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SOME ORGANOSILICON COMPOUNDS CONTAINING FUNCTIONAL GROUPS

by

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The author is desirous of expressing deep appreciation to Dr. Henry Gilman for stimulating and encouraging guidance proffered while this investigation was in progress.

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INTRODUCTION

Organosilicon compounds are those in which at least one carbon-silicon linkage exists.[1] Organosilicon compounds containing functional groups usually have these groups attached to the organic radicals. Some exceptions are the aminosilanes and the isocyanato- and isothiocyanatosilanes in which these respective radicals are attached to the silicon atom.

The introduction of functional groups into organosilicon molecules can be effected by suitably modifying usual procedures. Compounds containing nitro, amino, carboxyl, hydroxyl, and carbonyl groups have been described. It is of interest to note that unsaturated groups are generally not found attached directly to the silicon atom.

If organosilicon compounds containing functional groups were relatively readily accessible, then it might be possible to prepare from such compounds other silicon-containing chemicals which might be of value in medicine and agriculture.

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[1] (a) H. Gilman, "Organic Chemistry, An Advanced Treatise," John Wiley and Sons, Inc., New York, N. Y., 1943; (b) C. E. Burkhard, E. G. Rochow, H. S. Booth, and J. Hartt, Chem. Revs., 41, 98 (1947); (c) R. O. Sauer, J. Chem. Ed., 21, 303 (1944).

HISTORICAL

In this survey, the only organosilicon compounds included are those containing functional groups attached to the silicon atom and those in which organic radicals containing functional groups are linked to silicon through carbon.

Nitroarylsilanes

The nitroarylsilanes have been synthesized by suitably modifying ordinary nitration processes. By treating a solution of tetraphenylsilane in carbon tetrachloride with fuming nitric acid at 0°, Kipping obtained a 93% yield of nitrated products.[2] By carefully separating the components of the mixture, *tetrakis-(m-nitrophenyl)-silane*, $(m\text{-}O_2NC_6H_4)_4Si$, was isolated in 10% yield. This compound crystallised in the form of six-sided plates melting at 225-226°. The structure was proved by cleaving the compound with bromine, the product obtained being *m*-nitrobromobenzene. Boiling sodium hydroxide converted the nitro compound into nitrobenzene.

p-Nitrophenyltriethylsilane, $p\text{-}O_2NC_6H_4Si(C_2H_5)_3$, was formed with some *m-nitrophenyltriethylsilane* $m\text{-}O_2NC_6H_4Si(C_2H_5)_3$, when triethylphenylsilane was nitrated

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[2] F. S. Kipping and J. C. Blackburn, *J. Chem. Soc.*, 2200 (1932).

with fuming nitric acid in acetic anhydride at 0°.[3] The mixture of *meta* and *para* isomers distilled with some decomposition over the range 140-160° at 12 mm. The presence of these isomers was established by treating the mixture with water and bromine in a closed tube at 110° for 3 hours. By this procedure *p*-nitrobromobenzene and *m*-nitrobromobenzene were obtained, the proportions being 82% and 5%, respectively. This observation led to the conclusion that the triethylsilyl group is strongly para orienting.[3]

The nitration of diphenyldiethylsilane with fuming nitric acid in acetic anhydride at 0° led to the formation of *bis*-(p-nitrophenyl)-diethylsilane, $(\underline{p}\text{-}O_2NC_6H_4)_2Si(C_2H_5)_2$, in 76% yield and *bis-(m-nitrophenyl)-diethylsilane*, $(\underline{m}\text{-}O_2NC_6H_4)_2Si(C_2H_5)_2$ in 14% yield.[3] The mixture boiled at 295-298° at 760 mm. The *meta* isomer slowly separated from the mixture; it boils at 102-103°. The structures of these compounds were proved by cleaving each of the isomeric substances with bromine.[3]

The subjection of ethyltriphenylsilane to the same method of nitration used in the case of diphenyldiethylsilane resulted in the preparation of *tris-(p-nitrophenyl)-ethylsilane*, $(\underline{p}\text{-}O_2NC_6H_4)_3SiC_2H_5$, and *tris-(m-nitrophenyl)-ethylsilane*, $(\underline{m}\text{-}O_2NC_6H_4)_3SiC_2H_5$, which comprised 40% and 60% respectively, of the nitration products.[3]

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[3] F. S. Kipping and N. W. Cusa, *ibid.*, 1088 (1935).

The nitration of phenyltrimethylsilane was effected in 65% yield by treating the silane with copper nitrate in acetic anhydride at 40° for 6 hours.[4] Some nitrobenzene (25%) formed as a consequence of cleavage. The resulting mixture of nitration products was found to contain _ortho_, _meta_, and _para_ isomers in the ratio 30:40:30. Separation was brought about by distilling _o_-nitrophenyltrimethylsilane and then chilling a pentane solution of the residue in a Dry Ice bath. Chilling in this way caused solidification of _p_-nitrophenyltrimethylsilane which was filtered, leaving _m_-nitrophenyltrimethylsilane in the filtrate.[4]

o-Nitrophenyltrimethylsilane, $o\text{-}O_2NC_6H_4Si(CH_3)_3$, was observed to boil at 117° at 10 mm., n_D^{20} 1.5321, d_4^{20} 1.073.[4]

m-Nitrophenyltrimethylsilane, $m\text{-}O_2NC_6H_4Si(CH_3)_3$, has a boiling point of 126° at 10 mm., n_D^{20} 1.5329, d_4^{20} 1.055.[4]

p-Nitrophenyltrimethylsilane, $p\text{-}O_2NC_6H_4Si(CH_3)_3$, was found to boil at 129° at 10 mm., and it melts at 38-39°.[4] This compound was also formed in 55% yield by nitrating trimethylphenylsilane with fuming nitric acid in acetic anhydride.[5]

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[4] R. A. Benkeser and P. E. Brumfield, _J. Am. Chem. Soc._, 73, 4770 (1951).

[5] R. A. Benkeser, Doctoral Dissertation, Iowa State College, 1947.

Benzyltrimethylsilane formed nitrobenzyltrimethylsilanes in 66% yield by the same method of nitration used for the preparation of the nitrophenyltrimethylsilanes, the ratio of *ortho* to *para* isomers being 80:20.[4] No *m*-nitrobenzyltrimethylsilane was detected.[4] The compounds can be separated by fractional distillation. Approximately 5% of the mixture was composed of nitrotoluenes.

o-Nitrobenzyltrimethylsilane, $o\text{-}O_2NC_6H_4CH_2Si(CH_3)_3$, boils at 125° at 10 mm., n_D^{20} 1.5276, d_4^{20} 1.045. It can be oxidized practically quantitatively to *o*-nitrobenzoic acid with hot nitric acid.

p-Nitrobenzyltrimethylsilane, $p\text{-}O_2NC_6H_4CH_2Si(CH_3)_3$, has a boiling point of 147° at 10 mm., n_D^{20} 1.5423, d_4^{20} 1.069. It was readily cleaved with sodium hydroxide to yield *p*-nitrotoluene and *p,p'*-dinitro-1,2-diphenylethane.[4]

Aminoarylsilanes

When tetrakis-(*m*-nitrophenyl)-silane was reduced in boiling acetic acid with zinc and hydrochloric acid or hydrogenated in ethyl acetate in the presence of platinum oxide catalyst, the corresponding amino compound, *tetrakis-(m-aminophenyl)-silane*, $(m\text{-}H_2NC_6H_4)_4Si$, was produced.[6] It melts at 380° and is not soluble in most organic solvents. However, the amine dissolves sparingly in boiling phenol, cyclohexanol, aniline, or pyridine. The free base is stable to acids and

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[6] F. S. Kipping and J. C. Blackburn, *J. Chem. Soc.*, 1085 (1935).

alkalis.[6]

Tetrakis-(*m*-aminophenyl)-silane forms several salts. The tetrahydrochloride is very soluble in water, but sparingly so in ethanol. The oxalate, picrate, platinichloride, and acetate all precipitate from a solution of the hydrochloride and the appropriate reagent, but they are unstable in water. The hydrochloride, when treated with bromine water, forms a bromo derivative which does not melt below 300°. The amine also forms tetrakis-(*m*-acetamidophenyl)-silane, which melts at 300-301°.[6]

Tetrakis-(m-isopropylaminophenyl)-silane, $[m\text{-}(CH_3)_2CHNHC_6H_4]_4Si$, was obtained when tetrakis-(*m*-nitrophenyl)-silane was reduced with tin and hydrochloric acid in boiling acetone.[6] The compound was reported to boil at 135°, and it is soluble in acetone, ethyl acetate, chloroform, and ethanol. The tetrahydrochloride is a water-soluble crystalline solid melting above 300°.[6] When the tetrahydrochloride was treated with sodium nitrite, a pale yellow precipitate developed, and the filtrate from this precipitate did not couple with alkaline β-naphtol.[6]

Trimethyl-(p-aminophenyl)-silane, $p\text{-}H_2NC_6H_4Si(CH_3)_3$, was obtained by the catalytic reduction of trimethyl-(*p*-nitrophenyl)-silane with Raney nickel.[5,7] It boils at

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[7] R. A. Benkeser and P. E. Brumfield, *J. Am. Chem. Soc.*, *74*,253 (1952).

51.5-55.5° at 0.5 mm., and 60-60.5° at 0.77 mm., n_D^{20} 1.5380, d_4^{20} 0.9477.[5] It is also reported to have the following constants: boiling point, 113° (10 mm.), n_D^{20} 1.5393, d_4^{20} 0.947.[7] The yields were 77-80%[5] and 85%.[7] The melting point of the anilide, trimethyl-(_p_-acetamidophenyl)-silane, is 169-170°.[7]

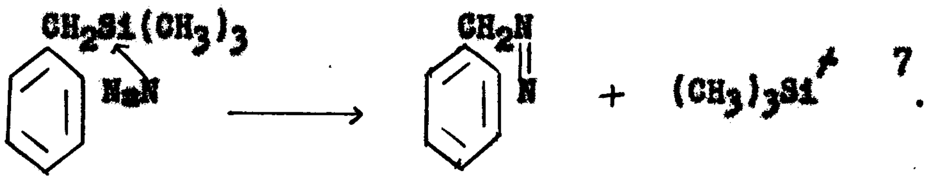
Trimethyl-(o-aminophenyl)-silane, _o_-$H_2NC_6H_4Si(CH_3)_3$, prepared by the same method as the _para_ isomer, was formed in 83% yield.[7] It boils at 101° at 10 mm., n_D^{20} 1.5388, d_4^{20} 0.952. The N-acetyl derivative melted at 130-130.5°.[7]

The catalytic reduction of trimethyl-(_m_-nitrophenyl)-silane resulted in the formation of _trimethyl-(m-aminophenyl)-silane_, _m_-$H_2NC_6H_4Si(CH_3)_3$, in 75% yield.[7] It boils at 110° at 10 mm., n_D^{20} 1.6362, d_4^{20} 0.947. Trimethyl-(_m_-acetamidophenyl)-silane melts at 114-115°.[7]

Trimethyl-(p-aminobenzyl)-silane, _p_-$H_2NC_6H_4CH_2Si(CH_3)_3$, can be prepared in 85% yield by the catalytic reduction of the corresponding nitro compound.[7] It boils at 119° (10 mm.) and melts at 33.5-34°. The N-acetyl derivative melts at 132-133°.

Trimethyl-(o-aminobenzyl)-silane, _o_-$H_2NC_6H_4CH_2Si(CH_3)_3$, was prepared in 90% yield in a manner analogous to that by which _para_ amino compound was synthesized. The boiling point is 114° at 10 mm., n_D^{20} 1.5345, d_4^{20} 0.939.[7] Trimethyl-(_o_-acetamidophenyl)-silane melts at 117-117.5°.

Each trimethyl-(aminophenyl)-silane and trimethyl-(*o*-aminobenzyl)-silane could be diazotized and coupled with *β*-napthol to yield red and orange-colored products. The reaction of trimethyl-(*o*-aminobenzyl)-silane with nitrosyl chloride resulted in the formation (16%) of indazole. It is proposed that the trimethylsilyl group underwent displacement as represented by the scheme



Triethoxy-(p-aminophenyl)-silane, *p*-$H_2NC_6H_4Si(OC_2H_5)_3$, was reportedly obtained when an ether solution of *p*-bromoaniline and ethyl orthosilicate reacted with lithium.[8] It was also prepared in 29% yield[9] from *p*-bromoaniline, ethyl orthosilicate, and *n*-butyllithium. It boils at 145-150° at 14 mm.,[8] and 148-153° at 16 mm., n_D^{20} 1.4950, d_4^{20} 1.0702.[9]

Triethoxy-(p-dimethylaminophenyl)-silane, *p*-$(CH_3)_2NC_6H_4Si(OC_2H_5)_3$, was synthesized by the reaction of *p*-dimethylaminophenyllithium upon ethyl orthosilicate.[8] It distills at 180-182° at 14 mm. pressure.[8]

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[8] R. E. Fleming, U. S. Patent 2,386,452, Oct. 9, 1945 [*C.A.*, **40**, 603 (1945)].

[9] R. N. Clark, Doctoral Dissertation, Iowa State College, 1946.

Several other organosilicon compounds containing the *p*-dimethylaminophenyl group have been prepared by Gilman and co-workers in order that their properties be studied.[10,14,15] These properties were found to be unusual when compared with those of their phenyl and *p*-tolyl analogs.

Triphenyl-(p-dimethylaminophenyl)-silane, $p\text{-}(CH_3)_2NC_6H_4Si(C_6H_5)_3$, was prepared by treating triphenylchorosilane in ether with *p*-dimethylaminophenyllithium.[10] The yield of product, melting at 233-235°, was 46%. Some tetraphenyl silane (10%) was also obtained. The hydrochloride of triphenyl-(*p*-dimethylaminophenyl)-silane can be formed by treating the amine with ethereal hydrogen chloride; it melts at 227-229° when recrystallized from absolute methanol.[10]

Diphenylbis-(p-dimethylaminophenyl)-silane, $[p\text{-}(CH_3)_2NC_6H_4]_2Si(C_6H_5)_2$, was obtained in 40% yield from diphenyldiethoxysilane and *p*-dimethylaminophenyllithium.[10] The compound melts at 180-181° after recrystallization from a mixture of ethanol and petroleum ether (boiling point 60-70°).

Phenyltris-(p-dimethylaminophenyl)-silane, $[p\text{-}(CH_3)_2NC_6H_4]_3SiC_6H_5$, can be prepared in 17% yield by the

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[10] H. Gilman, M. A. Plunkett, and G. E. Dunn, *J. Am. Chem. Soc.*, *73*, 1686 (1951).

interaction of phenyllithium and tris-(*p*-dimethylaminophenyl)-ethoxysilane.[10] It melts at 171-173° after recrystallization from petroleum ether (boiling point 60-70°).

Tetrakis-(p-dimethylaminophenyl)-silane, $[p\text{-}(CH_3)_2NC_6H_4]_4Si$, was synthesized by the interaction of silicon tetrachloride and *p*-dimethylaminophenyllithium followed by hydrolysis after addition of the organolithium compound was completed.[10] In this manner a yield of 41% was obtained. However, if the reactants are heated at the reflux temperature of ether until Color Test I[11] becomes negative, yields as high as 86% can be obtained.[10]

Tris-(p-dimethylaminophenyl)-silane, $[p\text{-}(CH_3)_2NC_6H_4]_3SiH$, was prepared by treating trichlorosilane with *p*-dimethylaminophenyllithium. The first equivalent of the organolithium compound was added at -10°, but the other two equivalents were introduced while the reactants were warming to room temperature. The reaction mixture was then refluxed for thirty hours. The yield of product melting at 157° after recrystallization from absolute ethanol was 49%.

Tris-(*p*-dimethylaminophenyl)-silane was obtained also by the reduction of tris-(*p*-dimethylaminophenyl)-chlorosilane with lithium aluminum hydride in ether solution. This pro-

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[11] H. Gilman and F. Schulze, *ibid.*, *47*, 2002 (1925).

cedure leads to a 98% yield of product of such a high degree of purity that recrystallization is unnecessary.[10]

This silane does not yield hydrogen when it is treated with potassium hydroxide in piperidine[10] as do most compounds containing the Si-H bond.[12] However, if tris-(*p*-dimethylaminophenyl)-silane is warmed to 60° in a 2% solution of ethanolic potassium hydroxide, the evolution of hydrogen is vigorous. In this manner, a yield of 85% of the corresponding silanol can be obtained after acidification of the reaction mixture.[10]

Tris-(p-dimethylaminophenyl)-silanol, $[p\text{-}(CH_3)_2NC_6H_4]_3SiOH$, was prepared in 58% yield.[10] The procedure followed was the addition of one equivalent of *p*-dimethylaminophenyllithium to silicon tetrachloride at -15° to -20° followed by the introduction of the other two equivalents while the mixture was warming to room temperature. The reaction mixture was refluxed until Color Test I[11] became negative, and then hydrolyzed. Some tetrakis-(*p*-dimethyl)-aminophenyl)-silane (8%) was also formed. The melting point of the silanol is 183-184° after recrystallization from benzene.[10]

Tris-(p-dimethylaminophenyl)-ethoxysilane, $[p\text{-}(CH_3)_2NC_6H_4]_3SiOC_2H_5$, can be prepared by refluxing an ether solution of ethyl orthosilicate and *p*-dimethylaminophenyllithium until Color Test I[11] becomes negative.[10] The

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[12] F. S. Kipping and J. E. Sands, *J. Chem. Soc.*, *119*, 848 (1921); N. W. Cusa and F. S. Kipping, *ibid.*, 1040 (1932).

yield was 11.5% when the reaction mixture was hydrolyzed, and 12% when the product was obtained without subjecting the reaction mixture to hydrolysis.[10] After recrystallization from a benzene-ethanol mixture, tris-(p-dimethylaminophenyl)-ethoxysilane was found to melt at 125-126°.[10]

Tris-(p-dimethylaminophenyl)-ethoxysilane was converted into the silanol to the extent of 80% when it was dissolved in dilute hydrochloric acid followed by treatment with 0.2 N sodium hydroxide solution.[10]

When p-dimethylaminophenyllithium was introduced into an ether solution of silicon tetrachloride at -15° to -20° over a period of 2 hours and the contents of the reaction vessel stirred for ½ hour at room temperature prior to hydrolysis, bis-(p-dimethylaminophenyl)-silanediol, $[p\text{-}(CH_3)_2NC_6H_4]_2Si(OH)_2$, was formed. The blue, sticky, crude product was crystallized from a benzene-petroleum ether mixture (the boiling range of the petroleum ether is 90-120°), and a 77% yield of pure product melting at 173-174° was obtained.[10]

Bis-(p-dimethylaminophenyl)-silanediol was prepared also by the hydrolysis of bis-(p-dimethylaminophenyl)-diethoxysilane with dilute sodium hydroxide.[13] The yield of product formed by this method was 63% (from benzene).[13]

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[13] H. Gilman and G. N. R. Smart, *J. Org. Chem.*, **15**, 720 (1950).

Diphenyl-(p-dimethylaminophenyl)-silanol, $[p\text{-}(CH_3)_2NC_6H_4](C_6H_5)_2SiOH$, was obtained by refluxing an ether solution of diphenyldichlorosilane and *p*-dimethylaminophenyllithium for 2 hours and then hydrolysing the reaction mixture. An ether-insoluble portion proved to be diphenylsilanediol. The residue was extracted with benzene from which solvent more diphenylsilanediol was obtained. The total yield of this compound was 49%. The silanol, on the other hand, was obtained pure in 21% yield from a mixed solvent of benzene and petroleum ether (the petroleum ether boils over a range of 90-120°), and melts at 65-66°.[10]

Bis-(p-dimethylaminophenyl)-diethoxysilane, $[p\text{-}(CH_3)_2NC_6H_4]_2Si(OC_2H_5)_2$, was prepared by adding *p*-dimethylaminophenyllithium slowly to ethyl orthosilicate and stirring the mixture for 24 hours at 20°.[13] The reaction mixture was filtered, and after distillation, the yield of bis-(*p*-dimethylaminophenyl)-diethoxysilane boiling at 222-224° at 2 mm. or 229-231° at 3 mm., n_D^{25} 1.571, was 55%.[13]

Diphenyl-(p-dimethylaminophenyl)-chlorosilane, $[p\text{-}(CH_3)_2NC_6H_4]Si(C_6H_5)_2Cl$, boils at 227-228° at 2.5 mm.[14] It was formed in 70% yield by refluxing an ether solution of diphenyldichlorosilane and *p*-dimethylaminophenyllithium 24 hours, distilling the ether while benzene was being added,

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[14] H. Gilman and G. E. Dunn, *J. Am. Chem. Soc.*, *73*, 3404 (1951).

and then obtaining the product from the benzene solution by fractionation.

Diphenyl-(m-dimethylaminophenyl)-chlorosilane, $[m\text{-}(CH_3)_2NC_6H_4]Si(C_6H_5)_2Cl$, was prepared by the same procedure as was the *para* isomer, except that refluxing of the solution was over a 4 hour period.[14] The yield of product, boiling at 184-185° at 0.2 mm., was 78%.

When diphenyl-(*m*-dimethylaminophenyl)-chlorosilane was reduced with lithium aluminum hydride, *diphenyl-(m-dimethylaminophenyl)-silane,* $[m\text{-}(CH_3)_2NC_6H_4]Si(C_6H_5)_2SiH$, boiling at 176-177° at 0.1 mm., was produced in 83% yield.[14]

Diphenyl-(p-dimethylaminophenyl)-silane, $[p\text{-}(CH_3)_2NC_6H_4](C_6H_5)_2SiH$, was prepared by the action of lithium aluminum hydride upon the corresponding chloro compound in 55% yield.[14] It has a boiling point of 186-187° at 0.15 mm.[14]

Trimethyl-(p-dimethylaminophenyl)-silane, $p\text{-}(CH_3)_2NC_6H_4Si(CH_3)_3$, prepared in 48% yield by refluxing a solution of trimethylchlorosilane and *p*-dimethylaminophenyllithium in ether for one hour, boils at 252-253°.[15] When subjected to cleavage with anhydrous hydrogen chloride in refluxing acetic acid for 1 hour, trimethyl-(*p*-dimethylaminophenyl)-silane was converted into dimethylaniline (73.5%) and trimethylchlorosilane (67%).[15]

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[15] H. Gilman and F. J. Marshall, *ibid.*, *71*, 2066 (1949).

In general, the formation of p-dimethylaminophenylsilanes occurs more slowly than does that of other arylsilanes when aryllithium compounds are reacted with silicon tetrachloride.[10] In refluxing ether, 60 hours were required before Color Test I[11] became negative in the synthesis of tetrakis-(p-dimethylaminophenyl)-silane, 48 hours in the preparation of tris-(p-dimethylaminophenyl)-chlorosilane, 36 hours in the formation of tris-(p-dimethylaminophenyl)-ethoxysilane, and 30 hours in the preparation of tris-(p-dimethylaminophenyl)-silane.[10] Further, the fact that diphenylsilanediol was obtained in 49% yield in the preparation of diphenyl-(p-dimethylaminophenyl)-silanol is evidence of the relative slowness with which p-dimethylaminophenyllithium reacts with chlorosilanes. In contrast, phenyl- and p-tolyllithium react almost instantaneously with silicon tetrachloride at 0°.[16]

The practically quantitative conversion of triarylsilanols into hexaaryldisiloxanes has been accomplished by the use of 98% formic acid[17] or glacial acetic acid.[17] However, when tris-(p-dimethylaminophenyl)-silanol was treated with either of these reagents, only blue-colored oils and

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[16] H. Gilman and R. N. Clark, _ibid._, _68_, 1675 (1946).

[17] H. Gilman, H. W. Melvin, and L. S. Miller, unpublished studies. See, also, H. Gilman and L. S. Miller, _J. Am. Chem. Soc._, _73_, 968 (1951).

glasses were obtained.[10] Refluxing a toluene solution containing tris-(*p*-dimethylaminophenyl)-chlorosilane and the sodium salt of tris-(*p*-dimethylaminophenyl)-silanol for 6 hours resulted in the formation of a solid which did not fuse at 400°.[10]

Arylsilanes Containing $SiNR_2$ Groups

Among arylsilicon compounds of this type is *hexaphenyldisilazane*, $[(C_6H_5)_3Si]_2NH$. It was prepared by the reaction of triphenylsilane with sodium in liquid ammonia.[18]

$$2(C_6H_5)_3SiH + NH_3 \xrightarrow{Na} [(C_6H_5)_3Si]_2NH + H_2$$

The product melts at 175° and is stable in air and even in boiling dilute sodium hydroxide.[18] It can be hydrolysed to triphenylsilanol with hydrochloric acid.

Triphenyl-(amino)-silane, $(C_6H_5)_3SiNH_2$, was obtained when triphenylchlorosilane reacted with liquid ammonia.[19] It was extracted with dry petroleum ether from which it was crystallised. It melted at 55-56°.[19]

An unusual substance, "*triphenylsilicyl ethylamine*," $(C_6H_5)_3Si.C_2H_5NH_2$, a solvated free radical, has been

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[18] H. H. Reynolds, L. A. Bigelow, and C. A. Kraus, *ibid.*, *51*, 3067 (1929).

[19] C. A. Kraus and R. Rosen, *ibid.*, *47*, 2739 (1925).

described by Kraus and Eatough.[20a] It was supposedly prepared by the reaction of lithium with triphenylbromosilane in ethylamine. This substance reportedly melts at 45°, and it can be distilled at 150° in high vacuum. It was described as

$$(C_6H_5)_3SiBr + Li + C_2H_5NH_2 \longrightarrow LiBr + (C_6H_5)_3Si.C_2H_5NH_2$$

being soluble in the usual organic solvents except low-boiling petroleum ether and ethanol.[20a]

"Triphenylsilicyl ethylamine" was said to undergo the reactions shown below, one product being the highly desirable triphenylsilyllithium. This latter substance was reported to

$$2(C_6H_5)_3Si.C_2H_5NH_2 \xrightarrow[\text{boiling ether}]{} (C_6H_5)_3SiSi(C_6H_5)_3 + C_2H_5NH_2$$

$$(C_6H_5)_3Si.C_2H_5NH_2 + Li \xrightarrow[C_2H_5NH_2]{} (C_6H_5)_3SiLi + C_2H_5NH_2$$

undergo reaction with ammonium bromide, bromobenzene, and trimethyltin chloride, respectively, in liquid ammonia to yield the expected triphenylsilane, tetraphenylsilane, and triphenyl-(trimethyltin)-silane.[20a]

Later researches, however, have shown that what had been regarded as "triphenylsilicyl ethylamine" was actually triphenyl-(ethylamino)-silane, $(C_6H_5)_3SiNHC_2H_5$.[20b] This

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[20] (a) C. A. Kraus and H. Eatough, ibid., 55, 5008 (1933); (b) R. A. Benkeser, R. E. Robinson, and H. Landesman, ibid., 74, 5699 (1952).

aminosilane, melting at 47-48°, was obtained by the action of lithium upon triphenylchlorosilane and triphenylbromosilane, respectively, in ethylamine, and also by the reaction of either halosilane with ethylamine in ether.[20b] The former procedure was supposed to form "triphenylcilicyl ethylamine,"[20a] but none of the reactions ascribed to this substance was given by the product.[20b]

When "triphenylsilicyl ethylamine" in ethylamine solution reacted with lithium, a red color was observed to develop. The appearance of the color supposedly attended the formation of triphenylsilyllithium.[20a] It would seem, however, that the development of the red color is associated with the reaction of lithium with aromatic nuclei and not with organosilicon compounds as such.[20b] In support of this view is the fact that benzene as well as triphenyl-(ethylamino)-silane and tetraphenylsilane react with lithium with the appearance of this red color, but tetramethylsilane and lithium do not give rise to the same phenomenon.[20b] Furthermore, analyses indicate that one phenyl group can absorb six equivalents of lithium.[20b]

By the reaction of lithium dialkylamides with triphenylchlorosilane or triphenylsilane, triphenyl-(dialkylamino)-silanes may be obtained.[21] Good results were had with triphenylsilane and lithium dialkylamides. The lithium salts of

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[21] H. Gilman, B. Hofferth, H. W. Melvin, and G. E. Dunn, *ibid.*, *72*, 5767 (1940).

hydrazine, carbazole, N-methylaniline, diphenylamine, and 2,5-dimethylpyrrole were without effect upon triphenylsilane.[21]

Triphenyl-(di-n-butylamino)-silane, $(C_6H_5)_3SiN(C_4H_9\text{-}n)_2$, can be prepared in 10% yield by adding lithium di-n-butylamide to a solution of triphenylchlorosilane in ether, removing the solvent by distillation, and heating the residue at 200° for 1 hour.[21] The crude product was distilled and crystallised from petroleum ether (boiling point 60-70°). The amine was also synthesized in 63% yield by refluxing an ether suspension of triphenylsilane and lithium di-n-butylamide for ½ hour. The melting point is 60-62° (from absolute ethanol.)[21]

Triphenyl-(dimethylamino)-silane, $(C_6H_5)_3SiN(CH_3)_2$, was prepared in 75.6% yield by the use of lithium dimethylamide and triphenylsilane. It melts at 80-81° after recrystallisation from absolute ethanol.[21]

Triphenyl-(diethylamino)-silane, $(C_6H_5)_3SiN(CH_3)_2$, was also prepared from triphenylsilane and the corresponding lithium dialkylamide.[21] The yield was 74.2%, and the product has a melting point of 84-85°.

Tris-(p-dimethylaminophenyl)-di-n-butylaminosilane, $[p\text{-}(CH_3)_2NC_6H_4]_3SiN(C_4H_9\text{-}n)_2$, was obtained when tris-(p-dimethylaminophenyl)-silanol and excess di-n-butylamine were refluxed for 30 minutes, the excess amine being slowly distilled so as to remove the water that formed during the reaction. The yield of product, melting at 62-64°, was 92% after recrystallisation from di-n-butylamine and washing with petroleum ether (boiling point 60-70°).[21]

Arylsilanes Containing the SiCOOH Group

By subjecting triphenyl-(phenylisopropyl)-silane in ether to cleavage with sodium-potassium alloy and then carbonating the products, triphenyl-(carboxy)-silane (triphenylsilane-carboxylic acid), $(C_6H_5)_3SiCOOH$, was obtained.[22] The acid is a white crystalline substance stable at room temperature, but decomposes into carbon monoxide and a mixture of triphenylsilanol and hexaphenyldisiloxane when heated. Upon treating the compound with acid, the same type of decomposition was effected. In no case was carbon dioxide a product.[22]

Haloarylsilanes

The haloarylsilanes have shown themselves to be important in many instances because the halogen atoms are frequently replaceable by other groups. They, therefore, may be considered to be important intermediates.

2-Methoxy-5-bromophenyltrichlorosilane, $Cl_3SiC_6H_3(OCH_3\text{-}2)(Br\text{-}5)$, boiling at 130-140° under 13 mm. pressure, was prepared by the interaction of silicon tetrachloride and 2-methoxy-5-bromophenyllithium.[8]

Trimethyl-(p-bromophenyl)-silane, $p\text{-}BrC_6H_4Si(CH_3)_3$, was prepared in 53% yield by treating trimethylchlorosilane with

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[22] R. A. Benkeser and R. G. Severson, ibid., 71, 1424 (1951).

p-bromophenylmagnesium bromide. It boiled at 146-148° at 50 mm., d_4^{20} 1.2197, n_D^{20} 1.5302.[23] The compound was also synthesized by the reaction of p-bromophenyllithium (prepared from p-dibromobenzene and n-butyllithium[24]) upon trimethylchlorosilane. The yield by this method of synthesis was 55-61%.[25]

Trimethyl-(p-bromophenyl)-silane can be converted into p-trimethylsilylbenzoic acid by the carbonation of its Grignard reagent or its organolithium compound,[26] and p-trimethylsilylbenzaldehyde can be prepared from p-trimethylsilylphenyllithium and N-methylformanilide (see p. 110 of EXPERIMENTAL).

Trimethyl-(p-chlorophenyl)-silane, p-$ClC_6H_4Si(CH_3)_3$, boiling at 119-120° at 50 mm., n_D^{20} 1.5182, d_4^{20} 1.0282, was formed in 83% yield by the reaction of p-chlorophenylmagnesium bromide with trimethylchlorosilane.[23] It sluggishly reacts with lithium and magnesium to form p-trimethylsilylphenyllithium and p-trimethylsilylphenylmagnesium chloride (see p. 102 of EXPERIMENTAL). The dipole moment of trimethyl-

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[23] C. E. Burkhard, ibid., 68, 2103 (1946).

[24] See H. Gilman, J. A. Beel, C. G. Branner, M. W. Bullock, G. E. Dunn, and L. S. Miller, ibid., 71, 1499 (1949) for the preparation of n-butyllithium, and H. Gilman and A. H. Haubein, ibid., 66, 1515 (1944) for the determination of the titer.

[25] R. G. Jones and H. Gilman in R. Adams, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 355.

[26] J. D. Roberts, E. A. McElhill, and R. Armstrong, J. Am. Chem. Soc., 71, 2923 (1949).

(p-chlorophenyl)-silane has been found to be 1.70 D.[26] Since the dipole moment of chlorobenzene is 1.57 D, the trimethylsilyl group in the para position apparently slightly releases electrons to the phenyl group, for the net vector component of the dipole moment in the direction of the ring due to the trimethylsilyl group is only 0.1-0.25 D.[26]

Trimethyl-(p-fluorophenyl)-silane, p-$FC_6H_4Si(CH_3)_3$, was prepared in 91% yield by the interaction of trimethylchlorosilane and p-fluorophenylmagnesium bromide.[26] It boils at 92-93° at 60 mm., n_D^{25} 1.4711, d_4^{25} 0.9452.

The dipole moment of fluorobenzene is 1.44 D, and that of trimethyl-(p-fluorophenyl)-silane is 1.69 D. These data also indicate the release of electrons by the trimethylsilyl group to the benzene nucleus.[26]

The Grignard reagent prepared from m-iodochlorobenzene reacted with trimethylchlorosilane to form trimethyl-(m-chlorophenyl)-silane, m-$ClC_6H_4Si(CH_3)_3$, in 53% yield.[26] It has a boiling point of 97-102.5° (23 mm.), n_D^{25} 1.5070. The Grignard reagent prepared from this compound can be converted into the corresponding acid by carbonation.[26]

Diphenyl-(p-chlorophenyl)-chlorosilane, p-$ClC_6H_4(C_6H_5)_2SiCl$, was synthesized by refluxing an ether solution containing diphenyldichlorosilane and p-chlorophenylmagnesium bromide for 72 hours. The yield of product, boiling at 149-150° at 0.3 mm., was 36%.[14] Diphenyl-(p-chlorophenyl)-chlorosilane can be converted into diphenyl-(p-chloro-

phenyl)-silane, $p\text{-ClC}_6\text{H}_4(\text{C}_6\text{H}_5)_2\text{SiH}$, boiling at 161-162° (1 mm.), in 56% yield by treatment with lithium aluminum hydride.[14]

Several chlorinated aryl silanes have been prepared in order that their insecticidal properties might be studied.[27] *p*-Chlorophenyllithium[28] was caused to react with phenylethoxy- or phenylchlorosilanes to form a series of silanes having the general formula $(\text{C}_6\text{H}_5)_n\text{Si}(\text{C}_6\text{H}_4\text{Cl-}p)_{4-n}$ where n = 0 to 3.[27] Methyltris-(*p*-chlorophenyl)-silane and dimethylbis-(*p*-chlorophenyl)-silane were prepared in a similar manner by treating methyltrichlorosilane and dimethyldiethoxy- or dimethyldichlorosilane, respectively, with *p*-chlorophenyllithium.[27]

Tris-(p-chlorophenyl)-ethoxysilane, $(p\text{-ClC}_6\text{H}_4)_3\text{SiOC}_2\text{H}_5$, was formed in 29.5% yield from *p*-chlorophenyllithium and ethyl orthosilicate. It is a white crystalline material which melts at 128° after recrystallization from 95% ethanol.[27]

Tris-(p-chlorophenyl)-silanol, $(p\text{-ClC}_6\text{H}_4)_3\text{SiOH}$, melting at 121°, was prepared in 93% yield by the hydrolysis of tris-(*p*-chlorophenyl)-ethoxysilane with potassium hydroxide in 1:1 dioxane-ethanol solution.[27]

Tetrakis-(p-chlorophenyl)-silane, $(p\text{-ClC}_6\text{H}_4)_4\text{Si}$, was synthesized by the interaction of *p*-chlorophenyllithium and

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[27] H. Gilman and L. S. Miller, *ibid.*, *73*, 968 (1951).

[28] H. Gilman, W. Langham, and F. W. Moore, *ibid.*, *62*, 2327 (1940).

ethyl orthosilicate. The yield of product, melting at 181°, was 65%.[27]

Hexakis-(p-chlorophenyl)-disiloxane, $[(\underline{p}\text{-}ClC_6H_4)_3Si]_2O$, was formed when tris-(p-chlorophenyl)-ethoxysilane was refluxed for 20 minutes with 90% formic acid. It melts at 210° after recrystallization from methanol.[27]

Phenyltris-(p-chlorophenyl)-silane, $(\underline{p}\text{-}ClC_6H_4)_3SiC_6H_5$, was prepared in 47.5% yield and melts at 134°.[27]

Bis-(p-chlorophenyl)-diphenylsilane, $(\underline{p}\text{-}ClC_6H_4)_2Si(C_6H_5)_2$, was formed in 61.5% yield by the action of p-chlorophenyllithium upon diphenyldiethoxysilane. It melts at 131°.[27]

Triphenyl-(p-chlorophenyl)-silane, $\underline{p}\text{-}ClC_6H_4Si(C_6H_5)_3$, may be prepared by treating triphenylethoxysilane with p-chlorophenyllithium. This method of synthesis resulted in a 54% yield of product melting at 157°.[27]

Methyltris-(p-chlorophenyl)-silane, $(\underline{p}\text{-}ClC_6H_4)_3SiCH_3$, was formed in 53% yield from methyltrichlorosilane and p-chlorophenyllithium.[27] It melts at 86° (from methanol).[27]

Trichloromethyltris-(p-chlorophenyl)-silane, $(\underline{p}\text{-}ClC_6H_4)_3SiCCl_3$, can be prepared by treating methyltris-(p-chlorophenyl)-silane with chlorine in the presence of ultra-violet light at 170°.[27] After extraction of the product with methanol and recrystallization from petroleum ether (boiling point 79-119°), the yield of material melting at 210° was 22%. Trichloromethyltris-(p-chlorophenyl)-silane is stable in boiling water and in 30% hydrochloric acid, but it is cleaved by 50% aqueous sodium hydroxide to form hexakis-(p-chlorophenyl)-disiloxane.[27]

Dimethylbis-(p-chlorophenyl)-silane, $(p\text{-}ClC_6H_4)_2Si(CH_3)_2$, can be synthesized in 71-80% yields by the action of p-chlorophenyllithium upon dimethyldichlorosilane or dimethyldiethoxysilane.[27] It melts at 47°. When this compound was subjected to chlorination by the same procedure as that used in the case of methyltris-(p-chlorophenyl)-silane, the only product isolated was p-dichlorobenzene.

By chlorinating dimethylbis-(p-chlorophenyl)-silane in carbon tetrachloride under the influence of ultraviolet light, methyl-(dichloromethyl)-bis-(p-chlorophenyl)-silane, $(p\text{-}ClC_6H_4)_2Si(CHCl_2)CH_3$, was formed.[27] This distilled at 165-170° at 10^{-5} mm., n_D^{20} 1.6062, d_4^{20} 1.340. This product was made also by the chlorination of dimethylbis-(p-chlorophenyl)-silane without a solvent at 50°, and by treating this silane with sulfuryl chloride and benzoyl peroxide. No methyl-(trichloromethyl)-bis-(p-chlorophenyl)-silane was isolated in any of these preparations.[27] When methyl-(trichloromethyl)-dichlorosilane[29] was treated with p-chlorophenyllithium, only p-dichlorobenzene was obtained upon distillation, and none of the desired product was isolated.[27]

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[29] R. H. Krieble and J. R. Elliott, ibid., 67, 1810 (1945).

n-Dodecyltris-(p-chlorophenyl)-silane, (p-$ClC_6H_4)_3SiC_{12}H_{25}$-$n$, resulted from the reaction of p-chlorophenyllithium with n-dodecyltrichlorosilane.[27] It is a viscous, straw-colored liquid obtained by distillation in a Hickman molecular still. The constants are n_D^{22} 1.5679, d_4^{22} 1.106. The yield was 64.1%.[27]

p-Bromophenyldimethylethoxysilane, p-$BrC_6H_4Si(CH_3)_2OC_2H_5$, was prepared from p-dibromobenzene, magnesium, and dimethyldiethoxysilane in 13.3% yield.[30] It boils at 148° at 34 mm., n_D^{25} 1.5131, d_4^{25} 1.2212.[30]

p-Bromophenyldimethylchlorosilane, p-$BrC_6H_4Si(CH_3)_2Cl$, can be prepared from p-bromophenylmagnesium bromide and dimethyldichlorosilane in 46.5% yield.[30] It boils at 135.5° (18 mm.), n_D^{25} 1.5438, d_4^{25} 1.3904.[30]

The reaction of a benzene solution of p-bromophenyldimethylethoxysilane with 75% sulfuric acid produced 1,3-bis-(p-bromophenyl)-tetramethyldisiloxane, $[p$-$BrC_6H_4Si(CH_3)_2]_2O$, in 92% yield.[30] The boiling point is 119-121° at 0.7 mm., n_D^{25} 1.5550, d_4^{25} 1.3641.[30] When p-bromophenyldimethylchlorosilane was used, the yield of product was 72%.[30]

Triphenyl-(p-bromophenyl)-silane, p-$BrC_6H_4Si(C_6H_5)_3$, can be prepared in 78% yield by the reaction of p-bromophenyllithium (from p-dibromobenzene and n-butyllithium[24]) and tri-

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[30] D. W. Lewis and G. C. Gainer, ibid., 74, 2931 (1952).

phenylchlorosilane.[31] After recrystallization from benzene containing ethanol, it melts at 167-168°.[31]

Triphenyl-(*p*-bromophenyl)-silane reacts with lithium dimethylamide to produce triphenyl-(*p*-dimethylaminophenyl)-silane.[31]

Hydroxyarylsilanes

Diethoxybis-(p-hydroxymethylphenyl)-silane, $(p\text{-}HOCH_2C_6H_4)_2Si(OC_2H_5)_2$, was produced from the appropriate organolithium compound and ethyl orthosilicate.[8] It boils at 200-210° at 15 mm.

Among silicon-containing napthalenes which have been synthesized are some hydroxynaphthalene derivatives. They are prepared by treating chlorosilanes with the appropriate hydroxynaphthyllithium compounds.[32]

1-(2-Hydroxynaphthyl)-trimethylsilane, $C_{10}H_6[Si(CH_3)_3\text{-}1]$ (OH-2) was formed in 53% yield by reacting 1-lithio-2-lithoxynaphthalene (from 1-bromo-2-hydroxynaphthalene and *n*-butyllithium[24]) with trimethylchlorosilane at the reflux temperature of ether for 4 to 5 hours.[32] It boils at 126-127° at 0.5 mm., n_D^{20} 1.5569, d_4^{20} 1.002.

6-(2-Hydroxynaphthyl)-triphenylsilane, $C_{10}H_6[Si(C_6H_5)_3\text{-}6]$ (OH-2), was prepared in similar manner from

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[31] H. Gilman and H. W. Melvin, *ibid.*, *72*, 995 (1950).

[32] S. V. Sunthankar and H. Gilman, *ibid.*, *72*, 4884 (1950).

6-bromo-2-hydroxynaphthalene and triphenylchlorosilane in 51% yield.[32] The compound melts at 139-140°.

6-(2-Hydroxynaphthyl)-trimethylsilane, $C_{10}H_6[Si(CH_3)_3\text{-}6]$ (OH-2), melting at 107-108°, was prepared in 48% yield by the same general procedure as the other hydroxynaphthylsilanes.[32]

None of these hydroxynaphthylsilanes[32] gives a color reaction with ferric chloride, but each one of them can be converted into its methyl ether by the use of dimethyl sulfate.[32] 1-(2-Hydroxynaphthyl)-trimethylsilane and 6-(2-hydroxynaphthyl)-trimethylsilane are cleaved by 20% hydrochloric acid and 20% potassium hydroxide; 6-(2-hydroxynaphthyl)-triphenylsilane can be cleaved by dry hydrogen chloride in refluxing acetic acid solution.[15,32] In each instance of cleavage, 2-hydroxynaphthalene is formed.[32]

An interesting procedure for the preparation of silicon compounds containing the hydroxyl group in organic radicals has been developed.[33] The series of equations below exemplifies this method when applied to the synthesis of silicon-containing phenols.

$$\textit{p}\text{-}ClC_6H_4OH + (CH_3)_3SiCl \longrightarrow \textit{p}\text{-}ClC_6H_4OSi(CH_3)_3 + HCl$$

$$\textit{p}\text{-}ClC_6H_4OSi(CH_3)_3 + (CH_3)_3SiCl + 2Na \longrightarrow \textit{p}\text{-}(CH_3)_3SiC_6H_4OSi(CH_3)_3 + 2NaCl$$

$$\textit{p}\text{-}(CH_3)_3SiC_6H_4OSi(CH_3)_3 + H_2O \xrightarrow{H^+} \textit{p}\text{-}(CH_3)_3SiC_6H_4OH + (CH_3)_3SiOH$$

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[33] J. L. Speier, *ibid.*, *74*, 1003 (1952).

The yields of phenols prepared by this procedure are reportedly quantitative.[33]

Trimethyl-(p-hydroxyphenyl)-silane, *p*-$HOC_6H_4Si(CH_3)_3$, melting at 74-74.2°, was prepared in 96% yield.[33] *p*-Trimethylsilylphenyl 3,5-dinitrobenzoate melts at 142.5-143°, and the $\underline{\alpha}$-naphthylurethan derivative melts at 153.5-155°.[33]

Trimethyl-(o-hydroxyphenyl)-silane, *o*-$HOC_6H_4Si(CH_3)_3$, melts at 8.6-9.2° and boils at 113° at 26 mm., d_4^{25} 0.966, n_D^{25} 1.515.[33] *o*-Trimethylsilylphenyl 3,5-dinitrobenzoate melts at 123-124°.[33] This phenol was formed also when 2,4-bis-(trimethylsilyl)-phenoxytrimethylsilane was hydrolyzed in aqueous acetone. Apparently the trimethylsilyl group *para* to the $(CH_3)_3SiO$ group was cleaved in the process.

Each of these two phenols, when heated in a sealed tube at 250° for 24 hours, rearranges to phenoxytrimethylsilane having a boiling point of 180-181°.[33]

Trimethyl-(2-methyl-4-hydroxyphenyl)-silane, $(CH_3)_3SiC_6H_4(CH_3\text{-}2)(OH\text{-}4)$, has a melting point of 51-51.5°.[32] The 3,5-dinitrobenzoate of this phenol melts at 129-129.5°.[33]

Dimethylethyl-(p-hydroxyphenyl)-silane, *p*-$HOC_6H_4Si(CH_3)_2C_2H_5$, has as its melting point 32.2-33°, and it boils at 148° at 24 mm.[33]

Dimethylbis-(p-hydroxyphenyl)-silane, $(p\text{-}HOC_6H_4)_2Si(CH_3)_2$, melts at 170-171°.[33]

Dimethylbis-(2-methyl-4-hydroxyphenyl)-silane, $(CH_3)_2Si[C_6H_4(CH_3\text{-}2)(OH\text{-}4)]_2$, melts at 208-210°.[33]

Carboxyarylsilanes

Triethyl-(4-methoxy-3-carboxyphenyl)-silane, $(C_2H_5)_3SiC_6H_4(OCH_3\text{-}4)\ (COOH\text{-}3)$, was prepared in 47% yield by the metalation of triethyl-*p*-anisylsilane with *n*-butyllithium[24] and then subjecting the organolithium compound to carbonation.[5] It melts at 52-56° with preliminary softening. Cleavage of triethyl-(4-methoxy-3-carboxyphenyl)-silane with bromine[2,3,6] showed metalation to have occurred *ortho* to the methoxyl group since 2-methoxy-5-bromobenzoic acid was obtained.

Trimethyl-(p-carboxyphenyl)-silane, *p*-$HOOCC_6H_4Si(CH_3)_3$, was prepared from *p*-trimethylsilylphenylmagnesium bromide by carbonation of the organometallic compound.[26] The yield was 28%[26] and the melting point of the acid was 117-118°.[26] It was also formed in 60% yield, melting at 110-111°, by the carbonation of the corresponding RLi compound.[9]

Trimethyl-(m-carboxyphenyl)-silane, *m*-$HOOCC_6H_4Si(CH_3)_3$, was obtained in 47% yield when *m*-chlorophenyltrimethylsilane was converted into *m*-trimethylsilylphenyllithium and the organolithium compound carbonated.[26] The acid melts at 113.7-114°.[26]

The ionization constants of the trimethyl-(carboxyphenyl)-silanes were measured and compared with that of benzoic acid. The ionization constant for benzoic acid was found to be

1.78×10^{-6} while trimethyl-(*m*-carboxyphenyl)-silane (*m*-trimethylsilylbenzoic acid) and trimethyl-(*p*-carboxyphenyl)-silane (*p*-trimethylsilylbenzoic acid) have respective constants of 0.96×10^{-6} and 1.41×10^{-6}.[26] These data are in agreement with the observation that the trimethylsilyl group is electron-releasing.[26]

2-(5-Carboxyfuryl)-trimethylsilane, $C_4H_2O(COOH\text{-}5)[Si(CH_3)_3\text{-}2]$ resulted from the carbonation of 2-(5-lithiofuryl)-trimethylsilane [from trimethyl-(2-furyl)-silane and *n*-butyllithium[24]]. The yield of product, melting at 110-111°, was 62%.[34]

The carbonation of 2-(5-lithiothienyl)-trimethylsilane formed *2-(5-carboxythienyl)-trimethylsilane*, $C_4H_2S(COOH\text{-}5)[Si(CH_3)_3\text{-}2]$, in 62% yield.[34] This acid has a melting point of 134-135° after recrystallization from dilute ethanol.[34]

2-(5-Carboxythienyl)-triphenylsilane, $C_4H_2S[Si(C_6H_5)_3\text{-}2]\,(COOH\text{-}5)$ may be synthesized in 45% yield by the metalation of triphenyl-(2-thienyl)-silane with *n*-butyllithium[24] followed by carbonation of the RLi compound.[5] It melts at 188-190° with some prior softening.

1,3-Bis-(p-carboxyphenyl)-tetramethyldisiloxane, $[p\text{-}HOCOC_6H_4Si(CH_3)_2]_2O$, resulted in 63% yield by the oxida-

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[34] R. A. Benkeser and R. B. Currie, *ibid.*, *70*, 1780 (1948).

tion of 1,3-bis-(*p*-tolyl)-tetramethyldisiloxane with chromium trioxide in acetic acid-acetic anhydride solvent containing sulfuric acid.[30] The temperature of the reaction was kept between -5° and 5°. The melting point of the pure acid is 241-242° (from acetone).[30]

This acid can be prepared also by the hydrolysis of 1,3-bis-(*p*-cyanophenyl)-tetramethyldisiloxane (prepared from 1,3-bis-(*p*-bromophenyl)-tetramethyldisiloxane and cuprous cyanide). The melting point of the compound obtained by this method of preparation is 239-241°.[30]

Arylsilicon Compounds Containing the Carbonyl Group

The reaction of trimethyl-2-thienylsilane with acetic anhydride in the presence of iodine as a catalyst has been used to prepare *2-(5-acetylthienyl)-trimethylsilane*, $C_4H_2S(COCH_3\text{-}5)[Si(CH_3)_3\text{-}2]$ in 13% yield. It is a yellow oil which boils at 104-105° at 4 mm., n_D^{20} 1.5289, d_4^{20} 1.028.[34]

The oxidation of 2-(5-acetylthienyl)-trimethylsilane by means of selenium dioxide in dioxane under reflux for 2½ hours forms *(5-trimethylsilyl-2-thienyl)-glyoxal*, $C_4H_2S(COCHO\text{-}2)[Si(CH_3)_3\text{-}5]$ in 73% yield.[35] It is a pale yellow oil which boils at 89-90° at 0.6 mm. This compound forms a monohydrate melting at 102-109°, and its semicarbazone

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[35] R. A. Benkeser and H. Landesman, *ibid.*, 71, 2493 (1949).

melts at 221-224° with decomposition.[35]

The furan derivatives analagous to the thiophene compounds listed above are prepared in the same way.[35] *2-(5-Acetylfuryl)-trimethylsilane*, $C_4H_2O(COCH_3\text{-}5)[Si(CH_3)_3\text{-}2]$, is a yellow oil boiling at 78.5-79° at 3-4 mm., n_D^{20} 1.4925, d_4^{20} 0.978.[35] The semicarbazone has a melting point of 200-201°.[35] The yield of ketone is 25%.

(5-Trimethylsilyl-2-furyl)-glyoxal, $C_4H_2O[(CH_3)_3Si\text{-}5](COCHO\text{-}2)$, formed in 40% yield. It is a yellow oil boiling at 71° at 0.6 mm. pressure.[35] The compound rapidly darkens and solidifies on standing at room temperature in a nitrogen atmosphere. The monohydrate melts at 108-114°.[35]

Phenyl Silicon Isocyanates and Isothiocyanates

Triphenylchlorosilane reacts with inorganic cyanates and thiocyanates to form triphenylsilyl isocyanate and isothiocyanate.[36] In addition to this method of synthesis, the isocyanate can be prepared by the treatment of triphenylchlorosilane with urea[37] and sodium urethan,[37] and the isothiocyanate can be formed by the reaction of thiourea with triphenylchlorosilane.[37]

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[36] (a) G. S. Forbes and H. H. Anderson, *ibid.*, *62*, 761 (1949); (b) *ibid.*, *70*, 1943 (1948); (c) H. H. Anderson, *ibid.*, *70*, 1220 (1948).

[37] H. Gilman, B. Hofferth, and H. W. Melvin, *ibid.*, *72*, 3045 (1950).

Triphenylsilyl isocyanate, $(C_6H_5)_3SiNCO$, can be synthesized in yields of 80-85% by the reaction of triphenylchlorosilane with excess silver cyanate in refluxing benzene.[36b] The melting point is given as 95±1°,[36b] and 100-101°.[37] The compound was also formed in a yield of 67% when the chlorosilane was fused with urea for four hours,[37] and in 48% yield when triphenylchlorosilane reacted with sodium urethan in refluxing xylene.[37]

Triphenylsilyl isocyanate is converted into triphenylsilanol and benzamide when it reacts with phenyllithium or with phenylmagnesium bromide,[37] but it is not affected by absolute ethanol in refluxing benzene.[37]

When triphenylchlorosilane reacted with silver thiocyanate,[36c,37] ammonium thiocyanate,[37] lead thiocyanate,[37] or thiourea,[37] the yields of *triphenylsilyl isothiocyanate*, $(C_6H_5)_3SiNCS$, were 73%, 56%, 97%, and 68%, respectively. It is reported to melt at 76±1°[36c] and at 100-101°.[37]

Triphenylsilyl isothiocyanate reacts with phenyllithium to form triphenylsilanol,[37] tetraphenylsilane,[37] and thiobenzamide.[37] Phenylmagnesium bromide causes the production of triphenylsilanol and hydrogen sulfide.[37] If, however, the reaction with phenylmagnesium bromide is carried out at elevated temperatures, some benzophenone is obtained.[37]

Both triphenylsilyl isocyanate and triphenylsilyl isothiocyanate can be hydrolyzed to triphenylsilanol.[37]

Cyanoarylsilanes

1,3-Bis-(p-cyanophenyl)-tetramethyldisiloxane, $[p\text{-}NCC_6H_4(CH_3)_2Si]_2O$, can be prepared by treating 1,3-bis-(p-bromophenyl)-tetramethyl-disiloxane with a mixture containing cuprous cyanide, potassium cyanide, and copper powder.[30] It is a liquid boiling at 190-200° at 1-2 mm., n_D^{25} 1.5351, d_4^{25} 1.0460.

Alkylsilicon Compounds Containing $SiNR_2$ Groups

Compounds of the type R_3SiNR_2 have been synthesized by treating R_3SiX or $(R_3Si)_2SO_4$ types with ammonia or amines. The R groups may be hydrogen or radicals. These compounds are liquids which undergo hydrolysis, alcoholysis, polymerization, and conversion into disiloxanes, disilazanes, and silyl halides.

Trimethyl-(methylamino)-silane, $(CH_3)_3SiNHCH_3$, was prepared in 55% yield by the action of liquid methylamine or an ether solution of methylamine upon trimethylchlorosilane.[38] It distills at 71° at 755 mm., n_D^{20} 1.3905, d_4^{20} 0.7395.

Trimethyl-(dimethylamino)-silane, $(CH_3)_3SiN(CH_3)_2$, was formed when dimethylamine reacted with trimethylchlorosilane in xylene.[39] It boils at 85-86°.

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[38] R. O. Sauer and R. H. Hasek, ibid., 68, 241 (1946).

[39] E. Larrson and O. Mjorne, Trans. Chalmers Univ. Gothenburg, No. 87, 29 (1949) [C. A., 44, 1402 (1950)].

Trimethyl-(ethylamino)-silane, $(CH_3)_3SiNHC_2H_5$, is the product of reaction between trimethylchlorosilane and ethylamine in ether.[38] The yield of compound by this method of synthesis was 25%. It boils at 90.1-90.8°, n_D^{20} 1.3912.[38]

Trimethyl-(diethylamino)-silane, $(CH_3)_3SiN(C_2H_5)_2$, was formed by merely adding trimethylchlorosilane to an ether solution of diethylamine.[38] The yield of product, boiling at 126.1-126.4°, n_D^{20} 1.4112, was 28%.[38]

Trimethyl-(heptylamino)-silane, $(CH_3)_3SiNHC_7H_{15}$, was obtained by refluxing equimolecular quantities of hexamethyldisilazane and heptylamine.[40] The compounds boil at 92-93° at 26 mm.

Trimethyl-(benzylamino)-silane, $(CH_3)_3SiNHCH_2C_6H_5$, was prepared from hexamethyldisilazane and benzylamine in the same way as was the above described compound.[40] It boils at 98-99° at 22 mm. The reaction between hexamethyldisilazane and β-phenylethylamine resulted in the formation of *trimethyl-(phenethylamino)-silane*, $(CH_3)_3SiNHCH_2CH_2C_6H_5$, which boils at 107° at 22 mm.[40]

Trimethyl-(phenylamino)-silane, $(CH_3)_3SiNHC_6H_5$, prepared from hexamethyldisilazane and aniline, has a boiling point of 96-98° at 24 mm.[40]

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[40] O. Mjorne, *Svensk* *Kem*. *Tid*., *62*, 120 (1950) [*C*. *A*., *44*, 9342 (1950)].

Hexamethyldisilazane, $[(CH_3)_3Si]_2NH$, was obtained in 61-68% yield by the reaction of gaseous ammonia with an ether solution of trimethylchlorosilane.[41] It can also be prepared by treating trimethylchlorosilane with liquid ammonia[38] (45% yield) or trimethylsilyl sulfate[42] with gaseous ammonia.[42] Hexamethyldisilazane boils at 125.2-125.7°, n_D^{20} 1.4081. It does not react with sodium but is hydrolyzed to trimethylsilanol by water and hydrochloric acid.[38]

A by-product formed during the synthesis of trimethyl-(methylamino)-silane from trimethylchlorosilane and methylamine is *N-methylhexamethyldisilazane,* $[(CH_3)_3Si]_2NCH_3$. It boils at 125.2-125.7°.

Triethyl-(amino)-silane, $(C_2H_5)_3SiNH_2$, boiling at 136.8-137.8° at 753 mm., n_D^{20} 1.4259, was prepared in 26% yield by adding triethylchlorosilane to liquid ammonia.[38] If the reaction is carried out in a low temperature bath, the yield of product boiling at 134°, n_D^{20} 1.4267, is 70%.[43]

Triethyl-(amino)-silane reacts with the halogen acids to form the respective triethylhalogenosilanes.[43] Thus, triethylchlorosilane can be obtained in 80% yield from hydrochloric

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[41] R. O. Sauer, *J. Am. Chem. Soc.*, *66*, 1707 (1944).

[42] L. H. Sommer, G. T. Kerr, and F. C. Whitmore, *ibid.*, *70*, 445 (1948).

[43] D. L. Bailey, L. H. Sommer, and F. C. Whitmore, *ibid.*, *70*, 435 (1948).

acid and in 70% yield when hydrogen chloride is made to react with an ether solution of the aminosilane.[43] Triethylfluorosilane is prepared in 89% yield when hydrofluoric acid is used.[43] Triethylbromosilane is prepared in 70% yield by the action of hydrogen bromide upon triethyl-(amino)-silane, and in 55% yield by the action of a mixture of hydrobromic and sulfuric acids with triethyl-(amino)-silane.[43]

Triethyl-(ethylamino)-silane, $(C_2H_5)_3SiNHC_2H_5$, was prepared by the action of lithium upon triethylsilane in ethylamine.[44] Seemingly the lithium acted as a catalytic agent.

$$(C_2H_5)_3SiH + Li + C_2H_5NH_2 \longrightarrow (C_2H_5)_4SiNHC_2H_5 + Li + H_2$$

The amine can also be prepared from triethylbromosilane, ethylamine, and lithium[44], or by refluxing a 1:2 ratio of

$$(C_2H_5)_3SiBr + Li + C_2H_5NH_2 \longrightarrow (C_2H_5)_3SiNHC_2H_5 + LiBr + \tfrac{1}{2}H_2$$

triethylchlorosilane and ethylamine in benzene.[39] Triethyl-(ethylamino)-silane is a clear liquid having a camphor-like odor,[44] and it boils at 63° at 22 mm.[39] Triethyl-(ethylamino)-silane can be hydrolysed to triethylsilanol,[44] and when warmed with absolute methanol for 30 minutes, it is converted

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[44] C. A. Kraus and W. K. Nelson, ibid., 56, 195 (1934).

into trimethylmethoxysilane.[39] It does not react with lithium in ethylamine solution.[44]

Triethyl-(phenylamino)-silane, $(C_2H_5)_3SiNHC_6H_5$, was synthesized from triethylchlorosilane and aniline by refluxing a chloroform solution of the reactants.[39] It boils at 130-132° at 12 mm.[39]

Triethyl-(benzylamino)-silane, $(C_2H_5)_3SiNHCH_2C_6H_5$, boiling at 148° at 20 mm., was prepared by the same procedure as was the phenylamino compound.[39]

Triethyl-(p-methylphenylamino)-silane, $(C_2H_5)_3SiNHC_6H_3CH_3$-*p*, was formed by interacting triethylchlorosilane and *p*-toluidine in boiling benzene.[39] It boils at 147° at 16 mm.

Hexaethyldisilazane, $[(C_2H_5)_3Si]_2NH$, can be prepared by the following sequence of reactions:[44]

$$(C_2H_5)_3SiH + KNH_2 \xrightarrow{\text{liq. } NH_3} [(C_2H_5)_3Si]_2NK + H_2$$

$$[(C_2H_5)_3Si]_2NK + NH_4Br \longrightarrow [(C_2H_5)_3Si]_2NH + KBr + NH_3.$$

No Si-K bond apparently formed.[44]

Hexaethyldisilazane boils at 100° at 1 mm., and is a clear colorless oil with a faint camphor-like oder.[44] It is not soluble in liquid ammonia and is denser than that solvent.[44]

Dimethylbis-(methylamino)-silane, $(CH_3)_2Si(NHCH_3)_2$, was formed by reacting dimethyldichlorosilane and methylamine in dry ether at -15° and then refluxing the mixture for 45 minutes.[45] The yield of product boiling at 66° at 165 mm. was 66%.[45]

When dimethylbis-(methylamino)-silane is distilled at atmospheric pressure, it decomposes into methylamine, N-methyl-1,3-bis-(methylamino)-tetramethyldisilazane, $[(CH_3)_2SiNHCH_3]_2NCH_3$, and a small quantity of a polymeric substance.[45]

Dimethylbis-(ethylamino)-silane, $(CH_3)_2Si(NHC_2H_5)_2$, was prepared from ethylamine and dimethyldichlorosilane in benzene, the yield being approximately 69%.[45] The boiling point is 139° at 775 mm.[45]

Dimethylbis-(phenylamino)-silane, $(CH_3)_2Si(NHC_6H_5)_2$, was obtained by the reaction between dimethyldichlorosilane and aniline in carbon tetrachloride solution.[45] It boils at 174° at 4-5 mm., and, after recrystallization from petroleum ether, it melts at 56°.[45] The yield was about 66%.[45]

The reaction between dimethyldichlorosilane and benzylamine resulted in the formation of *dimethylbis-(benzylamino)-silane*, $(CH_3)_2Si(NHCH_2C_6H_5)_2$, in 62% yield.[45] It boils at 174-178° at 5 mm., n_D^{20} 1.5409, d^{20} 1.0090.[45]

α-Chloroethyldiethyl-(amino)-silane, $CH_3CHCl(C_2H_5)_2SiNH_2$, was prepared by slowly adding α-chloro-

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[45] E. Larrson and B. Smith, *Acta Chem. Scand.* *3*, 487 (1949) [C. A., *44*, 1897 (1950)].

ethyldiethylchlorosilane to liquid ammonia in a Dry Ice-acetone bath. The yield of amine boiling at 93° at 38 mm., n_D^{20} 1.4570, d^{20} 0.9604, was 88%.[43]

α-Chloroethyldiethyl-(amino)-silane can be converted into α-chloroethyldiethylhalogenosilanes when it is treated with halogen acids. By this means, α-chloroethyldiethylchlorosilane (79%), α-chloroethyldiethylfluorosilane (82%), and α-chloroethyldiethylbromosilane (26%) were prepared.[43] Anhydrous hydrogen chloride reacts with an ether solution of the silane to produce α-chloroethyldiethylchlorosilane in 76% yield, and a mixture of hydrobromic and sulfuric acids converts α-chloroethyldiethyl-(amino)-silane into the corresponding bromosilane in 81% yield.[43]

β-Chloroethyldiethyl-(amino)-silane, $ClCH_2CH_2(C_2H_5)_2SiNH_2$, can be prepared in 60% yield by the action of liquid ammonia upon β-chloroethyldiethylchlorosilane.[46] It has a boiling point of 65-65.5° at 7 mm., n_D^{20} 1.4624, d^{20} 0.9769. β-Chloroethyldiethyl-(amino)-silane is reportedly quite unstable, and decomposes slowly into ethylene, ammonium chloride, and other products.[46]

Haloalkylsilanes

Organosilicon compounds containing halogens in the alkyl group can be prepared by (1) direct halogenation in the

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[46] L. H. Sommer, D. L. Bailey, and F. C. Whitmore, *J. Am. Chem. Soc.*, *70*, 2869 (1948).

presence of ultraviolet light, (2) the use of sulfuryl chloride with benzoyl peroxide catalyst, (3) the action of phosphorus halides upon hydroxy compounds, and (4) the reaction between allyl compounds and hydrogen halides. They are liquids which may form esters and amines, and they can be cleaved and hydrolyzed.

Methyl-(chloromethyl)-dichlorosilane, $CH_3(CH_2Cl)SiCl_2$, was formed in 37% yield by the photochemical chlorination of dimethyldichlorosilane.[29] It distills at 121.3°.[29] Methyl-(chloromethyl)-dichlorosilane reacts with phenylmagnesium bromide to produce methylphenyl-(chloromethyl)-chlorosilane and diphenylmethyl-(chloromethyl)-silane. Hydrolysis studies show that the chlorines attached to silicon are easily affected by simply placing the compound in water.[29]

Methyl-(dichloromethyl)-dichlorosilane, $CH_3(CHCl_2)SiCl_2$, was produced to the extent of 38.3% along with the monochloromethyl compound.[29] It boils at 107-108° at 225 mm. Only the chlorines attached to silicon are hydrolyzed under mild conditions.[29]

(Trichloromethyl)-triphenylsilane, $Cl_3CSi(C_6H_5)_3$, was prepared by the chlorination of methyltriphenylsilane at 150° in ultraviolet light.[27] The yield of product melting at 194° was 38.6%.[27]

Methyl-(trichloromethyl)-dichlorosilane, $CH_3(CCl_3)SiCl_2$, was obtained in 6.5% yield when dimethyldichlorosilane was photochemically chlorinated.[29] It boils at 109° at 150 mm. and has a melting point of 99°.

The action of sulfuryl chloride upon methylethyldichlorosilane in the presence of benzoyl peroxide catalyst resulted in the formation of the methyl-(chloroethyl)-dichlorosilanes.[47] *Methyl-(α-chloroethyl)-dichlorosilane*, $CH_3(CH_3CHCl)SiCl_2$, has a boiling point of 135-136° at 760 mm.,[47] and *methyl-(β-chloroethyl)-dichlorosilane*, $CH_3(CH_2ClCH_2)SiCl_2$, boils at 156-157° at 760 mm.[46]

These silanes will react with a 30% excess of quinoline to form vinylmethyldichlorosilane.[47]

Dimethyl-(chloromethyl)-chlorosilane, $(CH_3)_2CH_2ClSiCl$, prepared by the photochemical chlorination of trimethylchlorosilane, distills at 115° at 760 mm.[29]

Dimethylbis-(chloromethyl)-silane, $(CH_3)_2Si(CH_2Cl)_2$, can be prepared in 63% yield by the action of methylmagnesium bromide upon bis-(chloromethyl)-dichlorosilane.[48] It boils at 160° (724 mm.), n_D^{25} 1.4579, d_4^{25} 1.075.[48]

Dimethylbis-(chloromethyl)-silane was heated and shaken with potassium acetate in acetic acid solution in a stainless

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[47] D. T. Hurd, *ibid.*, *67*, 1813 (1945).

[48] J. L. Speier and B. F. Daubert, *ibid.*, *70*, 1400 (1948).

steel autoclave at 118-130° for 4 hours and then at 148-160° for 16 hours to form bis-(acetoxymethyl)-dimethylsilane, boiling at 124° at 27 mm., and 223° at 739 mm., n_D^{25} 1.4309, d_4^{25} 1.0135, in 90% yield.[48]

Trimethyl-(chloromethyl)-silane, $(CH_3)_3SiCH_2Cl$, was prepared in 33% yield by the chlorination of tetramethylsilane irradiated with ultraviolet light.[49] It boils at 97.1° at 734 mm., n_D^{20} 1.4180.

Trimethyl-(chloromethyl)-silane forms trimethylsilylmethylmagnesium chloride in 90% yield,[49] and the corresponding lithium compound has been prepared in 86% yield in boiling pentane.[50] It also reacts with R_3SiX types and sodium in hexadecane solution to yield compounds of the general formula $(CH_3)_3SiCH_2SiR_3$.[50] The Grignard reagent prepared from trimethyl-(chloromethyl)-silane can be made to react with mercuric chloride to form trimethyl-(chloromercurimethyl)-silane which melts at 74-76°,[49] and with phenyl isocyanate to form acetanilide (80%).[48] Trimethyl-(chloromethyl)-silane rearranges to dimethylethylchlorosilane when heated with aluminum chloride, some trimethylchlorosilane and methyldiethylchlorosilane being formed also.[51]

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[49] F. C. Whitmore and L. H. Sommer, *ibid.*, *68*, 481 (1946).

[50] J. T. Goodwin, Brit. Patent 627,809, Aug. 16, 1949 [C. A., 44, 3518 (1950)].

[51] F. C. Whitmore, L. H. Sommer, and J. Gold, *J. Am. Chem. Soc.*, *69*, 1976 (1947).

Trimethyl-(iodomethyl)-silane, $(CH_3)_3SiCH_2I$, can be formed by the reaction of sodium iodide with trimethyl-(chloromethyl)-silane in dry acetone solution.[49] At 744 mm. pressure, it boils at 139.5°, n_D^{20} 1.4917.[49] The compound is inert to boiling 20% aqueous silver nitrate and boiling 20% ethanolic silver nitrate.[49]

Trimethyl-(dichloromethyl)-silane, $(CH_3)_3SiCHCl_2$, was prepared in 70% yield when methylmagnesium bromide reacted with dichloromethyltrichlorosilane.[48] The compound boils at 133° at 730 mm., n_D^{25} 1.4430, d_4^{25} 1.0395.[48]

Trimethyl-(dichloromethyl)-silane reacts vigorously with sodium ethoxide in absolute ethanol forming methylene chloride (71% yield) and hexamethyldisiloxane (73% yield).[48] When heated in a sealed tube at 200° for 3 hours with potassium acetate in acetic acid, it is cleaved, yielding formaldehyde.[48]

Trimethyl-(α-chloroethyl)-silane, $(CH_3)_3SiCHClCH_3$, can be prepared in 53% yield by the reaction of methylmagnesium bromide with α-chloroethyltrichlorosilane for 14 hours.[52] It has a boiling point of 117.8° at 735 mm., n_D^{20} 1.4242. The Grignard reagent formed from trimethyl-(α-chloroethyl)-silane reacts with mercuric chloride to form trimethyl-(α-chloromercurio-ethyl)-silane with a melting point of 97°. Trimethyl-(α-chloroethyl)-silane is not affected by 20% aqueous silver nitrate.[52]

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[52] L. H. Sommer and F. C. Whitmore, *ibid.*, *68*, 485 (1946).

Trimethyl-(γ-bromopropyl)-silane, $(CH_3)_3Si(CH_2)_3Br$, was obtained when trimethyl-(γ-hydroxypropyl)-silane was treated with phosphorus tribromide under reflux for 4 hours.[53] It boils at 70° at 25 mm., n_D^{20} 1.4541, d^{20} 1.1173.[53] The yield was 84%.[52]

Trimethyl-(γ-bromopropyl)-silane can be converted into cyclopropane (92%) and trimethylbromosilane (82%) in the presence of aluminum chloride.[53] When its Grignard reagent (γ-trimethylsilylpropylmagnesium bromide) reacts with ethylene oxide, trimethyl-(5-hydroxypentyl)-silane is produced in 64% yield.[53]

Trimethyl-(5-bromopentyl)-silane, $(CH_3)_3Si(CH_2)_5Br$, boils at 113° at 23 mm., n_D^{20} 1.4570.[52] It is prepared by treating trimethyl-(5-hydroxypentyl)-silane with phosphorus tribromide, allowing the mixture to stand for 18 hours, and then heating it at 95-99° for 1 hour.[53] The yield of product obtained by this procedure is 78%.[53]

It is interesting to note that trimethyl-(5-bromopentyl)-silane does not form cyclopentane in the presence of aluminum chloride, some pentene-1 and trimethylbromosilane being obtained instead.[52] These observations are in line with the γ-elimination mechanisms proposed by these investigators[53] for silicon-containing compounds. The formation of cyclopropane from trimethyl-(γ-bromopropyl)-silane and aluminum chloride is

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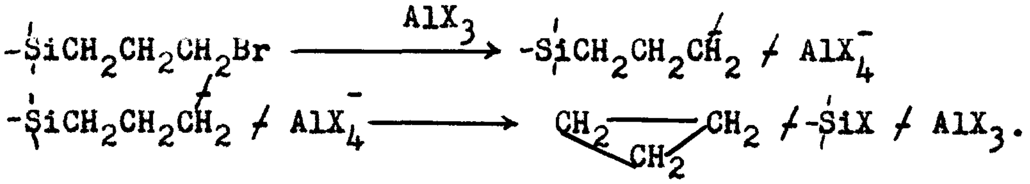
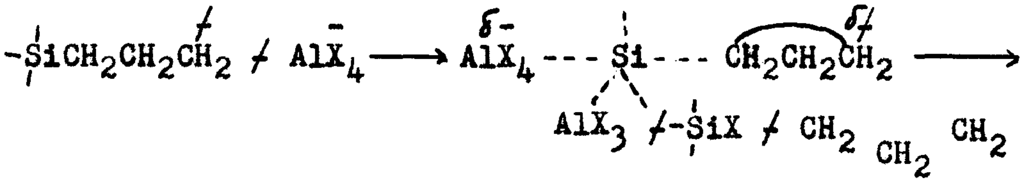
[53] L. H. Sommer, R. E. Van Strien, and F. C. Whitmore, *ibid.*, *71*, 3056 (1949).

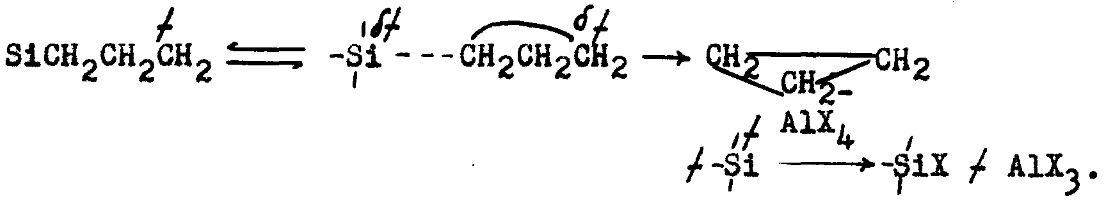
explained by the following scheme:[53]



The formation of a transition complex might be considered, or



the liberation of a siliconium ion prior to combination with halogen from AlX_4^- might occur.



There is no contention by these workers[53] that a siliconium ion is involved in these reactions. The major driving force is the ability of electropositive silicon to release an electron pair to electronically deficient carbon. The absence of cyclopentane formation is felt to be traceable to the distance between silicon and the electronically deficient carbon, which distance would prevent intramolecular transmission of charge sufficient for cyclization, despite the lesser strain involved in a 5-membered ring.[53]

Trimethyl-(β-bromopropyl)-silane, $(CH_3)_3SiCH_2CHBrCH_3$, was formed in 70% yield by the action of hydrogen bromide upon allyltrimethylsilane.[54] The reaction was initiated at room temperature and continued in a Dry Ice-ether bath. The compound boils at 31° (6 mm.), n_D^{20} 1.4580, d^{20} 1.113. The use of benzoyl peroxide in the reaction did not result in the formation of any of the *γ*-isomer.[54]

The product, on being slowly heated, decomposes above 40° yielding propene and trimethylbromosilane (88%).[54]

Trimethyl-(β-iodopropyl)-silane, $(CH_3)_3SiCH_2CHICH_3$, was similarly prepared in 48% yield.[54] The boiling point is 57° (6 mm.), n_D^{20} 1.496. It fumes in the air, and decomposes into propene (55%) and trimethyliodosilane (46%) when it is heated at 80° for 30 minutes.[54]

Trimethyl-(β,γ-dichloropropyl)-silane, $(CH_3)_3SiCH_2CHClCH_2Cl$, can be obtained in 56% yield when chlorine is led into trimethylallylsilane at -70°.[54] This compound boils at 36° at 4 mm., n_D^{20} 1.4581, d^{20} 1.030. No comparable reaction with bromine was observed when that reagent was used with allyltrimethylsilane. In that instance, allyl bromide and trimethylbromosilane were formed.[54]

Trimethyl-(β,γ-dichloropropyl)-silane is decomposed into allyl chloride (87%) and trimethylchlorosilane (87%) when it is heated above 90° for 30 minutes.[54]

α-Chloroethyltrichlorosilane, $CH_3CHClSiCl_3$, and *β-chloroethyltrichlorosilane,* $CH_2ClCH_2SiCl_3$, were produced together

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[54] L. H. Sommer, L. J. Tyler, and F. C. Whitmore, *ibid.*, *70*, 2872 (1948).

when ethyltrichlorosilane was treated with sulfuryl chloride and benzoyl peroxide catalyst.[52] The α-isomer, formed in 21% yield, boils at 138° (734 mm.) while the β-isomer (53% yield) has a boiling point of 152°. Only the chlorine attached to silicon can be titrated in α-chloroethyltrichlorosilane while all the chlorine atoms in β-chloroethyltrichlorosilane can be so determined.[52]

When *n*-propyltrichlorosilane (from silicon tetrachloride and *n*-propylmagnesium bromide in 41% yield[55]) and sulfuryl chloride were heated together for 12 hours, all three isomeric chloropropyltrichlorosilanes were produced.[55] The ratio of α-:β-:γ- was 1:3.5:3.1. *α-Chloropropyltrichlorosilane*, $CH_3CH_2CHClSiCl_3$, distills at 157° at 739 mm. and was obtained in a yield of 13.3%. *β-Chloropropyltrichlorosilane*, $CH_3CHClCH_2SiCl_3$, has a boiling point of 162° at 729 mm., and was formed in about 47% yield. *γ-Chloropropyltrichlorosilane*, $CH_2ClCH_2CH_2SiCl_3$, obtained in 41% yield, boils at 178.5° at 732 mm.

γ-Chloropropyltrichlorosilane reacts with potassium hydroxide in aqueous ethanol to form cyclopropane in a yield of 31%.[53] However, the compound did not react in the presence of aluminum chloride. This latter observation is explained on the basis that halogens, being electronegative, would inhibit the release of electrons to carbon by silicon, thus rendering

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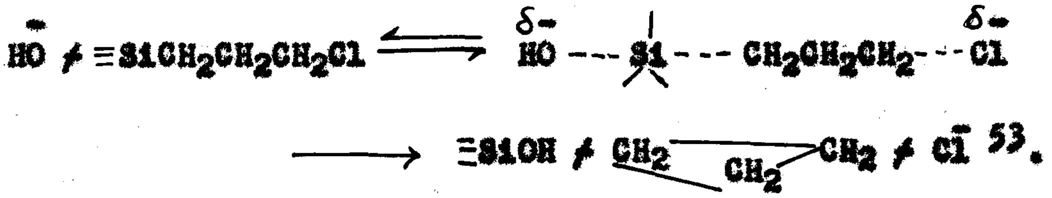
[55] L. H. Sommer, E. Dorfman, G. M. Goldberg, and F. C. Whitmore, *ibid.*, **68**, 488 (1946).

silicon less vulnerable to nucleophilic attack.[53] The mechanism involving base in the formation of cyclopropane from *γ*-chloropropyltrichlorosilane is suggested to be



$$\overset{-}{HO} + \equiv SiCH_2CH_2CH_2Cl \rightleftarrows \overset{\delta-}{HO} --- \overset{|}{\underset{\diagup\diagdown}{Si}} --- CH_2CH_2CH_2 --- \overset{\delta-}{Cl}$$

$$\longrightarrow \equiv SiOH + CH_2CH_2CH_2 + \overset{-}{Cl}\ ^{53}.$$

Trimethyl-(3-methyl-3-chlorobutyl)-silane, $(CH_3)_3SiCH_2CH_2CCl(CH_3)CH_3$, was obtained by shaking trimethyl-(3-methyl-3-hydroxybutyl)-silane with concentrated hydrochloric acid in a separatory funnel for 15 minutes.[56] The yield of product, boiling at 90° under 55 mm. pressure, was 48%, n_D^{20} 1.4338, d^{20} 0.869.[56]

Diethyl-(α-chloroethyl)-fluorosilane, $CH_3CHCl(C_2H_5)_2SiF$, was formed in 82% yield when diethyl-(*α*-chloroethyl)-aminosilane[43] was added dropwise to 48% hydrofluoric acid cooled in an ice bath and the mixture stirred for 10 minutes.[43] It boils at 149-150°, d^{20} 0.9961.[43] The compound may also be prepared with the *β*-isomer by chlorinating triethylfluorosilane with sulfuryl chloride with benzoyl peroxide catalyst.[57]

Diethyl-(β-chloroethyl)-fluorosilane, $CH_2ClCH_2(C_2H_5)_2SiF$, boils at 101° at 77 mm.[57]

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[56] L. H. Sommer and N. S. Marans, *ibid.*, *72*, 1935 (1950).

[57] L. H. Sommer, D. L. Bailey, W. A. Strong, and F. C. Whitmore, *ibid.*, *68*, 1881 (1946).

Diethyl-(α-chloroethyl)-chlorosilane, $CH_3CHCl(C_2H_5)_2SiCl$, can be prepared by passing hydrogen chloride into an ether solution of diethyl-(α-chloroethyl)-aminosilane.[43] The yield was 76%. The constants are boiling point 179-181°, d^{20} 1.0385, n_D^{20} 1.4553.[42] It was also formed by chlorinating triethylchlorosilane with sulfuryl chloride.[57]

Diethyl-(β-chloroethyl)-chlorosilane, $CH_2ClCH_2(C_2H_5)_2SiCl$, was formed with the α-isomer when triethylchlorosilane reacted with sulfuryl chloride.[57] It boils at 153° at 200 mm., or 201° at 760 mm., d_4^{20} 1.0552, n_D^{20} 1.4636.

Diethyl-(α-chloroethyl)-bromosilane, $CH_3CHCl(C_2H_5)_2SiBr$, can be synthesized in 26% yield by treating diethyl-(α-chloroethyl)-aminosilane in ether with hydrogen bromide,[43] or by treating the aminosilane, cooled in an ice bath, with 48% hydrobromic acid followed by the dropwise addition of concentrated sulfuric acid.[43] The yield by the latter method of preparation was 81%. Diethyl-(α-chloroethyl)-bromosilane boils at 194-196° at atmospheric pressure and 105-106° at 46 mm., n_D^{20} 1.4752 and 1.4764.[43]

Diethylmethyl-(α-chloroethyl)-silane, $(C_2H_5)_2CH_3SiCHClCH_3$, can be obtained in 87% yield by the interaction of diethyl-(α-chloroethyl)-chlorosilane and methylmagnesium bromide.[57] The compound boils at 80° at 40 mm., 125° at 200 mm., 172° at 760 mm., d^{20} 0.9036, n_D^{20} 1.4452.[57]

Diethylphenyl-(α-chloroethyl)-silane, $(C_2H_5)_2C_6H_5SiCHClCH_3$, boils at 104° at 4 mm., 219° at 200 mm., 274° at 760 mm.,

d_4^{20} 1.0109, n_D^{20} 1.5229. It can be prepared in 52% yield from diethyl-(α-chloroethyl)-chlorosilane and phenylmagnesium bromide.[57]

Diethyl-(α-chloroethyl)-silanol, $(C_2H_5)_2CH_3CHClSiOH$, was obtained by the hydrolysis of diethyl-(α-chloroethyl)-chlorosilane on cracked ice containing sodium hydroxide.[57] The compound boils at 101° at 29 mm., 150° at 200 mm., 195° at 760 mm., d_4^{20} 1.0238, n_D^{20} 1.4067.[57] This method of preparation seemingly does not make for disiloxane formation, the only product isolated being the silanol (84%).[57]

The action of chlorine on cooled tetraethylsilane resulted in the formation of both isomers of triethyl-(chloroethyl)-silane.[58] *Triethyl-(α-chloroethyl)-silane*, $(C_2H_5)_3SiCHClCH_3$, boils at 72-73° at 9 mm., d_{17}^{17} 0.9143, n_D^{17} 1.4538,[58] and *triethyl-(β-chloroethyl)-silane*, $(C_2H_5)_3SiCH_2CH_2Cl$, has the boiling point of 80-82° at 9 mm., d_{17}^{17} 0.9158, n_D^{20} 1.4562.[58]

The α-isomer is converted into triethylvinylsilane when heated in a sealed tube with alkali at 145°,[58] and triethyl-(β-chloroethyl)-silane forms the vinyl derivative upon being warmed with alkali.[58] Triethylvinylsilane reportedly does not polymerize even in the presence of benzoyl peroxide or sulfuric acid.[58]

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[58] S. M. Ushakov and A. M. Itenberg, *J. Gen. Chem.* (U.S.S.R.) *7*, 2495 (1937) [(*C. A.*, *32*, 2083 (1938)].

(Chloromethyl)-pentamethyldisiloxane, $(CH_3)_2CH_2ClSiOSi(CH_3)_3$, was obtained by the hydrolysis of a mixture of trimethylchlorosilane and dimethyl-(chloromethyl)-chlorosilane and then heating the mixture.[29] It boils at 204-204.5°, n_D^{20} 1.4106, d_4^{20} 0.9105. Some hexamethyldisiloxane was also isolated.[29] The main product was formed in a yield of approximately 38%.

1.3-Bis-(chloromethyl)-tetramethyldisiloxane, $[(CH_3)_2CH_2ClSi]_2O$, was formed by the hydrolysis of dimethyl-(chloromethyl)-chlorosilane.[29] The product boils at 204.5°, n_D^{20} 1.4390, d_4^{20} 1.045. The yield was approximately 94%.

Hydroxyalkylsilanes

Organosilicon compounds containing the hydroxyalkyl group may be synthesized by several methods. The basic hydrolysis of esters (particularly acetates) and the reaction of Grignard reagents with appropriate compounds (esters, ketones, and ethylene oxide) are means successfully employed. Compounds prepared by these methods are described below.

Phenyldimethyl-(3-hydroxy-3-methylbutyl)-silane, $C_6H_5(CH_3)_2SiCH_2CH_2COH(CH_3)CH_3$, was obtained by the reaction of methylmagnesium bromide with ethyl (*β*-phenyldimethylsilyl)-propionate.[56] The yield of compound, boiling at 118° (3 mm.), n_D^{20} 1.5058, d^{20} 0.347, was 80%.[56]

Trimethyl-(3-hydroxypropyl)-silane, $(CH_3)_3SiCH_2CH_2CH_2OH$, was prepared by the reaction of ethylene oxide in ether with trimethylsilylmethylmagnesium chloride.[53] The mixture was stirred for 3 days after which time the ether was replaced with benzene in which the reaction was run under reflux for 20 hours. Trimethyl-(3-hydroxypropyl)-silane boils at 83° at 27 mm., n_D^{20} 1.4290, d^{20} 0.8316 and was obtained in 71% yield.[53]

Trimethyl-(3-hydroxypropyl)-silane can be converted into trimethyl-(3-bromopropyl)-silane by treatment with hydrogen bromide.[53]

Trimethyl-(3-hydroxy-3-methylbutyl)-silane, $(CH_3)_3SiCH_2CH_2COH(CH_3)CH_3$, has a boiling point of 48° at 4 mm. and was obtained in 63% yield by the reaction of ethyl *β*-trimethylsilylpropionate with methylmagnesium bromide,[56] and from methylmagnesium bromide and 4-trimethylsilylbutanone-2 in 82% yield.[56] It melts at 12-13°, n_D^{20} 1.4315, d^{20} 0.8255.[56]

Triethyl-(hydroxyethyl)-silane, $(C_2H_5)_3SiC_2H_4OH$, has been called "siliconony1 alcohol" by one investigator, the position of the hydroxyl group not being given.[59] Triethyl-(chloroethyl)-silane was converted into the acetate by treating the chloroethylsilane with fused potassium acetate in acetic acid.[59] Hydrolysis of the acetate with ethanolic potassium hydroxide resulted in the formation of triethyl-(hydroxyethyl)-silane in 48% yield.[59] It boils at 190°.

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[59] E. L. Niedzielski, *J. Am. Chem. Soc.*, *62*, 3519 (1940).

Dimethylbis-(hydroxymethyl)-silane, $(CH_3)_2Si(CH_2OH)_2$, was formed by the slow hydrolysis of dimethylbis-(acetoxymethyl)-silane in methanol containing hydrochloric acid.[48] The boiling point of this compound is 130° at 27 mm., n_D^{25} 1.4611, d_4^{11} 0.993.

Trimethyl-(hydroxymethyl)-silane, $(CH_3)_3SiCH_2OH$, was prepared by slowly hydrolyzing trimethyl-(acetoxymethyl)-silane /prepared by heating potassium acetate and trimethyl-(chloromethyl)-silane in an autoclave in acetic acid solution/.[60] The yield of product, boiling at 121.6° at 729 mm., n_D^{25} 1.4169, d_4^{25} 0.8261, was 80%.

Trimethyl-(hydroxymethyl)-silane (trimethylsilylmethanol) forms a 3,5-dinitrobenzoate (95%) which melts at 70-70.5°.[60] The alcohol also reacts with trimethylchlorosilane in a chloroform-quinoline mixture to yield (trimethylsilylmethoxy)-trimethylsilane (84%) which boils at 129.8° (738 mm.), n_D^{25} 1.3971, d_4^{25} 0.7781. Trimethylsilylmethanol slowly reacts with sodium with the evolution of hydrogen, and dissolves in boiling 75% potassium hydroxide to form a clear solution from which an infusible combustible gel is obtained upon acidification. Apparently potassium hydroxide causes cleavage of the silicon-carbon bond, resulting in the production of a polymeric siloxane upon acidification of the solution.[60]

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[60] J. L. Speier, B. F. Daubert, and R. R. McGregor, ibid., 70, 1117 (1948).

Trimethylsilylmethanol was found to be more reactive with regard to phenyl isocyanate than were neopentyl, methyl, and ethyl alcohols.[60] Mixtures containing equivalent quantities of trimethylsilylmethanol and each of the other alcohols were reacted with phenyl isocyanate and the ratios of rate constants were found to be trimethylsilylmethanol/neopentyl alcohol, 6.56; trimethylsilylmethanol/ethanol, 3.57; trimethylsilylmethanol/methanol, 2.92.[60]

Silicon-containing alcohols have been prepared by a recently developed procedure utilizing chloroalkoxysilanes.[33] The reactions involved are

$$\mathrm{SiO(CH_2)_xCl + 2Na + ClSi \longrightarrow SiO(CH_2)_xSi\text{-} + 2NaCl} \qquad (1)$$

$$\mathrm{SiO(CH_2)_xCl + 2M \longrightarrow Si(CH_2)_xOM + MCl} \qquad (2)$$

$$\mathrm{R_3SiO(CH_2)_xCl + Mg \longrightarrow R_3SiO(CH_2)_xMgCl \xrightarrow{\text{elevated temp.}} R_3Si(CH_2)_xOMgCl.} \qquad (3)$$

The compounds resulting from reaction (1) can be hydrolyzed to the corresponding hydroxyalkylsilanes, while in reactions (2) and (3), rearrangements are involved in the formation of silicon-containing alcohols.[33]

In these preparations, x must be greater than two. When x = 2, ethylene is produced.[33]

$$\mathrm{(CH_3)_3SiO(CH_2)_2Cl + 2Na + ClSi(CH_3)_3 \longrightarrow [(CH_3)_3Si]_2O + C_2H_4 + 2NaCl}$$

When x = 3, magnesium does not react. If x = 4 or 5, sodium, lithium, and magnesium all react smoothly provided only one chloroalkoxy group is attached to silicon. When more than one such group is linked to silicon, only sodium and lithium are effective. Too, if x = 4 or 5, the Grignard reagent formed is stable at room temperature, rearranging only at elevated temperatures.[33] Trimethyl-(3-hydroxypropyl)-silane, previously described, was prepared in 60-61% yield by the action of lithium or sodium upon trimethyl-(3-chloropropoxy)-silane [see reaction (2)].[33]

Dimethylbis-(3-hydroxypropyl)-silane, $(CH_3)_2Si(CH_2CH_2CH_2OH)_2$, was obtained in 47% yield by the hydrolysis of the product obtained when sodium reacted with a mixture of trimethyl-(3-chloropropoxy)-silane and dimethyldichlorosilane.[33] It boils at 176° (24 mm.), n_D^{25} 1.4649, d_4^{25} 0.940.

Dimethylethyl-(3-hydroxypropyl)-silane, $(CH_3)_2C_2H_5SiCH_2CH_2CH_2OH$, formed in 63% yield by the acid hydrolysis of dimethylethyl-[3-(dimethylethylsilyl)-propoxy]-silane in ethanol,[33] has a boiling point of 101°, n_D^{25} 1.4370, d_4^{25} 0.839.

Dimethylethyl-(5-hydroxypentyl)-silane, $(CH_3)_3C_2H_5SiCH_2CH_2CH_2CH_2CH_2OH$, was prepared by the hydrolysis of dimethylethyl-[5-(dimethylethylsilyl)-pentoxy]-silane, and boils at 124° (24 mm.), n_D^{25} 1.4421, d_4^{25} 0.838.[33]

Trimethyl-(4-hydroxybutyl)-silane, $(CH_3)_3SiCH_2CH_2CH_2CH_2OH$, can be obtained by the action of lithium or magnesium upon trimethyl-(4-chlorobutoxy)-silane in 56% and 63% yields, respectively.[33] When sodium was used, only a small quantity of the product formed.[33] If trimethyl-(4-chlorobutoxy)-silane is treated with a sodium emulsion in tetralin, the product is n-butanol (75%).[33]

Trimethyl-(4-hydroxybutyl)-silane boils at 96° at 25 mm., n_D^{25} 1.4315, d_4^{25} 0.830.[33]

Trimethyl-(5-hydroxypentyl)-silane, $(CH_3)_3SiCH_2CH_2CH_2CH_2CH_2OH$, was prepared in 14%, 45%, and 79% yields, respectively, by the reaction of sodium, magnesium, and lithium with trimethyl-(5-chloropentoxy)-silane.[33] It boils at 110° (25 mm.), n_D^{25} 1.4358, d_4^{25} 0.841.[33] It was also obtained in a yield of 64% when 3-trimethylsilylpropylmagnesium bromide reacted with ethylene oxide.[53]

These alcohols are said to be of stable structures possessing the reactivities typical of alcohols.[33] They do not rearrange at elevated temperatures as do the phenols, nor are they cleaved by dilute acids or bases even under prolonged refluxing.[33]

Carboxyalkylsilanes and Their Derivatives

Organosilicon compounds containing carboxyalkyl groups may be prepared by (1) the carbonation of Grignard reagents, (2) the reaction of ethyl malonate and ethyl acetoacetate with certain haloalkylsilanes, and (3) the hydrolysis of esters containing silicon. They show the same chemical characteristics as do other organic acids since they can be converted into esters, acid chlorides, and amides in the customary manner.

Trimethyl-(carboxymethyl)-silane (trimethylsilylacetic acid), $(CH_3)_3SiCH_2COOH$, was formed in 88% yield when trimethylsilylmethylmagnesium chloride was carbonated. It has a melting point of 40°.[61]

Trimethyl-(carbethoxymethyl)-silane (ethyl trimethylsilylacetate), $(CH_3)_3SiCH_2COOC_2H_5$, was prepared in 74.5% yield by the action of the Grignard reagent of trimethyl-(chloromethyl)-silane upon ethyl chloroformate, the mixture being heated on a water bath for 5 hours.[62] It boils at 157° at 730 mm. and 75.5° at 42 mm., n_D^{20} 1.4149, d^{20} 0.8762, and is a colorless, stable liquid possessing a pleasant, fruity odor.[62]

Trimethyl-(carboethymethyl)-silane reacts with refluxing dilute hydrochloric acid and with sodium hydroxide solution (both cold and refluxing) to yield hexamethyldisiloxane in excess of 80% yield, and acetic acid.[62] Interaction between the ester and hydrogen chloride results in the formation of trimethylchlorosilane and ethyl acetate in respective yields

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[61] L. H. Sommer, J. R. Gold, G. M. Goldberg, and N. S. Marans, *ibid.*, *71*, 1509 (1949).

[62] J. R. Gold, L. H. Sommer, and F. C. Whitmore, *ibid.*, *70*, 2974 (1948).

of 71% and 66%.[62] Bromine cleaves the ester into trimethylbromosilane (73%) and ethyl bromoacetate (73%). Absolute ethanol reacts with the compound to form trimethylethoxysilane and ethyl acetate.[62]

Dimethylphenyl-(carboxymethyl)-silane (dimethylphenylsilylacetic acid), $(CH_3)_2C_6H_5SiCH_2COOH$, melting at 90°, was prepared in 69% yield by the carbonation of dimethylphenylsilylmethylmagnesium chloride.[61]

Dimethylphenyl-(β-carboxyethyl)-silane (β-dimethylphenylsilylpropionic acid), $(CH_3)_2C_6H_5SiCH_2CH_2COOH$, has a boiling point of 132° at 2 mm., n_D^{20} 1.5149, d^{20} 1.037.[56] It was formed in 82.4% yield by the hydrolysis of the ester with 10% sodium hydroxide.

Dimethylphenyl-(β-carbethoxyethyl)-silane (ethyl β-dimethylphenylsilylpropionate), $(CH_3)_2C_6H_5SiCH_2CH_2COOC_2H_5$, was obtained by the reaction of the sodium salt of ethyl acetoacetate with dimethylphenyl-(iodomethyl)-silane for 40 hours at the reflux temperature of the mixture.[56] The yield of product, boiling at 106° (2 mm.), n_D^{20} 1.4972, d^{20} 0.9856, was 67%.[56]

β-Dimethylphenylsilylpropionyl chloride, $(CH_3)_2C_6H_5SiCH_2CH_2COCl$, was prepared in 61% yield by heating the corresponding acid with thionyl chloride for 2 hours.[56] The product boils at 114° at 3 mm., n_D^{20} 1.5188, d^{20} 1.0664.[56]

Trimethyl-(β-methyl-β-carboxyethyl)-silane (α-methyl-β-trimethylsilylpropionic acid), $(CH_3)_3SiCH_2CH(CH_3)COOH$, a liquid boiling at 92° at 4 mm., n_D^{20} 1.4310, d^{20} 0.9121, was synthesized by the reaction of sodium ethoxide upon ethyl α-methyl α-trimethylsilylmethylacetoacetate followed by hydrolysis with hydrochloric acid.[56] The yield was 67%.

Trimethyl-(β-carboxyethyl)-silane (β-trimethylsilylpropionic acid), $(CH_3)_3SiCH_2CH_2COOH$, was obtained in respective yields of 66% and 63% when the sodium salts of ethyl malonate and ethyl acetoacetate reacted with trimethyl-(chloromethyl)-silane. The acid has a boiling point of 147° under 65 mm. pressure, n_D^{20} 1.4279. It melts at 22°.[60]

The acid also formed when the ethyl ester was hydrolyzed with 10% sodium hydroxide at 90° for 2 hours.[56] The yield by this method of synthesis was 89%, n_D^{20} 1.4280, d^{20} 0.9196.[56]

The reaction between β-trimethylsilylpropionic acid and thionyl chloride at 90° for 1 hour resulted in the formation of *β-trimethylsilylpropionyl chloride*, $(CH_3)_3SiCH_2CH_2COCl$, in yields of 89%[52] and 96.6%[63]. It boils at 92° (65 mm.), n_D^{20} 1.4375, d^{20} 0.9609.[52] It reacts with dimethylcadmium and diphenylcadmium to form the corresponding ketones.[53]

β-Trimethylsilylpropionamide, $(CH_3)_3SiCH_2CH_2CONH_2$, was obtained by reaction between β-trimethylsilylpropionyl chloride

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[63] L. H. Sommer and J. Rockett, *ibid.*, 73, 5130 (1951).

and liquid ammonia.[63] It is a white flaky solid which has a melting point of 95-96°.[63] The conversion of the acid chloride into the amide occurs to the extent of 94.3%.[63]

β-Trimethylsilylpropionitrile, $(CH_3)_3SiCH_2CH_2CN$, can be synthesized from β-trimethylsilylpropionamide by heating the amide with phosphorus pentoxide.[63] It is a clear, colorless liquid possessing a pleasant minty odor, and boils at 94° under 49 mm. pressure, n_D^{20} 1.4240, d_4^{20} 0.8270.[63] The yields were 71-86%.

Trimethyl-(β-carbethoxyethyl)-silane (ethyl β-trimethylsilylpropionate), $(CH_3)_3SiCH_2CH_2COOC_2H_5$, was prepared by refluxing a mixture of trimethyl-(iodomethyl)-silane and the sodium salt of ethyl acetoacetate for 14 hours.[56] The cooled mass was neutralised with glacial acetic acid and then fractionated. The yield of product, boiling at 93° at 40 mm., n_D^{20} 1.4198, d^{20} 0.8763, was 70%.[56]

The ester was formed also by reacting sodium ethoxide with ethyl α-(trimethylsilylmethyl)-acetoacetate at 90° for 12 hours. After neutralising the mixture with glacial acetic acid, the yield was 64%.[56]

Ethyl α-(trimethylsilylmethyl)-acetoacetate, $CH_3COCH[CH_2Si(CH_3)_3]COOC_2H_5$, was prepared by refluxing the sodium derivative of ethyl acetoacetate and trimethyl-(iodomethyl)-silane for 30 hours. The compound has a boiling point of 126° (50 mm.), n_D^{20} 1.4405, d^{20} 0.949 and was obtained in 48% yield [based on unrecovered trimethyl-(iodomethyl)-

silane].[56] Some ethyl β-trimethylsilylpropionate (22%) was also produced.[55]

Ethyl α-methyl-α-(trimethylsilylmethyl)-acetoacetate, $CH_3COC(CH_3)[CH_2Si(CH_3)_3]COOC_2H_5$, was formed by the treatment of the sodium salt of ethyl α-(trimethylsilylmethyl)-acetoacetate with methyl iodide under reflux for 30 minutes.[56] This compound, boiling at 87° at 55 mm., n_D^{20} 1.4420, d^{20} 0.9512, was obtained in 72% yield.[56]

If ethyl iodide is used in the procedure given above, *ethyl α-ethyl-α-(trimethylsilylmethyl)-acetoacetate*, $CH_3COC(C_2H)_5[CH_2Si(CH_3)_3]COOC_2H_5$, is obtained in 58% yield.[56] It has a boiling point of 92° at 3 mm., n_D^{20} 1.4453, d^{20} 0.9509.

Pentamethyl-(β-carboxyethyl)-disiloxane, $(CH_3)_3SiOSi(CH_3)_2CH_2CH_2COOH$, was prepared by the carbonation of the Grignard reagent formed from pentamethyl-(chloromethyl)-disiloxane in a yield of 85%.[61] The compound melts at 17°, n_D^{20} 1.4149.

The acid strengths of trimethylsilylacetic acid, β-dimethyl-(trimethylsiloxy)-silylpropionic acid, dimethylphenylsilylacetic acid, and β-trimethylsilylpropionic acid were determined and the respective ionization constants were found to be 0.6×10^{-5}, 0.6×10^{-5}, 0.54×10^{-5}, and 1.24×10^{-5}.[61] These observations indicate that electron-release by the silicon-containing groups is rather strong in the first three instances, but that this effect rapidly diminishes as the saturated chain is lengthened.[61] The release in the first three acids is greater than that by hydrogen or alkyl groups.

Triphenyl-(carboxydecyl)-silane (triphenylsilylhendecanoic acid), $(C_6H_5)_3SiC_{10}H_{20}COOH$, was formed in 96% yield by the reaction of triphenylsilane with 9-hendecenoic acid in hexane at 75° in a nitrogen atmosphere for 14 hours, the reaction being catalyzed by benzoyl peroxide.[64] The product distills at 250-270° at 7×10^{-5} mm., and crystallizes from benzene in needles which melt at 58.5-59°. The compound does not react with iodine.[64] The position occupied by the carboxyl group was not specified.

When the acid was esterfied or when ethyl 9-hendecenoate was made to react with triphenylsilane, *ethyl triphenylsilylhendecanoate*, $(C_6H_5)_3SiC_{10}H_{20}COOC_2H_5$, was obtained.[64] The ester melts at 49° and distills at 255-280° (7×10^{-5} mm.).

Silicon derivatives of acids containing sulfur have been prepared by the reaction of alkenylsilanes with acids containing the sulfhydryl group.[65] The two classes of substances were shaken together until homogeneity was effected, the products being obtained by distillation.[65] Thus *3-thia-6-sila-6,6-dimethylheptanoic acid*, $(CH_3)_3SiCH_2CH_2SCH_2COOH$, was prepared in 25% yield from trimethylvinylsilane and thioglycolic

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[64] H. Gadsby, *Research*, *3*, 339 (1950) [*C.A.*, 44, 8881 (1950)].

[65] C. E. Burkhard, *J. Am. Chem. Soc.*, *72*, 1078 (1950).

acid.[65] This compound boils at 143-144° at 7 mm., n_D^{20} 1.4811, d^{20} 1.0139.[65]

<u>3-Thia-7-sila-7,7-dimethyloctanoic acid</u>, $(CH_3)_3Si(CH_2)_3SCH_2COOH$, boiling at 164-166° at 9 mm., n_D^{20} 1.4790, d_4^{20} 1.009, formed in 54% yield by the reaction of thioglycolic acid with allyltrimethylsilane.[65]

<u>3-Thia-7,7-dimethyl-7-trimethylsiloxy-7-silaheptanoic acid</u>, $(CH_3)_3SiOSi(CH_3)_2(CH_2)_3SCH_2COOH$, was prepared from thioglycolic acid and allylpentamethyldisiloxane in a yield of 46%.[65] The constants are boiling point 149-150.2° (2 mm.), n_D^{20} 1.4588, d_4^{20} 0.9902.[65]

The reaction of allytrimethylsilane with ethyl thioglycolate resulted in the formation of <u>ethyl 3-thia-7,7-dimethyl-7-silaoctanoate</u>, $(CH_3)_3Si(CH_2)_3SCH_2COOC_2H_5$, in 63% yield.[65] The compound boils at 148-149° at 24 mm., n_D^{20} 1.4630, d_4^{20} 0.9493.[65]

Ethyl 3-thia-7,7-dimethyl-7-silaoctanoate was sponified and the acid treated with thionyl chloride and then <u>p</u>-toluidine to prepare <u>3-thia-7,7-dimethyl-7-sila-N-p-tolyloctanamide</u>, $(CH_3)_3Si(CH_2)_3SCH_2CONHC_6H_4CH_{3-\underline{p}}$.[65] This amide melts at 72.5-73°.[65]

Alkylsilanes Containing the Carbonyl Group

<u>Trimethyl-(β-acetylethyl)-silane (4-trimethylsilyl-2-butanone)</u>, $(CH_3)_3SiCH_2CH_2COCH_3$, was prepared by heating a mixture containing ethyl α-(trimethylsilylmethyl)-acetoacetate,

hydrochloric acid and ethanol at 90° until homogeneity was observed.[56] After ether was added, the organic portion was salted out with a saturated sodium chloride solution. The yield of 4-trimethylsilyl-2-butanone, distilling at 84° at 65 mm., n_D^{20} 1.4228, d^{20} 0.833 was 59%.[56]

The ketone may be obtained in 81% yield by the hydrolysis of ethyl α-(trimethylsilylmethyl)-acetoacetate with 10% sodium hydroxide, and in 50% yield by the reaction of dimethylcadmium with β-trimethylsilylpropionyl chloride.[56] The last method of synthesis was used to establish the structure of the ketone.[56]

When 4-trimethylsilyl-2-butanone reacted with sodium hypobromite solution below 5°, a 41% yield of β-trimethylsilylpropionic acid was obtained.[56]

Dimethylphenyl-(β-acetylethyl)-silane (4-dimethylphenylsilyl-2-butanone), $(CH_3)_2C_6H_5SiCH_2CH_2COCH_3$, was obtained in a yield of 45% by the interaction of β-dimethylphenylsilylpropionyl chloride and dimethylcadmium.[56] This ketone boils at 109° (4 mm.), n_D^{20} 1.5065, d^{20} 0.963.[56]

Trimethyl-(β-acetylbutyl)-silane [3-(trimethylsilylmethyl)-2-pentanone], $(CH_3)_3SiCH_2CH(CH_2CH_3)COCH_3$, was formed when ethyl α-ethyl-α-(trimethylsilylmethyl)-acetoacetate was subjected to ketonic cleavage with 10% sodium hydroxide.[56] The yield of ketone was 20%, approximately 40% of the ester being recovered unchanged.[56] 3-Trimethylsilylmethyl-2-pentanone has a boiling point of 88° at 30 mm., n_D^{20} 1.4295, d^{20} 0.843.[56]

Trimethyl-(β-benzoylethyl)-silane (2-trimethylsilylethyl phenyl ketone), $(CH_3)_3SiCH_2CH_2COC_6H_5$, boils at 115° at 4 mm., n_D^{20} 1.5085, d^{20} 0.955.[56] It was prepared by the action of diphenylcadmium upon β-trimethylsilylpropionyl chloride.[56]

Trimethyl-(β-methyl-β-acetylethyl)-silane (4-trimethylsilyl-3-methyl-2-butanone), $(CH_3)_3SiCH_2CH(CH_3)COCH_3$, was obtained by hydrolyzing ethyl α - methyl- α - trimethylsilylmethylacetoacetate with 10% sodium hydroxide.[56] The ketone, boiling at 83° (40 mm.), n_D^{20} 1.4280, d^{20} 0.836, formed in 53% yield.[56]

Aminoalkylsilanes

Silicon compounds containing aminoalkyl groups may be synthesized by (1) the reduction of nitriles, (2) the hydrolysis of carbamates, (3) the Gabriel synthesis, and (4) the reaction of halomethylsilanes with liquid ammonia or amines in an autoclave. In the reaction between halomethylsilanes and liquid ammonia or primary amines no tertiary amines were isolated.[66] If secondary amines were used, tertiary amines which sluggishly formed quaternary salts did result.[66] Reaction of ethanolamine with chloromethylsilanes caused cleavage of the

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[66] J. E. Noll, J. L. Speier, and B. F. Daubert, *ibid.*, 73, 3871 (1951).

chloromethyl group, the product isolated being N-methylethanolamine.[66]

Trimethyl-(aminomethyl)-silane, $(CH_3)_3SiCH_2NH_2$, was prepared in 67% yield by hydrolysing N-(trimethylsilylmethyl)-phthalimide with hydrochloric acid and then liberating the free base with potassium hydroxide solution.[63] The amine was also formed when trimethyl-(chloromethyl)-silane and liquid ammonia were interacted in an autoclave, the yield being 50%.[66] The constants reported are boiling point 94° at 729 mm., n_D^{20} 1.4139, d_4^{25} 0.7646.[66]

The bicarbonate of trimethyl-(aminomethyl)-silane sublimes at room temperature,[66] and the sulfate melts at 213-216° with decomposition.[66] N-(Trimethylsilylmethyl)-p-nitrobenzamide has a melting point of 123.5-124°.[66] The hydrochloride of the amine melts at 242-243°.[66]

Attempts to prepare the amine by the reaction of trimethyl-(chloromethyl)-silane with sodium in liquid ammonia resulted in cleavage and rearrangement to trimethyl-(methylamino)-silane which was converted into N-methylhexamethyldisilazane.[66] The reactions probably are

$$(CH_3)_3SiCH_2Cl + NaNH_2 \longrightarrow (CH_3)_3SiNHCH_3 + NaCl$$

$$2(CH_3)_3SiNHCH_3 \longrightarrow [(CH_3)_3Si]_2NCH_3 + CH_3NH_2.^{66}$$

When methyl N-(β-trimethylsilylethyl)-carbamate was refluxed with potassium hydroxide in methanol and the product steam-distilled, *trimethyl-(β-aminoethyl)-silane*,

$(CH_3)_3SiCH_2CH_2NH_2$, was obtained in a yield of 83.5%.[63] It boils at 121° at 735 mm., n_D^{20} 1.4244, and the hydrochloride melts at 300°.[63] The formation of N,N'-bis-(β-trimethylsilylethyl)-urea, melting at 77-78°, occurs to some extent in this preparation.[63] The amine also forms by subjecting _-trimethylsilylpropionamide to the Hoffmann reaction.[67]

Trimethyl-(γ-aminopropyl)-silane, $(CH_3)_3SiCH_2CH_2CH_2NH_2$, is a liquid which has a boiling point of 145° under a pressure of 726 mm., n_D^{20} 1.4301, d_4^{20} 0.7866.[63] It was obtained in a yield of 82% by the reduction of γ-trimethylsilylpropionitrile with lithium aluminum hydride.[63] The melting point of the hydrochloride is 183-184°.[63]

Trimethyl-(iodomethyl)-silane and liquid ammonia can be made to react at 100° under a pressure of 510 pounds to produce *bis-(trimethylsilylmethyl)-amine*, $[(CH_3)_3SiCH_2]_2NH$, in a yield of 23.7%.[63] The boiling point is 90° (57 mm.), n_D^{20} 1.4267, d_4^{20} 0.7863. The melting point of the hydrochloride is 158°.[63]

This amine is also formed along with trimethyl-(aminomethyl)-silane when trimethyl-(chloromethyl)-silane reacts with liquid ammonia.[66] In addition to the hydrochloride, bis-(trimethylsilylmethyl)-amine forms a sulfate which hydrolyzes to a polymeric substance. The proposed structure of the polymer is $-[OSi(CH_3)_2CH_2NHCH_2Si(CH_3)_2]$.[66]

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[67] L. H. Sommer, N. S. Marans, G. M. Goldberg, J. Rockett, and R. P. Pioch, *ibid.*, *71*, 882 (1941).

Dimethylphenyl-(aminomethyl)-silane, $(CH_3)_2C_6H_5SiCH_2NH_2$, was prepared by the reaction of dimethylphenyl-(chloromethyl)-silane [from (chloromethyl)-dimethylchlorosilane and phenylmagnesium bromide] with liquid ammonia in an autoclave in 68% yield.[66] It boils at 226.5° (744 mm.), n_D^{25} 1.5205, d_4^{25} 0.940. The hydrochloride melts at 198-200°.[66]

The by-product of the above-described reaction is bis-(dimethylphenylsilylmethyl)-amine, $[(CH_3)_2C_6H_5SiCH_2]_2NH$, which has a boiling point of 215.2° at 23 mm., n_D^{25} 1.5332, d_4^{25} 0.958.[66]

Dimethylethoxy-(aminomethyl)-silane, $(CH_3)_2C_2H_5OSiCH_2NH_2$, was obtained when liquid ammonia and dimethyl-(chloromethyl)-ethoxysilane [from ethanol and dimethyl-(chloromethyl)-chlorosilane] interacted.[66] The yield of product, boiling at 131.8° at 740 mm., n_D^{25} 1.411, d_4^{25} 0.849, was 37%.[66] The compound is quite stable to hydrolysis, the hydrochloride (melting point 183-187°) being prepared by evaporating a hydrochloric acid solution of the amine to dryness.[66]

Bis-(ethoxydimethylsilylmethyl)-amine, $[(CH_3)_2C_2H_5OSiCH_2]_2NH$, boiling at 160-170° at 24 mm., n_D^{25} 1.433, d_4^{25} 0.892, was prepared in 37% yield by the process described above.[66]

Triethoxy-(aminomethyl)-silane, $(C_2H_5O)_3SiCH_2NH_2$, was obtained in 51% yield when triethoxy-(chloromethyl)-silane reacted with liquid ammonia.[66] It has a boiling point of 93°

at 26 mm., n_D^{25} 1.4080, d_4^{25} 0.955. Triethoxy-(aminomethyl)-silane hydrolyzes in the air to produce a silica-like material.[66]

Bis-(triethoxysilylmethyl)-amine, $[(C_2H_5O)_3SiCH_2]_2NH$, a by-product in the preparation of triethoxy-(aminomethyl)-silane was formed to the extent of 25%.[66] The constants are boiling point 117° (0.4 mm.), n_D^{25} 1.4132, d_4^{25} 0.973.

Tetramethyl-1,3-bis-(aminomethyl)-disiloxane dihydrochloride, $[(CH_3)_2NH_2CH_2Si]_2O.2HCl$, melts at 247-249°.[66] It was formed in practically quantitative yields when trimethyl-(aminomethyl)-silane reacted with sulfuric acid and the resulting compound subjected to treatment with hydrogen chloride. The by-product of the sulfuric acid reaction is methane. The reactions are

$$2(CH_3)_3SiCH_2NH_2 + 2H_2SO_4 \longrightarrow 2HOSO_3Si(CH_3)_2CH_2NH_2 + 2CH_4$$

$$2HOSO_3Si(CH_3)_2CH_2NH_2 + H_2O \longrightarrow [(CH_3)_2NH_2CH_2Si]_2O + 2H_2SO_4.$$[65,66]

Trimethyl-(methylaminomethyl)-silane, $(CH_3)_3SiCH_2NHCH_3$, was obtained by the action of trimethyl-(chloromethyl)-silane upon methylamine in 50% yield.[66] It has a boiling point of 101.6° at 735 mm., n_D^{25} 1.4094, d_4^{25} 0.754. The amine forms a water azeotrope which boils at 83° (735 mm.), n_D^{25} 1.4132.[66] The hydrochloride of trimethyl-(methylaminomethyl)-silane has a melting point of 198-199°.[66]

Trimethyl-(dimethylaminomethyl)-silane, $(CH_3)_3SiCH_2N(CH_3)_2$, [from trimethyl-(chloromethyl)-silane and dimethylamine] is found to boil at 110.1° (746 mm.), n_D^{25} 1.4102, d_4^{25} 0.746.[66] It was formed in 64% yield. The amine hydrochloride melts at 185-186°. The quaternary salts, trimethyl-(trimethylsilylmethyl)-ammonium bromide and iodide, melt at 260-262° and 241.5-242.5°, respectively.[66]

Trimethyl-(octadecylaminomethyl)-silane, $(CH_3)_3SiCH_2NHC_{18}H_{37}$-*n*, may be prepared in 67.5% yield from octadecylamine and trimethyl-(chloromethyl)-silane.[65] Its boiling point is 193-194° at 2 mm., n_D^{26} 1.4507, d_4^{26} 0.815, and its melting point is 26-32°.[66] The amine hydrochloride melts at 101-102°.[66]

Trimethyl-(isopropylaminomethyl)-silane, $(CH_3)_3SiCH_2NHCH(CH_3)_2$, can be obtained in 83% yield from isopropylamine and trimethyl-(chloromethyl)-silane. It boils at 129.5° at 736.5 mm., n_D^{25} 1.4141, d_4^{25} 0.758.[66] The melting point of the hydrochloride is 136-137°.

Tetramethyl-1,3-bis-(isopropylaminomethyl)-disiloxane, $[(CH_3)_2\ \textit{iso} - C_3H_7NHCH_2Si]_2O$, was prepared by treating trimethyl-(isopropylaminomethyl)-silane with sulfuric acid and then hydrolyzing the product with alkali.[66] The compound has a boiling point of 245° (736.8 mm.), n_D^{25} 1.4278, d_4^{25} 0.850.[66] The dihydrochloride melts at 179-180°.[66]

Trimethyl-(cyclohexylaminomethyl)-silane, $(CH_3)_3SiCH_2NHC_6H_{11}$-cyclo, was synthesized by treating trimethyl-(chloromethyl)-silane with cyclohexylamine[66] and by catalytic reduction of trimethyl-(phenylaminomethyl)-silane.[66] The yields by these respective methods were 90% and 88%. The compound boils at 211° at 736.5 mm., n_D^{25} 1.4519, d_4^{25} 0.839.[66] The melting point of the hydrochloride is 235-239°, and the phenylthiourea derivative melts at 136.5-137°.[66]

After trimethyl-(cyclohexylaminomethyl)-silane was treated with sulfuric acid and then with aqueous alkali, *tetramethyl-1,3-bis-(cyclohexylaminomethyl)-disiloxane*, $[(CH_3)_2\text{cyclo-}C_6H_{11}NHCH_2Si]_2O$, was produced in 80% yield, n_D^{25} 1.4679, d_4^{25} 0.922.[66] The dihydrochloride melts at 228-232°.

Trimethyl-(phenylaminomethyl)-silane, $(CH_3)_3SiCH_2NHC_6H_5$, [from aniline and trimethyl-(chloromethyl)-silane] has a boiling point of 242° at 740.8 mm., n_D^{25} 1.5213, d_4^{25} 0.918.[66]

Triethoxy-(cyclohexylaminomethyl)-silane, $(C_2H_5O)_3SiCH_2NHC_6H_{11}$ -cyclo, boils at 162° (99 mm.), n_D^{25} 1.4488, d_4^{25} 0.889, and was obtained in 64% yield from cyclohexylamine and trimethyl-(chloromethyl)-silane.[66]

Studies as to the base strength of the aminoalkylsilanes showed them to be stronger bases than their carbon analogs.[63] For example, trimethyl-(aminomethyl)-silane is nearly six times as strong as neopentylamine. It is observed, also, that while the α-trimethylsilyl group has a strong effect on increasing the basic dissociation constants of amines, the effect of phenyl- or oxygen-substituted silyl groups is in the opposite direction.[68] Electronegative substituents such as phenyl or oxygen generally weaken amines.

The fact that the amines containing silicon are generally stronger than corresponding carbon compounds causes questioning of the idea that silicon coordinates with the electrons on nitrogen in these amines.[69] If such coordination were to occur, then amines containing silicon should be weak.[63] Further, cryoscopic determinations of molecular weights of these amines show them to be monomolecular.[68] These considerations tend to rule out intramolecular or intermolecular association among these compounds.[63,68]

The Alkyl Silicon Isocyanates and Isothiocyanates

The general method by which these substances are prepared is the reaction between silicon halides and silver cyanate and silver thiocyanate, respectively, in benzene solution.[36,69,70,71]

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[68] J. E. Noll, B. F. Daubert, and J. L. Speier, ibid., 73, 3871 (1951).

[69] See C. G. Swain, R. M. Esteve, and R. H. Jones, ibid., 71, 965 (1949) for mechanisms involving pentacovalent silicon.

[70] H. H. Anderson, ibid., 69, 3049 (1947).

[71] H. H. Anderson, ibid., 72, 193 (1950).

Methyltriisothiocyanatosilane, $CH_3Si(NCS)_3$, boils at 266-267°, d_4^{20} 1.304, and melts at 72.4°.[70] The density was determined in solution.

Dimethyldiisothiocyanatosilane, $(CH_3)_2Si(NCS)_2$, boils at 217.3 ± 1°, and melts at 18°, d_4^{20} 1.143, n_D^{20} 1.5677 ± 0.0005.[70]

Trimethylisothiocyanatosilane (trimethylsilyl isothiocyanate), $(CH_3)_3SiNCS$, boils at 143.1 ± 0.3° and melts at -32.8°, d_4^{20} 0.931, n_D^{20} 1.482 ± 0.0005.[70]

The methyl silicon isothiocyanates were studied as to their chemical properties. Each of them is easily hydrolyzed, though the rate of hydrolysis is moderately slow. The hydrolysis product of dimethyldiisothiocyanatosilane is a liquid which floats on water and which, when dried, boils at 260°. It is assumed to be a cyclic dimethylsiloxane.[70] The isothiocyanate groups can be determined by titrating the hydrolyzed compounds with silver nitrate using ferric nitrate indicator.[70]

Several physical constants were measured. The molar refraction values favor the isothiocyanate structure rather than the thiocyanate configuration.[70] In addition, heats of vaporization, Trouton's constants, and the constants in the vapor pressure equations for each compound were ascertained.

Benzyltriisothiocyanatosilane, $C_6H_5CH_2Si(NCS)_3$, has a boiling point of 348.9 ± 1° (171-172° at 3 mm.), and it melts at 36 ± 1°, d_4^{20} 1.275 (determined on the supercooled liquid.)[71]

Benzyltriisocyanatosilane, $C_6H_5CH_2Si(NCO)_3$, boils at 111-112° at 3 mm. and 265 ± 2° at atmospheric pressure and has the constants n_D^{20} 1.5230, d_4^{20} 1.225.[71] It melts at 11 ± 1°.

n-Butyltriisothiocyanatosilane, *n*-$C_4H_9Si(NCS)_3$, boils at 135-136° at 3 mm. and 300.6 ± 1° at atmospheric pressure, n_D^{20} 1.5928, d_4^{20} 1.189.[71] This compound melts at -0.5°.

Each of the latter three compounds is a colorless liquid when pure, and each hydrolyzes without the evolution of heat. The isothiocyanate groups were titrated with standard silver nitrate with ferric ion indicator, while the isocyanate moiety was analyzed for nitrogen by the Dumas method.[71]

Ethyltriisocyanatosilane, $C\ H\ Si(NCO)_3$, has a boiling point of 183.5°, d_4^{20} 1.2191, n_D^{20} 1.4468.[72]

Diethyldiisocyanatosilane, $(C_2H_5)_2Si(NCO)_2$, boils at 176.7°, d_4^{20} 1.0223, n_D^{20} 1.4348.[72]

Triethylisocyanatosilane (triethylsilyl isocyanate), $(C_2H_5)_3SiNCO$, was prepared in a 60-40 nitromethane-benzene mixture by the interaction of triethylchlorosilane and silver cyanate.[72] The synthesis did not proceed to completion in benzene. The significance of the role of nitromethane is being investigated.[72] Triethylsilyl isocyanate boils at 161.1°, d_4^{20} 0.8895, n_D^{20} 1.4295.[72]

n-Propyltriisocyanatosilane, *n*-$C_3H_7Si(NCO)_3$, was prepared in a 9:1 benezene-nitromethane solvent. It boils at 198.2°, n_D^{20} 1.4462, d_4^{20} 1.1726.[72]

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[72] H. H. Anderson, *ibid.*, *72*, 196 (1950).

Isopropyltriisocyanatosilane, $(CH_3)_2CHSi(NCO)_3$, was prepared in the same solvent as was the n-propyl compound. Its boiling point is 192°, d_4^{20} 1.162, n_D^{20} 1.444.[72]

Both preparations involving the propyl compounds were slow in starting. However, reaction in each case reached completion after being refluxed for 1 hour.

n-Propyltriisothiocyanatosilane, $n\text{-}C_3H_7Si(NCS)_3$, prepared in benzene, boils at 289.5°, d_4^{20} 1.2248, n_D^{20} 1.6014.[72]

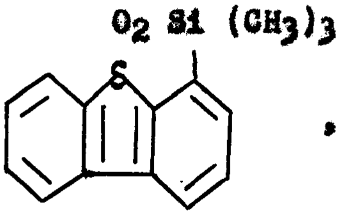
Isopropyltriisothiocyanatosilane, $(CH_3)_2CHSi(NCS)_3$, boiling at 279°, d_4^{20} 1.2177, n_D^{20} 1.6066, was prepared in benzene.[72]

Among the ethylsilicon isocyanates, the rate of hydrolysis increases as the number of ethyl groups decreases.[72] Trimethylsilyl isocyanate can be heated to 85° and shaken with water at that temperature without a reaction of detectable speed or heat. However, if triethylsilyl isocyanate is shaken with 50% ethanol, it reacts rapidly with the evolution of heat.[72]

Each propyltriisocyanatosilane, when emulsified with water, hydrolyzes at an initially slow rate, but after approximately 5 minutes, the hydrolysis rate rapidly increases. However, each compound is more slowly hydrolyzed than is silicon tetraisocyanate.[71] All these compounds - ethyl and propyl - decompose completely in 95% ethanol within 5 minutes.[72]

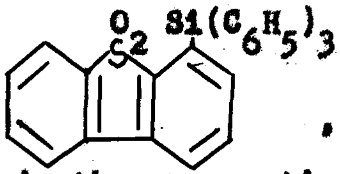
Miscellaneous Compounds

4-Trimethylsilyldibenzothiophene - 5 - dioxide,



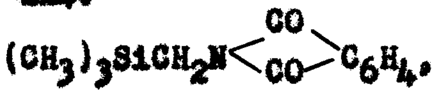
, was prepared in 42% yield by the oxidation of 4-trimethylsilyldibenzothiophene with 30% hydrogen peroxide in glacial acetic acid.[73] The compound melts at 146-147°.

4-Triphenylsilyldibenzothiophene-5-dioxide,



, was formed in a manner similar to that used in the preparation of the compound described above.[73] It has a melting point of 212-213° (from ethyl acetate).

Neither of these compounds is cleaved by hydrogen chloride. 4-Trimethylsilyldibenzothiophene-5-dioxide can be nitrated to form a nitro derivative of undetermined structure.[73] The nitro compound melts at 223-224.°



N-Trimethylsilylmethylphthalimide, $(CH_3)_3SiCH_2N\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_4$, was obtained in 89.8% yield by the reaction of trimethyl-(chloromethyl)-silane with phthalimide and potassium carbonate.[63] It is a water-clear oil boiling at 117° at 2 mm., n_D^{20} 1.5427, and it freezes at 23°.

Methyl N-(β-trimethylsilylethyl)-carbamate, $(CH_3)_3SiCH_2CH_2NHCOOCH_3$, is a clear water-white liquid which boils at 108° at 12 mm., n_D^{20} 1.4410. It was obtained in 82.2% yield when β-trimethylsilylpropionamide in methanol was reacted with bromine and sodium methoxide.[63]

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[73] H. Gilman and J. F. Nobis, ibid., 72, 2629 (1950).

Methyl N-(β-trimethylsilylethyl)-carbamate can be hydrolyzed to β-trimethylsilylethylamine, some *N,N'-bis-(β-trimethylsilylethyl)-urea*, $[(CH_3)_3SiCH_2CH_2NH]_2CO$, melting at 77-78° also being formed.[63]

EXPERIMENTAL

The apparatus used in experiments involving organometallic compounds consisted of a suitably sized three-necked round bottom flask fitted with a mechanical stirrer, a reflux condenser, and a dropping funnel. The reactions were run under a positive pressure of dry nitrogen prepared by passing high grade nitrogen through a train containing, respectively, sulfuric acid, alkaline pyrogallol, and soda lime or Drierite. Modifications were made as required.

Silicon Analysis[74]

Polyarylsilanes were analyzed for silicon by placing a sample of each compound into a previously ignited platinum crucible with cover and adding 1-3 ml. of concentrated sulfuric acid dropwise to the sample in the partially covered crucible. Sufficient time was allowed for the sample to become thoroughly wetted by the acid. Wetting may be facilitated by previously introducing acetic acid, or by adding 2 or 3 drops of concentrated nitric acid to the sulfuric acid and sample in the crucible. The partially covered crucible was then placed on the wire support of a Rogers ring burner and the flame so adjusted as to impinge on the crucible just above the level of the acid. As the acid evaporated, the crucible was raised so that acid fumes were constantly being evolved. After all the

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[74] See ref. 27 for the microdetermination of silicon.

acid had vaporized, the crucible was ignited at dull red heat by means of a Meker burner until the weight of the crucible and silica became constant.

However, compounds containing the trimethylsilyl group cannot handily be analyzed by the procedure described above because the volatility of this group is such that low results are almost invariably obtained.[75] These compounds were analyzed by decomposing a sample of each by the Parr fusion method. The resulting melt was dissolved in distilled water, acidified with a 20 ml. excess of perchloric acid and the solution evaporated to fumes of the acid. The solution was then diluted with distilled water, cooled, and filtered. The precipitate thus obtained was washed with four to six 100 ml. portions of dilute hydrochloric acid (3 ml. of acid and 97 ml. of water) and once with 100 ml. of dilute ammonium hydroxide (1 ml. of base and 99 ml. of water). The filter was next transferred to a previously tared platinum crucible in which it was carefully charred and finally ignited at dull red heat until the weight of the crucible and its contents became constant.

Liquid silanes were weighed in gelatin capsules, and the capsules containing the samples were introduced into the Parr bomb with the fusion mixture.

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[75] See ref. 15 for a discussion of the volatility of the trimethylsilyl group.

The samples weighed 0.15-0.25 g. The factor for converting silica into silicon is 0.4672.

The Preparation of Triphenylsilane and Triphenyltin Hydride

Triphenylsilanol.- Triphenylsilanol was prepared by two methods. In the first, silicon tetrachloride and phenylmagnesium bromide were used in essential accordance with the directions of earlier workers.[76] The yield of product was 96 g. (71%) using 0.5 mole of silicon tetrachloride. In a second experiment, beginning with 0.3 mole of silicon tetrachloride, the yield of triphenylsilanol was 59.6 g., or 72%. The melting point was 150-151°.

In the second method, phenyllithium (2.83 moles) was added to 0.94 mole of silicon tetrachloride in ether, the reaction flask being kept in an ice bath.[16] The yield of triphenylsilanol, after hydrolyzing and working up the reaction mixture, was 83% (215 g.). In addition, 35 g. of tetraphenylsilane was obtained.

Attempted reduction of triphenylsilanol.- A solution containing 4.8 g. (0.0174 mole) of triphenylsilanol dissolved in 50 ml. of absolute ethanol containing Raney nickel was subjected to a pressure of 59 pounds of hydrogen for 17 hours. At the end of that period, the pressure of hydrogen had not

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[76] W. Dilthey and F. Eduardoff, Ber., 37, 1139 (1904).

changed. After filtering the mixture and removing the ethanol by distillation, 4.6 g. of triphenylsilanol was recovered (mixed melting point identification). Two other attempts at the reduction of triphenylsilanol resulted in 95-96% recoveries of triphenylsilanol when the reaction times were 20 hours and 24 hours, respectively.

Triphenylsilanol and formic acid.- A procedure for the conversion of triphenylcarbinol into triphenylmethane by treating the carbinol with formic acid has been described.[77] Accordingly, 5 g. (0.018 mole) of triphenylsilanol was refluxed for 16 hours with 25 ml. of 98% formic acid. After cooling and filtering the mixture and recrystallizing the residue from ethanol, there was obtained a quantitative yield of hexaphenyldisiloxane[78] melting at 220-222°. No triphenylsilane was isolated.

Anal. Calcd. for $C_{36}H_{30}OSi_2$: Si, 10.48. Found: Si, 10.46 and 10.52.

Triphenylsilanol and sulfuric acid in ethanol.- It has been reported that triphenylcarbinol or triphenylchloromethane

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[77] H. Kauffmann and A. D. Pannwitz, ibid., 45, 776 (1912).

[78] W. C. Schumb and C. M. Saffer, J. Am. Chem. Soc., 61, 366 (1939).

can be converted into triphenylmethane by heating either substance with concentrated sulfuric acid in ethanol.[79] Therefore, 50 ml. of concentrated sulfuric acid was added to 5 g. (0.017 mole) of triphenylchlorosilane[80] dissolved in 50 ml. of ethanol and the solution heated with stirring at 70-80° for 6 hours. The reaction mixture was cautiously poured into 400 ml. of solution containing a 10% excess of the sodium carbonate calculated to neutralize the acid. After filtering the suspension, a gummy residue that was not appreciably soluble in the usual organic solvents was collected. This material did not melt at temperatures as high as 380°.

Extraction of the aqueous portion with ether resulted in the isolation of a small quantity of solid which charred without melting at 350°. These results suggest that cleavage and hydrolysis might have occurred.

Trichlorosilane and phenylmagnesium bromide.- The directions of earlier workers[18] were followed in this method. In one preparation, when 0.62 mole of trichlorosilane was used, the yield of triphenylsilane was 88%. Hydrolysis was effected by pouring the reaction mixture on cracked ice containing sulfuric acid. Since this product, after two recrystallizations

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[79] J. Schmidlin and A. Garcia-Banus, *Ber.*, *45*, 3189 (1912).

[80] Prior to the availability of commercial triphenylchlorosilane, the compound was prepared by passing anhydrous hydrogen chloride through an ether solution of triphenylsilanol. See C. A. Kraus and R. Rosen, *J. Am. Chem. Soc.*, *47*, 2746 (1925).

from ethanol, melted at 44-45° instead of 36-37° as previously reported,[18] it was analyzed.

Anal. Calcd. for $C_{18}H_{16}Si$: Si, 10.77. Found: Si, 10.67 and 10.72.

The yield in a second preparation, starting with 0.99 mole of trichlorosilane, was 86% of pure product melting at 45-45.5°.[81]

Triphenylchlorosilane and lithium aluminum hydride.- To 4 g. (0.105 mole) of lithium aluminum hydride in 75 ml. of ether was slowly added 10 g. (0.034 mole) of triphenylchlorosilane in 25 ml. of ether, and the resulting suspension was refluxed for 5 hours. The reaction mixture was hydrolyzed with dilute hydrochloric acid and worked up in the customary manner. The yield of triphenylsilane, melting at 43-44° (mixed melting point 44-45°), was 7 g., or 79.5%.

Triphenyltin chloride.- Triphenyltin chloride was prepared by a modification[82] of the procedure of Kocheshkow, Nadi, and Aleksandrow[83] from 55 g. (0.1785 mole) of tetra-

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[81] See J. W. Jenkins, N. Lavery, P. R. Guenther, and H. W. Post, J. Org. Chem., 13, 862 (1948), for the preparation of R_3SiH types.

[82] C. E. Arntzen, Doctoral Dissertation, Iowa State College, 1942.

[83] K. A. Kocheskow, M. M. Nadi, and A. R. Aleksandrow, Ber., 67, 1348 (1934).

phenyltin and 11.2 g. (0.0429 mole) of stannic chloride. The yield of triphenyltin chloride, melting at 103-104°, was 47.2 g. (72%). Repeated recrystallization from petroleum ether (boiling point 77-115°) did not raise the melting point.

Triphenyltin hydride.- Triphenyltin chloride instead of the bromide was used in this synthesis.[84] From 20 g. (0.0518 mole) of triphenyltin chloride was obtained 1.5 g. (8.3%) of triphenyltin hydride. In a second run, using 17.8 g. (0.046 mole) of triphenyltin chloride, the yield was 6.8 g. (42%) of triphenyltin hydride. The compound was purified by distillation *in vacuo* from an apparatus previously swept with nitrogen. No percentage yield was reported by the earlier workers.[84]

Triphenyltin chloride and lithium aluminum hydride.- Several efforts were made to prepare triphenyltin hydride by the reduction of triphenyltin chloride with lithium aluminum hydride since this reagent was used successfully in the formation of triphenylsilane from triphenylchlorosilane. To 0.6 g. (0.0163 mole) of lithium aluminum hydride suspended in 50 ml. of ether was added 12 g. (0.03 mole) of triphenyltin chloride in 70 ml. of ether and the mixture refluxed for 2½ hours on a hot plate. The reaction mixture was hydrolyzed with 1:4 hydrochloric acid and the organic layer separated and dried over

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[84] R. F. Chambers and P. C. Scherer, *J. Am. Chem. Soc.*, *48*, 1059 (1926).

anhydrous sodium sulfate. After the ether was removed by distillation, there was recovered 10.4 g. of triphenyltin chloride. This was a recovery of 87.5%.

In a second experiment in which the weights of reactants and conditions were the same as those used in the above procedure, the recovery of triphenyltin chloride was 10 g. (83.3%).

In a third reaction, 15 g. (0.039 mole) of triphenyltin chloride and 0.6 g. (0.0163 mole) of lithium aluminum hydride were used and the ether suspension refluxed for 6 hours. After working up the reaction mixture, the quantity of triphenyltin chloride recovered was 12.7 g., or 84.7%.

Some Reactions[85] of Triphenylsilane and Triphenyltin Hydride

Triphenylsilane and phenyllithium.- To 26 g. (0.1 mole) of triphenylsilane in 50 ml. of ether was added 0.1 mole of phenyllithium in 107 ml. of ether. A white precipitate immediately formed. At the conclusion of the addition of the phenyllithium solution, Color Test I[11] was negative. A portion of the precipitate was removed and analyzed as described below. Subsequent to hydrolysis and recrystallization from benzene, there was obtained 30.3 g. (90%) of tetraphenylsilane melting at 230-232°.

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[85] H. Gilman and H. W. Melvin, ibid., 71, 4050 (1949).

Anal. Calcd. for $C_{24}H_{20}Si$: Si, 8.33. Found: Si, 8.3 and 8.3.

Triphenyltin hydride and phenyllithium.- In the first of two runs, 1.6 g. (0.0043 mole) of triphenyltin hydride was treated with 0.0044 mole of phenyllithium, a white precipitate being formed at once. Then 0.0044 mole of benzyl chloride was added to react with any triphenyltinlithium[86] that might have formed. Color Test I[11] became negative immediately after the addition of the benzyl chloride. The reaction mixture was hydrolyzed with 1:4 hydrochloric acid and the ether-insoluble solid separated by filtration. This residue was washed with five 5-ml. portions of ether and dried in a vacuum desiccator over sulfuric acid. The yield of tetraphenyltin melting at 228-230° (mixed melting point 228-230°) was 1.7 g., or 91%.

In the second experiment, using 4.1 g. (0.0117 mole) of triphenyltin hydride, 0.0119 mole of phenyllithium and 0.0119 mole of benzyl chloride, a portion of the precipitate that appeared was removed for analysis. Subsequent to working up the mixture, there was obtained 4.5 g. of tetraphenyltin, a yield of 90%. The compound was identified by the mixed melting point method.

Analysis of the precipitate.- The precipitate that formed in each of the two preceeding reactians was allowed to settle

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[86] H. Gilman and S. D. Rosenberg, ibid., 74, 531 (1952).

and the ether decanted in a nitrogen atmosphere. The residue was then centrifuged for 1½ hours and the supernatant ether decanted. The solid was twice washed with anhydrous ether, centrifuged, and the ether decanted. Residual solvent was removed by heating the solid on a steam bath *in vacuo*. The combined ether washings completely distilled at 36-38°, indicating the absence of benzene.

A sample of the dried precipitate was hydrolysed and the total alkalinity determined, the inert portion being recovered. From 1.4300 g. of the precipitate formed in the reaction between triphenylsilane and phenyllithium was obtained 1.3968 g. of tetraphenylsilane. The total alkali, 0.00415 mole, was in agreement with the loss in weight of the sample (0.0332 g.) when this was calculated as lithium hydride (0.00418 mole). Hydrolysis of 0.2895 g. of the precipitate formed in the reaction between triphenyltin hydride and phenyllithium yielded 0.2842 g. of tetraphenyltin, and the total alkali (0.00067 mole) again checked with the loss in weight of the sample (0.0053 g.) when this was calculated as lithium hydride (0.00067 mole).

Triphenylsilane and methyllithium.- Triphenylsilane (11.4 g., 0.044 mole) and 0.044 mole of methyllithium were interacted as described in the reaction between triphenylsilane and phenyllithium. Color Test I[11] became negative within 5 minutes. After working up the mixture in the customary manner and recrystallizing the product from ethanol, 11.6 g. (93%) of methyltriphenylsilane, melting at 66-67°[87] was obtained. The compound was identified by the mixed melting point method.[88]

Triphenylsilane and n-butyllithium.- To 13 g. (0.05 mole) of triphenylsilane dissolved in 25 ml. of ether was added 0.045 mole of n-butyllithium[24] in ether, Color Test I[11] becoming negative after 30 minutes. After pouring the reaction mixture into 1:4 hydrochloric acid, the hydrolysate was extracted with hot benzene. The benzene layer was separated and dried over anhydrous sodium sulfate, and the solvent removed by distillation. The residue, a gummy solid, was extracted with 95% ethanol and the material remaining proved to be tetraphenylsilane (10.7% of the product). From the ethanol was obtained 10 g. (63.5% yield) of n-butyltriphenylsilane melting at 86°. Disproportionation[89] has been reported to occur among silicon compounds, and this phenomenon might account for the presence of tetraphenylsilane.

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[87] H. Marsden and F. S. Kipping, J. Chem. Soc., 93, 198 (1908).

[88] The authentic specimen of methyltriphenylsilane was kindly provided by Dr. R. N. Clark.

[89] A. Ladenberg, Ann., 173, 159 (1873); G. Calingaert, H. Soroos, and V. Hnisda, J. Am. Chem. Soc., 62, 1107 (1940); G. Calingaert and H. A. Beatty, Ch. 24, ref. 1(a).

Anal, Calcd. for $C_{22}H_{19}Si$: Si, 8.86. Found: Si, 8.67 and 8.72.

Triphenylsilane and phenylmagnesium bromide.- Three experiments in which triphenylsilane and phenylmagnesium bromide were used as reactants were conducted.[85] In the first, 0.023 mole of the Grignard reagent was added to 8 g. (0.0308 mole) of triphenylsilane in ether and the solution refluxed for 24 hours. Color Test I[11] remained positive throughout the period of reaction. After hydrolyzing and working up the reaction mixture, 92.5% (7.4 g.) of the triphenylsilane was recovered. No tetraphenylsilane was isolated.

In the second instance, 4 g. (0.0154 mole) of triphenylsilane in 15 ml. of ether was treated with 0.012 mole of phenylmagnesium bromide in 10 ml. of ether. Most of the ether was then distilled and replaced with 20 ml. of pure xylene in which the reactants were refluxed for 24 hours. Color Test I[11] remained positive during this time. After working up the reaction mixture, 3.5 g. (88%) of the silane was recovered.

The third reaction was carried out by first adding 3 ml. of pure dioxane to 0.022 mole of phenylmagnesium bromide in 21 ml. of ether. Grignard reagents so treated have been found to be more reactive.[90] Then was added 5 g. (0.019 mole) of triphenylsilane in 20 ml. of ether, and the syspension stirred

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[90] H. Gilman and G. C. Gainer, J. Am. Chem. Soc., 69, 877 (1947); E. Bergmann and W. Rosenthal, J. prakt. Chem., [2] 135, 267 (1932).

at room temperature for 24 hours. The quantity of triphenylsilane recovered was 4.5 g. (90%).

Triphenylsilane and acridine.- Twenty-six grams (0.1 mole) of triphenylsilane and 4.8 g. (0.027 mole) of acridine were dissolved in 80 ml. of dry xylene in an apparatus connected to a trap[91] and the solution refluxed for 30 hours. The solid which separated upon cooling the solution was dissolved in acetone and treated with ethanolic hydrogen chloride to precipitate acridine hydrochloride which, in turn, was treated with 10% sodium hydroxide to liberate the base. The base was recrystallized from ethanol, and 4.7 g. (98%) of acridine, melting at 106°, was recovered. No depression occurred when a mixed melting point determination with an authentic specimen was made. From the acetone solution 24.7 g. (95%) of triphenylsilane was obtained.

Triphenyl-(m-dimethylaminophenyl)-silane from Triphenyl-(p-bromophenyl)-silane

Triphenyl-(p-bromophenyl)-silane[31].- p-Bromophenyllithium was prepared by dissolving 13 g. (0.055 mole) of p-dibromobenzene in sufficient ether to insure complete solution at -15°, the reaction flask being submerged in an acetone-Dry Ice bath. To this solution was added 0.05 mole of n-butyllithium[24] at the

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[91] H. Gilman and A. P. Hewlett, Rec. trav. chim., 48, 1124 (1929).

rate of 5 ml. per minute. Color Test II-A[92] became negative after 20 minutes. Then, 13.3 g. (0.045 mole) of triphenylchlorosilane in ether was added to the solution of p-bromophenyllithium at such a rate that the temperature of the reaction did not rise above -10°.[93] A precipitate was immediately formed. After all the triphenylchlorosilane had been added, the bath was removed. The suspension was stirred for 2 hours, and then refluxed with stirring for an hour. The reaction mixture was hydrolyzed by pouring it into 1:3 hydrochloric acid, and most of the solid product settled at the ether-water interface. This material was collected on a filter.

The ether layer was separated, dried over anhydrous sodium sulfate, and the solvent removed by distillation. A small quantity of solid was thus obtained. The total product was dissolved in the minimum volume of hot benzene and 95% ethanol was added until the hot solution began to assume a

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[92] H. Gilman and J. Swiss, J. Am. Chem. Soc., 62, 1847 (1940).

[93] In the preparation of triphenyl-(p-bromophenyl)-silane and trimethyl-(p-bromophenyl)-silane (see p. 101 for this latter preparation), it was found that better yields of the respective products are obtained if the halogen-metal interconversion reaction and subsequent addition of R_3SiCl compounds are carried out at -20° to -10°. If these precautions are not observed, lower yields result and side-products are formed. See H. Gilman, W. Langham, and F. W. Moore, ibid., 62, 2327 (1940) for the effects of temperature upon halogen-metal interconversion reactions.

cloudy appearance. After cooling the solution, the precipitate that formed was collected on a filter and dried in a vacuum desiccator over sulfuric acid. The yield of triphenyl-(p-bromophenyl)-silane, melting at 167-168°, was 14.5 g. (78%, based on the quantity of triphenylchlorosilane used).

Anal. Calcd. for $C_{24}H_{19}BrSi$: Br, 19.3; Si, 6.7. Found: Br, 19.2; Si, 6.7.

In two other preparations, the yields were 73% and 77%, respectively.

Triphenyl-(p-bromophenyl)-silane and lithium dimethylamide.- Lithium dimethylamide[94] was prepared by passing dimethylamine through an ether solution containing 0.03 mole of n-butyllithium[24] against a pressure of 2-3 cm. of mercury. Color Test II-A[92] was negative at the end of the reaction and Color Test IV[95] was positive.

To the suspension of lithium dimethylamide was added 10 g. (0.024 mole) of solid triphenyl-(p-bromophenyl)-silane and the mixture refluxed for 36 hours. On working up the reaction mixture in the usual manner, a viscous oil which could not be resolved by crystallization was obtained. This material was then suspended in ether, in which some of the product was soluble, and the suspension treated with anhydrous hydrogen

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[94] H. Gilman, N. N. Crounse, S. P. Massie, R. A. Benkeser, and S. M. Spatz, ibid., 67, 2106 (1945).

[95] H. Gilman and L. A. Woods, ibid., 65, 33 (1943).

chloride. The precipitate was extracted with petroleum ether (boiling point 77-115°), and the insoluble portion was recrystallized from 95% ethanol. From the ethanolic solution was obtained 1.4 g. (14%) of a solid, the hydrochloride of triphenyl-(m-dimethylaminophenyl)-silane, which melted with decomposition at 210-211°. The quantity of unreacted triphenyl-(p-bromophenyl)-silane (mixed melting point) recovered from the petroleum ether was 4.2 g. (42%). A viscous oil was also obtained.[31]

In a second experiment conducted in refluxing ether for 38 hours, the yield of the hydrochloride was 1.5 g. (15%). The weight of starting silane recovered was 4.1 g. (41%), and a viscous oil was obtained.[31]

On the basis of the quantities of triphenyl-(p-bromophenyl)-silane reacting, the yields of the hydrochloride of triphenyl-(m-dimethylaminophenyl)-silane were 24.5% and 25.8%, respectively.[31]

In each of two other experiments using the same quantities of starting materials as before, most of the ether was removed by distillation and replaced with 100 ml. of pure benzene, and the suspension refluxed for approximately 40 hours. From one run were obtained 3 g. (30%) of the hydrochloride, 4 g. (40% recovery) of triphenyl-(p-bromophenyl)-silane, and a viscous oil. From the second experiment, the products were 3.2 g. (32%) of the hydrochloride, 4.1 g. (41% recovery) of triphenyl-(p-bromophenyl)-silane, and an oil. A mixed melting point determination of the hydrochlorides formed in each experiment showed no depression.[31]

In the second set of reactions, the yields of the hydrochloride of triphenyl-(m-dimethylaminophenyl)-silane, based on the amount of triphenyl-(p-bromophenyl)-silane reacting, were 50% and 55%, respectively.[31]

Anal. Calcd. for $C_{26}H_{26}NClSi$: N, 3.4; Cl, 8.5; Si, 6.7. Found: N, 3.3; Cl, 8.6; Si, 6.6.

Triphenyl-(m-dimethylaminophenyl)-silane[31].- To 9.4 g. (0.034 mole) of triphenylchlorosilane dissolved in 50 ml. of ether was added 0.0375 mole of m-dimethylaminophenyllithium (prepared from 0.043 mole of m-bromodimethylaniline[96] and 0.09 g. atom of lithium in 87% yield). Color Test I[11] remained negative during addition, indicating prompt reaction. However, a slight excess of the organolithium compound was used, and Color Test I[11] became positive at the conclusion of the addition. The mixture was hydrolyzed and worked up in the customary manner. The yield of crude product, melting at 90-95° was 11 g. (85%). After it was recrystallized from petroleum ether (boiling point 77-115°) to a constant melting point of 95-96°, the yield of pure triphenyl-(m-dimethylaminophenyl)-silane was 7 g. (58%).

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[96] Kindly supplied by Dr. S. V. Sunthankar.

Anal. Calcd. for $C_{26}H_{25}NSi$: N, 3.7; Si, 7.4. Found: N, 3.7; Si, 7.3.

Identification of the amination product[30].- A portion of the hydrochloride of the amination product was dissolved in ethanol and gently heated with a solution of 10% sodium hydroxide in 50% ethanol. The precipitated free base was recrystallized from ethanol and melted at 94-95°. A mixture of this compound and authentic triphenyl-(*m*-dimethylaminophenyl)-silane (melting point 95-96°) melted at 95-96°.

An ethereal solution of authentic triphenyl-(*m*-dimethylaminophenyl)-silane was treated with anhydrous hydrogen chloride, and the resulting precipitate recrystallized from 95% ethanol. The melting point of this hydrochloride was 210-211° (dec.). The melting point of a mixture of this hydrochloride with that of the amination product was 210-211° (dec.).

Each free base formed a picrate melting at 203-205° with decomposition, and a mixture of the two picrates melted at the same temperature.

Anal. Calcd. for $C_{32}H_{28}O_7N_4Si$: N, 9.36; Si, 4.68. Found: N, 9.4; Si, 4.4.

The Attempted Preparation of Triphenyl-(*p*-carboxyphenyl)-silane

Triphenyl-(p-bromophenyl)-silane[31] *and n-butyllithium*[24].- Several attempts to prepare triphenyl-(*p*-carboxyphenyl)-silane (p-triphenylsilylbenzoic acid) by this method were undertaken. In a typical experiment, 10 g. (0.024 mole) of triphenyl-(p-bromophenyl)-silane[31] dissolved in 70 ml. of a 5:2 benzene-ether mixture was interacted with 0.0277 mole of n-butyllithium[24] for 4 hours with stirring at room temperature. In no case was appreciable heat of reaction detected. The mixture was carbonated by pouring it jet-wise into a slurry of Dry Ice in ether. After the Dry Ice had sublimed, the ether suspension was hydrolyzed, acidified, and filtered. The crude material on the filter had no definite melting point, fusion occurring over the range 185-205°. Recrystallization from various solvents did not materially improve the melting point.

From the organic layer was obtained a product which melted at 180-205° after recrystallization from petroleum ether, ethanol, dioxane, and benzene, respectively.

When the reactants were heated to reflux for 2 hours and worked up in the usual way for the preparation of acids, a solid melting over a range of 170-220° was formed. The weight of this non-acidic material formed in each experiment averaged 6 to 7 grams.

Triphenyl-(p-bromophenyl)-silane and lithium.- To 0.1 g. (0.0144 g. atom) of lithium in 10 ml. of ether was added 2 g. (0.0048 mole) of triphenyl-(p-bromophenyl)-silane suspended in 20 ml. of ether. The mixture was refluxed for 48 hours after which time Color Test I[11] was still negative. The carbonation procedure which followed resulted in a 95% recovery of the silane, none of the acid being obtained.

In a second experiment, 10 g. (0.024 mole) of triphenyl-(p-bromophenyl)-silane and 0.42 g. (0.06 g. atom) of lithium were suspended in 250 ml. of ether in which medium the reactants were heated at the reflux temperature for 70 hours. Again Color Test I[11] did not become positive. Working up the reaction after carbonation yielded 9.7 g. (97% recovery) of unreacted silane.

Triphenylchlorosilane and lithium p-lithiobenzoate.- To 0.16 mole of n-butyllithium[24] in ether at -75°[97] was added 15 g. (0.061 mole) of p-iodobenzoic acid. After an hour, 14.4 g. (0.049 mole) of triphenylchlorosilane in 50 ml. of ether was added to the solution, the temperature of the reaction medium being maintained at -75° during the addition. After the introduction of the triphenylchlorosilane solution, the Dry Ice-acetone bath was removed and the mixture stirred for 16 hours. The reaction mixture was hydrolyzed with dilute hydrochloric acid and the ether layer dried. Subsequent to the removal of ether by distillation, 8 g. of a solid having a melting point of 110-111° after three recrystallizations from ethanol was obtained.

Anal. Calcd. for $C_{25}H_{20}O_2Si$: Si, 7.37. Found: Si, 6.75; 6.88 and 6.78.

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[97] H. Gilman and C. E. Arntzen, J. Am. Chem. Soc., 69, 1537 (1947).

These data are inconclusive. If the compound were n-butyl p-triphenylsilylbenzoate, the silicon content would be 6.42%. However, attempts to saponify this substance with 20% sodium hydroxide in 50% ethanol did not cause any change in the melting point or in the analysis of the compound. p-Triphenylsilylphenyl valerate (6.42% Si) is also ruled out on these bases.

p-Triphenylsilylvalerophenone (6.66% Si) might be considered as a possible product of the reaction. The inertness of the substance to hydrolysis could be considered as evidence favoring the formation of such a compound. Presently, however, no assumption as to the nature of this substance is being made.

Trimethyl-(p-halophenyl)-silanes

Trimethyl-(p-chlorophenyl)-silane.- To 20.8 g. (0.12 mole) of silicon tetrachloride in 100 ml. of anhydrous ether was added 0.36 mole of metyllithium.[98] Color Test I[11] became negative after 20 minutes. Then, to the solution of trimethylchlorosilane was added 0.107 mole of p-chlorophenyllithium (prepared from n-butyllithium[24] and p-chlorobromobenzene). The reaction was completed in 10 minutes since Color Test I[11] became negative in that period. After hydrolysis and

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[98] H. Gilman, E. A. Zoellner, and W. M. Selby, ibid., 55, 1252 (1933). See, also, H. Gilman, E. A. Zoellner, W. M. Selby, and C. Boatner, Rec. trav. chim., 54, 584 (1935).

the separation and drying of the ether layer, the solvent was distilled, and there was obtained 14 g. (71% yield) of trimethyl-(p-chlorophenyl)-silane boiling at 45-49° at 0.2 mm., n_D^{20} 1.5125, d_4^{20} 1.0285. The constants previously reported are d_4^{20} 1.0282, n_D^{20} 1.5128.[23]

Anal. Calcd. for $C_9H_{13}ClSi$: Cl, 19.2; Si, 15.17. Found: Cl, 19.3; Si, 15.2.

Trimethyl-(p-bromophenyl)-silane.- To 47.2 g. (0.2 mole) of p-dibromobenzene dissolved in enough ether to insure complete solution at -15° (about 150 ml. of ether was required) was added 0.194 mole of n-butyllithium[24] at the rate of 5 ml. per minute.[93] Color Test II-A[92] became negative after 20 minutes. Then, 19.5 g. (0.18 mole) of trimethylchlorosilane[99] in ether was added to the solution of p-bromophenyllithium at such a rate that the temperature of the reaction mixture did not rise above -10°. After all the trimethylchlorosilane had been added, the Dry Ice-acetone bath was removed. The suspension was stirred for 2½ hours, and then refluxed for an hour. The reaction mixture was worked up in the usual way, and the product distilled. The yield of trimethyl-(p-bromophenyl)-silane, boiling at 53-56° at 0.2 mm., was 32.6 g., or 79%, n_D^{20} 1.5285, d_{20}^{20} 1.2206.

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[99] Purchased from the Anderson Laboratories, Inc., Adrian, Michigan.

Anal. Calcd. for $C_9H_{13}BrSi$: Br, 34.9; Si, 12.2; MR_D, 57.63.[100] Found: Br, 34.7; Si, 12.1; MR_D, 57.53.

In subsequent preparations using 0.18 mole, 0.138 mole, and 0.4 mole of trimethylchlorosilane, the yields were 89.8%, 75%, and 85%, respectively.

The following constants were reported by Burkhard: n_D^{20} 1.5302, d_4^{20} 1.2197.[23]

Studies with Trimethyl-(*p*-bromophenyl)-silane

Trimethyl-(p-carboxyphenyl)-silane (p-trimethylsilylbenzoic acid) from trimethyl-(p-chlorophenyl)-silane.- To 0.25 g. (0.036 g. atom) of lithium in 25 ml. of anhydrous ether was added 3.4 g. (0.018 mole) of trimethyl-(*p*-chlorophenyl)-silane in 10 ml. of ether. The suspension was heated with stirring at the reflux temperature for 8 hours after which time most of the lithium had disappeared. The degree of sluggishness with which the RLi compound formed cannot be overemphasized, Color Test I[11] becoming positive only after refluxing for an hour. At the conclusion of the refluxing period, the solution was poured jet-wise into a Dry Ice-ether slurry, and the carbon dioxide allowed to sublime. After working up the reaction mixture in the usual way, there was obtained 1.7 g. (48.7%

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[100] Molar refractions were calculated from the values of R. O. Sauer, *J. Am. Chem. Soc.*, *68*, 954 (1946), and E. L. Warwick, *ibid.*, *68*, 2455 (1946).

yield) of product melting at 108-109°. Recrystallization of the compound from petroleum ether (boiling point 60-70°) raised the melting point to 110-111°.[101] The trimethyl-(*p*-carboxyphenyl)-silane was identified by the mixed melting point method.[102]

Trimethyl-(p-carboxyphenyl)-silane (p-trimethylsilylbenzoic acid) from trimethyl-(p-bromophenyl)-silane.- To 0.4 g. (0.057 g. atom) of lithium suspended in 30 ml. of ether was added 5 g. (0.021 mole) of trimethyl-(*p*-bromophenyl)-silane in 20 ml. of ether and the mixture stirred for 25 minutes at room temperature. The yield of *p*-trimethylsilylphenyllithium was 92% (0.0193 mole).

The organolithium compound was carbonated by pouring the solution jet-wise into a slurry of Dry Ice in anhydrous ether. After the Dry Ice had sublimed, the ether mixture was hydrolyzed and then acidified with dilute hydrochloric acid. The aqueous layer was separated and extracted twice with 25 ml. of ether. The ether portions were combined and dried over anhydrous sodium sulfate. After the solvent was removed by distillation, 3.3 g. (89%) of crude *p*-trimethylsilylbenzoic acid, melting at 107-109° was obtained. The acid was recrystallized

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[101] The melting point of this compound has been reported to be 117-118°. See ref. 26.

[102] The authentic specimen of this acid was graciously provided by Dr. R. N. Clark.

from petroleum ether (boiling point 60-70°), and 2.7 g. (72.2%) melting at 111-112° was obtained (identified by the mixed melting point method).

This acid was prepared in 70% yield from another run when 0.051 mole of *p*-trimethylsilylphenyllithium was used (mixed melting point identification).

p-Trimethylsilylbenzoyl chloride.- Ten grams (0.0515 mole) of *p*-trimethylsilylbenzoic acid was placed in a 100 ml. round bottom flask connected to a reflux condenser fitted with a calcium chloride tube, and 11.1 g. (0.08 mole) of thionyl chloride added. The mixture was heated on a steam bath for an hour. The contents of the flask were cooled, transferred to a Claisen flask, and distilled. The yield of *p*-trimethylsilylbenzoyl chloride, boiling at 74° at 0.2 mm., was 5.5 g. (50.5%), n_D^{20} 1.5309, d_{20}^{20} 1.1023.

Anal. Calcd. for $C_{10}H_{13}OClSi$: Cl, 16.7; MR_D, 59.57.[100] Found: Cl, 16.7 and 16.8; MR_D, 59.62.

In another preparation using the same quantities of reactants, the yield of *p*-trimethylsilylbenzoyl chloride was 8 g., or 73.4%.

p-Trimethylsilylphenyllithium and gaseous carbon dioxide.- Good yields of ketones have been obtained by the reaction of gaseous carbon dioxide with RLi compounds.[103] Attempts to

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[103] H. Gilman and P. R. Van Ess, *J. Am. Chem. Soc.*, *55*, 1258 (1933).

prepare bis-(p-trimethylsilylphenyl) ketone by this method were therefore undertaken. Carbon dioxide was passed over or through an ether solution containing 0.04-0.06 mole of p-trimethylsilylphenyllithium with stirring at the rate of 8 to 10 bubbles per second. The rate of flow of gas was measured by letting the gas pass through sulfuric acid before it entered the reaction flask. Color Test I[11] became negative within 5 minutes in each instance, and the contents of the flask assumed a tan color practically immediately.

The reaction mixture was hydrolysed with 1:1 hydrochloric acid and the organic phase separated and dried over anhydrous sodium sulfate. After removing the solvent by distillation, a solid, which after recrystallization from ethanol melted at 108-111°, was obtained. The weight of product in each of four reactions was approximately 43-47% of the theoretical (calculated as the ketone).

Analytical data for this substance are not conclusive. The silicon content of bis-(p-trimethylsilylphenyl) ketone is 17.18%, but six analyses gave 15.2%, 15.3%, 15.4%, 15.3%, 15.4%, and 15.6%, respectively.

The compound reacted with hydroxylamine and 2,4-dinitrophenylhydrazine. However, the analyses for nitrogen in each case were not good. In the product from hydroxylamine, the calculated nitrogen is 4.1%, but the nitrogen found was 6.4%, 6.5%, and 6.4%. Closer agreement between calculated and experimental values for nitrogen was observed in the product formed from 2,4-dinitrophenylhydrazine and the supposed ketone, they being 11.07%, and 11.7%, 11.65%, and 11.8%, respectively.

When these derivatives were hydrolyzed in ethanol containing hydrochloric acid, the original compound, melting at 108-110°, was regenerated. Attempts to prepare the ketone from bis-(*p*-trimethylsilylphenyl)-cadmium and *p*-trimethylsilylbenzoyl chloride resulted in oils and glasses.

Trimethyl-(p-bromophenyl)-silane and lithium dimethylamide.- Ten grams (0.0436 mole) of trimethyl-(*p*-bromophenyl)-silane in ether was added to lithium dimethylamide[94] (prepared from 0.057 mole of *n*-butyllithium in ether and dimethylamine) and the mixture refluxed with stirring for 48 hours. After hydrolysis, the ether layer was extracted with five 10-ml. portions of hydrochloric acid. From the ether layer was obtained 2 g. (20% recovery) of trimethyl-(*p*-bromophenyl)-silane. The aqueous layer was made basic with 20% sodium hydroxide and extracted with three 25-ml. portions of ether. Subsequent to drying the ether solution and removing the solvent by distillation, the residue was distilled at 73-76° at 1 mm. The yield was 4.7 g. (56%) of a silicon-containing amine, n_D^{20} 1.5211; d_{20}^{20} 0.9103; MR_D calcd. 64.80[100]; MR_D found 64.45. On the basis of the quantity of trimethyl-(*p*-bromophenyl)-silane entering the reaction, the yield of this amine was 82.4%.

Anal. calcd. for $C_{11}H_{19}NSi$: N, 7.25; Si, 14.5. Found: N, 7.22; Si, 14.35.

The picrate melted at 154-156°.[15]

In a second experiment, 16 g. (0.07 mole) of trimethyl-(*p*-bromophenyl)-silane in ether was added to an ether suspension of lithium dimethylamide (from 0.082 mole of *n*-butyllithium and dimethylamine). Most of the ether was removed by distillation and replaced with 65 ml. of pure benzene and the suspension refluxed for 108 hours. The yield of base was 8.3 g. (62.2%), and 3 g. (18.7%) of trimethyl-(*p*-bromophenyl)-silane was recovered. The melting point of the picrate of the amine was 153-155°[15] (from ethanol), and when mixed with the picrate of the product of the earlier run, no depression of the melting point was observed. On the basis of the quantity of trimethyl-(*p*-bromophenyl)-silane entering the reaction, the yield of the amine was 90.2%. The following constants were found: n^{20}_{D} 1.5280; d^{20}_{20} 0.9194; MR_D calcd. 64.80;[100] MR_D found 64.65.

Identification of the amine.- Trimethyl-(*p*-dimethylaminophenyl)-silane[15] was prepared in 78.6% yield from 0.075 mole of trimethylchlorosilane and 0.078 mole of *p*-dimethylaminophenyllithium. Its picrate melted at 154-155°, and the melting point of a mixture of this picrate with that of the amination product was 154-155°.

However, infra-red studies[104] showed the product formed by the reaction of lithium dimethylamide and trimethyl-(p-bromophenyl)-silane to be trimethyl-(m-dimethylaminophenyl)-silane. Substitution, then, occurred at the position ortho to that originally held by bromine.

p-Bromo-tert-butylbenzene and lithium dimethylamide.- To a suspension of lithium dimethylamide in ether (prepared from 0.05 mole of n-butyllithium[24] and dimethylamine) was added 10 g. (0.046 mole) of p-bromo-tert-butylbenzene[105] in 20 ml. of ether. The mixture was refluxed with stirring for 48 hours. After hydrolysis, the basic material was separated in the customary way, and 3 g. (37%) of p-dimethylamino-tert-butylbenzene, distilling at 68-70° at 1 mm., was obtained. The quantity of starting material recovered was 2.6 g. (26%). The yield of p-dimethylamino-tert-butylbenzene, calculated on the basis of p-bromo-tert-butylbenzene reacting, was 50%. A tarry residue, as yet unresolved, was obtained upon distilling each substance. The methiodide of p-dimethylamino-tert-butylbenzene melted at 194-195° (dec.).[106]

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[104] The author wishes to express deep appreciation to Mr. Jack Goodman who made this observation and who gave other invaluable assistance with this reaction. See H. Gilman, H. W. Melvin, and Jack Goodman, ibid., 76, 3219 (1954).

[105] Kindly supplied by Mr. William Meikle.

[106] W. C. Davies and F. L. Hulbert, J. Soc. Chem. Ind. (London), 57, 349 (1938).

p-Nitro-tert-butylbenzene[107].- This compound was prepared from 26.8 g. (0.2 mole) of *tert*-butylbenzene and an equal weight of nitric acid (d. 1.52). The yield of *p*-nitro-*tert*-butylbenzene, boiling at 84-86° at 2 mm., was 9.2 g. (35.07%). In a second experiment using 26.8 g. (0.2 mole) of the hydrocarbon and 40.2 g. of nitric acid (d. 1.52), the yield of product, boiling at 83-86° at 1.8 mm., was 22 g. (61.5%).

p-Amino-tert-butylbenzene[107b].- The yield of this amine, distilling at 75-78° at 1.5 mm., was 6 g. (85.7%) when prepared from 7 g. (0.0405 mole) of *p*-nitro-*tert*-butylbenzene, 24.4 g. (0.21 g. atom) of tin, and sufficient hydrochloric acid to completely dissolve the tin.

p-Dimethylamino-tert-butylbenzene[106].- Approximately 3 ml. of *p*-amino-*tert*-butylbenzene was treated with 5 ml. of 10% sodium hydroxide and 5 ml. of dimethyl sulfate and the mixture vigorously shaken. The oil that formed the top layer was withdrawn with a medicine dropper, placed in 5 ml. of ethanol, and the ethanolic solution treated with methyl iodide. The melting point of the methiodide (from ethanol) was 195° (dec.).[106] A mixture of this methiodide and that of the amination product (from *p*-bromo-*tert*-butylbenzene and lithium dimethylamide) melted at 194-195° (dec.). In addition, a melting point de-

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[107] (a) J. B. Shoesmith and A. Mackie, *J. Chem. Soc.*, 2336 (1928); (b) D. F. Malherbe, *Ber.*, *52*, 319 (1919).

termination on a mixture of the methiodide of the amination product and an authentic sample[108] showed no depression.

Since the use of picrates of the silicon-containing amino compound proved to be of questionable worth in establishing structure, it might be that the methiodide of the product obtained by the reaction of lithium dimethylamide and p-bromo-tert-butylbenzene cannot be relied upon for that purpose either. Therefore, the latter reaction is being restudied.

p-Trimethylsilylbenzaldehyde.- p-Trimethylsilylphenyllithium was prepared by the dropwise addition of 18.3 g. (0.08 mole) of trimethyl-(p-bromophenyl)-silane in 30 ml. of ether to 1.26 g. (0.18 g. atom) of lithium in 60 ml. of ether. The yield was 0.068 mole (83%).

To 0.068 mole of p-trimethylsilylphenyllithium was added 10.2 g. (0.075 mole) of N-methylformanilide[109] in 65 ml. of ether at such a rate as to maintain gentle refluxing. Color Test I[11] became negative after the anilide had been added. After working up the reaction mixture in the customary manner, there was obtained 7.2 g. (62% yield) of p-trimethylsilylbenzaldehyde boiling at 69-72° at 0.2 mm., n_D^{20} 1.5202,

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[108] Kindly provided by Dr. W. Cule Davies of Leeds, England.

[109] "Organic Syntheses," Vol. 20, John Wiley and Sons, Inc., New York, N. Y., 1940.

d^{20}_{20} 0.9820, MR_D calculated 54.7.[100]

Anal, Calcd. for $C_{10}H_{14}OSi$: Si, 15.73. Found: Si, 15.6 and 15.7; MR_D found 54.9.

The 2,4-dinitrophenylhydrazone[110] melted at 218-220° (from ethanol-ethyl acetate mixture).

Anal. Calcd. for $C_{16}H_{18}O_4N_4Si$: N, 15.64. Found: N, 15.75 and 15.69.

Triphenylsilane and Lithium Amides

Triphenyl-(di-n-butylamino)-silane[37].- To 0.034 mole of n-butyllithium[24] was added dropwise 5 g. (0.039 mole) of di-n-butylamine in 25 ml. of anhydrous ether. The suspension was refluxed for 30 minutes, after which time Color Test II-A[92] became negative and Color Test IV[95] became positive. Then, 8.8 g. (0.034 mole) of triphenylsilane in 50 ml. of dry ether was added to the suspension of lithium di-n-butylamide[94] and the mixture refluxed for 30 minutes. The suspension was filtered and the solvent removed by distillation. The residue was refluxed with benzene for an hour, filtered, and the solvent distilled. A similar treatment of this residue with

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[110] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 174.

petroleum ether (boiling point 60-70°) yielded a gummy solid which, after crystallization from absolute ethanol, weighed 7.6 g. (63%) and melted at 60-62°. A mixture of this product and that formed from lithium di-n-butylamide and triphenylchlorosilane (melting point 62°) melted at 61-62°.

Anal. Calcd. for $C_{26}H_{33}NSi$: Si, 7.23; N, 3.61. Found: Si, 7.6; N, 3.6.

Triphenyl-(diethylamino)-silane[37].- To 5.5 g. (0.075 mole) of diethylamine in 30 ml. of ether was added 0.075 mole of n-butyllithium[24] in ether. Color Test II-A[92] became negative within 5 minutes and Color Test IV[95] was positive. Then 19.9 g. (0.075 mole) of triphenylsilane in 40 ml. of ether was added dropwise and the mixture refluxed until Color Test IV[95] became negative (about 30 minutes). The product, triphenyl-(diethylamino)-silane, melting at 84-85°, was isolated in the same manner as was the di-n-butylamino derivative. The yield was 74.2%.

Anal. Calcd. for $C_{22}H_{25}NSi$: N, 4.23; Si, 8.46. Found: N, 4.32; Si, 8.58.

Triphenyl-(dimethylamino)-silane[37].- This compound was prepared from 0.035 mole of triphenylsilane and lithium dimethylamide[94] (from dimethylamine and 0.0385 mole of n-butyllithium) in the same way as were the above described compounds. The yield of triphenyl-(dimethylamino)-silane, melting at 80-81°, was 74.5%.

Anal. Calcd. for $C_{20}H_{21}SiN$: Si, 9.24; N, 4.67. Found: Si, 9.2; N, 4.6.

Portions of the triphenyl-(dialkylamino)-silanes were dissolved in anhydrous ether and treated with hydrogen chloride. This procedure resulted in cleavage of the compounds into triphenylchlorosilane and the hydrochloride of the respective dialkylamines. The cleavage products were identified by the mixed melting point method.

Triphenylsilane and N-lithio-2,5-dimethylpyrrole.- N-Lithio-2,5-dimethylpyrrole was prepared by adding 0.024 mole of *n*-butyllithium[24] to 2.4 g. (0.025 mole) of 2,5-dimethylpyrrole in 25 ml. of ether. Color Test II-A[92] immediately became negative, but Color Test IV[95] did not develop. To this lithium salt was added 5 g. (0.019 mole) of triphenylsilane in 20 ml. of ether and the suspension refluxed for 5 hours. The mixture was then filtered and the solvent removed by distillation. The residue from ether proved to be triphenylsilane (4 g., 80% recovery).

Triphenylsilane and N-lithiocarbazole.- To 3.4 g. (0.02 mole) of carbazole suspended in 150 ml. of ether was added 0.02 mole of *n*-butyllithium.[24] Color Test II-A[92] became negative immediately, but Color Test IV[95] did not develop. To the suspension was added 5 g. (0.019 mole) of triphenylsilane in 20 ml. of ether, and the mixture refluxed for 5 hours. After filtering the suspension and distilling the ether, 4.5 g.

(90%) of triphenylsilane was recovered.

Triphenylsilane and lithium hydrazide.- Lithium hydrazide was prepared by adding 0.015 mole of n-butyllithium to 0.6 g. (0.019 mole) of anhydrous hydrazine suspended in 100 ml. of dry ether. Color Test IV[95] failed to develop, but Color Test II-A[92] became negative within 15 minutes after the addition of n-butyllithium. Then was added 4 g. (0.015 mole) of triphenylsilane in 20 ml. of ether, and the whole refluxed for 18 hours. The mixture was filtered and the ether removed by distillation. The residue was then refluxed in 50 ml. of benzene for 30 minutes, filtered, the solvent distilled, and the residue refluxed in 50 ml. of petroleum ether (boiling point 77-115°) for 30 minutes. The petroleum ether solution was filtered and concentrated to about 1/3 the original volume. There was obtained 2 g. (45.7%) of a solid which contained nitrogen and reduced silver nitrate in dry acetone. During the process of recrystallization from petroleum ether, the melting point continued to change, becoming 150-158°, 155-170°, and 162-211°, for each successive recrystallization. The final substance did not contain any nitrogen. Apparently the compound which formed hydrolyzed rapidly.

Triphenylsilane and lithium diphenylamide.- Lithium diphenylamide was prepared from 3.4 g. (0.02 mole) of diphenylamine and 0.02 mole of phenyllithium. Color Test IV[95] remained negative, although Color Test I[11] immediately became negative. Then 5 g. (0.019 mole) of triphenylsilane in 30 ml. of ether was added and the suspension refluxed for 36 hours. After filtering and removing the ether by distillation, 4.5 g. (90%) of triphenylsilane was recovered.

Triphenylsilane and N-lithio-N-methylaniline.- N-lithio-N-methylaniline was prepared from 2.2 g. (0.02 mole) of methyaniline in 20 ml. of ether and 0.019 mole of phenyllithium. Color Test I[11] became negative at the end of the addition of the organolithium compound and Color Test IV[95] became positive. Then, 5 g. (0.019 mole) of triphenylsilane in 20 ml. of ether was added and the suspension refluxed for 4 hours, after which time Color Test IV[95] was negative. After filtering the mixture and distilling the solvent, 3 g. of triphenylsilane was obtained. This represents a recovery of 60%.

Triphenylchlorosilane and N-lithiocarbazole, and carbazole.- To N-lithiocarbazole (from 3.4 g., 0.02 mole of carbazole in 150 ml. of ether and 0.02 mole of phenyllithium) was added 5.9 g. (0.02 mole) of triphenylchlorosilane in 30 ml. of ether and the suspension refluxed for 20 hours. After filtering the mixture and distilling the solvent, there was recovered 5.3 g. (90%) of triphenylchlorosilane (mixed melting point).

In a second experiment, 5.9 g. (0.02 mole) of triphenylchlorosilane and 3.4 g. (0.02 mole) of carbazole were mixed with 0.5 g. of copper powder, and the mixture heated at 250° in a metal bath for 3 hours in a 22 x 175 mm. test-tube. The mass was extracted with petroleum ether (boiling point 72-115°), and 3.6 g. (61%) of triphenylchlorosilane and 2.9 g. (85.3%)

of carbazole were recovered. A considerable quantity of charred matter was also obtained.

Triphenylsilanol and Acetic Anhydride

Triphenylsilyl acetate.- Five grams (0.017 mole) of triphenylsilanol was dissolved in 20 ml. of acetic anhydride and the solution was refluxed for 5½ hours. On cooling the solution, a solid was formed. This was filtered and dried, and the weight of this material, melting at 89-93°, was 3.5 g. An additional 0.7 g. melting at 83-86° was obtained after concentrating the mother liquors. The total weight of this product was 4.2 g., or 78%. Upon recrystallisation from petroleum ether (boiling point 77-115°) there was obtained 3.7 g. (68.5%) of triphenylsilyl acetate melting at 93-94°.

Anal. Calcd. for $C_{20}H_{18}O_2Si$: Si, 8.81. Found: Si, 8.7 and 8.8.

This product is apparently unstable in the air, for some triphenylsilanol was obtained from the petroleum ether concentrates. After 1 week in a stoppered vial, the melting point changed to 160-210°, and analyses showed the silicon content to have changed to 10.2% and 10.25%, which values are close to that for hexaphenyldisiloxane. It has been observed that mixtures of triphenylsilanol and hexaphenyldisiloxane melt over ranges similar to the one given.[111]

Triphenylsilanol, acetic anhydride, and aluminum chloride.- The apparatus used in these experiments was a three-necked round bottom flask fitted with a mechanical stirrer, a Y-tube holding both a thermometer with the bulb immersed in the solution and a dropping funnel, and a reflux condenser connected to a hydrogen chloride absorption trap through a calcium chloride tube. Into the flask was placed 27.6 g. (0.1 mole) of triphenylsilanol dissolved in pure carbon disulfide, and 23.4 g. (0.25 mole) of aluminum chloride was added. Hydrogen chloride began to evolve immediately. The reaction flask was submerged in an ice bath, and then was added 10.2 g. (0.1 mole) of freshly distilled acetic anhydride at such a rate as to keep the internal temperature below 10°. When all the acetic anhydride had been added, the bath was removed and the reaction mixture stirred at room temperature for 18 hours. The suspension was hydrolysed on cracked ice containing hydrochloric acid, extracted with three 20-ml. portions of carbon disulfide, and the separated solvent layer dried over anhydrous sodium sulfate. After distillation of the solvent, a brownish gummy residue was deposited. This residue did not crystallise after being treated with several solvents.

These residues were probably cleavage products. When diphenyldichlorosilane, aluminum chloride and ethyl bromide were

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[111] Studies by Dr. Burt Hofferth.

interacted, the products isolated were silicon tetrachloride, phenyltrichlorosilane, and ethyl derivatives of benzene.[112] Since this reaction was hydrolyzed, any polychlorosilanes would probably polymerize to the gummy masses obtained.

Triphenylsilanol, acetic anhydride, and stannic chloride.- Investigations of the Friedel-Crafts reaction show that frequently milder catalysts can be used to effect the desired results when sensitive compounds are being treated.[113] In this experiment, therefore, the milder stannic chloride was the catalyst selected. Triphenylsilanol (13.8 g., 0.05 mole) was dissolved in 200 ml. of pure carbon disulfide and 26.5 g. (0.1 mole) of stannic chloride added dropwise to the solution. The reaction flask was then submerged in an ice bath, and 5.1 g. (0.05 mole) of acetic anhydride was added slowly. No rise in temperature was noted, nor were fumes of hydrogen chloride evolved. The bath was removed and the solution was stirred at room temperature for 24 hours.

After hydrolyzing and working up the reaction mixture, 13.6 g. (98% recovery) of triphenylsilanol was obtained. Identification was made by the mixed melting point method.

Triphenylsilanol, zinc chloride, and acetic anhydride.- When 0.05 mole of triphenylsilanol in 200 ml. of carbon disul-

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[112] W. E. Evison and F. S. Kipping, J. Chem. Soc., 2774 (1931).

[113] H. Gilman and N. O. Calloway, J. Am. Chem. Soc., 55, 4197 (1933).

fide, 0.1 mole of freshly fused zinc chloride and 0.05 mole of acetic anhydride reacted at room temperature with stirring for 24 hours, 13.2 g. of the original 13.8 g. of triphenylsilanol was recovered.

Triphenylsilanol, acetic anhydride, and aluminum chloride-sulfuric acid catalyst.- A catalyst useful in condensations, alkylations, and isomerizations can be prepared by slowly heating a mixture of molar quantities of anhydrous aluminum chloride and sulfuric acid to 120°, forming, supposedly, $AlCl_2 \cdot HSO_4$.[114] This catalyst is described as being less hygroscopic than aluminum chloride.[114] The substance was prepared by heating 0.5 mole of aluminum chloride and 0.5 mole of sulfuric acid in an Erlenmeyer flask fitted with a thermometer and a large glass tube so gases could escape. The product was ground in a mortar, and 0.1 mole added to 0.05 mole of triphenylsilanol in 200 ml. of carbon disulfide. After following the procedure described previously, triphenylsilanol was recovered (97.8%).

Attempted Preparation of Triphenyl-(carboxy)-silane

Triphenylchlorosilane, lithium, and carbon dioxide.- To 0.3 g. (0.042 g. atom) of lithium in 20 ml. of ether was added 6 g. (0.02 mole) of triphenylchlorosilane in 30 ml. of ether,

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[114] L. Schmerling and V. N. Ipatieff, U. S. Patent 2,369,691, Feb. 20, 1945 [C. A., 39, 5254 (1945)].

and the suspension refluxed for 51 hours. Even though Color Test I[11] remained negative after that time and the quantity of lithium appeared not to have diminished, the suspension was filtered jet-wise into a slurry of Dry Ice in ether. After working up the solution, there was collected 4.9 g. of triphenylsilanol (a 90% conversion of the chlorosilane into the silanol) and none of the desired triphenyl-(carboxy)-silane.

Triphenylchlorosilane, carbon tetrachloride, and magnesium.- To 5 g. (0.017 mole) of triphenylchlorosilane and 0.31 g. (0.017 g. atom) of magnesium in 30 ml. of toluene was added 2.6 g. (0.017 mole) of carbon tetrachloride in 10 ml. of toluene and the mixture refluxed for 24 hours. After the suspension was hydrolyzed and worked up, 4.3 g. of triphenylsilanol was obtained and none of the desired carboxysilane was isolated. The weight of triphenylsilanol formed represents an 86% conversion of the chlorosilane.

The Preparation of Triphenyl-(benzyl)-silane

Triethoxychlorosilane.- Freshly distilled silicon tetrachloride (81.2 g., or 0.477 mole) was dissolved in 100 ml. of pure benzene in a three-necked round bottom flask of 500 ml. capacity which was submerged in an ice-salt bath. The flask was fitted with a stirrer, condenser and a Y-tube into one arm of which was placed a thermometer so that the bulb was in the solution. A dropping funnel containing 66.6 g. (1.448 moles) of absolute ethanol was fitted into the other arm, and the top of the funnel was attached to the nitrogen line. The ethanol was added at such a rate as to keep the temperature of the solution at 0° or below. When all the ethanol had been added, the bath was removed and the solution allowed to warm to room temperature. The reaction was then heated to 60° at which temperature it was maintained for an hour.

The solvent was distilled and the residue fractionated at 55-57° at 11 mm. The weight of triethoxychlorosilane[9] was 66.1 g. (69.8% yield).

Benzyltriethoxysilane.- Benzylmagnesium chloride[115] was prepared in 91% yield from 4.3 g. (0.18 g. atom) of magnesium and 0.2 mole of benzyl chloride. To 33.3 g. (0.168 mole) of triethoxychlorosilane in 50 ml. of ether was added 0.168 mole of benzylmagnesium chloride in 190 ml. of ether. After Color Test I[11] became negative, the mixture was refluxed for 30 minutes and then filtered. The ether was removed by distillation and the residue fractionated at 84-85.5° at 0.5 mm. The yield of benzyltriethoxysilane was 35.2 g. or 82.4%, d_{20}^{20} 0.9864.[116]

Triphenylbenzylsilane.- To 20.3 g. (0.08 mole) of benzyltriethoxysilane was added 0.264 mole (a 10% excess) of phenyllithium. After stirring at room temperature for an hour, the

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[115] H. Gilman, E. A. Zoellner, and J. B. Dickey, *J. Am. Chem. Soc.*, *51*, 1576 (1929).

[116] W. Melzer, *Ber.*, *41*, 3391 (1908).

mixture was hydrolyzed on ice containing hydrochloric acid. The ether layer was separated and the aqueous portion extracted with ether. The ether portions were combined, dried over anhydrous sodium sulfate, and the solvent removed by distillation. The crude product weighed 29.6 g. (99%) and melted at 91-94°. Repeated recrystallization from a 1:1 methanol-ethyl acetate mixture raised the melting point to 97-98°, 23.8 g. (85%) being obtained.

Anal. Calcd. for $C_{25}H_{22}Si$: Si, 8. Found: Si, 7.9 and 8.1.

In another preparation from 0.14 mole of benzyltriethoxysilane, the yield was 84% of pure product.

Attempted Preparation of Triphenyl-(benzoyl)-silane

Lithium, benzoyl chloride, and triphenylchlorosilane.- To 90 ml. of an ether solution of 5 g. (0.017 mole) of triphenylchlorosilane and 0.3 g. (0.034 g. atom) of lithium was added 2.4 g. (0.017 mole) of benzoyl chloride. The mixture was heated with stirring at the reflux temperature of the suspension for 19 hours, but there appeared to be no diminution in the quantity of lithium.

The volume of ether was reduced by distillation and 50 ml. of pure toluene was added. This mixture was refluxed for 5 hours. After the suspension was filtered and the solvent distilled, 4.3 g. (86% recovery) of triphenylchlorosilane was obtained. No triphenyl-(benzoyl)-silane was detected.

Triphenylchlorosilane, benzoyl chloride, and magnesium.- To 0.5 g. (0.017 g. atom) of magnesium in 25 ml. of ether was added 5 g. (0.017 mole) of triphenylchlorosilane in 20 ml. of ether and the whole refluxed for 12 hours. The quantity of magnesium appeared not to decrease during this period. Then was added 2.4 g. (0.017 mole) of benzoyl chloride. Most of the ether was distilled and replaced with 50 ml. of pure toluene, and the new suspension refluxed for 5 hours. The recovery of triphenylchlorosilane was 95% of the theoretical and no triphenyl-(benzoyl)-silane was discerned.

Triphenylsilane and benzoyl chloride.- To a solution of 5 g. (0.019 mole) of triphenylsilane in 20 ml. of ether was added 2.7 g. (0.019 mole) of benzoyl chloride in 10 ml. of ether. After the addition was completed, 2 ml. of dry pyridine was introduced, and the mixture refluxed for 21 hours. After removing the ether by distillation, a solid was formed in the residue. The solid weighed 3.7 g. (74% recovery) and was proved to be triphenylsilane (mixed melting point identification).

Triphenylsilane and benzoyl chloride in pyridine.- Five grams (0.019 mole) of triphenylsilane, 2.7 g. (0.019 mole) of benzoyl chloride and 3 g. (0.038 mole) of dry pyridine were placed in a 125 ml. flask attached to a reflux condenser fitted with a calcium chloride tube and the solution refluxed for 3 hours. The solution was treated with dilute hydrochloric acid until acid to litmus to remove the pyridine. The mixture was extracted with benzene and the benzene portion extracted with three 20-ml. portions of 10% sodium carbonate and then washed with water. The benzene solution was dried over anhydrous sodium sulfate and the solvent distilled. The residual solid was recrystallized from petroleum ether (boiling point 77-115°), and 4.3 g. (80%) of triphenylsilanol (mixed melting point) was obtained.

Triphenylbenzylsilane and tert-butyl nitrite.- The procedure followed in this instance is essentially that described for the preparation of *o*- and *p*-nitroacetophenone from *p*-ethylnitrobenzene.[117] Into 100 ml. of *tert*-butyl alcohol in an Erlenmeyer flask was placed 2.5 g. (0.109 g. atom) of sodium wire and the suspension refluxed on a steam bath until the sodium had dissolved. Then to the solution, cooled in an ice bath, was slowly added a cold solution containing 17.5 g. (0.05 mole) of triphenylbenzylsilane and 28.8 g. (0.28 mole) of *tert*-butyl nitrite[118] in 30 ml. of pure benzene. Upon completing the addition, the flask was fitted with a calcium chloride tube and the mixture left standing for 24 hours. A reflux condenser was then attached and the suspension refluxed for 5½ hours, and then steam-distilled. The residue which solidified

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[117] A. H. Ford-Moore and H. N. Ryden, *J. Chem. Soc.*, 679 (1946).

[118] "Organic Syntheses," Collective Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 108.

in the flask melted at 92-93°. After recrystallization of this solid from a 1:1 methanol-ethyl acetate mixture, the melting point was raised to 96-97°. This material was shown to be triphenylbenzylsilane by the method of mixed melting points. The recovery of the silane was 97% complete.

It is to be noted that all operations involving *tert*-butyl nitrite were carried out in the hood behind a shield.

Triphenylsilyl cyanide and phenylmagnesium bromide.- Silver cyanide (2.3 g. or 0.017 mole) suspended in 20 ml. of ether was added to 5 g. (0.017 mole) of triphenylchlorosilane in 25 ml. of ether. After refluxing the suspension with stirring for 2 hours, the mixture was filtered. The ether was distilled, and 4.5 g. of the triphenylchlorosilane was recovered. No triphenylsilyl cyanide was obtained.

In a second trial, using the same quantities of reactants and pure benzene as the solvent and refluxing the suspension for 18 hours, a benzene-insoluble portion which was identified as silver chloride was obtained after filtering the mixture. The benzene-soluble material, about 1.5 g., melted at 216-218°. Since the weight of silver chloride formed was 2.4 g. or 0.017 mole, the reaction must have been quantitative. The organic solid, however, did not give a nitrogen test, and its melting point suggested hexaphenyldisiloxane. A mixed melting point determination proved this substance to have been formed as a result of exposure to air. The odor of hydrogen cyanide was quite strong. These observations suggest that triphenylsilyl cyanide did form.

A third experiment was undertaken using the same quantities of reactants in benzene solution. After refluxing for 18 hours, the suspension was filtered under nitrogen, and the filtrate treated with 0.02 mole of phenylmagnesium bromide. When the Grignard reagent was added, the solution assumed a deep violet color with the evolution of heat. After the initial heat of reaction had subsided, the mixture was refluxed over a period of 14 hours. Subsequent to hydrolyzing and working up the mixture, 1.7 g. (30%) of tetraphenylsilane (mixed melting point), 2 g. (42.5%) of triphenylsilanol, and an oil which was not further investigated were obtained.

Attempted Preparation of Sulfanilamide Derivatives

Triphenylchlorosilane and *p*-acetamidobenzenesulfonamide.- A xylene solution containing 4.8 g. (0.017 mole) of triphenylchlorosilane and 3.7 g. (0.017 mole) of *p*-acetamidobenzenesulfonamide was refluxed for 20 hours. A solid precipitated after the solution had cooled. This residue was collected on a filter and it was shown to be unreacted *p*-acetamidobenzenesulfonamide melting at 215-217° (mixed melting point identification). The quantity recovered was 3.6 g. (97.4%).

Hydrolysis of the xylene-soluble material yielded 72% of the theoretical amount of triphenylsilanol.

Dry pyridine was used as the solvent for the next experiment. Into 15 ml. of pyridine were placed 4.8 g. (0.017 mole) of triphenylchlorosilane and 3.7 g. (0.017 mole) of *p*-acetamidobenzenesulfonamide and the solution refluxed for 20 hours. After filtering the cooled solution, 3.5 g. of the sulfonamide was collected.

Triphenylchlorosilane and N^1-sodium p-acetamidobenzenesulfonamide.- Four grams (0.014 mole) of triphenylchlorosilane and 3.3 g. (0.014 mole) of N^1-sodium *p*-acetamidobenzenesulfonamide (from *p*-acetamidobenzenesulfonamide in ethanol and sodium hydroxide) were suspended in 50 ml. of dry xylene and refluxed for 22 hours. After filtering the suspension, the residue was twice extracted with hot xylene and then dried in a vacuum desiccator over calcium chloride. The solid weighed 3.3 g. (quantitative recovery of the salt), and upon acidification of it, *p*-acetamidobenzenesulfonamide was obtained.

Hydrolysis of the xylene-soluble material yielded 62.5% of the theoretical quantity of triphenylsilanol.

In the next run, 0.014 mole of N^1-sodium *p*-acetamidobenzenesulfonamide and 0.014 mole of triphenylchlorosilane were suspended in xylene containing 0.3 g. of copper powder. The mixture was refluxed for 8 hours. After filtering the suspension, 3.2 g. (80%) of the triphenylchlorosilane was recovered. The solid was dissolved in water and the solution filtered so as to remove the copper. Acidification of the filtrate caused the formation of 2.8 g. (94% conversion) of *p*-acetamidobenzenesulfonamide.

In the high-temperature reaction next used, 2.2 g. (0.009 mole) of N^1-sodium *p*-acetamidobenzenesulfonamide, 2.7 g. (0.009 mole) of triphenylchlorosilane, and 0.3 g. of copper powder were mixed and heated at 195° for 4 hours in a metal bath in a 22 x 175 mm. Pyrex test tube fitted with a calcium chloride tube. Only a charred mass which could not be resolved was produced.

The Isopropylsilanes[119]

Phenyltriethoxysilane and isopropyllithium.- To 14 g. (2 g. atoms) of lithium in 250 ml. of freshly distilled, anhydrous petroleum ether (boiling point 28-38°) was added a few ml. of a solution of isopropyl chloride in petroleum ether (boiling point 28-38°). The mixture was heated on a water bath to initiate reaction. After reaction began, more of the isopropyl chloride in solution was added until one mole of the alkyl halide had been introduced. The yield of isopropyllithium was 0.48 mole or 48%.

Isopropyllithium (0.23 mole) in petroleum ether (boiling point 28-38°) was added to 16.8 g. (0.07 mole) of phenyltriethoxysilane dissolved in 100 ml. of petroleum ether (boiling point 28-38°). During the addition of the first equivalent of the organolithium compound, Color Test I[11] was negative, but

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[119] H. Gilman and R. N. Clark, *J. Am. Chem. Soc.*, *69*, 1499 (1947).

the test remained positive while the other two equivalents were being introduced. The suspension was stirred with refluxing for 14 hours after which time Color Test I[11] became negative. Subsequent to working up the reaction mixture, there was obtained 11.3 g. (a 70% yield) of phenyltris-(isopropyl)-silane, d $_4^{20}$ 0.9189, n $_D^{20}$ 1.4938, boiling at 81-83° at 0.6 mm.

The constants of this compound have been reported to be boiling point, 90-91° at 4 mm., d $_4^{20}$ 0.9055, n $_D^{20}$ 1.5102.[119]

Phenyltris-(isopropyl)-silane was also prepared from 0.03 mole of phenylbis-(isopropyl)-ethoxysilane and 0.033 mole of isopropyllithium refluxed in petroleum ether (boiling point 23-28°) for 48 hours. The yield of product boiling at 80° at 0.5 mm., n $_D^{20}$ 1.4950, d $_4^{20}$ 0.9220, was 5.2 g. (74%).

<u>Phenylbis-(isopropyl)-ethoxysilane</u>.- To 15.8 g. (0.066 mole) of phenyltriethoxysilane in 100 ml. of petroleum ether (boiling point 28-38°) was added dropwise 0.14 mole of isopropyllithium in 193 ml. of petroleum ether, and Color Test I[11] became negative after two equivalents of the organolithium compound had been added. The mixture was filtered and the solvent distilled. The residue boiled at 75-77° at 0.3 mm., d $_4^{20}$ 0.9265, n $_D^{20}$ 1.4940. The yield of phenylbis-(isopropyl)-ethoxysilane was 10 g. or 63.7%.

<u>Anal</u>. Calcd. for $C_{14}H_{24}OSi$: Si, 11.86. Found: Si, 11.82 and 11.91.

Attempted Preparation of Triphenyl-(aminophenyl)-silane

Tetraphenylsilane and nitric acid.- In each of these reactions, the object was to obtain triphenyl-(nitrophenyl)-silane from which the corresponding aminophenyl compound could possibly be formed. The first experiment was a modification of a procedure described earlier.[120] Ten grams (0.03 mole) of tetraphenylsilane was placed in a three-necked round bottom flask fitted with a reflux condenser, a mechanical stirrer and a dropping funnel. The flask was submerged in an ice bath, and a mixture of 2 ml. (0.0368 mole, d. 1.45) of nitric acid and 10 ml. of sulfuric acid was added slowly with stirring. The addition was accompanied by much charring of the tetraphenylsilane. The mixture was poured into ice water, filtered, and the solid extracted with benzene. From the benzene was obtained 6.2 g. of tetraphenylsilane, a 62% recovery (identified by the mixed melting point method). The insoluble portion, weighing 0.67 g. and corresponding to 3.8 g. of tetraphenylsilane, was silica.

A second experiment in which 5 g. (0.015 mole) of tetraphenylsilane in 80 ml. of acetic acid was treated with 1.3 ml. (0.03 mole) of fuming nitric acid (measured in a buret) in 10 ml. of acetic acid was carried out. The flask containing the reactants was submerged in an ice bath while the fuming nitric

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

acid in acetic acid was added.[121] The mixture was stirred at 60-65° for 4 hours and then poured into ice water. The solid that formed was collected on a filter and was found to melt at 229°. After recrystallization from benzene, there was obtained 4.7 g. (94% recovery) of tetraphenylsilane melting at 231-232° (mixed melting point identification).

In a third reaction, 5 g. (0.015 mole) of tetraphenylsilane in 25 ml. of freshly distilled acetic anhydride which had been cooled to 3° was treated with a mixture of 2 ml. of fuming nitric acid in 12 ml. of acetic anhydride, which mixture was slowly added over a period of 5 minutes. The temperature of the reaction was kept at 3-6° during the addition. Then the suspension was allowed to warm to room temperature at which temperature it was stirred for 2 hours. A sample of the suspension was removed, placed into water, filtered and dried. This material proved to be tetraphenylsilane.

Since reaction seemed to be inappreciable under these conditions, the mixture was heated with stirring at 60° for 4 hours. After working up the reaction mixture, a 92% recovery of tetraphenylsilane was obtained.

Triphenylchlorosilane, p-bromoaniline, and n-butyllithium.- To 42 ml. of an ether solution containing 0.044 mole of n-

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[121] Ref. 116, p. 390

butyllithium[24] was slowly added 3.8 g. (0.022 mole) of p-bromoaniline in 30 ml. of ether. The solution was refluxed gently for 30 minutes. Then, 6.5 g. (0.022 mole) of triphenylchlorosilane in 50 ml. of ether was added and the resulting mixture refluxed for 1½ hours after which time Color Test I[11] became negative.

The solution, which was yellow, was treated with ethanol in order to decompose any organolithium compound remaining,[9] and then filtered. The solvent was removed by distillation, leaving a solid. Upon recrystallization of the solid from petroleum ether (boiling point 77-115°) there was obtained 5 g. (77% yield) of triphenylsilanol melting at 149-151° (mixed melting point 149-150°).

In a second experiment 0.063 mole of n-butyllithium[24] and 3.6 g. (0.021 mole) of p-bromoaniline were refluxed in ether for 30 minutes.[122] Then was added 6.2 g. (0.021 mole) of triphenylchlorosilane in 50 ml. of ether and the solution refluxed for 5 hours. Treatment with ethanol followed in order to destroy any lithium derivatives in the mixture. A purple color developed when the ethanol was added. After the reaction mixture was worked up, there was obtained 5.2 g. (89.6%) of triphenylsilanol melting at 148-150°.

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[122] C. G. Stuckwisch, Doctoral Dissertation, Iowa State College, 1943.

In the next experiment, clear *n*-butyllithium,[24] filtered under nitrogen, was used. To 2.8 g. (0.016 mole) of *p*-bromoaniline in 30 ml. of ether was added 0.049 mole of *n*-butyllithium[24] in ether and the solution stirred at room temperature for an hour. The organolithium compound was then slowly added to 4.7 g. (0.016 mole) of triphenylchlorosilane in 30 ml. of ether. After 5 minutes Color Test I[11] became negative. The mixture was then poured into ice water, the ether layer separated, washed with dilute hydrochloric acid, and dried over anhydrous sodium sulfate. The dry solution was afterwards distilled to remove the ether and the residue, an oily solid, crystallized from petroleum ether. The yield of triphenylsilanol, melting at 149-151°, was 3.9 g. (89%).

In this run, the liquid was drained from the yellow solid formed when 2.8 g. (0.016 mole) of *p*-bromoaniline in 30 ml. of ether and 0.049 mole of *n*-butyllithium interacted at room temperature with stirring for an hour. The solid was suspended in 100 ml. of dry ether prior to the addition of 4.7 g. (0.16 mole) of triphenylchlorosilane in 50 ml. of ether. The solution was stirred at room temperature for an hour, hydrolyzed with ammonium chloride solution, and the organic layer separated and dried over anhydrous sodium sulfate. After removal of the ether by distillation, a red-purple oil was obtained. This oil was suspended in water, the suspension made alkaline with ammonia and extracted with ether. After separating and drying the ether layer and distilling the solvent, a solid which was impure triphenylsilanol separated. This was recrystallised from petroleum ether (boiling point 77-115°) to yield 4.2 g. (95.4%).

Next, 5.9 g. (0.034 mole) of *p*-bromoaniline in 50 ml. of ether was treated with 0.0965 mole of *n*-butyllithium[24] and the solution stirred for 30 minutes at room temperature. To this solution was added 5 g. (0.017 mole) of triphenylchlorosilane in 50 ml. of ether. Most of the ether was removed and replaced with 100 ml. of pure benzene and the solution refluxed for 15 hours. Hydrolysis of the mixture was effected by pouring it into iced ammonium chloride solution. The organic layer was separated, dried over anhydrous sodium sulfate, and the solvent distilled. A red-brown oil which did not crystallise from a variety of organic solvents was obtained. Attempts to distill this material *in vacuo* resulted in decomposition as evidenced by charring.

Triphenylchlorosilane, sodium, and p-bromoaniline.- Into 30 ml. of pure benzene were placed 5 g. (0.017 mole) of triphenylchlorosilane, 0.8 g. (0.034 g. atom) of sodium and 3 g. (0.017 mole) of *p*-bromoaniline, and the mixture refluxed for 41 hours. The suspension was filtered and the sodium destroyed with ethanol. The filtrate was hydrolysed with hydrochloric acid, and the organic phase separated and dried over anhydrous sodium sulfate. The material found in this layer did not contain nitrogen and melted over a range of 195-210°. After this was recrystallised from ethanol, 4.2 g. of hexaphenyldisiloxane was obtained. This weight of the disiloxane corresponds to 95%

of the chlorosilane. The acqueous layer yielded 92% of p-bromoaniline (mixed melting point identification).

Attempted amination of triphenyl-(p-bromophenyl)-silane with sodium amide.- Sodium amide[123] was prepared by adding 1.1 g. (0.048 g. atom) of sodium piecemeal to 200 ml. of liquid ammonia containing 0.5 g. of ferric nitrate. A blue color appeared. Then was added 5 g. (0.012 mole) of triphenyl-(p-bromophenyl)-silane in small portions. After addition of the silane was finished, the suspension was stirred for 2 hours and the excess sodium amide destroyed by adding ammonium chloride in small quantities until the blue color disappeared. The ammonia was allowed to evaporate and the residue extracted with benzene in a Soxhlet apparatus. From the benzene solution was recovered 4.3 g. (86%) of triphenyl-(p-bromophenyl)-silane (mixed melting point identification).

This attempted reaction was repeated using the same quantities of sodium and triphenyl-(p-bromophenyl)-silane, but the volume of liquid ammonia was increased to 500 ml. and the stirring time increased from 2 to 6 hours. After working up the reaction mixture, 4.4 g. (88%) of unreacted triphenyl-(p-bromophenyl)-silane was recovered.

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[123] T. H. Vaughn, R. R. Vogt, and J. A. Nieuwland, J. Am. Chem. Soc., 56, 2120 (1934).

Silanes for Steric Hindrance Studies[13]

Tris-(o-anisyl)-chlorosilane.- To 11.8 g. (0.069 mole) of silicon tetrachloride in 50 ml. of ether was added 0.228 mole of o-anisyllithium (prepared from 0.7 g. atom of lithium and 0.3 mole of o-bromoanisole in 90% yield). The reaction flask was immersed in an ice bath during the introduction of the organolithium compound. The bath was removed after addition had been completed and the mixture stirred for 4 hours at room temperature. The suspension was filtered free of inorganic salts and the solvent removed by distillation. The residue was dissolved in a 1:3 benzene-petroleum ether mixture (the boiling point of the petroleum ether was 77-115°) and filtered. The filtrate was concentrated until a cloudiness appeared and then cooled. The yield of tris-(o-anisyl)-chlorosilane, melting at 204-205°, was 16.1 g. or 60.3%.

Anal. Calcd. for $C_{21}H_{24}O_3SiCl$: Si, 7.28; Cl, 9.23. Found: Si, 7.24; Cl, 9.5.

Tris-(o-tolyl)-chlorosilane.- o-Tolyllithium was prepared in 90% yield from 7 g. (1 g. atom) of lithium metal suspended in 80 ml. of ether and 85.5 g. (0.5 mole) of o-bromotoluene in ether.

To 25.6 g. (0.15 mole) of silicon tetrachloride in 40 ml. of ether was added 0.45 mole of o-tolyllithium in 300 ml. of ether. Color Test I[11] remained negative during the addition of the first equivalent but persisted to be positive during further addition. The solution was refluxed for 4 hours after which time the test became negative. The mixture was then poured on cracked ice containing 10 ml. of concentrated hydrochloric acid. The ether layer was separated, dried over anhydrous sodium sulfate, and the ether removed by distillation. The glassy solid that remained was recrystallized from petroleum ether (boiling point 60-70°) and 34.2 g. (68%) of tris-(*p*-tolyl)-chlorosilane, melting at 113-115° was obtained. From the mother liquors was obtained an additional 12 g. after concentration of the solution. The total mass was recrystallized from petroleum ether (boiling point 60-70°), and 44.8 g. (89%) of tris-(*p*-tolyl)-chlorosilane melting at 114-115° was obtained. This product was identified by the method of mixed melting points with a sample melting at 115-116°.[13]

Attempts to Form a Silicon-Sulfur Linkage

Triethoxychlorosilane and lithium p-thiocresoxide.- To an ether suspension of lithium *p*-thiocresoxide (prepared from 0.053 mole of *p*-thiocresol and 0.041 mole of phenyllithium) was added 0.041 mole (8.1 g.) of triethoxychlorosilane in 20 ml. of ether. The mixture was refluxed for 2 hours. After the suspension was filtered and the solvent distilled from the filtrate, the residue was fractionated. The distillate (boiling point 55-57° at 10-14 mm.) was unreacted triethoxychlorosilane, and weighed 7.3 g. (90% recovery). Acidification of the solid on the filter resulted in the recovery of *p*-thiocresol.

In two subsequent runs, the quantities of triethoxychlorosilane recovered were 89.7% and 91.1%, respectively.

Triethoxychlorosilane[9] and silver p-toluenesulfinate.- Into 50 ml. of pure benzene was placed 4.9 g. (0.017 mole) of silver *p*-toluenesulfinate and 3.4 g. (0.017 mole) of triethoxychlorosilane[9] and the solution refluxed for 45 hours. The suspension was filtered, and 4.4 g. of silver *p*-toluenesulfinate was recovered (94%). The benzene solution was treated with 10 ml. of absolute ethanol and warmed so that any unreacted triethoxychlorosilane[9] would be converted into ethyl orthosilicate. The quantity of ethyl orthosilicate obtained was 3 g. (86%).

In another experiment, 0.017 mole of triethoxychlorosilane[9] and 0.017 mole of silver *p*-toluenesulfinate were mixed and refluxed for 4½ hours. The recovery of silver *p*-toluenesulfinate was 4.7 g. (96%).

Triethoxychlorosilane[9] and sodium p-toluenesulfinate.- When 0.019 mole of triethoxychlorosilane[9] and 0.019 mole of sodium *p*-toluenesulfinate were used, 3.3 g. (97%) of the salt was recovered.

Triphenylchlorosilane and sodium p-thiocresoxide.- Sodium sand (0.8 g. or 0.035 g. atom) was prepared in 30 ml. of dry boiling xylene. To the suspension was added 5 g. (0.04 mole) of *p*-thiocresol in 25 ml. of dry xylene and the mixture heated gently. After the reaction had ceased, 8.8 g. (0.03 mole) of triphenylchlorosilane dissolved in 25 ml. of dry xylene was added to the suspension of sodium p-thiocresoxide, and the mixture refluxed for 18 hours. After filtration of the suspension and removal of the solvent under reduced pressure, there was obtained 8.2 g. of a viscous liquid. This material was crystallized from petroleum ether (boiling point 60-70°), and 7.7 g. (87.5%) of triphenylchlorosilane was recovered (mixed melting point determination). A small portion of the product was hydrolyzed to triphenylsilanol melting at 148-150° (mixed melting point 149-151°).

In another attempt, 4.7 g. (0.0166 mole) of triphenylchlorosilane and 2.7 g. (0.017 mole) of sodium p-thiocresoxide were placed in a 22 x 175 mm. test tube fitted with a calcium chloride tube and fused for an hour at 180-200° in a metal bath. During the heating the reactants turned brown. The cooled mass was removed, crushed, and extracted with two 50-ml. portions of petroleum ether (boiling point 77-115°). After removal of approximately 2/3 of the solvent by distillation, a solid residue was obtained. This residue gave a negative sulfur test and proved to be triphenylchlorosilane. Hydrolysis of this product gave 3.7 g. (86%) of triphenylsilanol melting at 149-151° (mixed melting point 150-151°).

Triphenylchlorosilane and sodium p-toluenesulfinate.- To 15.3 g. (0.052 mole) of triphenylchlorosilane in 80 ml. of dry xylene was added 9.3 g. (0.052 mole) of solid sodium p-toluenesulfinate, and the suspension refluxed for 6 hours. The xylene was distilled under reduced pressure after filtration and 14.7 g. (96% recovery) of triphenylchlorosilane was obtained.

In a second experiment, 0.0153 mole of triphenylchlorosilane and 0.017 mole of sodium p-toluenesulfinate were suspended in 50 ml. of xylene and the mixture refluxed for 18 hours. The recovery of triphenylchlorosilane was 89% complete.

A third run was made in which 4 g. (0.014 mole) of triphenylchlorosilane and 2.5 g. (0.014 mole) of sodium p-toluenesulfinate were thoroughly mixed and fused at 180-200° for 6 hours in a 22 x 175 mm. test tube fitted with a calcium chloride tube. The solid mass was extracted with dry acetone and the acetone distilled. Only a viscous, glassy mass which could not be crystallized remained.

Tris-(o-tolyl)-chlorosilane and sodium p-toluenesulfinate.- Two grams (0.0059 mole) of tris-(o-tolyl)-chlorosilane and 1 g. (0.0059 mole) of sodium p-toluenesulfinate were suspended in 25 ml. of dry xylene and refluxed for 55 hours. After filtering the suspension and removing the xylene by distillation under reduced pressure (water aspirator), 1.8 g. of solid melting at 113-114° was obtained. This was proved to be unchanged tris-(o-tolyl)-chlorosilane by the method of mixed melting points.

The same quantities of reactants were used in a different experiment in which the substances were intimately mixed and placed in a 22 x 175 mm. Pyrex test tube fitted with a calcium chloride tube. The tube was heated in a metal bath at 140-150° for 3 hours. The fused mass was crushed and extracted with petroleum ether (boiling point 60-70°). After filtering the extract, the solution was concentrated to one-half the original volume by distillation. All attempts to crystallize the product resulted in the formation of an oil.

Triphenylchlorosilane and silver p-toluenesulfinate.- A mixture of 2.5 g. (0.0085 mole) of triphenylchlorosilane, 2.3 g. (0.0085 mole) of silver p-toluenesulfinate, and 0.3 g. of copper powder was placed in a test tube fitted with a calcium chloride tube and heated at 200° for 6 hours. The charred mass that resulted was extracted with petroleum ether (boiling point 60-70°), but only a gummy material uncrystallizable from the usual organic solvents was obtained.

When the same quantities of reactants were refluxed in xylene for 20 hours, the suspension filtered and the filtrate concentrated, 2 g. (80%) of triphenylchlorosilane was recovered and identified by the method of mixed melting points.

Triphenylsilane and lithium p-thiocresoxide.- Lithium p-thiocresoxide was prepared from 5 g. (0.04 mole) of p-thiocresol in 20 ml. of ether and 0.036 mole of phenyllithium in ether. Color Test I[11] was negative at the end of the addition, and a solid separated. Then was added 7.8 g. (0.03 mole) of triphenylsilane dissolved in 25 ml. of ether. The mixture was refluxed by external heating for 24 hours with stirring. After working up the mixture, 7.5 g. (95%) of triphenylsilane was recovered. From the aqueous layer, 4.4 g. (88%) of p-thiocresol (mixed melting point) was obtained.

In a second experiment, 0.020 mole of lithium p-thiocresoxide and 0.019 mole of triphenylsilane were refluxed in 20 ml. of ether for 49 hours. From the mixture was recovered 95% of triphenylsilane and 85% of p-thiocresol.

In a third run, 0.019 mole of triphenylsilane in 20 ml. of ether was added to an ether suspension containing 0.02 mole of lithium p-thiocresoxide. Most of the ether was removed by distillation and replaced with 35 ml. of toluene. The mixture was refluxed for 72 hours. After working up the reaction mixture, 91% of the silane and 87% of p-thiocresol were recovered (identified by the method of mixed melting points.)

Triphenylchlorosilane and diphenyl sulfide.- The general directions for previous investigations[124] were used in these reactions. Five grams (0.017 mole) of triphenylchlorosilane, 3.2 g. (0.017 mole) of diphenyl sulfide,[125] and 6.1 g. (0.017 mole) of mercuric bromide were dissolved in 70 ml. of dry acetone. Complete solution was observed after the mixture had been refluxed for 2½ hours. After that time, test portions of the solution were found to form precipitates in ether and in ethanol. In their syntheses, the earlier workers[124] found these tests to be indicative of the formation of these salts. Then 0.0531 mole of solid silver nitrate was added to the mixture

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[124] R. R. Renshaw and O. S. Searles, ibid., 55, 4951 (1933).

[125] The diphenyl sulfide used was freshly distilled Eastman White Label grade boiling at 296° at atmospheric pressure and 120-122° at 0.5 mm., n_D^{20} 1.632.

and this treatment was followed by the passage of hydrogen sulfide through the solution in order to precipitate the silver and the mercury. After filtering the suspension, the filtrate was treated with ether. An oil mixed with a solid material remained after distillation of the solvent. The oil boiled at 296°, n_D^{20} 1.631, showing it to be diphenyl sulfide. The solid (2.5 g., 50%) was triphenylsilanol.

In a second reaction, 0.017 mole of triphenylchlorosilane and 0.017 mole of diphenyl sulfide were dissolved in dry acetone and the solution refluxed for 24 hours. The substances obtained were diphenyl sulfide (85%) and the chlorosilane (72%).

In a third attempt, 0.017 mole of triphenylchlorosilane, 0.017 mole of diphenylsulfide and 0.017 mole of mercuric bromide were heated together at 200-250° for 4 hours in an oil bath. After cooling the mixture, dry acetone was added and the solution treated with solid silver nitrate. Then the solution was warmed for 30 minutes, treated with hydrogen sulfide, and filtered. Only triphenylsilanol (67%) and diphenyl sulfide (87.5%) were obtained.

<u>Trimethylchlorosilane and diphenyl sulfide</u>.- Into 50 ml. of dry acetone were placed 4.3 g. (0.04 mole) of trimethylchlorosilane, 7.4 g. (0.04 mole) of diphenylsulfide, and 14.4 g. (0.04 mole) of mercuric bromide, and the solution stirred for 30 minutes. The mixture assumed a tan color after it had been stirred for about 5 minutes. Then was added 21 g. (0.124 mole) of silver nitrate, the consistency of the mixture becoming

pasty at that point. The suspension was stirred until a muddy-brown precipitate appeared. The suspension was then filtered, and the filtrate was treated with hydrogen sulfide to remove any residual silver and mercury. The solids were separated by filtration and the solvent removed by distillation. From the residue was obtained 6.9 g. (93% recovery) of diphenylsulfide. No attempt was made to recover any trimethylchlorosilane or its hydrolysis products.

The Triphenyl-(hydroxyphenyl)-silanes

Triphenyl-(o-hydroxyphenyl)-silane.- *o*-Hydroxyphenyllithium[97] was prepared from 0.28 mole of *n*-butyllithium[24] and 24.2 g. (0.14 mole) of *o*-bromophenol by refluxing an ether solution of these reactants until Color Test II-A[92] became negative (about 3 hours). Then was added 15.7 g. (0.053 mole) of triphenylchlorosilane in 50 ml. of ether. Most of the ether was removed by distillation and replaced with 125 ml. of pure benzene, and the solution refluxed for 24 hours. After working up the reaction mixture in the customary way, there was obtained 12 g. (a 61% yield) of triphenyl-(*o*-hydroxyphenyl)-silane melting at 229-231°. When recrystallized from a 1:1 mixture of ethanol and ethyl acetate, the melting point was raised to 231-232°.

Anal. Calcd. for $C_{24}H_{20}OSi$: Si, 7.96. Found: Si, 7.9 and 7.89.

Yields of 55%, 59%, and 65% were obtained in other experiments (based on the quantity of triphenylchlorosilane used).

It should be emphasized that in this preparation it is necessary that the halogen-metal interconversion reaction be allowed to proceed until Color Test II-A[92] becomes negative, or *n*-butyltriphenylsilane will also be formed. In every instance in which this precaution was not observed, the yield of the desired product was low and a considerable quantity of *n*-butyltriphenylsilane was obtained.

Triphenyl-(p-hydroxyphenyl)-silane.- The procedure followed in this synthesis is the same as that described for the preparation of triphenyl-(*o*-hydroxyphenyl)-silane, the same precautions being observed. In a reaction using 16.2 g. (0.055 mole) of triphenylchlorosilane and *p*-hydroxyphenyllithium[97] (from 0.145 mole of *p*-bromophenol and 0.29 mole of *n*-butyllithium[24]), the yield of product, melting at 225-226°, was 16 g., or 82%. After recrystallization from ethanol, the melting point of the silane was raised to 226-227°.

Anal. Calcd. for $C_{24}H_{20}OSi$: Si, 7.96. Found: Si, 7.88 and 7.91.

In each of three other preparations employing 5 g. of triphenylchlorosilane, the yields were 77%, 79%, and 81%, respectively (based on the chlorosilane used).

Chloracetic acid and the triphenyl-(hydroxyphenyl)-silanes.- Each silane (0.6 g., 0.0017 mole) was dissolved in 40 ml. of 20% potassium hydroxide and warmed to effect solution. To each solution was added 2 g. (0.0021 mole) of chloroacetic acid in

20 ml. of ethanol, and the flasks containing the solutions were placed in boiling water for 5 minutes.[109] The solutions were cooled, diluted with 15 ml. of water, and then made acid to Congo red with 1:5 hydrochloric acid. The acidified solutions were extracted with ether and the ether extracts washed with three 10-ml. portions of 5% sodium carbonate solution. The washings were carefully acidified, but no precipitate formed in either case.

The ether portions were dried over anhydrous sodium sulfate and the solvent removed by distillation. In each instance a quantitative recovery of the starting silane was made (identified by the mixed melting point method).

In a second attempt, 0.0017 mole of each hydroxyphenylsilane was dissolved in 5 ml. of 33% potassium hydroxide solution and each mixture warmed on a steam bath. Ethanol was added until solution was practically complete. To each solution was added 0.0021 mole of chloroacetic acid and the mixtures heated as described above for an hour. Each silane was quantitatively recovered.

Neither silane gave a color reaction with ferric chloride.

Cleavage[15] of the hydroxyphenylsilanes with hydrogen chloride.- Dry hydrogen chloride was passed into a stirred refluxing solution containing 5.5 g. (0.0156 mole) of each silane in 100 ml. of glacial acetic acid for 15 hours. On cooling, the reaction mixture was cautiously made basic with sodium carbonate solution. The resulting mixture was filtered to remove silicon compounds. The precipitate was extracted with ether and dried over anhydrous sodium sulfate. Triphenylsilanol was obtained from the ether. Hexaphenyldisiloxane, which is not appreciably soluble in ether, was recrystallized from petroleum ether (boiling point 77-115°). The silicon compounds were identified by the mixed melting point method.

The aqueous layer was acidified with 1:2 hydrochloric acid, extracted with ether, and the ethereal solution dried over anhydrous sodium sulfate. Phenol (identified as phenoxyacetic acid) was obtained by this procedure.

Triphenyl-(p-hydroxyphenyl)-silane yielded 0.9 g. (64.3%) of phenol, and 3.3 g. of silicon-containing compounds of which hexaphenyldisiloxane comprised 1.3 g. (39%), the remainder being triphenylsilanol (2 g., or 60.6%).

The ortho isomer formed 0.8 g. (57%) of phenol, and 3.4 g. of silicon compounds of which 1.6 g. (47%) was hexaphenyldisiloxane and 1.8 g. (53%) was triphenylsilanol.

Attempted Ketone Formation from Triphenyl-(phenylethynyl)-silane

Triphenyl-(phenylethynyl)-silane.- Phenylethynyllithium was prepared from 1.8 g. (0.0178 mole) of phenylacetylene in ether and 0.017 mole of phenyllithium. Then to the solution of phenylethynyllithium was added 5 g. (0.017 mole) of triphenylchlorosilane in 30 ml. of ether. Color Test I[11] became negative after 20 minutes. Subsequent to hydrolysis of the reaction mixture and separation and drying of the organic layer, the solvent was distilled. There was obtained 6 g. of a gummy product which was recrystallized from ethanol. The yield of pure product, melting at 97-98°, was 4.5 g., or 75%. This was identified by the method of mixed melting points.

Triphenyl-(phenylethynyl)-silane and sulfuric acid.- The reagent[126] for this reaction was prepared by dissolving 10 g. of sulfuric acid and 1 g. of mercuric oxide in 22 ml. of water. To 15 ml. of this solution was added 2 g. (0.006 mole) of triphenyl-(phenylethynyl)-silane, and the mixture stirred for 5 hours. The solid that settled was soluble in hot ethanol and was shown to be unchanged starting material. A part of the recovered silane was placed in the solution and refluxed for 10 minutes. Upon filtering the cooled solution, an infusible solid was collected. The overall recovery of triphenyl-(phenylethynyl)-silane was 1.7 g. (85%).

In a second experiment, the same procedure with the same quantities of materials was followed except that the solution was stirred while being warmed on a water bath at 50° for 18 hours. Subsequent to working up the mixture, 1.8 g. (90%) of triphenyl-(phenylethynyl)-silane was recovered. No ketonic material was found in either instance.

Triphenyl-(phenylethynyl)-silane and ethanolic hydrogen

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[126] C. Weygand, "Organic Preparations," Interscience Publishers, Inc., New York, N. Y., 1945, p. 125.

chloride.- Into 35 ml. of 5.8 M ethanolic hydrogen chloride was placed 1.8 g. (0.0054 mole) of triphenyl-(phenylethynyl)-silane and the solution refluxed for an hour. There was recovered 1.3 g. of the original silane after cooling the solution. After the solvent distilled, an oil and a solid remained. The solid proved to be hexaphenyldisiloxane (0.2 g.). Treatment of the oil with 2,4-dinitrophenylhydrazine resulted in the formation of 0.3 g. of the 2,4-dinitrophenylhydrazone of acetophenone.

The Preparation and Properties of Triphenylsilyl Isocyanate[36]

Diphenyldichlorosilane and urea.- Diphenyldichlorosilane was prepared *in situ* by treating 6.6 g. (0.038 mole) of silicon tetrachloride in ether with 0.0776 mole of phenyllithium. The reaction flask was submerged in an ice bath while the organolithium compound was being introduced. Then 2.3 g. (0.0388 mole) of urea was added and the suspension refluxed for 24 hours. The mixture was hydrolyzed and the ether layer separated and dried over anhydrous sodium sulfate. The diphenylsilanediol obtained after distillation of the solvent weighed 6.2 g. (75% yield) and melted at 158-161°. The compound was identified by the mixed melting point method.[127]

The melting point of diphenylsilanediol has been reported to be 139°[76]; 155° when heated at 2° per minute, with prelimi-

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[127] Mr. Norman Benedict graciously provided the authentic sample.

nary softening at 135°[128a]; 145°[128b]; and 128-132°[128c].

Urea and triphenylchlorosilane.- To 8.8 g. (0.03 mole) of triphenylchlorosilane in 50 ml. of dry xylene were added 2.1 g. (0.035 mole) of urea and 2.8 g. (0.035 mole) of dry pyridine to react with any hydrogen chloride that might have formed, and the mixture refluxed for 24 hours. The suspension was filtered and the xylene removed by distillation. The solid that remained weighed 7.5 g. and was proved to be unreacted triphenylchlorosilane.

In a second experiment, 5 g. (0.017 mole) of triphenylchlorosilane and 1 g. (0.017 mole) of urea were thoroughly mixed and placed in a 22 x 175 mm. test tube fitted with a calcium chloride tube and the tube heated at 190-200° for 4 hours in a metal bath. The solid was removed, crushed and extracted with three 25-ml. portions of petroleum ether (boiling point 77-115°). After concentrating and cooling the solution, 3.4 g. (67%) of triphenylsilyl isocyanate, melting at 96-97° was obtained. Slow recrystallization from the petroleum ether raised the melting point to 99-100°.

Anal. Calcd. for $C_{19}H_{15}ONSi$: Si, 9.3; N, 4.6. Found: Si, 9.4; N, 4.2.

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[128] (a) G. Martin, *Ber.*, *45*, 403 (1912); (b) G. E. Burkhard, *J. Am. Chem. Soc.*, *67*, 2173 (1945); (c) F. S. Kipping, *J. Chem. Soc.*, *101*, 2108 (1912).

The material that did not dissolve in the petroleum ether (boiling point 77-115°) was soluble in distilled water and gave a positive chloride test, and ammonia was evolved when the solution was warmed with sodium hydroxide. The weight of the ammonium chloride formed was 0.9 g. (quantitative).

Triphenylchlorosilane and sodium urethan.- Sodium urethan[129] was prepared from 0.5 g. (0.022 mole) of sodium and 2.2 g. (0.025 mole) of urethan in 30 ml. of dry xylene, the mixture being heated until the sodium disappeared. To the suspension was added 5 g. (0.017 mole) of triphenylchlorosilane and the mixture refluxed for 15 hours. The solid that remained after distilling the xylene from the filtered solution was dissolved in petroleum ether (boiling point 77-115°). An additional quantity of solid was obtained from the mother liquors. The total crude product was recrystallized from petroleum ether (boiling point 77-115°) and 2.8 g. (48% yield) of triphenylsilyl isocyanate, melting at 97-98°, was obtained. No depression in the melting point of a mixture of this product and that previously formed was observed.

Triphenylsilyl isocyanate and phenyllithium.- To 3 g. (0.01 mole) of triphenylsilyl isocyanate in 50 ml. of ether was added dropwise 11 ml. of an ether solution containing 0.01 mole

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[129] L. G. R. Tompkins and E. F. Degering, *J. Am. Chem. Soc.*, *69*, 2616 (1947).

of phenyllithium. A white precipitate began to form after the first 5 or 6 ml. of phenyllithium had been added, and refluxing ceased when the equivalent of phenyllithium had been introduced. After hydrolysis of the reaction mixture, the ether layer was separated and dried, and a solid remained after distillation of the solvent. This material was extracted with hot water, and the water-insoluble portion, after recrystallization from petroleum ether (boiling point 77-115°), weighing 1.7 g. (62%), was proved to be triphenylsilanol (mixed melting point). From the cooled water solution was obtained 0.7 g. (63.6%) of benzamide melting at 125-127° (mixed melting point 126-128°).

In another reaction, the ether suspension was treated with anhydrous hydrogen chloride, and 1.9 g. (65%) of triphenylchlorosilane and 0.9 g. (85%) of benzamide were isolated.

The Preparation and Properties of Triphenylsilyl Isothiocyanate[37]

Thiourea and triphenylchlorosilane.- Five grams (0.017 mole) of triphenylchlorosilane and 1.3 g. (0.017 mole) of thiourea were thoroughly mixed in a 22 x 175 mm. test tube fitted with a calcium chloride tube and heated in a metal bath at 190-200° for 4 hours. The fused mass was crushed and extracted with petroleum ether (boiling point 77-115°) in a manner similar to that employed in the reaction between urea and triphenylchlorosilane. The yield of triphenylsilyl isothiocyanate, melting at 96-97°, was 3.6 g. (68%). Slow recrystallization from petroleum ether caused the melting point to be raised to 99-100°.

Anal. Calcd. for $C_{19}H_{15}NSSi$: Si, 8.82; N, 4.41; S, 10.09. Found: Si, 8.8; N, 4.35; S, 9.9.

The yield in another preparation was 3.8 g., or 70%.

Triphenylchlorosilane and silver thiocyanate.- A suspension of 5 g. (0.017 mole) of triphenylchlorosilane and 3.1 g. (0.0187 mole) of silver thiocyanate in 40 ml. of pure benzene was refluxed for 3 hours with stirring. After filtering the mixture and distilling the benzene, a tan oil which crystallised from petroleum ether (boiling point 77-115°) remained. The product thus obtained weighed 3.9 g. (73% yield) and melted at 98-99° (mixed melting point 98-99°).

Triphenylchlorosilane and ammonium thiocyanate.- Five grams (0.017 mole) of triphenylchlorosilane and 1.5 g. (0.02 mole) of ammonium thiocyanate were suspended in 50 ml. of pure benzene and the mixture refluxed for 7 days. The hot suspension was filtered and the solvent distilled, and the residual oil crystallised from petroleum ether (boiling point 77-115°). The weight of triphenylsilyl isothiocyanate, melting at 97-99° (mixed melting point 98-99°), was 3.5 g. (56%).

Triphenylchlorosilane and lead thiocyanate.- A suspension of 8.5 g. (0.025 mole) of lead thiocyanate[130] and 7.4 g.

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[130] "Inorganic Syntheses," Vol. I, McGraw-Hill Book Company, Inc., New York and London, 1939, p. 85.

(0.025 mole) of triphenylchlorosilane in 100 ml. of pure benzene was refluxed for 10 hours. The suspension was filtered, the solid washed with dry benzene, and the solvent distilled. A syrupy liquid which dissolved in petroleum ether (boiling point 77-115°) remained. Since a pink color developed when the material crystallized, the product was redissolved in 20 ml. of petroleum ether and refluxed with Norit and filtered. From the clear filtrate was obtained 6.7 g. (97% yield) of triphenylsilyl isothiocyanate melting at 97-98° (mixed melting point 98-99°).

Triphenylsilyl isothiocyanate and phenyllithium.- To 5 g. (0.0157 mole) of triphenylsilyl isothiocyanate in 60 ml. of ether was added 0.0157 mole of phenyllithium in 18.3 ml. of ether. A white precipitate formed while the phenyllithium was being introduced. The suspension was stirred for 2 hours at room temperature, hydrolyzed, and filtered. The insoluble material, weighing 0.9 g. (17%), proved to be tetraphenylsilane (mixed melting point identification). The ether layer was separated, dried over anhydrous sodium sulfate, and distilled. The solid residue thus obtained was extracted with hot water, and 1.1 g. (57% yield) of thiobenzamide, melting at 114-115°, was obtained. The melting point of a mixture of this product with authentic thiobenzamide[131] was 114-116°.

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[131] Thiobenzamide was prepared by the method of S. Gabriel and P. Heymann, *Ber.*, *21*, 158 (1890). See, also, A. Bernthsen, *ibid.*, *10*, 1241 (1877).

The water-insoluble portion was recrystallised from petroleum ether (boiling point 77-115°) and 2.4 g., or 56%, of triphenylsilanol was obtained.

Triphenylsilyl isothiocyanate and phenylmagnesium bromide.- To 130 ml. of an ether solution containing 0.142 mole of phenylmagnesium bromide was added 15 g. (0.0473 mole) of triphenylsilyl isothiocyanate dissolved in 70 ml. of dry ether and the solution refluxed with stirring for 20 hours. The mixture was hydrolyzed with dilute hydrochloric acid and the evolved gas passed through a solution of lead acetate (0.175 mole). The weight of the dried lead sulfide was 0.5 g., corresponding to 4.5% of hydrogen sulfide.

The ether and aqueous layers were separated, the ether portions washed with water, and the washings combined with the original aqueous layer. The combined aqueous portions were in turn extracted with ether and the combined ether extracts dried over sodium sulfate. The solid obtained from the ether solution was recrystallised from petroleum ether (boiling point 77-115°), and 9.1 g. (70% yield) of triphenylsilanol was isolated. No organic matter was found in the aqueous portions.

In a subsequent reaction, 0.145 mole of phenylmagnesium bromide and 0.055 mole of triphenylsilyl isothiocyanate were refluxed in ether for 20 hours. During the heating, condenser difficulty ensued and the solvent boiled away. This made for a "forced" reaction. Upon hydrolysis of the reaction mixture, a strong odor of hydrogen sulfide was noted and a yellow solid was produced. The hydrolysate was extracted with ether, and after the usual procedure, 10.6 g. (70%) of triphenylsilanol and a red oil which did not contain nitrogen or sulfur were obtained. The oil was dissolved in a small volume of ethanol and after chilling, 1.7 g. (17%) of benzophenone was obtained.

Attempts to Form Silicon-Containing Azo Dyes

Triphenyl-(p-hydroxyphenyl)-silane and p-nitrobenzenediazonium salts.- Many experiments were conducted in an effort to prepare an azo dye containing silicon. In a typical procedure, *p*-nitroaniline (0.01 mole) was dissolved in 5 ml. of concentrated hydrochloric acid, and 0.01 mole of sodium nitrite which had been made into a 10% solution was slowly added to the amine hydrochloride solution which was kept at a temperature of 0-5°. After 30 minutes, solid sodium acetate was introduced until the solution became neutral to Congo red paper.

Triphenyl-(*p*-hydroxyphenyl)-silane (4 g., or 0.011 mole) was dissolved in 40 ml. of hot ethanol containing 10 ml. of 20% sodium hydroxide. The solution of the silane was cooled in an ice bath until the temperature of the solution fell to 0-5°. Then over a period of approximately 45 minutes to an hour was added the diazonium salt (the acetate), the temperature being held below 5° meanwhile. A cardinal color first appeared, but after about one-half of the diazonium salt had been added, the solution assumed a brownish color. The mixture was stirred during this operation and for periods of 30 minutes to 15 hours after addition; the temperature was maintained at 0-5°.

The solid was collected on a filter and dried, the crude material melting over a range of 160-190°. Attempts to purify the substance from a variety of solvents (ethanol, toluene, benzene, chlorobenzene, chloroform) resulted in an orange-colored solid which melted over a range of 185-215°.

Some of the material was suspended in sodium hydroxide solution and filtered. The undissolved matter melted over a range of 148-150°. Since it did not give a positive nitrogen test, a mixed melting point with triphenylsilanol was taken, and no depression was observed.

Another portion (about 0.5 g.) was dissolved in chloroform and subjected to chromatographic separation, the column being activated alumina. A colored zone did appear, and the material in that zone was extracted with ether. After distilling the solvent, a slightly yellow solid melting over a range of 110-140° was collected. It did not contain nitrogen.

In one instance, when the mixture was acidified after coupling, filtered, and the solid placed on a wad of paper towels under a watch glass to dry, the precipitate spontaneously ignited after approximately 2 hours. Since triphenyl-(p-hydroxyphenyl)-silane was recovered (90%), the spontaneously inflammable substance was assumed to have been the free diazonium salt. In each experiment, the odor of nitrobenzene was strong. Apparently either hydrolysis and cleavage or no reaction occurred.

In every case in which triphenyl-(*o*-hydroxyphenyl)-silane was used, a practically quantitative recovery of that silane was made.

DISCUSSION

The Reaction of Triphenylsilane with Organometallic Compounds, and with Lithium Dialkylamides

In the carbon series, organometallic compounds are frequently and conveniently used to introduce functional groups into the molecules from which the organometallic compounds are prepared. The procedure for synthesizing carboxylic acids from either Grignard reagents or organolithium compounds is well known. In addition, ketones,[103] aldehydes,[132] and sulfinates[133] are among other classes of compounds that are preparable by the use of organometallic compounds.

Since organosilicon compounds containing functional groups were felt to be desirable for possible pharmacological and agricultural studies, triphenylsilane was treated with organolithium compounds in an effort to obtain triphenylsilyllithium. Instead of the creation of a silicon-lithium linkage, however, a tetrasubstituted silane was formed in each instance.[85,134]

$$R_3SiH + R'Li \longrightarrow R_3SiR' + LiH$$

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[132] G. Wittig, *Angew. Chem.*, *53*, 243 (1940).

[133] H. Gilman and L. F. Cason, *J. Am. Chem. Soc.*, *72*, 3469 (1950).

[134] H. Gilman and S. P. Massie, *ibid.*, *68*, 1128 (1946); R. N. Meals, *ibid.*, *68*, 1880 (1946); U. S. Patent 2,444,784 [*C. A.*, *42*, 7317 (1948)].

In extending the examination of the reaction of organolithium compounds to other similar hydrides of Group IV elements,[135] it was found that triphenyltin hydride reacts with phenyllithium to form tetraphenyltin in 90% yields.[85] Triphenylgermane undergoes a similar reaction with phenyllithium when that organolithium compound is in great excess, tetraphenylgermane being produced in almost quantitative yield.[136] It is highly probable that R_3PbH[137] compounds would react like the corresponding silicon, tin and germanium compounds. All this is in contrast with the manner in which triphenylmethane and RLi compounds interact since triphenylmethyllithium is produced from this hydrocarbon.[138]

$$(C_6H_5)_3CH + RLi \longrightarrow (C_6H_5)_3CLi + RH$$

While substances of the type R_2NLi are not classed as organometallic compounds,[1] they were found to react with triphenylsilane like organolithium compounds.[21] Thus, compounds of the type $(C_6H_5)_3SiNR_2$ were synthesized in yields of 63-75% by the reaction

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[135] H. Gilman and G. E. Dunn, Chem. Revs., 52, 77 (1953).

[136] O. H. Johnson and D. M. Harris, J. Am. Chem. Soc., 72, 5566 (1950).

[137] Compounds of the type R_3PbH have not been isolated. See H. Gilman and J. C. Bailie, ibid., 61, 731 (1939); R. W. Leeper, L. Summers, and H. Gilman, Chem. Revs., 54, 101 (1954).

[138] H. Gilman and R. V. Young, J. Org. Chem., 1, 330 (1936).

$$(C_6H_5)_3SiH + LiNR_2 \longrightarrow (C_6H_5)_3SiNR_2 + LiH$$

where R is n-C_4H_9, C_2H_5, or CH_3.

When triphenylsilane was treated with phenylmagnesium bromide, no tetraphenylsilane was formed; instead, upwards of 90% of the silane was recovered even when the reaction was run at the reflux temperature of xylene.[85] Since it has been shown that the reactivity of Grignard reagents is increased when dioxane is added to their solutions,[139] triphenylsilane was treated with phenylmagnesium bromide containing this compound. Apparently reaction was inappreciable because triphenylsilane was recovered to the extent of 90%.[85]

While it is true that in these instances only RLi compounds reacted with triphenylsilane to form tetrasubstituted derivatives while phenylmagnesium bromide was without effect, the much less reactive dipropylzinc was found to react with trichlorosilane in a sealed tube at 150° for 6 hours to produce tetrapropylsilane as well as the expected tripropylsilane.[140] The formation of tetrapropylsilane along with free zinc and

$$2SiHCl_3 + 4Zn(C_3H_7)_2 \longrightarrow SiH(C_3H_7)_3 + 3ZnCl_2 + Zn + C_3H_8 + Si(C_3H_7)_4$$

propane might be explained by a reducing action of the silicon-hydrogen bond in tripropylsilane. It appears not unlikely, however, that the tetrapropylsilane might have been formed by

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[139] Possibly $(C_6H_5)_2Mg$, which is more reactive than C_6H_5MgBr, was precipitated. See ref. 1(a), p. 498, and ref. 89.

[140] C. Pape, Ber., 14, 1873 (1881).

$$SiH(C_3H_7)_3 + Zn(C_3H_7)_2 \longrightarrow Si(C_3H_7)_4 + Zn + C_3H_8$$

a reaction similar to that described with RLi compounds. Organometallic compounds differ largely in rate of reaction rather than in kind of reaction,[141] and the "forced" conditions used by Pape might have been the determining factor in the results obtained by him. Inasmuch as Grignard reagents lie between organolithium and organozinc compounds in reactivity, it is probable that they also would react like organolithium compounds under appropriate conditions.

Only one experiment was conducted to see if triphenylsilane is a reducing agent. Acridine and an excess of triphenylsilane were heated in xylene solution.[142] However, no products that might be formed by such a reduction were isolated.

The displacement of hydrogen by the negative radicals of organolithium compounds may be explained on the basis that the hydrogen atom is the negative end of the dipole in the silicon-hydrogen bond. The physical data on the carbon-hydrogen and the silicon-hydrogen bonds are: bond energy, kcal./mole[143]--

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[141] See pp. 518-524, ref. 1(a), for a discussion of relative reactivities of organometallic compounds.

[142] J. L. Towle, in unpublished studies, has shown that thiols, under these conditions, will reduce acridine and unrelated compounds. See, also, H. Gilman and J. B. Dickey, J. Am. Chem. Soc., 52, 4573 (1930).

[143] K. S. Pitzer, ibid., 70, 2140 (1948).

Si-H 76, C-H 98.2; bond length, Å[144]--Si-H 1.49, C-H 1.09; percent ionic character[143]--Si-H 3, C-H 4. The bond energies differ somewhat, the silicon-hydrogen bond being less stable. The bond lengths are such that the silicon-hydrogen bond is longer. The percent of ionic character is about the same in each case. However, the relative electronegativities of carbon, hydrogen, and silicon are 2.5, 2.1, and 1.8, respectively.[144] This makes for greater displacement of electrons toward hydrogen by silicon than by carbon. Therefore, silicon is more susceptible to nucleophilic attack by R^- and NR_2^- than is carbon. Thus, the hydrogen in silicon-hydrogen bonds would be more easily displaced by anions than would be hydrogen in carbon-hydrogen bonds. In the latter case, the hydrogen being more acidic, would more likely be replaced by metals.

Later researches have revealed that silicon-metal bonds may be formed by using various silicon compounds and the appropriate metal. The silicon-potassium bond has been made from hexaphenyldisilane and sodium-potassium alloy in ethyl ether and in *n*-butyl ether;[145] from triphenylchlorosilane and the alloy in ethyl ether;[145] and from triphenyl-(phenylisopropyl)-silane in ethyl ether.[22] Triphenylsilane, triphenylethoxysi-

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[144] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945.

[145] H. Gilman and T. C. Wu, *J. Am. Chem. Soc.*, *73*, 4031 (1951); *ibid.*, *75*, 2509 (1953); *J. Org. Chem.*, *18*, 753 (1953).

lane, tris-(p-xenyl)-silane, diphenylsilane, and phenylsilane all react with sodium-potassium alloy to form a silicon-potassium linkage.[146] Seemingly at least one aryl group has to be in the silicon-containing molecule, because triethylsilane did not react with the alloy.[146]

Silicon-sodium and silicon-lithium bonds have been formed by treating solutions of hexaphenyldisilane in ethylene glycol dimethyl ether with the respective metals.[147] The products were triphenylsilylsodium and triphenylsilyllithium. Since solutions of these compounds deteriorate with time, they should be used as soon as they are prepared.[147]

Possible reactions of compounds containing silicon-metal bonds might be promising. Tetrasubstituted silanes[20,146] and other derivatives have been synthesized from them.[147]

The Amination of p-Bromophenylsilanes

Amination of *ortho*-halogenated ethers[148a] and sulfides and sulfones[148b] by sodium amide in liquid ammonia results in the formation of *meta*-amino derivatives.[148] The same type of reaction was observed to occur when these halogenated ethers

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[146] R. A. Benkeser, H. Landesman, and D. J. Foster, *J. Am. Chem. Soc.*, *74*, 648 (1952).

[147] A. G. Brook and H. Gilman, *ibid.*, *76*, 278 (1954).

[148] (a) H. Gilman and R. H. Kyle, *ibid.*, *74*, 3027 (1952); (b) H. Gilman and G. A. Martin, *ibid.*, *74*, 5317 (1952).

reacted with lithium dialkylamides in ether.[148] Further, _-halogenated napthalenes, *o*-bromodimethylaniline and *p*-bromoanisole also formed products in which the amino groups occupy positions adjacent to those originally held by the halogen atoms.

In amination studies involving halophenylsilanes, it was found that triphenyl-(*p*-bromophenyl)-silane reacted with lithium dimethylamide in ether or an ether-benzene mixture to yield triphenyl-(*m*-dimethylaminophenyl)-silane. Some unreacted starting material was recovered. The rearrangement also occurred when trimethyl-(*p*-bromophenyl)-silane and lithium dimethylamide were interacted.[104] The analogous carbon compound, *p*-*tert*-butylbromobenzene, seemingly yielded only the *para*-derivative.

In the trimethylsilylbenzoic acids, data have been collected showing the trimethylsilyl group to be electron-releasing with regard to the benzene nucleus.[26] This release of electrons makes for the weakening of the acids to a greater degree than does the release of electrons by the *tert*-butyl group. Since the haloanisoles and other compounds which undergo the rearrangement reaction with metal amides have *o*-*p*-directing groups *ortho* or *para* to the halogen atom, it follows that trimethyl-(*p*-bromophenyl)-silane would also react in an analagous manner with metal amides. The apparent failure of the carbon analoge, *p*-*tert*-butylbromobenzene, to behave similarly might be traceable to the weak electron-releasing property of the tert-butyl group.[26]

In the case of triphenyl-(p-bromophenyl)-silane, the situation is possibly somewhat different. The meager evidence that does exist concerning the orienting influence of the triphenylsilyl group suggests it to be meta directing.[2,149] This radical, then, is electron-attracting. Since bromine also withdraws electrons,[150] the phenyl radical containing both these substituents would become positive. Further, the attacking species (the dimethylamido group), being nucleophilic, would cause a greater displacement of electrons towards both electron-withdrawing groups. If displacement towards bromine is greater than that towards the triphenylsilyl group, the position ortho to bromine would acquire a positive charge. These combined influences, then, would cause the attacking dimethylamido group to enter the position ortho to bromine.

The data on the yields of products by amination of the two silanes with lithium dimethylamide might be interesting in this connection. Trimethyl-(m-dimethylaminophenyl)-silane was formed in 82.4% and 90% yields in refluxing ether (48 hours) and in a refluxing ether-benzene mixture (108 hours), respectively,

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[149] E. G. Rochow, "An Introduction to the Chemistry of the Silicones," John Wiley and Sons, Inc., New York, N. Y., 1946.

[150] See C. K. Ingold, J. Chem. Soc., 1120 (1933), for substitution in haloaryl compounds.

with 18-20% recovery of the starting material, while the corresponding yields of triphenyl-(m-dimethylaminophenyl)-silane were 25% (36 hours) and 50-55% (40 hours) with a recovery of 40-42% of unreacted triphenyl-(p-bromophenyl)-silane.[31] (The yields are based on the quantities of the silanes reacting.) Since, except in one experiment, the conditions under which these syntheses were effected were roughly the same, the reactivity of trimethyl-(p-bromophenyl)-silane might be considered to be greater than that of triphenyl-(p-bromophenyl)-silane with respect to lithium dimethylamide.

The mode by which amido groups enter into positions ortho to those originally held by halogen to form meta-amino derivatives is not clear. More data must be assembled in order that these reactions be better understood.

Attempts to Prepare Triphenyl-(p-carboxyphenyl)-silane

Three procedures were followed in the effort to prepare triphenyl-(p-carboxyphenyl)-silane (p-triphenylsilylbenzoic acid). In the first, a halogen-metal interconversion reaction was tried. Some reaction did occur, for heat was evolved. The product, though, was not acidic, because it was not possible to titrate it with standard alkali. The melting point was quite indefinite, the range (180-205°) suggesting the substance to be impure hexaphenyldisiloxane.[111] Cleavage of the p-bromophenyl group by n-butyllithium followed by hydrolysis would result in the formation of the disiloxane.[151] While no evidence has been gathered conclusively favoring the presence of hexaphenyldisiloxane in the reaction mixture, possibly it did form.

In the second procedure, several efforts were made to form p-triphenylsilylphenyllithium from lithium and triphenyl-(p-bromophenyl)-silane by refluxing the suspension for as long as three days in ether. No reaction occurred, since after carbonation, practically all the silane was recovered.

In a third method, triphenylchlorosilane and lithium p-lithiobenzoate were interacted at -75°.[97] The substance isolated did not appear to be an acid or an ester. The analyses (Si found 6.75%, 6.88%, and 6.79% vs. 7.37% calculated) seemed to more nearly fit the data for triphenylsilylvalerophenone $[(C_6H_5)_3SiC_6H_4COC_4H_9]$ which has a calculated silicon content of 6.66%.

The class to which this substance belongs has not been established. It might be well to point out that since an excess of n-butyllithium was used, the silane might have undergone a halogen-metal interconversion reaction at the low temperature used and some ketonic material might have formed when the mixture was carbonated. It has been mentioned before that ketones are formed in high yields when gaseous carbon dioxide reacts with RLi compounds.[103] While an ether-Dry Ice slush was em-

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[151] H. Gilman, R. A. Benkeser, and G. E. Dunn, J. Am. Chem. Soc., 72, 1689 (1950); H. Gilman and H. Hartzfeld, ibid., 73, 5878 (1951).

ployed in this case, the formation of a ketone cannot be ruled out without further careful study.

Compounds Formed from Trimethyl-(p-bromophenyl)-silane

Trimethyl-(p-bromophenyl)-silane underwent reaction with lithium to form the corresponding organolithium compound in good yields. This is in contrast with triphenyl-(p-bromophenyl)-silane which did not react with lithium. p-Trimethylsilylphenyllithium was converted into p-trimethylsilylbenzaldehyde by treating it with N-methylformanilide,[118] and into the acid by the usual method. The acid reacted with thionyl chloride to produce p-trimethylsilylbenzoyl chloride in fairly high yields (60-70%). Each of these substances could be well characterized.

Attempted Ketone Syntheses

The attempts to prepare bis-(p-trimethylsilylphenyl) ketone from gaseous carbon dioxide and p-trimethylsilylphenyllithium were not as rewarding as were other reactions involving trimethyl-(p-bromophenyl)-silane. The product of the reaction had a silicon content 1.8-2% too low. While the substance did react with 2,4-dinitrophenylhydrazine and hydroxylamine, the nitrogen analyses were such as to leave one much in doubt (see EXPERIMENTAL for analyses). Hydrolysis of the nitrogen-containing compounds regenerated the original substance. No final conclusion has been reached as to the nature of this substance.

The Friedel-Crafts reaction was also employed in an effort to acylate organosilicon compounds. Triphenylsilanol was treated with acetic anhydride and aluminum chloride catalyst in carbon disulfide solution. Only cleavage products were formed as evidenced by the appearance of viscous tars.

Cleavage of organosilicon compounds by aluminum chloride has been previously reported.[111] In the case of tetraphenylsilane, cleavage occurred as follows:[149]

$$(C_6H_5)_4Si + AlCl_3 \longrightarrow (C_6H_5)_3SiCl + C_6H_5AlCl_2$$
$$(C_6H_5)_3SiCl + AlCl_3 \longrightarrow (C_6H_5)_2SiCl_2 + C_6H_5AlCl_2$$
$$(C_6H_5)_2SiCl_2 + AlCl_3 \longrightarrow C_6H_5SiCl_3 + C_6H_5AlCl_2$$
$$C_6H_5SiCl_3 + AlCl_3 \longrightarrow SiCl_4 + C_6H_5AlCl_2.$$

Finally, silicon tetrachloride and a tarry residue resulted.[149]

Because aluminum chloride causes cleavage of the molecule of triphenylsilanol, other catalysts were selected. Stannic chloride,[113] fused zinc chloride, and dichloroaluminum bisulfate ($AlCl_2.HSO_4$)[114] were employed, but they proved to be ineffective, the silanol being recovered in high yields. Later researches have shown that iodine is a catalyst of choice in the acylation of organosilicon compounds. Trimethyl-(2-thienyl)-silane and trimethyl-(2-furyl)-silane were acylated with acetic anhydride by means of iodine catalyst.[35] The acetyl group entered the 5-position of the thienyl and furyl parts of the respective molecules.

Next, experiments were undertaken to prepare triphenyl-(benzoyl)-silane. Benzoyl chloride, triphenylchlorosilane and lithium or magnesium were heated together in ether and/or toluene. No reaction took place. When triphenylsilane and benzoyl chloride were heated at the reflux temperature of pyridine, only triphenylsilanol was obtained as the silicon compound. The attempted oximation of triphenyl-(benzyl)-silane with <u>tert</u>-butyl nitrite was without effect since 97% of the starting silane was recovered. Each of these efforts was of no avail.

Another route by which a benzoyl silane might be prepared was then selected. It was thought that if phenylmagnesium bromide could be interacted with triphenylsilyl cyanide,[152] triphenyl-(benzoyl)-silane might be formed. The cyanide could not be isolated because the compound seems to be unstable in the air. Evidence of its preparation was indirect, the silver chloride formed being used as an indication of the synthesis of the cyanide. Phenylmagnesium bromide was introduced into the solution after the silver chloride had been filtered off, and reaction did occur. Apparently the cyanide group acted like a pseudo-halogen because tetraphenylsilane and some triphenylsilanol were isolated.[151] In no case was the desired product obtained. The hoped-for reaction was

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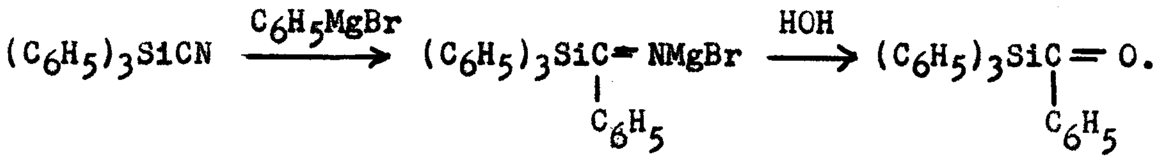
[152] The possibility of the formation of the isocyanide cannot be ruled out. See J. J. McBride, Jr., and H. C. Beachell, <u>ibid</u>., <u>74</u>, 5247 (1952) for an account of the preparation and properties of methylisocyanosilanes.



$$(C_6H_5)_3SiCN \xrightarrow{C_6H_5MgBr} (C_6H_5)_3Si\underset{C_6H_5}{C}{=}NMgBr \xrightarrow{HOH} (C_6H_5)_3Si\underset{C_6H_5}{C}{=}O.$$

Next, triphenyl-(phenylethynyl)-silane was subjected to hydrolysis with sulfuric acid containing mercuric oxide. Again the procedure yielded no ketone. Instead, triphenyl-(phenylethynyl)-silane was recovered to the extent of 97%.

In the last effort, triphenyl-(phenylethynyl)-silane was treated with ethanolic hydrogen chloride. It was hoped that the reaction

$$(C_6H_5)_3SiC\ CC_6H_5 \xrightarrow{HCl} (C_6H_5)_3SiCCl_2CH_2C_6H_5$$

$$[\text{or } (C_6H_5)_3SiCH_2CCl_2C_6H_5] \xrightarrow{H_2O} (C_6H_5)_3SiCOCH_2C_6H_5$$

$$[\text{or } (C_6H_5)_3SiCH_2COC_6H_5]$$

would occur. Instead, however, the compound was cleaved, some triphenyl-(phenylethynyl)-silane being recovered, and hexaphenyldisiloxane and acetophenone being produced.

It is quite probable that the difficulty of forming a silicon-carbonyl bond is traceable to the positive charge on each connecting atom. Silicon is electropositive,[143] and the carbonyl group in ketones and aldehydes is polarized so that carbon has a formal positive charge.

$$C{=}O \longleftrightarrow \overset{+}{C}-\overset{-}{O}$$

These conditions would lead to relatively small affinity between silicon and the carbonyl group. It is noteworthy that compounds of the type R_3SiCOR' are not known.

The Attempted Synthesis of Triphenyl-(aminophenyl)-silane

Four approaches to this preparation were made. In the first, several experiments to mononitrate tetraphenylsilane were conducted. Cleavage and charring took place when the method of Polis was used.[120] The reagents next tried were fuming nitric acid dissolved in acetic acid, and fuming nitric acid dissolved in acetic anhydride. Even when the latter two solutions containing tetraphenylsilane were heated, no reaction occurred, the silane being recovered to the extent of 92-94%. More rigorous conditions led to charring.

A series of experiments was next undertaken in which p-bromoaniline was converted into the lithium compound by means of a halogen-metal interconversion reaction with n-butyllithium. The organolithium compound was then treated with triphenylchlorosilane. In each instance triphenylsilanol was obtained along with some oil which charred when subjected to distillation.

Next, p-bromoaniline, triphenylchlorosilane, and sodium were heated in benzene, but no reaction took place. The only silicon compound isolated after hydrolysis was hexaphenyldisiloxane.

Finally, triphenyl-(p-bromophenyl)-silane was treated with sodium amide in liquid ammonia. From each of two such experiments, approximately 90% of the starting silane was recovered.

Attempts to Synthesize Sulfur-Containing Organosilicon Compounds

The types of compounds desired in these instances were (1) those containing a silicon-sulfur bond and (2) N^1-silicon derivatives of p-acetamidobenzenesulfonamide. In the aliphatic series, several mercaptosilanes have been prepared,[153] but aromatic silicon compounds of this type are few.[154] No N^1-silicon derivatives of sulfanilamide are reported.[1b]

No sulfides of the type R_3SiSAr were produced when triethoxychlorosilane, triphenylchlorosilane, and triphenylsilane, respectively, were treated with sodium or lithium p-thiocresoxide. Too, all efforts to form sulfones from chlorosilanes and p-toluenesulfinates met with no success. Finally, no sulfonium salts were prepared when triphenylchlorosilane and trimethylchlorosilane, respectively, were treated with diphenyl sulfide.

Cleavage studies[15] show aryl groups to be relatively easily removed, indicating them to have a rather strong affinity for electrons. It is possible, then, that the sulfur atom connected to the aryl group would have a residual positive charge, making for a weak bond between it and the rather electropositive silicon atom. The existence of such a condition would perhaps

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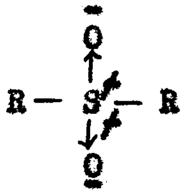
[153] H. J. Backer and F. Stienstra, *Rec. trav. chim.*, *52*, 912 (1933); H. J. Backer and H. A. Klasens, *ibid.*, *61*, 500 (1942).

[154] H. Gilman and G. N. R. Smart, *J. Org. Chem.*, *16*, 424 (1951).

account for the lack of formation of both R_3SiSAr types and sulfonium compounds.

The failure to obtain compounds of the type R_3SiSO_2Ar might also be traceable to the positiveness of silicon and sulfur. In sulfones, the electron distribution is such that the sulfur atom has a formal positive charge of two.[155] This would make for a weak bond between sulfur and silicon.



Gilman and Smart[154] succeeded in preparing tris-(*p*-tolyl)-*p*-tolylmercaptosilane, but their attempts to oxidize the compound to the sulfone led to cleavage. Thus compounds of the type R_3SiSO_2Ar were not obtained by indirect or direct methods.

The value of the sulfa drugs in medicine is well known. It was thought that it would be interesting, therefore, if silicon derivatives of sulfonamides could be made. The silicon-nitrogen bond is observed to be sensitive to moisture; therefore, strictly anhydrous conditions were maintained in each attempted reaction between *p*-acetamidobenzenesulfonamide or its N^1-sodium salt and the chlorosilane selected.

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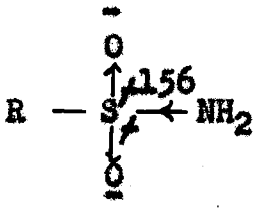
[155] R. Q. Brewster, "Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1953. See, also, Ch. 10, ref. 1(a), for a discussion of sulfur compounds.

Unfortunately, the results of efforts to obtain these compounds were negative. Again, the relative positiveness of the atoms to be linked might be a factor. In the aryl sulfonamides, the sulfur atom is positive, and this would cause electrons to have a tendency to move towards sulfur, leaving the nitrogen slightly positive.[155] If this is a true picture



$$R-\underset{\underset{-}{O}}{\underset{\downarrow}{\overset{\overset{-}{O}}{\overset{\uparrow}{S}}}}\xleftarrow{156}NH_2$$

of the position of charges, it is apparent that a compound of the type $R_3SiNHSO_2R'$ might be quite unstable.

Triphenylsilyl Isocyanate and Isothiocyanate

The treatment of triphenylchlorosilane with urea was undertaken in the hope that a silicon derivative of urea might be obtained, thus opening the way to the synthesis of silicon-containing barbiturates. The observation that the use of the malonic ester synthesis (and presumably the acetoacetic ester synthesis) with organosilicon compounds resulted in the formation of siloxy compounds[157] excludes these processes in the preparation of the desired products. The obtaining of tri-

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[156] The symbol ⟵ is used to indicate the direction in which electrons tend to be displaced. See Ch. 25, ref. 1(a).

[157] H. Gilman and R. N. Clark, J. Am. Chem. Soc., 69, 967 (1947).

phenylsilyl isocyanate was not anticipated. However, triphenylsilyl isocyanate was also produced when triphenylchlorosilane was treated with sodium urethan,[129] no N-triphenylsilylurethan being isolated.

Triphenylsilyl isocyanate reacts with phenyllithium to form triphenylsilanol and benzamide. If, however, treatment with hydrogen chloride instead of hydrolysis follows the addition of phenyllithium, the products are triphenylchlorosilane and benzamide.

$$(C_6H_5)_3SiNCO \xrightarrow{C_6H_5Li} (C_6H_5)_3SiN{=}C(OLi)C_6H_5 \xrightarrow{HOH}$$

$$(C_6H_5)_3SiNHCOC_6H_5 \xrightarrow{HOH} (C_6H_5)_3SiOH + C_6H_5CONH_2$$

$$\xrightarrow{HCl} (C_6H_5)_3SiCl + C_6H_5CONH_2 .$$

The reaction of triphenylchlorosilane with thiourea resulted in the synthesis of triphenylsilyl isothiocyanate. This compound reacts with phenyllithium to form some tetraphenylsilane, triphenylsilanol, and thiobenzamide. Since tetraphenylsilane did appear among the products, seemingly the scheme given above for the reaction between triphenylsilyl isocyanate and phenyllithium is not representative of that between the isothiocyanate and phenyllithium. The isothiocyanate moiety apparently behaved as a pseudo-halogen undergoing reaction like that observed with triphenylchlorosilane.

Triphenylsilyl isothiocyanate reacted with phenylmagnesium bromide at the reflux temperature of an ether solution of reactants to form triphenylsilanol. However, if "forced" conditions are used (fairly high temperature), some benzophenone is also obtained. No thiobenzamide was isolated in the reaction with phenylmagnesium bromide.

Phenylmagnesium bromide was used in a three-fold excess in these reactions. The fate of the phenyl group in the instance of reaction in refluxing ether is not known. However, in the case of heating in the absence of ether ("forced" conditions), the course of the reaction might have been as follows:

$$(C_6H_5)_3SiNCS \xrightarrow{C_6H_5MgBr} (C_6H_5)_3SiNC(SMgBr)C_6H_5 \xrightarrow{C_6H_5MgBr}$$

$$(C_6H_5)_3SiN=C(C_6H_5)_2 \xrightarrow{HOH} (C_6H_5)_3SiOH + (C_6H_5)_2C=NH$$

$$(C_6H_5)_2C=NH \xrightarrow{HOH} (C_6H_5)_2CO + NH_3.$$

This scheme would account for the presence of benzophenone.

These observations lead one to the conclusion that triphenylsilyl isocyanate and triphenylsilyl isothiocyanate are not exact analogs in their reactions with phenyllithium and phenylmagnesium bromide.

The Triphenyl-(hydroxyphenyl)-silanes

Triphenyl-(o-hydroxyphenyl)-silane and triphenyl-(p-hydroxyphenyl)-silane were synthesized in fairly high yields. However, the formation of triphenyl-(o-hydroxyphenyl)-silane took place at a slower rate and to a lesser extent than did that of triphenyl-(p-hydroxyphenyl)-silane. These results are not surprising in view of the observations made in steric hindrance studies.[13,119] Neither of these silanes gave a color reaction with ferric chloride, nor did they form the corresponding phenoxyacetic acids. However, both substances underwent cleavage[15] with anhydrous hydrogen chloride, yielding phenol, hexaphenyldisiloxane, and triphenylsilanol.

Attempts to couple these compounds with *p*-nitrobenzenediazonium salts were fruitless. In the case of triphenyl-(*o*-hydroxyphenyl)-silane, no reaction occurred, quantitative recoveries of the silane having been made.

Triphenyl-(*p*-hydroxyphenyl)-silane, on the other hand, underwent some reaction, apparently. However, what did actually occur is obscure. The melting points of whatever formed were so indefinite as to imply the presence of some sort of mixture. In at least one instance, the free diazonium salt was separated. At best the reaction can be described as sluggish and unclear.

Silicon-containing azo dyes have been prepared from trimethyl- and triphenyl-(*m*-dimethylaminophenyl)-silane,[158a] and their effectiveness and properties studied.[158b]

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[158] (a) S. V. Sunthankar and H. Gilman, *J. Org. Chem.*, **15**., 1200 (1950); *ibid.*, **18**, 47 (1953). (b) S. V. Sunthankar and H. Gilman, *Textile Research J.*, **22**, 574 (1952); *ibid.*, **23**, 53 (1953).

SUMMARY

A survey of some organosilicon compounds containing functional groups has been made.

In addition to the established means of synthesis, triphenylsilane was prepared smoothly and in a high degree of purity from triphenylchlorosilane and lithium aluminum hydride. Triphenyltin hydride could not be prepared from triphenyltin chloride by this method. In an effort to form triphenylsilane from triphenylsilanol, a new synthesis for hexaphenyldisiloxane was found.

Triphenylsilane and triphenyltin hydride did not form compounds of the type $(C_6H_5)_3MLi$ (where M may be Si or Sn) when they were treated with organolithium compounds, good yields of tetra-substituted products being obtained instead.

Triphenyl-(dialkylamino)-silanes were obtained by the action of lithium salts of di-*n*-butylamine, dimethylamine, and diethylamine, respectively, upon triphenylsilane. The lithium salts of 2,5-dimethylpyrrole, methylaniline, diphenylamine, and carbazole were without effect. Lithium hydrazide gave a compound which hydrolyzed on attempted purification.

Triphenylsilane did not reduce acridine.

Triphenyl-(*p*-bromophenyl)-silane and trimethyl-(*p*-bromophenyl)-silane reacted with lithium dimethylamide to yield *meta*-amino compounds. Triphenyl-(*p*-bromophenyl)-silane did not react with lithium, and its reaction with *n*-butyllithium resulted in indefinite products.

Trimethyl-(p-bromophenyl)-silane was converted into its organolithium compound from which the corresponding aldehyde and acid were prepared. p-Trimethylsilylbenzoyl chloride was obtained from the acid.

Attempts to prepare bis-(p-trimethylsilylphenyl) ketone from p-trimethylsilylphenyllithium and gaseous carbon dioxide were unsuccessful. The use of the cadmium compound with p-trimethylsilylbenzoyl chloride led to the formation of oils and glasses.

Efforts to acylate triphenylsilanol resulted in either no reaction or cleavage. The reaction between triphenylsilyl cyanide and phenylmagnesium bromide yielded tetraphenylsilane and triphenylsilanol, no triphenyl-(benzoyl)-silane being obtained.

Triphenyl-(nitrophenyl)-silane and triphenyl-(aminophenyl)-silane could not be synthesized by the procedures used.

All attempts to form compounds containing silicon to sulfur bonds, and compounds with a carbonyl or carboxyl group linked to silicon, did not succeed. Too, N^1-silicon derivatives of p-acetamidobenzenesulfonamide could not be prepared.

Two new methods for the synthesis of triphenylsilyl isocyanate and one for that of triphenylsilyl isothiocyanate have been devised. The reactions of these compounds with organometallic compounds have been described.

Triphenyl-(o-hydroxyphenyl)-silane and its para isomer were prepared. They did not give a color reaction with ferric chloride, nor did they form the corresponding phenoxyacetic acids. When treated with p-nitrobenzenediazonium salts, the para isomer gave indefinite products while the ortho compound did not react.