ORGANIC AND BIOLOGICAL CHEMISTRY

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

Cyclic Organosilicon Compounds. II. Reactions Involving Certain Functional and Related Dibenzosilole Compounds

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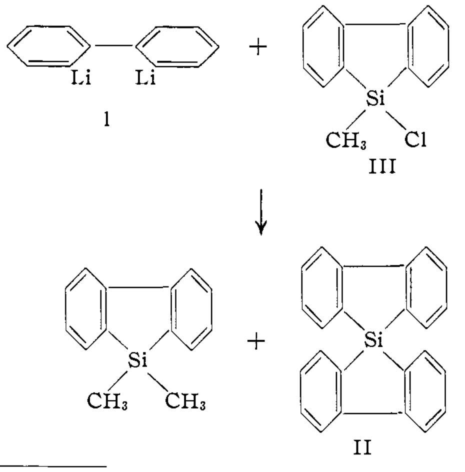
It has been demonstrated that 2,2′-biphenylenedilithium (I) reacts with 5-chloro-5-methyldibenzosilole (III) to give 5,5′-spirobi-[dibenzosilole] (II) and 5,5-dimethyldibenzosilole. Furthermore, II was the only compound isolated from the reaction of I with hexachlorodisilane. Compound II was readily cleaved by phenyllithium in diethyl ether or in tetrahydrofuran to yield 5-(2-biphenylyl)-5-phenyldibenzosilole, a compound which has been synthesized unambiguously from 2-biphenylyllithium and 5-chloro-5-phenyldibenzosilole. Functional dibenzosilole compounds reacted with sodium, lithium aluminum hydride and water in an expected manner. The silicon–silicon bond in 5,5′-dimethyl-5,5′-bi-[dibenzosilole] (VI) has been cleaved smoothly by lithium in tetrahydrofuran.

To our knowledge, there is no reported instance in organosilicon chemistry wherein an aryl or alkyl group of a tetraaryl- or arylalkylsilane is displaced by an organolithium compound. In fact it has been demonstrated that such compounds are unaffected by *n*-butyllithium in diethyl ether.[1] Benzyltriphenylsilane appeared to be an exception, but even in this case it was shown that the cleavage occurred during work-up of the reaction mixture.[2]

During the course of some studies concerned with the synthesis of some functional dibenzosilole compounds from 2,2′-biphenylenedilithium (I) and an alkyl- or aryltrichlorosilane, it was observed that in addition to obtaining the 5-alkyl- or 5-aryl-5-chlorodibenzosilole in a good yield there was concurrently found small amounts of 5,5′-spirobi-[dibenzosilole] (II).[3a,3b] The formation of II was indeed surprising since this implied that an alkyl or aryl group attached to the 5-position was being displaced by an organolithium compound.

In order to elucidate the reaction path, 5-chloro-5-methyldibenzosilole (III) was treated with an equimolar quantity of I in diethyl ether to yield almost equimolar amounts of II and 5,5-dimethyldibenzosilole, both of which were synthesized previously by unambiguous methods.[3]



Thus, it seems that I first participates in a reaction with the silicon–chlorine bond; then, the methyl–silicon linkage is cleaved simultaneously or in a very rapid stepwise fashion by the second anion of I to yield II and methyllithium which, in turn, can couple with unreacted III to give the dimethyl derivative. The fact that approximately equimolar amounts of products were obtained strongly supports a concerted or rapid coupling–cleavage type of reaction. That the reaction seems to be intimately related to the formation of II is illustrated by the failure of I to react in a similar fashion with triethylchlorosilane to give 5,5-diethyldibenzosilole.

A noteworthy and somewhat unexpected reaction was one wherein II was attacked by phenyllithium in tetrahydrofuran or in diethyl ether to give 5-(2-biphenylyl)-5-phenyldibenzosilole, a compound which was synthesized unambiguously from 2-biphenylyllithium and 5-chloro-5-phenyldibenzosilole (IV). The reaction was unexpected in that it is essentially the reverse of the one in which II was formed from the reaction of I with III but for one striking difference. In the reaction in which II was formed, the methyllithium arising from the scission of the methyl–silicon linkage can interact with unreacted III. On the other hand, in the reaction of II with phenyllithium, no silicon–chlorine bond is available for a possible organolithium intermediate resulting from the ring opening of III to react with. This reaction appears to be peculiar to II since 5,5-diphenyldibenzosilole was unaffected by phenyllithium under similar conditions.

5,5-Diphenyldibenzosilole was cleaved by formic acid to give biphenyl and an impure silicon-containing fragment. This reaction is reminiscent of similar cleavages of 2-biphenylyl-substituted organosilicon compounds by formic acid.[4]

In general, reactions of 5-alkyl- or 5-aryl-5-chlorodibenzosiloles with various reagents proceeded in an expected manner. Thus, 5-benzyl-5-chlorodibenzosilole and IV were both reduced by lithium aluminum hydride to yield 5-benzyldibenzosilole and 5-phenyldibenzosilole, respectively. Although the latter was not analytically pure, it reacted with phenyllithium to give a high yield of 5,5-diphenyldibenzosilole.

Neutralization of III with sodium hydroxide

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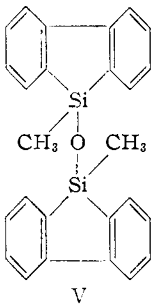
[1] H. Gilman, R. A. Benkeser and G. E. Dunn, THIS JOURNAL, **72**, 1689 (1950).

[2] H. Gilman and H. Hartzfeld, *ibid.*, **73**, 5878 (1951).

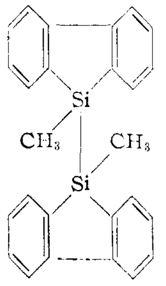
[3] (a) H. Gilman and R. D. Gorsich, *ibid.*, **80**, 1883 (1958). (b) The nomenclature employed herein was recommended by the editorial staff of "Chemical Abstracts."

[4] H. Gilman and K. Oita, THIS JOURNAL, **77**, 3386 (1955).

yielded 5,5′-oxybis-[5-methyldibenzosilole] (V). Likewise, 5-chloro-5-*n*-dodecyldibenzosilole gave a disiloxane compound on hydrolysis with either water or dilute base.



V



VI

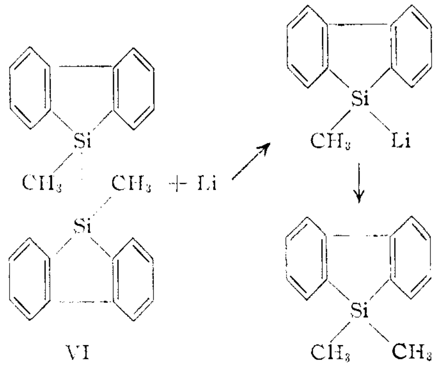
Two dibenzosilole compounds containing a silicon–silicon bond, 5,5′-dimethyl-5,5′-bi-[dibenzosilole] (VI) and the analogous *n*-dodecyl derivative, were prepared in mediocre yields by sodium condensations from the respective 5-alkyl-5-chlorodibenzosiloles. In surprising contrast, a similar reaction between sodium and IV gave 5,5′-oxybis-[5-phenyldibenzosilole] subsequent to hydrolysis of the reaction mixture. The disiloxane may well have been formed by hydrolysis of starting material.

Another approach to the synthesis of dibenzosilole compounds containing a silicon–silicon bond was one in which one mole of hexachlorodisilane was treated with two moles of I. The only pure organosilicon compound separated from the reaction mixture was II. A considerable amount of material which appeared to be inorganic in nature also was isolated but not purified. Also, some biphenyl was found.

In all likelihood, the expected coupling product, 5,5′-dichloro-5,5′-bi-[dibenzosilole] may have been formed to some extent as an intermediate; but this compound, or even possibly 5-chloro-5-trichlorosilyldibenzosilole, might be attacked further by I to form a carbon–silicon bond followed by a rapid or simultaneous cleavage of the silicon–silicon bond by the second anion of I. This reaction resembles that of III with I except for one notable difference. In one case, a carbon–silicon bond is cleaved, while in the other a silicon–silicon bond is ruptured.

It has been well-established that a silicon–silicon bond can be cleaved when treated with certain arylating and alkylating reagents, *e.g.*, when octachlorotrisilane was treated with phenylmagnesium bromide, a mixture of tetraphenylsilane and hexaphenyldisilane was obtained. Even the treatment of halogenated disilane compounds with zinc alkyls, Grignard reagents and metallic sodium resulted in some scission of the single silicon–silicon bond.[5] It might be expected, therefore, that after one of the carbon–lithium bonds of I interacts with the silicon–chlorine bond of the dibenzosilole compound, the scission of the silicon–silicon bond by the second anion would be more facile than cleavage of a carbon–silicon bond.

The high yield of triphenylsilyllithium obtained from hexaphenyldisilane and lithium in tetrahydrofuran was the impetus for a similar study with a dibenzosilole compound containing a silicon–silicon bond. Treatment of VI with an excess of lithium metal in tetrahydrofuran gave 5-lithio-5-methyldibenzosilole which, when allowed to react with dimethyl sulfate, afforded 5,5-dimethyldibenzosilole. This type of cleavage reaction has potential of being an excellent method for obtaining intermediates of synthetic utility.



VI

Interestingly enough, 5,5-dimethyldibenzosilole did not appear to be cleaved by lithium in tetrahydrofuran but rather seemed to absorb the metal in some unknown fashion, as was evidenced by the recovery of considerable starting material after hydrolysis of the reaction mixture.

Experimental[6]

Reaction of 2,2′-Biphenylenedilithium (I) with 5-Chloro-5-methyldibenzosilole (III).—Two grams (0.0087 mole) of impure 5-chloro-5-methyldibenzosilole and 30 ml. of an ethereal solution containing 0.009 mole of 2,2′-biphenylenedilithium[7] were stirred at room temperature for 29 hours, after which the mixture was poured onto a slurry of Dry Ice and diethyl ether. The organic layer was separated, extracted once with 5% sodium hydroxide, and dried over sodium sulfate. The solvent was distilled, the residue was washed with petroleum ether (b.p. 28–38°), and a crystalline material was filtered off to give 1.08 g. (38%) of 5,5′-spirobi-[dibenzosilole], m.p. 225–227°, whose melting point was undepressed when admixed with an authentic sample.

Removal of the solvent from the filtrate left an oil which was distilled to yield 0.15 g. of forerun followed by 0.65 g. (36%) of 5,5-dimethyldibenzosilole, b.p. 87–90° (0.005 mm.), which was crystallized from methanol to give 0.32 g. (18%) of white plates, m.p. 59–61°. A mixed melting point with an authentic sample[3] was undepressed.

Reaction of 2,2′-Biphenylenedilithium with Triethylchlorosilane (Attempted).—A solution of 4.18 g. (0.028 mole) of triethylchlorosilane and 0.018 mole of 2,2′-biphenylenedilithium was refluxed for 4 hours. Benzene was added and refluxing was continued at 55° for 12 hours and at 60° for 6 hours. The mixture was hydrolyzed and 0.75 g. of product, insoluble in the common organic solvents, was filtered off. Distillation of the residue, after evaporation of the solvent from the organic layer, gave 1.2 g. of forerun followed by 1.5 g. of unidentified liquid, b.p. 130–150° (0.022 mm.). Both fractions showed no infrared absorption bands at 8.9 μ, which would have been indicative of the dibenzosilole nucleus.[3a]

5-(2-Biphenylyl)-5-phenyldibenzosilole. (a) From 5,5′-Spirobi-[dibenzosilole] and Phenyllithium.—A solution of 1 g. (0.003 mole) of 5,5′-spirobi-[dibenzosilole] in about 15 ml. of diethyl ether and 5 ml. of a 1.1 molar phenyllithium solution was stirred at room temperature for 13 hours. Immediately after the addition of the phenyllithium a dense precipitate formed. The mixture was hydrolyzed with

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[5] E. G. Rochow, "An Introduction to the Chemistry of the Silicones," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 61.

[6] All melting points are uncorrected and all reactions involving organolithium and silyllithium compounds were carried out under an atmosphere of dry, oxygen-free nitrogen in sodium-dried solvents.

[7] H. Gilman and R. D. Gorsich, THIS JOURNAL, **77**, 6380 (1955).

water. The organic layer was separated, dried, and the solvent was distilled. The residual oil was crystallized from petroleum ether (b.p. 60–70°) to yield 1.02 g. (87%) of white prisms, m.p. 137–138.5°.

Anal. Calcd. for $C_{30}H_{22}Si$: C, 87.77; H, 5.40; Si, 6.84. Found: C, 87.82; H, 5.79; Si, 6.90.

When the same reaction was run in only tetrahydrofuran under comparable conditions, the yield of 5-(2-biphenylyl)-5-phenyldibenzosilole was 51%.

If this cleavage reaction occurs with alkyllithium compounds, it may provide access to high-boiling liquids. It is noteworthy that a higher yield of cleavage product was obtained in diethyl ether than in tetrahydrofuran.

(b) **From 2-Biphenylyllithium and 5-Chloro-5-phenyldibenzosilole.**—A mixture of 2.3 g. (0.0078 mole) of 5-chloro-5-phenyldibenzosilole and 35 ml. of an ethereal solution containing 0.009 mole of 2-biphenylyllithium[8] was stirred at room temperature for 15 minutes and refluxed for 45 minutes. The mixture was hydrolyzed and the organic layer was worked up as described in the preceding experiment. The residual oil was dissolved in benzene and chromatographed on alumina. Distillation of the solvent from the eluates left a white powder which was sublimed *in vacuo* to give 0.3 g. of biphenyl, m.p. 65–67°. The residue was crystallized from petroleum ether (b.p. 60–70°) to yield 1.17 g. of prisms, m.p. 137–138°, which showed no depression in melting point when admixed with the material obtained in the preceding experiment. Concentration of the filtrate yielded an additional 0.46 g. of product, m.p. 134–136°, total yield 1.63 g. (51%).

Reaction of Phenyllithium with 5,5-Diphenyldibenzosilole.—A solution of 0.62 g. (0.0018 mole) of 5,5-diphenyldibenzosilole[7] in 10 ml. of diethyl ether and 3 ml. of a 1.1 molar phenyllithium solution was stirred at room temperature for 13 hours. Hydrolysis and work-up of the organic layer yielded 0.52 g. (84%) of starting material. There appeared to be no trace of other product which could comprise (2-biphenylyl)-triphenylsilane.

Reaction of Formic Acid with 5,5-Diphenyldibenzosilole.—A mixture of 1 g. (0.003 mole) of 5,5-diphenyldibenzosilole and 50 ml. of 98% formic acid was refluxed for 22 hours. The formic acid was distilled and the residue was sublimed *in vacuo* to give 0.16 g. (35%) of biphenyl. The remaining material could not be purified.

5-Benzyldibenzosilole.—A solution of 6.46 g. (0.021 mole) of 5-benzyl-5-chlorodibenzosilole[3] in 20 ml. of diethyl ether was added, during 10 minutes, to a stirred suspension of 0.76 g. (0.02 mole) of lithium aluminum hydride in approximately 50 ml. of ether. The mixture was refluxed for 12 hours and then was filtered in a moisture-free atmosphere. Most of the ether was distilled and replaced by petroleum ether (b.p. 60–70°). Again the mixture was filtered and the petroleum ether was distilled. The residue was distilled to give 4.07 g. (72%) of colorless liquid, b.p. 135–138° (0.005 mm.), which crystallized on standing for 2 hours. The distillate was crystallized from ethanol to give white needles, m.p. 68.5–69.5°.

Anal. Calcd. for $C_{19}H_{16}Si$: C, 83.77; H, 5.92; Si, 10.30. Found: C, 83.72, 83.50; H, 6.01, 6.23; Si, 10.12.

5-Phenyldibenzosilole (impure) was prepared from 1.6 g. (0.042 mole) of lithium aluminum hydride and 11.1 g. (0.038 mole) of 5-chloro-5-phenyldibenzosilole as described in the preceding experiment. The crude product was distilled at 0.005 mm. to give 8.63 g. (88%) of liquid, b.p. 130–131°. Crystallization from methanol gave white needles m.p. 58–60°. The infrared spectrum of the compound in carbon tetrachloride solution showed bands at 4.85 and 8.9 μ characteristic of a Si–H bond and a dibenzosilole nucleus, respectively.[3]

Anal. Calcd. for $C_{18}H_{14}Si$: C, 83.67; H, 5.46; Si, 10.85. Found: C, 83.02; H, 5.58; Si, 10.59.

Further efforts to purify the compound were unsuccessful; when it was treated with phenyllithium, an 81% yield of 5,5-diphenyldibenzosilole was obtained.

5,5′-Oxybis-[5-methyldibenzosilole] (V).—A solution of 2.69 g. (0.0115 mole) of 5-chloro-5-methyldibenzosilole[3] in about 100 ml. of ether was neutralized with a 5% sodium hydroxide solution. The organic layer was separated, dried, and the solvent was evaporated leaving a crystalline material which was allowed to stand in a mixture of methanol and water for 6 weeks. Filtration and drying of the resulting crystals gave 1.8 g. (77%) of product, m.p. 125–127°. Recrystallization from a mixture of chloroform and methanol raised the melting point to 127–128°.

Anal. Calcd. for $C_{26}H_{22}OSi_2$: C, 76.85; H, 5.48. Found: C, 77.12; H, 5.69.

Infrared analysis showed a strong absorption band at 9.5 μ indicative of a Si–O–Si linkage, as well as a band at 8.9 μ characteristic of the dibenzosilole nucleus.[3]

The compound volatilized between 450–460° with no sign of decomposition.[9]

When the neutralization was carried out at 0° and when the work-up of the reaction mixture was carried out below 20°, a product was obtained which melted at 157–158° after one crystallization from a mixture of acetone and water. Although infrared analysis showed a band at 2.7 μ indicative of a Si–OH bond and no band at 9.5 μ, the carbon, hydrogen and silicon analyses were in accord with a compound having the molecular formula $C_{26}H_{22}OSi_2$ and not 5-hydroxy-5-methyldibenzosilole.

5,5′-Oxybis-[5-*n*-dodecyldibenzosilole].—An ethereal solution of 3 g. (0.0078 mole) of 5-chloro-5-*n*-dodecyldibenzosilole was neutralized with sodium hydroxide at room temperature. The crude product was distilled under reduced pressure to give 1.98 g. of product, b.p. 190–200° (0.003 mm.). The distillate was crystallized from ethanol to give 1.28 g. (46%) of colorless needles, m.p. 74–75°. The infrared spectrum showed a broad absorption band at 9.6 μ characteristic of a Si–O–Si linkage. Hydrolysis with water alone gave a comparable yield of the disiloxane compound. The compound volatilized between 470–480° with slight decomposition.

Anal. Calcd. for $C_{48}H_{66}OSi_2$: C, 80.62; H, 9.30. Found: C, 80.97, 80.75; H, 9.30, 9.42.

5,5′-Dimethyl-5,5′-bi-[dibenzosilole] (VI).—A mixture of 9.16 g. (0.0396 mole) of 5-chloro-5-methyldibenzosilole, 0.99 g. (0.043 g. atom) of sodium and 100 ml. of xylene was refluxed for 25 hours, after which ethanol was added to the purple mixture until the evolution of hydrogen ceased. Hydrolysis was effected with water. The organic layer was separated, combined with two ether extracts of the aqueous layer, and dried over sodium sulfate. Distillation of the solvents left a residue which was crystallized from ethanol to give 3.3 g. (43%) of white plates, m.p. 180–182°. Recrystallization from ethanol raised the melting point to 185–186°. The compound volatilized at 460° with no sign of decomposition.

Anal. Calcd. for $C_{26}H_{22}Si_2$: C, 79.97; H, 5.68; Si, 14.37. Found: C, 80.29; H, 5.73; Si, 14.21.

Concentration of the filtrate from the first crystallization deposited a solid which was crystallized from ethanol to give 1.05 g. of material melting over the range 107–119°. The infrared spectrum of the material indicated it to be impure 5,5′-oxybis-[5-methyldibenzosilole].

5,5′-Di-*n*-dodecyl-5,5′-bi-[dibenzosilole].—A mixture of 5 g. (0.013 mole) of 5-chloro-5-*n*-dodecyldibenzosilole, 0.30 g. (0.013 g. atom) of sodium and *ca.* 80 ml. of xylene was refluxed for 19 hours, after which the mixture was worked up as described in the preceding preparation. The residue was crystallized successively from a mixture of petroleum ether (b.p. 28–38°) and ethanol, and from a mixture of ethanol and ethyl acetate to yield 2.42 g. (53%) of product, m.p. 59–61°. The infrared spectrum showed no band at 9.5 μ characteristic of a Si–O–Si linkage. The compound volatilized between 470–480° with slight decomposition.

Anal. Calcd. for $C_{48}H_{68}Si_2$: C, 82.41; H, 9.52; Si, 8.03. Found: C, 82.75; H, 9.37; Si, 8.03, 8.09.

Reaction of Sodium with 5-Chloro-5-phenyldibenzosilole.—One hundred milliliters of xylene, 3.98 g. (0.0135 mole) of 5-chloro-5-phenyldibenzosilole and 0.5 g. (0.022 g. atom) of sodium were refluxed for 21 hours without any color change being observed. Work-up as described previously gave a product which was crystallized twice from ethyl acetate to give 1.52 g. (21%) of material, m.p. 203–204°. The infra-

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(8) H. Gilman and K. Oita, *J. Org. Chem.*, **20**, 862 (1955).

(9) Volatility was determined by inserting a melting point capillary containing a small amount of a sample into a copper block which was heated by means of a bunsen burner. The volatilization point or range was that temperature at which either all of the liquid disappeared from the bottom of the capillary or that temperature at which rapid refluxing was observed in the top of the capillary.

red spectrum in carbon disulfide solution showed an absorption band at 9.5 μ characteristic of a Si–O–Si linkage. This, together with the analytical data, indicate the compound to be 5,5'-oxybis-[5-phenyldibenzosilole]. Purification of the remaining crude product by crystallization could not be achieved.

Anal. Calcd. for $C_{36}H_{26}OSi_2$: C, 81.48; H, 4.94; Si, 10.57. Found: C, 81.26; H, 5.20; Si, 10.60, 10.57.

Reaction of 2,2'-Biphenylenedilithium with Hexachlorodisilane.—Three hundred and thirty milliliters of an ethereal solution containing 0.097 mole of 2,2'-biphenylenedilithium[7] was added, during 1.75 hours, to a stirred solution of 11.5 g. (0.043 mole) of hexachlorodisilane in 150 ml. of ether. The mixture was worked up in a manner similar to that described for 5-chloro-5-*n*-dodecyldibenzosilole except for using benzene instead of petroleum ether (b.p. 60–70°).[3a] Concentration and cooling of the benzene solution yielded 2.86 g. of crystals which, when crystallized from ethyl acetate, melted at 230–231° and showed no depression in melting point when admixed with an authentic sample of 5,5'-spirobi-[dibenzosilole] (II). From the mother liquor was obtained an additional 1.62 g. of II. Distillation of the remaining benzene left a residue which was sublimed at 130° (17 mm.) to give 1.75 g. of biphenyl, identified by mixed melting point. The residue was refluxed in acetone to give 7.25 g. of insoluble material which did not melt below 530°. Concentration of the acetone filtrate gave another 1.22 g. of II, m.p. 225–227°. The total yield of II was 5.70 g. (20% based on hexachlorodisilane).

An ethereal solution containing 4.69 g. of the residue obtained after removal of the benzene was treated with methyllithium. Work-up of the organic layer after hydrolysis yielded a viscous oil which could not be purified.

Reaction of Lithium with 5,5'-Dimethyl-5,5'-bi-[dibenzosilole].—Two grams (0.005 mole) of 5,5'-dimethyl-5,5'-bi-[dibenzosilole], 1.15 g. (0.166 g. atom) of finely cut lithium wire and 30 ml. of tetrahydrofuran were stirred at room temperature for 4 hours, after which the excess lithium was filtered off. To the resulting green mixture was added 1.5 g. (0.012 mole) of freshly distilled dimethyl sulfate dissolved in 10 ml. of tetrahydrofuran. The mixture was hydrolyzed with water, diethyl ether was added, and the organic layer was worked up in the usual manner. The crude product was distilled to give 0.2 g. of forerun followed by 1.15 g. (54%) of 5,5-dimethyldibenzosilole, b.p. 87° (0.005 mm.), which crystallized on cooling and melted at 55–57°. The melting point was undepressed when admixed with an authentic sample.[3]

Reaction of Lithium with 5,5-Dimethyldibenzosilole.—A mixture of 3.1 g. (0.0148 mole) of 5,5-dimethyldibenzosilole, 0.54 g. (0.072 g. atom) of finely cut lithium wire, 10 ml. of diethyl ether and 10 ml. of tetrahydrofuran was stirred at room temperature for 4.3 hours. The dark green mixture, which exhibited a positive Color Test I,[10] was hydrolyzed with water. The organic layer was separated and worked up in the usual manner. The residue was crystallized from methanol to give 1.60 g. of 5,5-dimethyldibenzosilole, m.p. 55–57°, identified by mixed melting point and infrared analysis. The solvent was evaporated from the filtrate and the residue was sublimed *in vacuo* to give an additional 0.35 g. of starting material, m.p. 53–55°, total yield 1.85 g. (60%). No reduction product was detected.

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(10) H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925).

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Silicon and Organosilicon Derivatives of Acetylacetone

BY ROBERT WEST

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Silicon and organosilicon derivatives of acetylacetone have been prepared and their structures have been investigated, principally by means of infrared spectroscopy. Chelated structures (I and II below) are proposed for the unsubstituted derivative $SiA_3Cl·HCl$ (A = acetylacetonate group)[1] and also for monoalkyl compounds of the type $RSiA_2Cl$. The dialkylsilyl and trialkylsilyl acetylacetonates have open-chain, O-silylated structures such as III. The reasons for these structural differences are discussed.

Organometallic enolates generally are little-known, and no organosilicon derivatives of β-diketones are described in the literature.[2] This paper reports the synthesis of a series of organosilicon acetylacetonates and a study of their structure by means of infrared spectroscopy in the sodium chloride region. The unsubstituted silicon derivative of acetylacetone (HA)[1] was first prepared in 1903 by Dilthey[7,8] who found the product resulting from the reaction of $SiCl_4$ and HA to have the empirical formula $C_{15}H_{22}O_6SiCl_2$. Dilthey proposed for this compound a novel structure, $(SiA_3)^+Cl^-·HCl$, containing a positively charged siliconium ion in which the silicon is chelated by 3 acetylacetonate groups. Dilthey prepared a number of derivatives of the tris-(2,4-pentanediono)-siliconium ion containing other anions, and proved the structure as well as possible using the techniques of his time. We have examined the infrared spectrum of $(SiA_3)^+Cl^-·HCl$ and, as will be shown below, we find that the observed absorption bands confirm the unusual structure proposed by Dilthey.

The silyl derivatives of acetylacetone were prepared by three different general reactions: the direct reaction of a chlorosilane with acetylacetone in an inert solvent (A), a similar reaction assisted by the presence of the base pyridine (B) and the metathetical reaction between a chlorosilane and sodium acetylacetonate (C). Method A was used for the preparation of acetylacetonates of $SiCl_4$ and

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(1) The symbol A will be used to represent the acetylacetonate group, $C_5H_7O_2$–, throughout the remainder of this paper.

(2) The trimethylsilyl and triethylsilyl derivatives of ethylacetoacetate are known[3,4]; their structures are controversial.[3-6] The structures of these compounds will be discussed in a forthcoming paper.

(3) H. Gilman and R. N. Clark, THIS JOURNAL, **69**, 967 (1947).

(4) F. C. Whitmore, L. H. Sommer, J. Gold and R. E. Van Strien, *ibid.*, **69**, 1551 (1947).

(5) C. R. Hance and C. R. Hauser, *ibid.*, **75**, 994 (1953).

(6) M. J. Hurwitz, P. L. de Benneville and R. A. Yoncoskie, Abstracts of Papers, 131st National Meeting, American Chem. Soc., 1957, p. 52-O.

(7) W. Dilthey, *Ber.*, **36**, 923 (1903); *Ann.*, **344**, 300 (1906).

(8) A. Rosenheim, W. Loewenstamm and L. Singer, *Ber.*, **36**, 1833 (1903).