days, the RLi was slowly consumed and phenolic materials were produced.

Depending on the properties of the product the run was worked up in one of three different ways. Water-stable substances were generally isolated following hydrolysis of the reaction mixture with water, ice, or dilute acid. If a solid was present at this point it was filtered. The ether layer was then separated, dried, and the solvent evaporated. The syrupy or solid residue was treated with cold petroleum ether[13] and any resulting crystalline material was separated and further purified. This purification was almost invariably effected by recrystallization from petroleum ether, alcohol, benzene, or some combination of these solvents. In those cases where crystals could not be obtained from the crude syrup by treatment with petroleum ether, other common solvents were tried. The preliminary removal of by-products by evacuation, steam-distillation, or adsorption on alumina often proved beneficial. Seeding techniques were used in the resolution of certain syrupy mixtures. In several cases unisolable arylchlorosilanes were treated with boiling ethanol in the presence of hydrogen chloride in an effort to produce the corresponding isolable arylethoxysilanes. For convenient reference in the tables this general method for recovering the product is designated as Method X.

If crystallization could not be effected by other means, the syrup obtained after hydrolysis was distilled at reduced pressures and the individual fractions were examined and, if possible, crystallized. In certain cases recovery by distillation was found to be superior to Method X even where the crudes could be crystallized. Distillation used in conjunction with crystallization afforded the means of obtaining excellent yields of good-quality products. This procedure is called Method Y.

Water-unstable substances were recovered by distillation under nitrogen without prior hydrolysis. Here the ether solution was siphoned away from the precipitated salts and distilled or, alternately, the ether and volatile product were removed from the reaction flask directly by distillation. (The concentration of reagents and heat-treatment characteristic of this method sometimes served to drive otherwise-reluctant reactions to completion.) In either case, separation was best effected by a preliminary rapid distillation followed by redistillation under more auspicious conditions. Further redistillation or crystallization gave good-quality products. This method is referred to as Method Z.

The results of this investigation are presented in the following manner. Table III records the analyses and chief physical properties of nineteen new aromatic organosilicon compounds.[14] The experimental conditions governing the preparation (and reactions of some) of these compounds are given in Tables IV to IX along with information on other runs which either failed to yield isolable products or which resulted in the formation of significant by-products. Considered together these results furnish a comprehensive picture of the nature of steric hindrance in highly-substituted organosilicon compounds. Tables IV, V, and VI survey those runs in which silicon tetrachloride, ethyl silicate, silicochloroform, or hexachlorodisilane was treated with a given aromatic organolithium compound or Grignard reagent. The runs in Table VII were characterized by the two-stage addition of two differing organolithium compounds to ethyl silicate. Tables VIII and IX summarize those runs in which a triarylchlorosilane, triarylethoxysilane, triarylsilane, or di-*o*-tolyldichlorosilane was treated with a given aromatic organolithium compound. This report also includes a detailed description of six runs, selected to illustrate as widely as possible the techniques which were used.

Tetra-o-methoxyphenylsilane (Table IV, run 9). To a solution of 9 g. (0.053 mole) of silicon tetrachloride in 100 ml. of ether was added 153 ml. of an ether solution containing an estimated 0.210 mole of *o*-methoxyphenyllithium (mole ratio 1:3.8). The first three equivalents were consumed very rapidly [as indicated by Color Test I (21)], but the fourth reacted so slowly that after 36 hours reflux Color Test I was still positive. The reaction

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[13] Petroleum ether in this report refers to the hydrocarbon fraction, b.p. 60–68°.

[14] The chemical properties of some of these compounds will be further discussed in a later report.

TABLE III
The Properties of Some Aromatic Organosilicon Compounds

FORMULA	M.P., °C.	B.P., °C.	SOLUBILITY	Si	
				Calc'd	Found
$(C_6H_5)_3Si(o\text{-}CH_3C_6H_4)$	186.5–187.5	—	s.B; vss.P, EA	8.01	8.17
$(C_6H_5)_2Si(o\text{-}CH_3C_6H_4)_2$	174.0–174.2	—	s.B; vss.P, EA	7.70	7.66
$(o\text{-}CH_3C_6H_4)_3SiH$	89–90	190–192/2 mm.	vs.B, P, EA	9.28	9.08
$(o\text{-}CH_3C_6H_4)_3Si(C_6H_5)$	195.5–195.9	—	s.B; ss.P, EA	7.41	7.32
$(o\text{-}CH_3OC_6H_4)_3Si(o\text{-}CH_3C_6H_4)$	193.5–194.0	—	s.B; ss.P, EA	6.37	6.53
$(o\text{-}CH_3OC_6H_4)_4Si$	224.0–224.5	—	s.B; vss.EA, EE	6.14	6.27
$(o\text{-}CH_3C_6H_4)_3Si(p\text{-}CH_3OC_6H_4)$	179–180	—	vs.B; ss.P, EA	6.88	6.80
$(o\text{-}CH_3OC_6H_4)_3Si(p\text{-}CH_3OC_6H_4)$	178–180	—	vs.B; ss.P, EA	6.14	6.01
$(o\text{-}CH_3C_6H_4)_3SiCl$	115.5–116.0	*ca.* 250/19 mm.	vs.B; s.P; ss.EA(d.)	8.33[a]	8.34
$(o\text{-}CH_3C_6H_4)_3SiOC_2H_5$	144.5–145.0	—	vs.B; ss.P, EA	8.10	8.02
$(o\text{-}CH_3C_6H_4)_3SiOC_6H_4CH_3\text{-}(o)$	153–154	*ca.* 225/2 mm.	vs.c.B, c.C, h.P, h.EA	6.88[b]	7.03
$(o\text{-}CH_3OC_6H_4)_3SiOC_2H_5$	102–104	—	vs.B; ss.P, EA; s.h.EA	7.11	7.03
$(o\text{-}CH_3C_6H_4)_2Si(OH)_2$	135.5–136.5	—	vs.A; s.h.P; ss.c.P	11.48[c]	11.56
$(o\text{-}CH_3C_6H_4)_2SiCl_2$	74–75	138–140/1 mm.	vs.A, h.P; ss.c.P; d.EA	10.00[d]	9.90
$(o\text{-}CH_3C_6H_4)_2Si(OC_2H_5)_2$	57.0–58.5	185–190/18 mm.	vs.B; s.c.P, h.M, h.EA	9.34	9.37
$[2,4,6\text{-}(CH_3)_3C_6H_2]_2Si(OC_2H_5)_2$	63.5–64.0	138–140/0.2 mm.	vs.B; s.P, EA	7.87	7.98
$[p\text{-}(CH_3)_2NC_6H_4]_2Si(OC_2H_5)_2$	—[e]	229–231/3 mm.	vs.; s.dil.acid (d.)	7.82[f]	7.76
$[p\text{-}(CH_3)_2NC_6H_4]Si(OC_2H_5)_3$	—[g]	144–146/2 mm.	vs.; s.dil.acid (d.)	9.90[h]	9.70
$[(o\text{-}CH_3C_6H_4)_2SiOH]_2$	158.0–158.5	—	s.B, EE, h.P; vss.c.P	12.35[i]	12.03

A = acetone; B = benzene; C = carbon tetrachloride; EA = ethyl alcohol; EE = ethyl ether; M = methyl alcohol; P = petroleum ether; vs. = very soluble; s. = soluble; ss. = slightly soluble; vss. = very slightly soluble; h. = hot; c. = cold; d. = decomposed.

[a] Calc'd for $C_{21}H_{21}ClSi$: Cl, 10.52. Found: Cl, 10.47. [b] Calc'd for $C_{28}H_{28}OSi$: C, 82.30; H, 6.92. Found: C, 81.78; H, 7.25. [c] Calc'd for $C_{14}H_{16}O_2Si$: Active hydrogens, 2.00. Found: Active hydrogens, 1.94, 2.10. (Zerewitinoff determinations by Mr. J. S. Ahmann). [d] Calc'd for $C_{14}H_{14}Cl_2Si$: Cl, 25.20. Found: Cl, 25.15. [e] d_4^{25} 1.102; n_D^{25} 1.5765. (The density may be in error). [f] Calc'd for $C_{20}H_{30}N_2O_2Si$: Neut. equiv., 179.3; MR_D^{25} 106.84. Found: Neut. equiv. 179.6; MR_D^{25} 107.76. [g] d_4^{25} 1.012; n_D^{25} 1.5012. (The density may be in error). [h] Calc'd for $C_{14}H_{25}NO_3Si$: MR_D^{25} 79.34. Found: MR_D^{25} 82.55. [i] Calc'd for $C_{28}H_{30}O_2Si_2$: Active hydrogens, 2.00. Found: Active hydrogens, 2.06. (Zerewitinoff determination by Mr. J. S. Ahmann).

TABLE IV

THE REACTION OF SILICON TETRACHLORIDE WITH RM COMPOUNDS; SEE EQUATIONS 1, 8, AND 14 (ALSO 11–13, 15–22)

NO.	MOLES $SiCl_4$	MOLES RM / G.-ATOM Si	REACTION CONDITIONS TIME/TEMP., °C.	PRODUCT	METHOD PRODUCT RECOVERY AND RECRYST. SOLVENT	YIELD[a], %	M.P., °C.
1[b]	0.400	2.1 o-$CH_3C_6H_4MgBr$	10 hr./35[c] —/dist.[d]	R_2SiCl_2[e, f]	$\underline{Z}$ (dist.) (2) P P (2)	45 35 12	65–69[g] 71.0–72.5[g] 74–75[g]
2	.018	5.0 o-$CH_3C_6H_4MgBr$	72 hr./170	—[h]	$\underline{X}$ and $\underline{Y}$		
3	.274	2.9 o-$CH_3C_6H_4Li$	15 hr./20 0.3 hr./35[d]	R_3SiCl[i]	$\underline{Y}$ (dist.)[j] P	65 55[k]	 110–114
4[b]	.350	3.0 o-$CH_3C_6H_4Li$	20 hr./20 1 hr./35[c]	R_3SiCl[e] $R_3SiOC_2H_5$[i, l]	$\underline{Y}$ EE, (dist.) P (dist.) P (3)	96 75 3 1	107–116 115.5–116.0 130–136 153–154
5	.012	4.9 o-$CH_3C_6H_4Li$	172 hr./35[c]	$R_3SiOC_2H_5$[i]	$\underline{Y}$[m] P EA	10 5	137–139 143–144
6	.040	5.2 o-$CH_3C_6H_4Li$	18 hr./35[c]	R_3SiCl[i]	$\underline{X}$[n] EE P	90 70	95–114 113–116
7	.022	4.5 m-$CH_3C_6H_4Li$	2 hr./35	R_4Si[o]	$\underline{X}$ EA EA	27 14	135–150 152.5–153.5
8	.045	4.4 p-$CH_3C_6H_4Li$	2 hr./20	R_4Si[p, q]	$\underline{X}$ EE B-EA	82 48	156–225 227.5–228.5
9[b]	.053	3.8 o-$CH_3OC_6H_4Li$	36 hr./35[c, r]	R_4Si-R_3SiCl[p, e] R_4Si[e]	$\underline{X}$ EE EE, B, B-P, B-EA	97 50	175–205 224.0–224.5
10	.007	4.2 p-$CH_3OC_6H_4Li$	10 hr./35	—[s]	$\underline{X}$		
11	.013	11.0 p-$CH_3OC_6H_4Li$	48 hr./35	—[s]	$\underline{X}$		
12[b]	.080	2.0 p-$(CH_3)_2NC_6H_4Li$	1 hr./20	R_2SiCl_2 (?)	$\underline{Z}$ (dist.)	3	140–155

Consult Table III on the use of abbreviations.

$\underline{X}$, $\underline{Y}$, and $\underline{Z}$ refer to the method of product recovery as described in the text of this report.

[a] Yields are calculated on the $SiCl_4$ basis. [b] This run is described in detail in the text of this report. [c] Color Test I was positive at this stage (See Ref. 21). [d] Color Test I was negative at this stage. [e] The product was characterized by analysis. [f] The by-product $RSiCl_3$ was not isolated in the pure state, but it apparently boils at about 230°/745 mm. [g] The analysis improved as the purification proceeded. Calc'd for $C_{14}H_{14}Cl_2Si$: Cl, 25.20; Si, 10.00. Found (after successive purifications): Cl, 21.85, 24.05, and 25.15; Si, 9.30, 9.90, and 9.90. [h] Crystalline products could not be obtained. This run confirms the earlier work of Schumb and Saffer (See Ref. 2). [i] The product was characterized by mixed melting point with an analyzed sample. [j] The fraction b.p. 245-265°/19 mm. was recrystallized. [k] When 2.8 moles RLi was used 45% R_3SiCl and 7% crude $R_3SiOC_2H_5$ were isolated. [l] The preparation of this compound by another method will be described in a later report. [m] No crystalline products could be isolated by the ordinary means. The $R_3SiOC_2H_5$ was isolated after a fraction boiling 165-175°/0.1 mm. was allowed to stand in contact with cold petroleum ether for three months. The result was confirmed by another run where $SiCl_4$ was added to 4.3 moles RLi. [n] No R_4Si could be found in a careful search. [o] Schumb and Saffer (Ref. 2) prepared this material in 8% yield by the action of m-$CH_3C_6H_4MgBr$ on $SiCl_4$ at 175°. Reported m.p. 150.8°. [p] The product was insoluble in ether and was filtered directly from the reaction liquor. [q] Schumb and Saffer (Ref. 2) prepared this material in 35% yield by the action of p-$CH_3C_6H_4MgBr$ on $SiCl_4$ at 175°. Reported m.p. 228°. [r] Note the reluctance with which the fourth o-anisyl group goes into the silicon. [s] No crystalline products could be obtained.

mixture was poured into water; 20 g. of solid material was filtered off. Since an additional 3.5 g. of crude solid was isolated after evaporation of the ether solution the conversion of silicon tetrachloride to solid anisylsilanes must have been near-quantitative (theoretical R_4Si, 24.2 g.). The crude product (m.p. 175–205°) was apparently a mixture of R_4Si and R_3SiCl and the separation of these materials proved difficult. Ether extraction followed by six wasteful crystallizations from benzene, benzene-petroleum ether, and benzene-alcohol gave 5 g. (20%) of tetra-*o*-methoxyphenylsilane, m.p. 224.0–224.5°. When the crude residues were refluxed for a prolonged period of time with a mixture of benzene and alcohol, the tri-*o*-methoxyphenylchlorosilane was apparently converted to the more soluble ethoxysilane

$$R_3SiCl + C_2H_5OH \xrightarrow[\text{Na, or Li}]{\text{aq. HCl,}} R_3SiOC_2H_5 + HCl \qquad 11.$$

(where $R = o\text{-}CH_3OC_6H_4-$) and additional tetra-*o*-methoxyphenylsilane (total 50%) was readily isolated. Tri-*o*-methoxyphenylchlorosilane could not be isolated in the pure state (although it was later prepared by the action of three moles of *o*-methoxyphenyllithium on silicon tetrachloride[3]), but a eutectic mixture containing 70 mole-percent of the chlorosilane and 30 mole-percent of the tetraarylsilane separated out. This material melted in the range 186–189° without previous shrinking and could be recrystallized from benzene-petroleum ether or from benzene-ethyl ether without changing its melting point.

Anal. Calc'd for 70 mole-% $C_{21}H_{21}ClO_3Si$ and 30 mole-% $C_{28}H_{28}O_4Si$: Si, 6.91; Cl, 6.12.
Found: Si, 6.71; Cl, 6.15.

That the mixture had this composition is supported by the fact that 4.4 g. of the eutectic after treatment with ethanol and benzene gave 1.4 g. of R_4Si. The ethoxysilane was not isolated here.

The formation of the R_3SiCl and R_4Si in the arylation reaction is represented by equations 1 and 8 where $R = o\text{-}CH_3OC_6H_4-$. The technique of product recovery is illustrative of Method X.

Sym-tetra-o-tolyldihydroxydisilane (I) (Table VI, run 5). To a solution of 3.16 g. (0.0118 mole) of hexachlorodisilane in 50 ml. ether was added 70 ml. of an ether solution containing an estimated 0.085 mole of *o*-tolyllithium (mole ratio 1:7.2). After refluxing for 26 hours Color Test I was still positive. Water was added to the reaction mixture and after standing for 36 hours, the ether layer was separated, washed, and dried. Subsequent to evaporation of the solvent and treatment of the residual syrup with petroleum ether, there was obtained 2.7 g. of a white crystalline solid, m.p. 156–158°, and 1.4 g. of less pure material, m.p. 147–153°. The total crude yield was 75%. One recrystallization from solution in benzene-petroleum ether (1:10) gave an over-all yield of 55% of pure I, m.p. 158.0–158.5°. This product contained no chlorine. The results of another run (Table VI, run 4) indicate that *sym*-tetra-*o*-tolyldichlorodisilane is the compound that is formed in the arylation reaction, I being produced only after prolonged standing with water. The over-all reaction is represented by equation 6 and the technique of product recovery is once again illustrative of Method X.

The properties of this interesting compound will be discussed in greater detail in a subsequent report. We favor the symmetrical over the unsymmetrical formula in view of the general instability of *gem*-diols among monosilanes and the high reactivity of diaryldichlorosilanes.

Tri-o-tolylchlorosilane (Table IV, run 4). To a cooled solution of 59.5 g. (0.350 mole) silicon tetrachloride in 220 ml. ether was slowly added 1136 ml. of 0.935 *M* *o*-tolyllithium in ether (mole ratio 1:3.0). The reaction mixture was stirred at room temperature for 20 hours and at 35° for one hour. Color Test I was still positive. The mixture was then poured onto 1000 g. of iced-water. The ether layer was separated and dried. During evaporation of the ether two crops of crystalline tri-*o*-tolylchlorosilane were filtered off: 71 g., m.p. 115–116°, and 28.5 g., m.p. 111–113°. The syrupy residue was distilled under reduced pressure. The fraction of b.p. 185–195°/2 mm. gave 13.6 g. of crude tri-*o*-tolylchlorosilane (m.p.

TABLE V

The Reaction of Ethyl Silicate with RM Compounds; See Equations 3 and 7

NO.	MOLES $Si(OC_2H_5)_4$	MOLES RM / G.-ATOM Si	REACTION CONDITIONS TIME/TEMP., °C.	PRODUCT	METHOD PRODUCT RECOVERY AND RECRYST. SOLVENT	YIELD[a], %	M.P., °C.
1	0.018	4.0 *o*-$CH_3C_6H_4MgBr$	240 hr./35[b]	—[c]	$\underline{X}$		
2[g]	.310	3.0 *o*-$CH_3C_6H_4Li$	3 hr./35[d]	$R_3SiOC_2H_5$[e]	$\underline{Y}$ P	57	139–145
			100 hr./20	$R_2Si(OC_2H_5)_2$[f]	(dist.)	30	36–41
					EA, M	18	57.0–58.5
3	.200	8.4 *o*-$CH_3C_6H_4Li$	48 hr./35[d, h]	$R_3SiOC_2H_5$[i, j]	$\underline{X}$ and $\underline{Y}$ B-EA	75	135–140
					B-P	50	143–144
				R_4Si (?)[k]	B-EA	2.3	290–330
					B-EA (2)	1.0	342–344
4	.020	12.7 *sym*-$(CH_3)_3C_6H_2Li$	120 hr./35[b]	$R_2Si(OC_2H_5)_2$[i]	$\underline{Y}$ (dist.)[p]	62	57–61
					EA (—20°)		63.5–64.0
5	.016	3.0 *o*-$CH_3OC_6H_4Li$	2 hr./35	$R_3SiOC_2H_5$[f]	$\underline{X}$ P	75	83–110
					EA (2)	35	102–104
6	.010	7.2 *o*-$LiOC_6H_4Li$[l, m]	10 hr./35[b]	—[n]	$\underline{X}$ M-H_2O	(1.7 g.)	50–90
	.030	1.8	30 hr./35[d]		From alk. with acid	(0.3 g.)	197–198
7	.025	4.8 *p*-$LiOC_6H_4Li$[l]	14 hr./35[d]	—[o]	$\underline{X}$		
8	.013	2.0 *p*-$(CH_3)_2NC_6H_4Li$	19 hr./20[d]	$R_2Si(OC_2H_5)_2$[f]	$\underline{Y}$[p] (dist.) (2)	37	—[q]
9[r]	.106	2.0 *p*-$(CH_3)_2NC_6H_4Li$	24 hr./20[d]	$R_2Si(OC_2H_5)_2$[s]	$\underline{Z}$ (dist.) (3)	55	—[u]
				$RSi(OC_2H_5)_3$[f, t]	(dist.) (2)	10	—[v]

[a] Yields are calculated on the $Si(OC_2H_5)_4$ basis. [b] Color Test I was positive. [c] Only syrupy products could be isolated. [d] Color Test I was negative. [e] This product was purified by recrystallization from petroleum ether and was identified by mixed melting point with an analyzed sample. [f] Characterized by analysis. [g] In a somewhat smaller run carried out under similar conditions the yield of crude $R_3SiOC_2H_5$ (m.p. 125–145°) was 61%. Recrystallization from petroleum ether and from ethanol gave a 55% over-all yield of pure $R_3SiOC_2H_5$ (m.p. 144.5–145.0°). Dr. R. N. Clark of these laboratories observed the formation of a little R_3SiCl along with the $R_3SiOC_2H_5$ when 0.040 mole of $Si(OC_2H_5)_4$ was treated with four equivalents of *o*-tolyllithium. The identity of this by-product was established by mixed melting point and by analysis, but we have been unable to confirm the formation of this material in other runs. It is possible that the ethyl silicate was contaminated with a little chlorosilane. Otherwise the only source of chlorine was the dilute hydrochloric acid used for hydrolysis; however, neither R_3SiOH nor $R_3SiOC_2H_5$ is changed into R_3SiCl under these conditions. [h] After refluxing under nitrogen for a short time the reaction mixture turned intensely red-brown. [i] Characterized by mixed melting point with an analyzed sample. [j] Actually, the reaction mixture was divided into several portions: one part was treated with methyl iodide before hydrolysis, a second with absolute ethanol, and a third with carbon dioxide. In each case the intense color of the reaction mixture was immediately discharged and, on working up, no significant differences in yields were apparent. The values given are for that portion which was treated with ethanol prior to hydrolysis. [k] This material is identical with that isolated in run 9, Table VIII. It may be an isomer of that tetra-*o*-tolylsilane which melts at 230° (See footnote 1).

$$4\ RLi + Si(OC_2H_5)_4 \xrightarrow{35^\circ} R_4Si + 4\ LiOC_2H_5$$

The properties of this material will be discussed in a later report. [l] These materials were prepared by treating *o*-or *p*-bromophenol with *n*-butyllithium:

$$HOC_6H_4Br + 2\ n\text{-}C_4H_9Li \rightarrow LiOC_6H_4Li + n\text{-}C_4H_9Br + n\text{-}C_4H_{10}$$

[m] Ethyl silicate (0.010 mole) was added to an estimated 7.2 equivalents of *o*-$LiOC_6H_4Li$ and the mixture was refluxed for ten hours. Since Color Test I was positive at this stage three additional 0.010-mole portions of ethyl silicate were added at intervals. When 0.040 mole had been added and the whole refluxed for 30 hours Color Test I was negative. The reaction mixture was hydrolyzed with dilute hydrochloric acid. [n] A small amount of solid was obtained from the syrupy reaction product by diluting a methanol solution with water. This material contained silicon and was alkali-soluble. Repeated precipitation from alkaline solution with acid gave a small amount of higher-melting material. This may have been a hydroxyphenylsilicon compound. [o] Some *p*-HOC_6H_4Br was recovered unchanged but besides this only syrupy products could be isolated. [p] Note the stability of the $R_2Si(OC_2H_5)_2$ to water. [q] Boiling range 222–224°/2 mm. [r] The results of this experiment were confirmed in all important details in another run. [s] Identified by comparison with an analyzed sample.

$$^{t}\ RLi + Si(OC_2H_5)_4 \xrightarrow{35^\circ} RSi(OC_2H_5)_3 + LiOC_2H_5$$

[u] Boiling range 229–231°/3 mm. [v] Boiling range 144–146°/2 mm.

TABLE VI

THE REACTION OF TRICHLOROSILANE AND HEXACHLORODISILANE WITH RM COMPOUNDS; SEE EQUATIONS 2 AND 6

NO.	MOLES $HSiCl_3$ OR Si_2Cl_6	$\frac{\text{MOLES RM}}{\text{G.-ATOM Si}}$	REACTION CONDITIONS TIME/TEMP., °C.	PRODUCT	METHOD PRODUCT RECOVERY AND RECRYST. SOLVENT	YIELD[a], %	M.P., °C.
1	0.250 $HSiCl_3$	4.7 *o*-$CH_3C_6H_4MgBr$	72 hr./35 48 hr./20[b]	R_3SiH[c]	Y (dist.)[d] (redist.)[d] EA, P (−20°)	65 50	75–80 85–90 89–90
2	.050 $HSiCl_3$	5.0 *o*-$CH_3C_6H_4Li$	14 hr./35[b]	R_3SiH[e, f]	X P EA (−20°)	50	85–90 89–90
3[g]	.350 $HSiCl_3$	5.0 *sym*-$(CH_3)_3C_6H_2Li$	120 hr./35[b, h]	—[i]	Y and Z		
4	.020 Si_2Cl_6[j]	1.9 *o*-$CH_3C_6H_4Li$ 0.3 *o*-$CH_3C_6H_4Li$	0.1 hr./35[k, l] 0.2 hr./35[h]	$(R_2SiOH)_2$[c, p] |	X P B-P (3)	42 20	120–135 156.0–158.5
5[m]	.012 Si_2Cl_6	3.6 *o*-$CH_3C_6H_4Li$	26 hr./35[h]	$(R_2SiOH)_2$[f] |	X P B-P	75 55	147–158 158.0–158.5
6	.002 Si_2Cl_6	12.5 *o*-$CH_3C_6H_4Li$	48 hr./135[m, h]	—[o]	X		

[a] Yields are calculated on the $HSiCl_3$ or Si_2Cl_6 basis. [b] No hydrogen was evolved on dilution. [c] Characterized by mixed melting point with an analyzed sample. [d] The crude reaction product was distilled. The R_3SiH came over in the range 185–195°/2 mm. and on redistillation in the range 190–192°/2 mm. Other syrupy products were isolated which gave proximate analyses for R_3SiOH and R_3SiCl but these could not be crystallized. The non-volatile residue (b.p. > 260°/2 mm.) analyzed for $(R_3Si)_2O$ but this too could not be crystallized. It is of interest that Taurke (26) has presented evidence that sodium, isoamyl chloride, and silicochloroform give hexaisoamyldisiloxane along with other products. [e] No tetra-*o*-tolylsilane could be found. [f] Characterized by analysis. [g] The run was carried out in collaboration with Mr. R. C. Wiley. [h] Color Test I was positive. [i] No crystalline products could be isolated. When distilled without prior hydrolysis 40% of the anticipated material boiled in the range 150–210°/0.5 mm. After redistillation a syrupy fraction (b.p. 165–175°/0.5 mm.) was obtained which gave a proximate silicon analysis for R_3SiH. However, this material discolored in air and contained appreciable amounts of chlorine. A portion of the original reaction liquor which was first hydrolyzed and then distilled gave only 10% of the anticipated material boiling in the range 150–210°/0.5 mm. Thus it appears that anhydrous distillation furthered the arylation reaction giving R_3SiH while hydrolysis stopped the arylation reaction and subsequent distillation resulted in decomposition of the lesser-substituted chloro- and hydroxy-silanes. [j] The hexachlorodisilane used in this run was of inferior quality. [k] Color Test I was negative. [l] The first four moles of RLi (per mole of Si_2Cl_6) reacted very rapidly, the next more slowly if at all. [m] This run is described in detail elsewhere in this report. [n] Xylene was added and the ether was removed by distillation. [o] The syrupy reaction products could not be crystallized. [p] The crude product was extensively contaminated with chlorine-containing compounds and was difficult to purify. This indicated that the *sym*-tetra-*o*-tolyldichlorodisilane was the intermediate product and tha this went over into the hydroxy compound on prolonged standing in contact with water. (In run 4 the hydrolysis time was 0.1 hour while in run 5 it was 100 hours.) When the crude chlorine-containing mixture was shaken with aqueous ammonia additional $(R_2SiOH)_2$ was isolated.

107–112°) after treatment with petroleum ether (total crude yield 96%). The fraction of b.p. 220–230°/2 mm. weighed 4.1 g.; this gave a crystalline solid, m.p. 130–136°, after treatment with petroleum ether. The tri-*o*-tolylchlorosilane was purified by recrystallization from petroleum ether and a 75% recovery of material was realized, m.p. 115.5–116.0°. The higher-melting solid was recrystallized from petroleum ether, benzene-alcohol, and several times from benzene-petroleum ether. The final product (yield 1%) had m.p. 153–154°. This compound, tri-*o*-tolyl-*o*-tolyloxysilane, was identical with that prepared directly from tri-*o*-tolylchlorosilane and sodium *o*-cresoxide, and on hydrolysis it gave tri-*o*-tolylsilanol and *o*-cresol.[15] The reactions which result in the formation of this compound may be the following:

$$o\text{-}CH_3C_6H_4Li + \tfrac{1}{2}O_2 \rightarrow o\text{-}CH_3C_6H_4OLi \qquad 12.$$

$$(o\text{-}CH_3C_6H_4)_3SiCl + o\text{-}CH_3C_6H_4OLi \xrightarrow{\text{distilled}} (o\text{-}CH_3C_6H_4)_3SiOC_6H_4CH_3\text{-}(o) + LiCl \qquad 13.$$

The formation of tri-*o*-tolylchlorosilane in the arylation reaction is represented by equation 1 where $R = o\text{-}CH_3C_6H_4-$. The technique of product recovery used here is illustrative of Method Y.

In another (smaller) run where the product was isolated by Method X the yield of crude R_3SiCl was 85% and the formation of R_3SiOR was not noted. When 2.9 and 2.8 moles of RLi were used per mole of silicon tetrachloride the yields of R_3SiCl were substantially lower (66% and 45%, respectively). Excess RLi probably does not affect the yield adversely (see run 6) although in a pair of runs where 4.3 and 4.9 moles of RLi were used no R_3SiCl could be isolated. $R_3SiOC_2H_5$ was isolated in small yield from each of three different runs. This by-product may have resulted from the interaction of R_3SiCl with sodium or lithium ethoxide [from the sodium-dried ether or from an ether cleavage reaction (22)]; the reaction would be similar to that represented by equation 13. In those runs where RLi was used in excess there was no suggestion whatever that any R_4Si was formed.

Ethyl silicate with mesityllithium and phenyllithium (Table VII, run 4). To 1.25 g. (0.006 mole) of ethyl silicate in 25 ml. of ether was added 0.078 mole of mesityllithium in 50 ml. of ether (mole ratio 1:13.0). The mixture was refluxed for 120 hours; at the end of this time Color Test I was still positive. Two-thirds of the reaction mixture was separated and treated with 0.024 mole of phenyllithium (mole ratio 1:6.0) and the whole was refluxed for an additional 48 hours. After acid hydrolysis and evaporation of the ether no crystalline material could be obtained, but distillation gave 0.7 g. (50% yield) of crude dimesityldiethoxysilane b.p. 138–140°/0.2 mm., m.p. 57–63°. Three recrystallizations of this material from petroleum ether gave 0.24 g. of pure dimesityldiethoxysilane, m.p. 64.8–65.2°. Dimesityldiethoxysilane of similar quality was recovered in approximately the same yield from the one-third of the original reaction mixture which had been treated with mesityllithium alone. There was no evidence to suggest that mesitylphenylsilanes had formed.

The arylation reaction is represented by equation 7 where $R = sym\text{-}(CH_3)_3C_6H_2-$, and the technique of product recovery is illustrative of Method Y.

Di-o-tolyldichlorosilane (Table IV, run 1). To a solution of 68.0 g. (0.400 mole) of silicon tetrachloride in 200 ml. of ether was slowly added a solution of 0.823 mole of *o*-tolylmagnesium bromide in 350 ml. of ether (mole ratio 1:2.1). The addition was carried out at 0° and the mixture was then heated at 35° for 10 hours. Color Test I was still positive. The clear solution was siphoned from the precipitated salts. As the ether was removed from this solution by distillation further reaction took place with the consumption of the remaining Grignard reagent and the precipitation of additional salt. The siphoning and distilling operations were carried out under nitrogen. The volatile material boiling in the range 55°/760 mm. to 210°/10 mm. was collected and then redistilled. There was obtained

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[15] This work will be described in a later report.

TABLE VII

THE TWO-STAGE REACTION OF ETHYL SILICATE WITH RM AND R'M; SEE EQUATIONS 3 AND 7

NO.	MOLES $Si(OC_2H_5)_4$	MOLES RM (R'M) / G.-ATOM Si	REACTION CONDITIONS TIME/TEMP., °C.	PRODUCT	METHOD PRODUCT RECOVERY AND RECRYST. SOLVENT	YIELD[a], %	M.P., °C.
1	0.003	3.0 *o*-$CH_3C_6H_4Li$ 6.0 C_6H_5Li[b]	(R) 5 hr./20[c] (R') 48 hr./35[d], [e]	—[f] $R_2SiR'_2$[g], [j]	X (evap. EE) B-EA (4)	95 5	95–130 174.0–174.2
2	.003	3.0 *o*-$CH_3C_6H_4Li$ 2.0 *m*-$CH_3C_6H_4Li$	(R) 24 hr./20[c] (R') 28 hr./35[c]	$R_3SiOC_2H_5$[g]	X P P	50	135–140 143–144
3	.003	3.0 *o*-$CH_3C_6H_4Li$ 2.0 *sym*-$(CH_3)_3C_6H_2Li$	(R) 160 hr./20[c] (R') 120 hr./35[d]	$R_3SiOC_2H_5$[g]	X P P	50	130–140 143–144
4[h]	.004	13.0 *sym*-$(CH_3)_3C_6H_2Li$ 6.0 C_6H_5Li	(R) 120 hr./35[d] (R') 48 hr./35[d]	$R_2Si(OC_2H_5)_2$[i]	Y (dist.) P P (3)	50 20	57–63 64.8–65.2

[a] The yields are calculated on the $Si(OC_2H_5)_4$ basis. [b] The phenyllithium was of inferior quality. [c] Color Test I was negative. [d] Color Test I was positive. [e] During the second stage of the reaction the ether evaporated and a much higher temperature was attained. [f] The crude product was probably a mixture of the $R_2SiR'_2$, R_3SiR', and $R_3SiOC_2H_5$. [g] This product was characterized by mixed melting point with an analyzed sample. [h] This run is described in detail elsewhere in this report. [i] This product was characterized by analysis. [j] $2\ RLi + 2\ R'Li + Si(OC_2H_5)_4 \xrightarrow{35°} R_2SiR'_2 + 4\ LiOC_2H_5$.

54 g. (50% yield) of crude di-*o*-tolyldichlorosilane b.p. 155–165°/5 mm., m.p. 65–69°. This fraction was itself distilled giving a 90% recovery of material b.p. 138–140°/1 mm., m.p. 65–69°. Analysis showed that this product was impure (see footnote *g*, Table IV). One recrystallization from petroleum ether gave a 75% recovery of moderately pure product, m.p. 71.0–72.5° (analysis Table IV). One gram of this material was twice recrystallized from petroleum ether with the resulting 35% recovery of pure di-*o*-tolyldichlorosilane, m.p. 74–75°. The reaction is represented by equation 14 where R = $o\text{-}CH_3C_6H_4-$ and M = – MgBr.

$$2\ RM + SiCl_4 \xrightarrow{35^\circ} R_2SiCl_2 + 2\ MCl \qquad 14.$$

The technique of product recovery is illustrative of Method Z.

Silicon tetrachloride with p-dimethylaminophenyllithium[16] (Table IV, run 12). To a solution of 13.6 g. (0.080 mole) of silicon tetrachloride in 50 ml. of ether was added 0.160 mole of *p*-dimethylaminophenyllithium in 150 ml. of ether (mole ratio 1:2.0). The temperature was held at 0° during the addition period. At the beginning of the reaction an intense blue color was produced[17] and a white precipitate formed. After 90 minutes at 0° and one hour at 25° the mixture was filtered under nitrogen and the precipitated white and blue solids were separated from the clear brown solution. The filtrate further precipitated a small amount of the blue solid after contact with air. This was filtered off and the filtrate now gave no reaction on exposure to the atmosphere (the solid materials removed by filtration as described above were not studied). A syrupy residue was obtained after evaporation of the ether; its weight corresponded to only about 10–15% of the expected yield of organosilicon products. This residue was distilled and three grams of material, b.p. 100–200°/0.5 mm., was collected. The non-volatile residue was a highly-colored (blue, brown, and orange), vile-smelling solid. The volatile portion solidified in the receiver. On treating this with petroleum ether two crops of crystals were obtained: 1.0 g., m.p. 140–155° (*Product A*, white, slowly turns pink on standing in air); and 0.5 g., m.p. *ca.* 70° (white, quickly turns red). Both materials gave purple liquids on fusion. Both gave negative results with Silicon Test I (although very soluble in acetic acid), but positive results with Silicon Test II. Product A was insoluble in water and in the common neutral organic solvents, but it was soluble in both dilute acid and dilute alkali. A nitric acid solution of *A* gave a heavy precipitate of silver chloride on treatment with aqueous silver nitrate, but a neutral aqueous suspension of *A* gave no reaction. On neutralization of either the acid or alkaline solution of *A*, a white solid precipitated (m.p. *ca.* 155°). This material itself was soluble in both acid and alkali, but repeated precipitation of the same sample or prolonged standing in acid or alkaline solution gradually reduced the alkali solubility to zero. The unused portion of *Product A* was redistilled in an atmosphere of nitrogen and at reduced pressure but extensive decomposition took place. The volatile material (*Product B*) solidified in the receiver; it melted at about 70°. The odor of dimethylaniline was prominent. *B* was insoluble in water, in dilute alkali, and in the common neutral organic solvents. It dissolved readily in dilute acid but not dilute alkali. The non-volatile residue was insoluble in all solvents and charred on a spatula without melting. It did not contain any significant amount of chlorine. Silicon Test I was negative, but Silicon Test II was positive.

In view of the low yields, questionable purity, and lack of analytical data, the nature of the products cannot be defined with confidence. The arylation reaction is certainly abnormal and distinctly novel products might justifiably be expected. It seems fairly certain that *Product A* is a *p*-dimethylaminophenylsilicon derivative, but the alkali solubility is

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[16] The observations reported here confirm and extend the earlier findings of Mr. R. C. Wiley.

[17] The blue color seems to be related directly to the reaction between silicon tetrachloride and the RLi compound since *p*-dimethylaminophenyllithium did not give the same reaction with anhydrous hydrogen chloride.

TABLE VIII

THE REACTION OF R_3SiCl, $R_3SiOC_2H_5$, AND R_3SiH COMPOUNDS WITH R'Li COMPOUNDS; SEE EQUATIONS 4, 9, AND 10

NO.	MOLES ORGANOSILICON COMPOUND	$\frac{\text{MOLES R'Li}}{\text{G.-ATOM Si}}$	REACTION CONDITIONS TIME/TEMP., °C.	PRODUCT	METHOD PRODUCT RECOVERY AND RECRYST. SOLVENT	YIELD[a], %	M.P., °C.
1	0.005 (o-$CH_3C_6H_4)_3SiCl$	2.5 C_6H_5Li	50 hr./35	R_3SiR'[b]	X EE (evap.) B-EA	80	190–193 195–196
2	.007 (o-$CH_3C_6H_4)_3SiCl$	10.0 o-$CH_3C_6H_4Li$	240 hr./35[c]	—[d]	X and Y		
3	.008 (o-$CH_3C_6H_4)_3SiCl$	1.4 p-$CH_3C_6H_4Li$[e]	10 hr./35[f]	R_3SiCl[b]	X P	30	114–116
4	.006 (o-$CH_3C_6H_4)_3SiCl$	4.0 o-$CH_3OC_6H_4Li$	48 hr./35	R_3SiCl[b]	X P P	90 65	112–116 115–116
5	.010 (o-$CH_3C_6H_4)_3SiCl$	5.4 p-$CH_3OC_6H_4Li$	36 hr./35	R_3SiR'[g]	X EE (evap.) P	90 60	169–175 179–180
6	.004 (o-$CH_3OC_6H_4)_3SiCl$	5.0 o-$CH_3OC_6H_4Li$	48 hr./35	R_3SiR'[b] (= R_4Si)	X B-EA B-EA	95	215–221 223.5–224.0
7	.005 (o-$CH_3C_6H_4)_3SiOC_2H_5$	2.5 C_6H_5Li	50 hr./35	—[h] R_3SiR'[b] $R_3SiOC_2H_5$[b]	X EE (evap.) B-EA (2) B-EA (2)	80 <20 >20	140–160 193.5–195.0 142–143
8	.005 (o-$CH_3C_6H_4)_3SiOC_2H_5$	10.0 C_6H_5Li	15 hr./150	R_3SiR'[b, i]	X P P	43	187–195 195–196
9	.029 (o-$CH_3C_6H_4)_3SiOC_2H_5$	2.0 o-$CH_3C_6H_4Li$	168 hr./35[j, f]	$R_3SiOC_2H_5$[b] $R_3SiR'(R_4Si)$[k]	X P B-EA B-EA (2)	60 2.5	135–140 143–144 342–344

10	.001 (o-$CH_3OC_6H_4)_3SiOC_2H_5$	8.0 o-$CH_3C_6H_4Li$	15 hr./35	$R_3SiR'^g$	$\underline{X}$ EE (evap.) P	85 75	180–188 193.5–194.0
11	.003 (o-$CH_3OC_6H_4)_3SiOC_2H_5$	1.1 p-$CH_3OC_6H_4Li$	24 hr./35^f	$R_3SiR'^g$	$\underline{X}$ EE (evap.) B-EA (2)	90 50	105–150 178–180
12	.012 $(C_6H_5)_3SiH^l$	1.5 o-$CH_3C_6H_4Li$	48 hr./35^m	$R_3SiR'^g$	$\underline{X}$ B-P	62	186.5–187.5
13	.020 (o-$CH_3C_6H_4)_3SiH$	2.1 C_6H_5Li	50 hr./35^{m,c}	$R_3SiR'^g$	$\underline{X}$ EE (evap.) B-EA	80 66	193–195 195.5–195.9
14	.010 (o-$CH_3C_6H_4)_3SiH$	1.1 o-$CH_3OC_6H_4Li$	48 hr./35^c	R_3SiH^b	$\underline{X}$ EE (evap.)	80	84–87
15	.007 (o-$CH_3C_6H_4)_3SiH$	2.0 p-$CH_3OC_6H_4Li$	15 hr./35	R_3SiH^b	$\underline{X}$ EE (evap.) EA (−20°)	95	78–87 87–88

[a] Yields are calculated on the R_3Si- basis. [b] Characterized by mixed melting point with an analyzed sample. [c] Color Test I was positive. [d] Many unsuccessful attempts were made to obtain a crystalline product: the crude syrup was treated with a variety of solvents and the solutions were seeded with R_3SiCl, R_3SiOH, $R_3SiOC_2H_5$, and R_4Si. Ultimately the syrup was distilled but little fractionation could be effected and no crystalline materials could be separated. [e] The p-tolyllithium was of questionable quality and the negative result should be accepted with reserve. [f] Color Test I was negative. [g] Characterized by analysis. [h] The separation of the $R_3SiOC_2H_5$ and R_3SiR' was difficult due to the similar solubility properties of the two substances; only a partial separation was achieved. [i] Additional R_3SiR' was obtained on reworking the syrupy residues. No $R_2SiR'_2$ could be found, however, indicating that the R-Si linkage is not cleaved by R'Li at elevated temperatures. [j] The anhydrous reaction mixture was an intense red-brown. This color was discharged instantly on dilution with water. [k] See Table V footnote *k*. [l] Prepared by Dr. R. A. Scibert from silicochloroform and phenyllithium. [m] A gas was evolved on hydrolysis. This was probably hydrogen from the by-product lithium hydride (see equation 10).

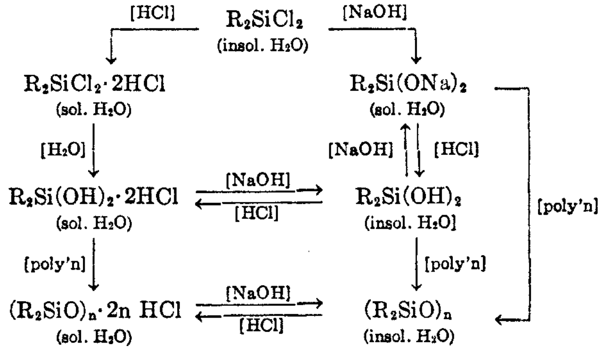
TABLE IX

THE REACTION OF DI-*o*-TOLYLDICHLOROSILANE (R_2SiCl_2) WITH R'M COMPOUNDS; SEE EQUATION 5

NO.	MOLES R_2SiCl_2[a]	$\frac{\text{MOLES R'M}}{\text{G.-ATOM Si}}$	REACTION CONDITIONS TIME/TEMP., °C.	PRODUCT	METHOD PRODUCT RECOVERY AND RECRYST. SOLVENT	YIELD[b], %	M.P., °C.
1	0.007	1.0 C_6H_5Li	10 hr./35[c]	—[d]	$\underline{X}$		
2	.007	7.0 C_6H_5Li	15 hr./20 2 hr./35	$R_2SiR'_2$[e]	$\underline{X}$ EE B-EA	100 80	167–174 173.2–174.5
3	.006	3.5 *p*-$CH_3C_6H_4Li$[f]	10 hr./35[c]	—[d]	$\underline{X}$		
4	.018	2.0 *sym*-$(CH_3)_3C_6H_2Li$	24 hr./35[g] 2 hr./100[g]	$R_2Si(OH)_2$[h]	$\underline{X}$ P (2)	50	135.5–136.5

[a] The R_2SiCl_2 used here melted in the range 71.0–72.5°; the pure material melted at 74–75°. [b] The yield is calculated on the R_2SiCl_2 basis. [c] Color Test I was negative. [d] The syrupy product which was obtained could not be crystallized. [e] This product was identified by analysis. [f] The *p*-tolyllithium was of poor quality and the run is of questionable value. [g] Color Test I was positive. [h] This product was identified by mixed melting point with an analyzed sample which had been prepared by direct hydrolysis of di-*o*-tolyldichlorosilane: $R_2SiCl_2 + 2\ H_2O \rightarrow R_2Si(OH)_2 + 2\ HCl$. (See subsequent report).

particularly disturbing. It suggests the presence of phenolic hydroxyls, perhaps derived from the RLi compound by oxidation or from a dimethylaminophenyl group by hydrolysis. We have considered and abandoned the possibility that one of the products might have been *p*-dimethylaminophenol (m.p. 78°). We suggest that *A* was impure bis-(*p*-dimethylaminophenyl)dichlorosilane, formed as indicated by equation 14 (where R = *p*-$(CH_3)_2NC_6H_4$- and M = Li). Its reactions could then be represented as follows:



15–22.

SUMMARY

1. Nineteen new aromatic organosilicon compounds have been prepared by reaction of organolithium compounds or Grignard reagents with some silicon chlorides, ethyl silicate, and related substances.

2. Tetra-*m*-tolylsilane and tetra-*p*-tolylsilane have been prepared in improved yields.

3. The failure of certain highly-substituted aromatic organosilicon compounds to form under the conditions of the arylation reaction appears to be related directly to steric factors.

4. It has been shown that tri-*o*-tolylchlorosilane is more reactive than tri-*o*-tolylsilane which, in turn, is more reactive than tri-*o*-tolylethoxysilane in the reaction of these substances with aryllithium compounds.

5 .Two useful tests for the presence of silicon in organic compounds are described.

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