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

o-Phenylene Silicon Derivatives. Dihydrosilanthrene and Related Compounds[1]

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From the reaction of *o*-phenylenedilithium (I) with diphenyldichlorosilane and with dibenzyldichlorosilane, 5,5,10,10-tetraphenyl-5,10-dihydrosilanthrene (II) and 5,5,10,10-tetrabenzyl-5,10-dihydrosilanthrene were obtained. The reaction of I with diphenylsilane afforded *o*-phenylenebis-(diphenylsilane) (III), along with other compounds. The functional derivative III has been treated with a variety of organolithium reagents.

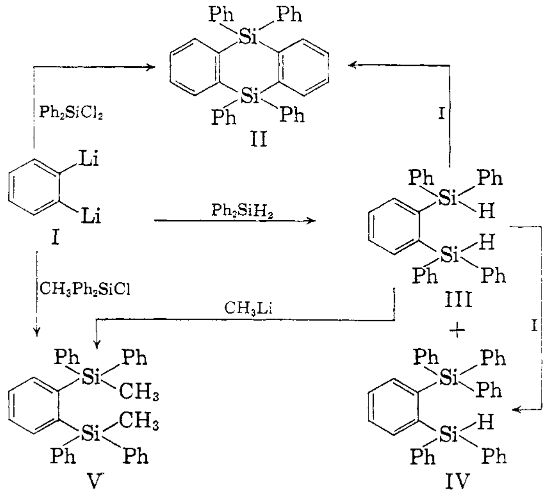
The synthesis of organometallic and organometalloidal derivatives containing the *o*-phenylene unit has been extremely arduous in some instances due to the inaccessibility of suitable Grignard and organolithium reagents. Grignard reagents, such as *o*-bromophenylmagnesium bromide[2,3] and *o*-bromophenylmagnesium iodide,[4] have been prepared but do not afford a practicable route for the synthesis of *o*-phenylene derivatives. Similarly, *o*-bromophenyllithium[5] has been prepared in low yields by the interaction of *o*-dibromobenzene and *n*-butyllithium, but is of limited utility as are the other *o*-halophenyllithium compounds.

Wittig and Bickelhaupt[6] recently have prepared *o*-phenylenedilithium (I) providing a new synthetic route to *o*-phenylene derivatives. The dilithium compound I was obtained by the lithium metal cleavage of *o*-phenylene–mercury, with the identity being confirmed by carbonation furnishing phthalic acid in 69% yield.

In the course of our studies, *o*-phenylenedilithium (I) has been allowed to react with various organosilicon compounds. Preliminary work in this Laboratory[7] on the reaction of the dilithium compound I with chlorosilanes showed the interactions to be complex. Contamination of the ethereal solution of the dilithium compound with finely divided lithium metal produced during the cleavage was thought to be the cause of this. After cleavage of the *o*-phenylene-mercury, the ethereal solution was filtered through a previously dried glass wool plug to give a red-brown solution containing a gray suspension. Acid titration of an aliquot of this solution always indicated base present in excess of 100%. Consequently, in an attempt to reduce the side reactions, the dilithium compound I was treated with an organosilicon hydride, diphenylsilane.

When *o*-phenylenedilithium (I) was allowed to react with diphenylsilane in an effort to synthesize 5,5,10,10 - tetraphenyl - 5,10 - dihydrosilanthrene (II), only *o*-phenylenebis-(diphenylsilane) (III) was isolated. A reaction with excess diphenylsilane gave an improved yield of di-silicon hydride III.

Subsequently, a suspension-free ethereal solution of *o*-phenylenedilithium (I) was obtained by filtering the cleavage solution through a sintered glass filter. This solution gave acceptable values of base present, upon acid titration of an aliquot, in line with conventional organolithium reagents. When this solution of the dilithium compound I was allowed to react with excess diphenylsilane, a good yield of *o*-phenylenebis-(diphenylsilane) (III) was obtained. The reaction of equal molar amounts of the dilithium compound I and diphenylsilane, in an attempt to prepare the cyclic derivative II, gave tetraphenylsilane, the di-silicon hydride III and (*o*-diphenylsilylphenyl)-triphenylsilane (IV).



Treatment of methyldiphenylchlorosilane with a suspension-containing solution of *o*-phenylenedilithium (I) afforded *o*-phenylenebis-(methyldiphenylsilane) (V) in low yield along with 1,2-dimethyl-1,1,2,2-tetraphenyldisilane. The formation of the disilane was thought to be due to a coupling reaction effected by the suspended lithium and not to the dilithium compound I. The dimethyl derivative V also was obtained from *o*-phenylenebis-(diphenylsilane) (III) and methyllithium. However, the reaction products were contaminated with Si–H containing material and were extremely difficult to purify, indicating incomplete reaction.

Two attempts to prepare the cyclic derivative, 5,5,10,10-tetraphenyl-5,10-dihydrosilanthrene (II), by the reaction of *o*-phenylenebis-(diphenylsilane) (III) and the dilithium compound I resulted only in the formation of (*o*-diphenylsilylphenyl)-triphenylsilane (IV). The cyclic derivative II, however, was finally obtained by treating equal molar amounts of *o*-phenylenedilithium (I) and diphenyldichloro-

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[1] For a preliminary account, see H. Gilman and E. A. Zuech, *Chemistry & Industry*, 120 (1960).

[2] H. Heaney, F. G. Mann and I. T. Millar, *J. Chem. Soc.*, 4692 (1956).

[3] G. Wittig and L. Pohmer, *Ber.*, **89**, 1334 (1956).

[4] H. Heaney, F. G. Mann and I. T. Millar, *J. Chem. Soc.*, 3930 (1957).

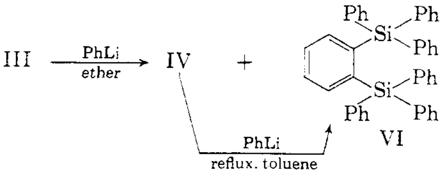
[5] H. Gilman and R. D. Gorsich, THIS JOURNAL, **78**, 2217 (1956).

[6] G. Wittig and F. Bickelhaupt, *Angew. Chem.*, **69**, 93 (1957); *Ber.*, **91**, 883 (1958).

[7] H. Gilman, D. Wittenberg and M. V. George, unpublished studies.

silane. In a similar fashion, 5,5,10,10-tetrabenzyl-5,10-dihydrosilanthrene was prepared from *o*-phenylenedilithium (I) and dibenzyldichlorosilane.

When *o*-phenylenebis-(diphenylsilane) was treated with an ethereal solution of phenyllithium, nearly equivalent amounts of (*o*-diphenylsilylphenyl)-triphenylsilane (IV) and *o*-phenylenebis-(triphenylsilane) (VI) were obtained. The silicon-hydride compound IV, however, was converted in good yield to the fully phenylated derivative VI by phenyllithium when forced conditions were used. An attempt to prepare the compound VI by treacting *o*-phenylenedilithium with triphenylchlorosilane was unsuccessful.



Attempts to make the molecular models of the dimethyl derivative V and the fully phenylated derivative VI using Stuart and Briegleb atomic models were unsuccessful, indicating a considerable amount of strain in the molecules due to the bulky substituents. This undoubtedly accounts for the slow reactions of methyl- and phenyllithium with *o*-phenylenebis-(diphenylsilane) (III). However, by comparison of the models, the dimethyl derivative V appears to be less strained than the corresponding phenylated derivative VI, which is in accord with the formation of V, but not of VI, from the respective reactions of methyldiphenylchlorosilane and of triphenylchlorosilane with the dilithium compound I. The molecular models of the other derivatives, including the cyclic silanthrene compounds, can be formed readily.

It is interesting to compare the melting points of the three phenylenebis-(triphenylsilane) isomers. The *p*-derivative[8] melts at 360° and the *m*-derivative[9] at 349°; while the sterically hindered *o*-derivative melts at 257.5–259°.

Experimental

All melting and boiling points are uncorrected and all reactions involving organolithium compounds were carried out under an atmosphere of dry, oxygen-free nitrogen in sodium-dried solvents. The *o*-phenylene-mercury was prepared according to Wittig and Bickelhaupt[6] using Eastman Kodak Co. white label *o*-dibromobenzene.

Reaction of *o*-Phenylenedilithium and Diphenylsilane. First Experiment.—A mixture of 8.28 g. (0.03 mole) of *o*-phenylene-mercury,[10] 6 g. of finely cut lithium wire and 100 ml. of dry ether was placed in a Schlenk tube and agitated for 4 days. The reaction mixture was filtered through a previously dried glass wool plug giving a reddish-brown solution containing a light gray suspension. This material was added over a period of 30 min. to 5.52 g. (0.03 mole) of diphenylsilane in 50 ml. of ether, while cooling in an ice-bath. After stirring for 24 hr. at room temperature, hydrolysis was carried out with 100 ml. of 5% hydrochloric acid. Ether was added and the insoluble gray solid filtered. This solid was then recrystallized from ethyl acetate three times to give 1.64 g. of *o*-phenylenebis-(diphenylsilane), m.p. 174–176°.

The layers of the filtrate were separated, and the aqueous layer extracted with ether. The combined organic solution was dried with anhydrous calcium sulfate and evaporated under an air-jet. The resulting material was taken up in ethyl acetate and seeded with some of the above solid to afford 0.95 g. of shiny crystals, m.p. 171–174°. This was recrystallized once more to give 0.77 g. of *o*-phenylenebis-(diphenylsilane), m.p. 174–176°. The total yield was 36.4% (based on the diphenylsilane), and the analytical sample melted at 174.5–176°. The infrared spectrum of the compound in carbon disulfide had characteristic absorption bands at 3.3, 9.0 and 13.3 μ, indicative of aromatic C–H, the silicon–phenyl linkage and *o*-disubstitution, respectively. As a carbon tetrachloride solution, the spectrum showed a large Si–H absorption at 4.7 μ.

Anal. Calcd. for $C_{30}H_{26}Si_2$: C, 81.39; H, 5.92; Si, 12.69. Found: C, 81.56, 81.38; H, 6.15, 5.98; Si, 12.78, 12.69.

Second Experiment.—*o*-Phenylenedilithium, prepared as described above from 10 g. (0.036 mole) of *o*-phenylene-mercury and 7 g. of lithium, was added dropwise to 14.7 g. (0.08 mole) of diphenylsilane dissolved in 100 ml. of ether. After stirring 16 hr. at room temperature, the reaction mixture was poured onto crushed ice containing a small amount of sulfuric acid. Following the same work-up procedure as given in the first experiment, there was obtained 3.71 g. (23.3%, based on the *o*-phenylene-mercury) of *o*-phenylenebis-(diphenylsilane), m.p. 173–176° (mixed m.p.).

Third Experiment.—A suspension of 10 g. (0.036 mole) of *o*-phenylene-mercury and 7 g. of lithium in 120 ml. of ether was agitated for 5 days. The reaction mixture was filtered through a sintered glass filter to give a red-brown, suspension-free, solution. A 2-ml. aliquot of the solution was titrated with standard acid indicating the presence of 0.024 mole of *o*-phenylenedilithium. (An assumption was made that all of the organolithium reagent was *o*-phenylenedilithium.) This reagent was added over a period of 45 min. to 11.0 g. (0.06 mole) of diphenylsilane in 150 ml. of ether, while cooling in an ice-bath. After stirring for 16 hr. at room temperature, the reaction mixture was poured on crushed ice containing a small amount of sulfuric acid. Work-up as described previously gave 4.05 g. (38.2%) of *o*-phenylenebis-(diphenylsilane) as colorless crystals, m.p. 173–176° (mixed m.p.).

Fourth Experiment.—An ethereal solution containing 0.023 mole of *o*-phenylenedilithium, filtered and titrated as described in the preceding experiment, was added to 4.23 g. (0.023 mole) of diphenylsilane in 25 ml. of ether. The reaction mixture was stirred at room temperature for 17 hr., 50 ml. of dry toluene was added, and the ether distilled. After refluxing the resulting suspension for 3 hr., Color Test I[11] was negative. Hydrolysis was carried out with 100 ml. of dilute sulfuric acid. The aqueous layer was separated, extracted with ether, and discarded. The combined organic solution was dried and evaporated under an air-jet. The brown oily residue was chromatographed on alumina.

Using petroleum ether (b.p. 60–70°) as an eluent, 0.1 g. of triphenylsilane (mixed m.p.) was obtained. Further elution with the same solvent gave a solid which was recrystallized twice from ethyl acetate to afford 0.21 g. (2.7%) of colorless needles, m.p. 234–237°, identified as tetraphenylsilane by mixed m.p. and by comparison of infrared spectra. Subsequently, cyclohexane was used as an eluent and the resulting solid was recrystallized from ethyl acetate to give 1.70 g. of colorless solid, m.p. 170–176°. An additional recrystallization afforded 1.58 g. (31.1%) of *o*-phenylenebis-(diphenylsilane), m.p. 175–177° (mixed m.p.). Further elution with cyclohexane, followed by recrystallization from ethyl acetate, afforded 0.68 g. of colorless solid, m.p. 210–216°. After recrystallization from the same solvent, there was obtained 0.54 g. (9.1%) of (*o*-diphenylsilylphenyl)-triphenylsilane, m.p. 214–217°, identified by mixed m.p. and by infrared spectrum (see below).

***o*-Phenylenebis-(methyldiphenylsilane) (V). (a) From *o*-Phenylenedilithium and Methyldiphenylchlorosilane.**—An ethereal solution containing 17.4 g. (0.075 mole) of methyldiphenylchlorosilane was treated with *o*-phenylenedilithium, prepared from 10 g. (0.036 mole) of *o*-phenylene-mercury and filtered through a glass wool plug, and refluxed for 18 hr. Since Color Test I[11] was positive, 80 ml. of dry toluene was added, the ether removed by distillation, and the

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[8] K. Oita and J. J. Goodman, unpublished studies.

[9] D. Wittenberg, T. C. Wu and H. Gilman, *J. Org. Chem.*, **23**, 1898 (1958).

[10] For convenience the molecular weight of *o*-phenylene-mercury was considered to be 276. The actual value is 1660 (G. Wittig and F. Bickelhaupt, *Ber.*, **91**, 883 (1958)).

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

resulting mixture heated at reflux for 24 hr. After cooling, the reaction mixture was hydrolyzed and worked up in the usual manner. The oily residue was treated with petroleum ether (b.p. 60–70°) depositing 4.75 g. of colorless crystals, m.p. 140–142°. Recrystallization from petroleum ether gave 4.34 g. (29.3%) of 1,2-dimethyl-1,1,2,2-tetraphenyldisilane, identified by mixed m.p. and by comparison of infrared spectra.

The petroleum ether solution then was concentrated affording 1.6 g. of solid, m.p. 157–165°. After two recrystallizations from petroleum ether (b.p. 60–70°), there was obtained 1.3 g. (7.7%) of colorless crystals, m.p. 172–174°. The analytical sample melted at 173–174°. The infrared spectrum of the material as a carbon disulfide solution showed absorption bands characteristic of aromatic and aliphatic C–H, the silicon–methyl linkage, the silicon–phenyl linkage and *o*-disubstituted benzene.

Anal. Calcd. for $C_{32}H_{30}Si_2$: C, 81.64; H, 6.42; Si, 11.94. Found: C, 82.10, 81.98; H, 6.31, 6.10; Si, 11.83, 11.55.

Concentration of the mother liquors gave only oils which could not be identified.

(b) **From Methyllithium and *o*-Phenylenebis-(diphenylsilane).**—Methyllithium (0.007 mole) was added to 1 g. (0.0023 mole) of *o*-phenylenebis-(diphenylsilane) in 50 ml. of ether. After refluxing for 18 hr., Color Test I[11] was only faintly positive; accordingly an additional 0.003 mole of methyllithium was added. Toluene (40 ml.) also was added, the ether distilled, and the toluene suspension refluxed for 1 hr. After work-up, there was obtained 0.82 g. of colorless solid, m.p. 125–152°. This material was recrystallized six times from petroleum ether (b.p. 60–70°) to give 0.18 g. (16.9%) of *o*-phenylenebis-(methyldiphenylsilane), m.p. 171–173° (mixed m.p. and infrared spectrum). (The difficulty in purifying the dimethyl derivative was due to contamination by Si–H containing compounds. A mixed m.p. with authentic *o*-phenylenebis-(methyldiphenylsilane) and *o*-phenylenebis-(diphenylsilane) melted over the range 150–165°.)

5,5,10,10-Tetraphenyl-5,10-dihydrosilanthrene (II). (a) **From *o*-Phenylenedilithium and Diphenyldichlorosilane.**—A solution of 7.1 g. (0.028 mole) of diphenyldichlorosilane in 25 ml. of ether was treated with an ether solution containing 0.028 mole of *o*-phenylenedilithium, determined by titration after filtering through a sintered glass filter. The reaction mixture was stirred at room temperature for 18 hr., 50 ml. of toluene was added, and the ether removed by distillation. After refluxing the toluene suspension for 6 hr., Color Test I[11] was negative. Subsequently, hydrolysis was carried out with dilute sulfuric acid, and the aqueous layer separated, extracted with ether, and discarded. The combined organic solution was dried and evaporated.

The brown reaction products were chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave a solid which was recrystallized from ethyl acetate to give colorless needles, m.p. 221–228°. Recrystallization from the same solvent gave 0.06 g. (0.6%) of tetraphenylsilane, m.p. 234–237° (mixed m.p.). Using cyclohexane as the eluent, there was obtained a colorless solid, m.p. 210–225°. This material was then recrystallized four times from ethyl acetate to afford 0.76 g. (10.4%) of large colorless crystals, m.p. 234–236°. The compound volatilized at 540° with slight decomposition. The infrared spectrum of the compound as a carbon disulfide solution had characteristic absorption bands at 3.3, 9.0, 13.3 and 13.6 μ, indicative of aromatic C–H, the silicon–phenyl linkage, *o*-disubstituted benzene and monosubstituted benzene, respectively.

Anal. Calcd. for $C_{36}H_{28}Si_2$: C, 83.67; H, 5.46; Si, 10.87; mol. wt., 517. Found: C, 84.05, 84.09; H, 5.57, 5.52; Si, 10.90, 10.88; mol. wt., 508, 487.

(b) **From *o*-Phenylenedilithium and *o*-Phenylenebis-(diphenylsilane) (Attempted).**—An ethereal solution of *o*-phenylenedilithium, prepared from 4.15 g. (0.015 mole) of *o*-phenylene-mercury and filtered through a glass wool plug, was added to 4.42 g. (0.01 mole) of *o*-phenylenebis-(diphenylsilane) suspended in 100 ml. of dry toluene. The ether then was removed by distillation and the toluene suspension heated at reflux for 5 hr. After cooling, the reaction mixture was poured onto crushed ice acidified with sulfuric acid. Ether was added and the organic layer worked up as usual. Subsequently the organic solution was evaporated and the resulting oily material treated with ethyl acetate, depositing 1.3 g. of solid, m.p. 165–200°. After two recrystallizations, there was obtained 0.76 g. (14.7%) of colorless crystals, m.p. 212–215°. The analytical sample melted at 214–216°, and the material was identified as (*o*-diphenylsilylphenyl)-triphenylsilane. The infrared spectrum of the compound showed the characteristic absorption bands for aromatic C–H, Si–H, the silicon-phenyl linkage and *o*-disubstituted benzene.

Anal. Calcd. for $C_{36}H_{30}Si_2$: C, 83.34; H, 5.83; Si, 10.83. Found: C, 83.15, 82.96; H, 5.83, 5.82; Si, 10.72, 10.79.

Concentration of the mother liquor gave a resin-like material which could not be crystallized or otherwise purified.

A repeat reaction employing 0.012 mole of *o*-phenylenebis-(diphenylsilane) and an ethereal solution containing 0.012 mole of *o*-phenylenedilithium afforded a 22.9% yield of (*o*-diphenylsilylphenyl)-triphenylsilane, plus a 38% recovery of the *o*-phenylenebis-(diphenylsilane).

5,5,10,10-Tetrabenzyl-5,10-dihydrosilanthrene.—A solution of 7.3 g. (0.026 mole) of dibenzyldichlorosilane in 75 ml. of ether, cooled in an ice-bath, was treated with an ether solution containing 0.026 mole of *o*-phenylenedilithium. The reaction mixture was allowed to warm to room temperature and stirred for 16 hr. Since Color Test I[11] was positive, 30 ml. of toluene was added, the ether removed by distillation, and the resulting suspension heated at reflux for 4 hr. Color Test I[11] was now negative and the reaction mixture was hydrolyzed. After the usual work-up, the reaction products were chromatographed on alumina.

Elution with petroleum ether (b.p. 60–70°) and then with cyclohexane gave only traces of oils. Using a 4:1 mixture of cyclohexane and benzene as the eluent, there was obtained 0.51 g. of colorless solid, m.p. 140–170°. This material was recrystallized three times from a 10:1 mixture of petroleum ether and benzene to give 0.21 g. (2.8%) of colorless crystals, m.p. 174.5–176°. The compound volatilized at 510° with decomposition. The infrared spectrum of this substance in carbon disulfide showed the characteristic absorption bands for aromatic and aliphatic C–H, and monosubstituted and *o*-disubstituted benzene, respectively.

Anal. Calcd. for $C_{40}H_{36}Si_2$: C, 83.86; H, 6.33. Found: C, 83.90, 84.07; H, 6.23, 6.30.

***o*-Phenylenebis-(triphenylsilane) (VI).** (a) **From *o*-Phenylenebis-(diphenylsilane) and Phenyllithium.**—An ethereal solution containing 0.015 mole of phenyllithium was added to 2.21 g. (0.005 mole) of *o*-phenylenebis-(diphenylsilane) in 100 ml. of ether and the reaction mixture was refluxed for 24 hr. After hydrolysis, ether was added and the colorless precipitate filtered. The organic layer was worked up in the usual manner and then evaporated. This material was combined with the solid which previously had been removed by filtration and chromatographed over alumina.

Using cyclohexane as the eluent, there was obtained a colorless solid melting over the range 190–230°. This material was recrystallized five times from ethyl acetate to give, 0.62 g. (23.9%) of impure (*o*-diphenylsilylphenyl)-triphenylsilane, m.p. 205–210°, identified by infrared spectrum. Further elution with cyclohexane gave another compound which was recrystallized four times from ethyl acetate to afford 0.91 g. (30.6%) of colorless crystals, m.p. 257.5–259°. The infrared spectrum of the compound contained characteristic absorption bands at 9.1, 13.35 and 13.6 μ, indicative of the silicon–phenyl linkage, *o*-disubstituted benzene and monosubstituted benzene, respectively.

Anal. Calcd. for $C_{42}H_{34}Si_2$: C, 84.80; H, 5.76; Si, 9.44. Found: C, 85.15, 85.06; H, 5.69, 5.69; Si, 9.49, 9.42.

(b) **From (*o*-Diphenylsilylphenyl)-triphenylsilane and Phenyllithium.**—A solution of 1.35 g. (0.0026 mole) of (*o*-diphenylsilylphenyl)-triphenylsilane in 50 ml. of dry toluene was treated with 0.01 mole of an ethereal solution of phenyllithium. The ether was removed by distillation and the toluene suspension refluxed for 16 hours. Color Test I[11] was only faintly positive; so, an additional 0.003 mole of phenyllithium was added. After refluxing 8 hr. longer, the reaction mixture was hydrolyzed with dilute sulfuric acid. The aqueous layer was separated, extracted with ether, and discarded. Subsequently the organic layer was dried and evaporated, and the residue treated with ethyl acetate to give 1.38 g. of colorless solid, m.p. 240–254°. This was recrystallized two times from ethyl acetate to give 1.12 g. (73.2%) of *o*-phenylenebis-(triphenylsilane), m.p. 256–259° (mixed m.p.).

(c) From *o*-Phenylenedilithium and Triphenylchlorosilane (Attempted).—An ethereal solution containing 0.014 mole of *o*-phenylenedilithium was added to 8.23 g. (0.028 mole) of triphenylchlorosilane in 100 ml. of ether. After adding 75 ml. of toluene, the ether was distilled, and the toluene solution heated at reflux for 24 hr. Work-up employing the usual chromatographic techniques gave an 11.7% yield of tetraphenylsilane, a 14.1% yield of hexaphenyldisiloxane and a 21.4% yield of triphenylsilanol, plus a resinous brown material.

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AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE UNIVERSITY]

The Aluminum Chloride-catalyzed Intramolecular Cyclization of Some Organosilicon Compounds. Studies in the Benzosilacyclanone Series

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The series of silyl-substituted carboxylic acids $(C_6H_5)_3Si(CH_2)_nCOOH$ (n = 1, 2, 3) was prepared by oxidation of the corresponding carbinols. Whereas triphenylsilylacetic acid decomposed under acidic conditions, triphenylsilylpropionic acid and triphenylsilylbutyric acid could be converted to acid chlorides. On treatment of the latter with aluminum chloride in nitrobenzene, an intramolecular cyclization occurred giving rise to the corresponding benzosilacyclanones.

The Friedel–Crafts coupling of acyl halides with aromatic silicon compounds has been described as being of limited utility for the preparation of aromatic silicon-containing ketones because of the susceptibility of silicon–aromatic bonds toward cleavage by acidic reagents. The principal reaction of tetraphenylsilane in chloroform with aluminum chloride is that of cleavage, resulting in an 80% yield of silicon tetrachloride.[1] Similarly, tetrabenzylsilane under these conditions also gave silicon tetrachloride.[1] Attempts to acylate triethylphenylsilane in the presence of aluminum chloride yielded benzene, hexaethyldisiloxane and the corresponding ketone in which the triethylsilyl group had been replaced by the acyl group.[2]

Benkeser and Currie,[3] however, were able to acetylate 2-trimethylsilylthiophene and 2-trimethylsilylfuran with iodine as a catalyst. The *m*- and *p*-trimethylsilylbenzoyl chlorides acetylate toluene smoothly in the presence of aluminum chloride,[4] but the *o*-isomer does not. Similarly, anisole has been acylated by *p*-trimethylsilylbenzoyl chloride.[4] Acetyl fluoride has been found to acylate silicon-substituted phenyl compounds satisfactorily in the presence of boron trifluoride.[5]

These results encouraged our studies in preparing cyclic organosilicon compounds containing functional groups by intramolecular acylation reactions. So far, only a few organofunctional silacyclanes have been reported in the literature.[6-8] As our starting materials, the series of triphenylsilyl-substituted alcohols $(C_6H_5)_3Si(CH_2)_nOH$ (n = 2,3,4) was used. These compounds have been made readily available by cleavage of ethylene oxide,[9] trimethylene oxide[10] and tetrahydrofuran[11] with triphenylsilyllithium. Chromic acid oxidation[12] of these alcohols furnished the corresponding acids. Triphenylsilylacetic acid was obtained only in poor yield, probably due to its low stability under acidic conditions. This is in accord with the known fact[13] that carboxylic acids containing silicon in the α-position are easily hydrolyzed. 3-Triphenylsilylpropionic acid and 4-triphenylsilylbutyric acid were prepared in satisfactory yields. The latter compound was also obtained by an alternative approach: 3-triphenylsilylpropanol was converted to the bromide using phosphorus tribromide,[14] and the corresponding Grignard reagent treated with carbon dioxide.

When an attempt was made to convert triphenylsilylacetic acid to its acid chloride, which on subsequent treatment with aluminum chloride was expected to cyclize, the work-up yielded only triphenylsilanol. This again demonstrates the relative ease of cleavage of the Si–C bond in this acid. Under the same conditions, 3-triphenylsilylpropionic acid, when allowed to react with thionyl chloride, followed by aluminum chloride in nitrobenzene, afforded a 47.9% yield of the expected cyclic ketone I, 2:3-benzo-1,1-diphenyl-1-silacyclohexen-2-one-4 (or 2,3-dihydro-1,1-diphenyl-4H-

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(9) H. Gilman, D. Aoki and D. Wittenberg, *ibid.*, **81**, 1107 (1959).

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