[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

SOME 2-BIPHENYLYL SUBSTITUTED ORGANOSILICON COMPOUNDS

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The effects of steric hindrance in connection with preparations and reactions of organosilicon compounds have been studied (1–8) and reviewed (6, 9) by many workers. From the relative ease with which bulky groups can be attached to a central silicon atom, the steric requirements of the groups can be estimated. The hydrolysis of trisubstituted chlorosilanes has been interpreted in a similar manner with the rate and extent inversely related to the bulk of the substituent (3-5, 10, 11). Both of these methods, however, have their limitations and only qualified conclusions can be drawn from such results.

Experimental conditions employed in the preparation or attempted preparation of tetrasubstituted silanes have not always been the same. Generally, silicon tetrachloride or substituted chlorosilanes and an excess amount of organolithium or Grignard reagent have been employed with diethyl ether as the solvent. However, tetra-*o*-tolylsilane has been isolated from the reaction of *o*-tolyllithium and tri-*o*-tolylchlorosilane at 170° (6) and tetra-1-naphthylsilane has been prepared from the reaction of di-1-naphthyldifluorosilane and 1-naphthyllithium in heavy kerosene at a temperature of 230–250° (7). The hydrolysis method is limited by by the lack of sufficient quantitative data as well as by the use of different experimental conditions for converting organochlorosilanes to the corresponding silanols.

We have extended the investigation to the 2-biphenylyl series in order to continue the studies of *ortho* substituted aryl silanes (5, 6, 8). The 2-biphenylyl group is of special interest because the *ortho* substituent is planar and by a suitable orientation of phenyl groups, Fischer-Hirschfelder-Taylor models of tetra-2-biphenylylsilane and hexa-2-biphenylyldisilane can be prepared. According to these models the 2-biphenylyl groups do not have free rotation; therefore, "propeller" type isomerism (12, 13) is theoretically possible. Some evidence is available that tetra-*o*-tolylsilane can exist in different stereoisomeric modifications because of restricted rotation of this kind (14). Hexa-2-biphenylyldisilane is also of interest because its bulky groups should aid its dissociation into tri-2-biphenylylsilyl radicals. However, the steric requirement of the 2-biphenylyl groups should prevent coplanar configuration of the radical and thereby prevent resonance stabilization of the type that is theoretically possible with the tri-4-biphenylylsilyl radical (9, 15). Unfortunately neither tetra-2-biphenylylsilane nor hexa-2-biphenylyldisilane has as yet been synthesized.

2-Biphenylyltriphenylsilane and di-2-biphenylyldiphenylsilane were prepared in low yields from the reaction of 2-biphenylyllithium and triphenylchlorosilane and diphenyldichlorosilane, respectively, using diethyl ether as the solvent.

$$\textit{2}\text{-}C_6H_5C_6H_4Li + (C_6H_5)_3SiCl \rightarrow (\textit{2}\text{-}C_6H_5C_6H_4)Si(C_6H_5)_3$$

$$\textit{2}\text{-}C_6H_5C_6H_4Li + (C_6H_5)_2SiCl_2 \rightarrow (\textit{2}\text{-}C_6H_5C_6H_4)_2Si(C_6H_5)_2$$

When an attempt to prepare tri-2-biphenylylphenylsilane from the interaction of 2-biphenylyllithium and phenyltrichlorosilane was carried out, the only pure product isolated was di-2-biphenylylphenylsilanol. However, the desired compound was prepared from the reaction of phenyllithium and tri-2-biphenylylchlorosilane at a xylene-reflux temperature.

$$(\mathit{2}\text{-}C_6H_5C_6H_4)_3SiCl + C_6H_5Li \rightarrow (\mathit{2}\text{-}C_6H_5C_6H_4)_3SiC_6H_5$$

When a suspension of tri-2-biphenylylchlorosilane and 2-biphenylyllithium was stirred at a benzene-reflux temperature for 3 days in an attempt to prepare tetra-2-biphenylylsilane, only tri-2-biphenylylchlorosilane and biphenyl were isolated. The reaction of silicon tetrachloride and 3 equivalents of 2-biphenylyllithium gave tri-2-biphenylylchlorosilane in fair yields.

The inverse relation of the ease of hydrolysis of chlorosilanes to steric hindrance is again illustrated by the stability of tri-2-biphenylylchlorosilane as compared to di-2-biphenylylphenylchlorosilane, which must have been an intermediate in the formation of di-2-biphenylylphenylsilanol mentioned previously.

The conversion of tri-2-biphenylylchlorosilane to tri-2-biphenylylsilanol and to tri-2-biphenylylsilane and the attempted preparations of hexa-2-biphenylyldisilane and hexa-2-biphenylyldisiloxane all indicated the effect of steric hindrance on reactions of triarylchlorosilanes.

Tri-2-biphenylylchlorosilane was converted to the corresponding silanol with 10% methanolic potassium hydroxide with benzene as a solvent. An aqueous 10% sodium hydroxide solution failed to hydrolyze tri-2-biphenylylchlorosilane suspended in hot methanol. Refluxing with 2-methoxyethanol, a method used for converting tri-1-naphthylchlorosilane to tri-1-naphthylsilanol in a quantitative yield (5), also failed to hydrolyze this chlorosilane. Tri-2-biphenylylsilanol was also obtained from the reaction of tri-2-biphenylylsilane and potassium hydroxide in piperidine (3, 16) as well as from the reaction of tri-2-biphenylylchlorosilane and dimethylformamide carried out according to the procedure reported by Rochow and Gingold (17) for converting chlorosilanes to the corresponding siloxanes.

$$(\mathit{2}\text{-}C_6H_5C_6H_4)_3SiCl + HCON(CH_3)_2 \rightarrow (\mathit{2}\text{-}C_6H_5C_6H_4)_3SiOH$$

Our inability to prepare hexa-2-biphenylyldisiloxane again must be attributed to steric hindrance. The reaction of tri-2-biphenylylsilanol with sodium followed by the addition of tri-2-biphenylylchlorosilane in accordance with the procedure described for preparing many disiloxanes (18) resulted in the recovery of tri-2-biphenylylchlorosilane and tri-2-biphenylylsilanol. When tri-2-biphenylylsilanol was refluxed with 98% formic acid according to the procedure for preparing hexaphenyldisiloxane in a quantitative yield from triphenylsilanol,[1] biphenylyl groups were cleaved from the silanol (19).

Even in the reduction of tri-2-biphenylylchlorosilane to tri-2-biphenylylsilane with lithium aluminum hydride (11, 20) the effect of steric hindrance was obvious. A quantitative recovery of tri-2-biphenylylchlorosilane was obtained from

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[1] See study of H. W. Melvin as reported by Gilman and Oita (ref. 19).

the attempted reduction with lithium aluminum hydride in diethyl ether; tri-1-naphthylchlorosilane afforded a 95% yield of tri-1-naphthylsilane under similar experimental conditions. The use of a higher-boiling solvent, tetrahydrofuran, and the extension of the reaction period gave a 21% yield of tri-2-biphenylylsilane. The use of an even higher-boiling solvent, ethylene glycol dimethyl ether, raised the yield to 71%.

$$(2\text{-}C_6H_5C_6H_4)_3SiCl + LiAlH_4 \xrightarrow[\text{dimethyl ether}]{\text{Ethylene glycol}} (2\text{-}C_6H_5C_6H_4)_3SiH$$

The use of ethylene glycol dimethyl ether has been reported (21) but further studies on its use as a solvent for lithium aluminum hydride reductions may be profitable.

An attempted preparation of hexa-2-biphenylyldisilane from 2-biphenylyllithium and hexachlorodisilane as well as the one by an attempted Wurtz type reaction between tri-2-biphenylylchlorosilane and sodium failed. From the first attempt tetra-2-biphenylyldichlorodisilane was isolated and from the second a very small amount of tri-2-biphenylylsilane was obtained.

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EXPERIMENTAL[2]

2-Biphenylyllithium. To a 3-necked, 1-liter flask fitted with an addition funnel, a stirrer, and a condenser was added 5.82 g. (0.84 g.-atom) of greasy, unwiped lithium ribbon[3] cut into pieces several mm. in length under a stream of nitrogen. The lithium pieces were rinsed with three 30-ml. portions of anhydrous ether; then 200 ml. of ether was added. Then 15 ml. of a solution of 93.2 g. (0.4 mole) of 2-bromobiphenyl in 200 ml. of ether was added and the reaction mixture was heated to a gentle reflux and stirred until the reaction started. The appearance of a yellow color in the ethereal solution indicated the initiation of the reaction. The heat was immediately removed and the dropwise addition of the 2-bromobiphenyl solution was started at a rate sufficient to maintain a gentle reflux. After the completion of the addition, which required 3 hours, the reaction was heated to a gentle reflux and stirred for 2 hours. The color of the reaction mixture at the end of this period was a dark reddish-brown. The yield of 2-biphenylyllithium as determined by titrating for the total alkalinity (22) was 96%.

When a three fold excess of lithium wire was used the yield was increased to 99%.

2-Biphenylyltriphenylsilane. To a rapidly stirred solution of 47.5 g. (0.16 mole) of triphenylchlorosilane[4] in 500 ml. of ether was added 248 ml. of an ethereal solution containing

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[2] All reactions involving organolithium compounds were carried out in a nitrogen atmosphere. Melting points reported are uncorrected.

[3] The technique of adding unwiped lithium ribbon is important in humid weather, but in an arid atmosphere the lithium may be wiped clean and used without rinsing.

[4] Triphenylchlorosilane, diphenyldichlorosilane, and phenyltrichlorosilane were Dow Corning's "purified grade" and were used without further purification.

0.16 mole of 2-biphenylyllithium. Color Test I (23) was negative after 4 hours of stirring at room temperature. The reaction mixture was carefully hydrolyzed with 2 *N* hydrochloric acid. The ether layer was separated from the aqueous layer and the ether was removed by distillation. The residue obtained weighed 40.4 g. and melted over the range 49–107°.

The crude product was worked up by fractional crystallization from petroleum ether. Those crystalline mixtures which could not be separated in this way were subjected to chromatography (alumina adsorbent and benzene eluant) or to molecular distillation.

There were finally isolated 6.7 g. of triphenylsilanol (16%, m.p. 152–155°), 4.0 g. of biphenyl (13%, m.p. 67–69°), and 8.0 g. of 2-biphenylyltriphenylsilane (12%, m.p. 136–137°). The triphenylsilanol and biphenyl were identified by the method of mixture melting point determination. The 2-biphenylyltriphenylsilane was recrystallized to constant melting point (137–137.5°) from petroleum ether.[5]

Anal.[6] Calc'd for $C_{30}H_{24}Si$: Si, 6.82. Found: Si, 6.83, 7.22.

2-Biphenylyltriphenylsilane volatilized at 450° without any apparent sign of decomposition.[7]

Di-2-biphenylyldiphenylsilane. To a solution of 20.2 g. (0.08 mole) of diphenyldichlorosilane in 100 ml. of ether was added 168 ml. of an ethereal solution containing 0.17 mole of 2-biphenylyllithium. The reaction mixture was stirred at an ether-reflux temperature for a week. Although Color Test I was still positive at the end of this period, the reaction mixture was allowed to cool and then was hydrolyzed with dilute potassium hydroxide. The crude product obtained on removal of the ether from the ethereal layer of the reaction mixture was dissolved in petroleum ether, dried over sodium sulfate, and chromatographed on 80–200 mesh alumina. Eluants used were petroleum ether, chloroform and methanol, respectively. A low-melting solid, a white viscous liquid, and a yellowish sticky resin were obtained.

The low-melting solid on recrystallization from methanol gave 5.0 g. (16%) of biphenyl melting at 67°. Mixture melting point with an authentic sample of biphenyl (m.p. 70–70.5°) was 69–70°.

The white viscous liquid was dissolved in petroleum ether and chromatographed on alumina. With petroleum ether as an eluant a product melting at 58–65° and a white resin were obtained. Using methanol as an eluant a white product melting at 134–139° was obtained. Recrystallization of this product from petroleum ether gave 0.87 g. of di-2-biphenylyldiphenylsilane melting at 137–137.5°.

The yellowish, sticky resin was worked up by chromatography on alumina followed by fractional recrystallizations from petroleum ether to give 1.91 g. of di-2-biphenylyldiphenylsilane melting at 137–137.5°. The total yield of this compound was 2.78 g. (7.1%).

Anal. Calc'd for $C_{36}H_{28}Si$: Si, 5.75. Found: Si, 5.78, 5.79.

Mixture melting point of di-2-biphenylyldiphenylsilane (m.p. 137–137.5°) with 2-biphenylyltriphenylsilane (m.p. 136–137°) was 114–135°.

Di-2-biphenylyldiphenylsilane volatilized at 490° without decomposition. At 530° a small amount of light yellow, glassy residue was left.

Tri-2-biphenylylphenylsilane. A solution of 0.05 mole of phenyllithium in 57 ml. of ether was added to 10.5 g. (0.02 mole) of tri-2-biphenylylchlorosilane. The reaction mixture was heated to a gentle reflux and vigorously stirred for 48 hours after which time Color Test I was still positive. Then 50 ml. of benzene was added and stirring at a reflux temperature was continued for 2 more days. Color Test I was still positive; therefore, 25 ml. of xylene was

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[5] The petroleum ether referred to in this paper boiled over the range 60–70°.

[6] Silicon analyses were carried out according to the procedure of Gilman, Hofferth, Melvin, and Dunn, *J. Am. Chem. Soc.*, **72**, 5767 (1950).

[7] Volatility was determined by inserting a melting point capillary containing a small amount of a sample into a copper block which was heated either electrically or with a Bunsen flame. The volatilization temperature was arbitrarily taken as the temperature at which approximately one eighth of an inch of condensate appeared in the capillary tube above the block.

added and the reaction mixture was stirred at reflux temperature for 5 hours after which time Color Test I was only weakly positive.

The reaction was carefully hydrolyzed with 2 *N* hydrochloric acid, stirred well, and filtered to remove the insoluble scum which was not identified. The benzene-xylene layer of the filtrate was separated from the aqueous layer, reduced in volume, and cooled. The precipitate obtained on filtration weighed 6.20 g. and melted at 175–178°. Recrystallization from toluene and xylene, respectively, yielded 2.43 g. (22%) of tri-2-biphenylylphenylsilane melting at 184°.

Anal. Calc'd for $C_{42}H_{32}Si$: Si, 4.96. Found: Si, 4.90, 4.91.

The compound volatilized at 490° without any apparent decomposition. The residue was a light yellow liquid which remained unchanged even when heated to 520°.

A 68% recovery of tri-2-biphenylylsilane was made in an attempted preparation of tri-2-biphenylylphenylsilane from the reaction of tri-2-biphenylylsilane and phenyllithium according to the procedure described for tri-2-biphenylylchlorosilane.

Di-2-biphenylylphenylsilanol. This compound was synthesized in an attempt to prepare tri-2-biphenylylphenylsilane from the reaction of phenyltrichlorosilane and 2-biphenylyllithium.

To a solution of 11.5 g. (0.054 mole) of phenyltrichlorosilane in 100 ml. of ether was added 216 ml. of an ethereal solution containing 0.18 mole of 2-biphenylyllithium. The reaction mixture was stirred at a reflux temperature. Color Test I which was carried out daily remained positive until the 13th day. The reaction was carefully hydrolyzed with 2 *N* hydrochloric acid and filtered to remove a small amount of scum that was present. The ether layer was separated from the aqueous layer and the ether was removed by distillation. The brownish oil left as a residue was cooled overnight in a refrigerator but it did not solidify. This material was dissolved in benzene and chromatographed on 80–200 mesh alumina using benzene, chloroform, and methanol, respectively, as eluants. Three principal products were obtained: the first melted near 60°, the second was a yellow semi-solid, and the third melted in the neighborhood of 110°.

The first fraction was purified by vacuum sublimation to give 3.7 g. (13%) of biphenyl melting at 69–70°. Mixture melting point with an authentic specimen of biphenyl was not depressed.

The second fraction could not be purified by vacuum sublimation followed by chromatography on alumina with chloroform and methanol, respectively, as eluants.

When the third fraction was chromatographed on alumina with chloroform and methanol as eluants, a material melting at 106–110° and another melting at 105–112° were obtained. These products were combined and recrystallized twice from petroleum ether to give 2.47 g. (10%) of di-2-biphenylylphenylsilanol melting at 115–116°.

Anal. Calc'd for $C_{30}H_{24}OSi$: Si, 6.54. Found: Si, 6.59, 6.63.

The infrared spectrum of this compound as a Nujol mull had a characteristic hydroxyl band at 2.75 μ.

Di-2-biphenylylphenylsilanol volatilized at 435° without leaving a residue. Microbubbles appeared above 410°.

Tri-2-biphenylylchlorosilane. Tri-2-biphenylylchlorosilane was first prepared in an attempt to synthesize tetra-2-biphenylylsilane from the reaction of silicon tetrachloride and 2-biphenylyllithium in a 4:1 molar ratio. Only 3 of the chloro groups were substituted even after stirring at an ether-reflux temperature for 16 days. Two equivalents of 2-biphenylyllithium reacted immediately but the third reacted much more slowly.

To a flask containing 13.6 g. (0.08 mole) of silicon tetrachloride was added 287 ml. of an ethereal solution containing 0.28 mole of 2-biphenylyllithium. The suspension was heated to a gentle reflux and stirred for 48 hours. The ether was slowly removed by distillation and 25 ml. of xylene was added. The reaction mixture was stirred at a reflux temperature until Color Test I became negative, then hydrolyzed with 50 ml. of water, stirred thoroughly, and filtered to give a product melting at 241–242° (cloudy). The product when digested with hot water and filtered weighed 23.3 g. (54%) and melted at 241–242°. The analytical sample obtained by recrystallization from benzene melted sharply at 242°.

Anal. Calc'd for $C_{36}H_{27}ClSi$: Si, 5.36. Found: Si, 5.35, 5.30.

The compound volatilized at 450° without decomposition although a reddish-brown liquid residue was still left at 472°.

When the reaction mixture containing 0.54 mole of 2-biphenylyllithium and 26.9 g. (0.16 mole) of silicon tetrachloride was stirred at a reflux temperature for 72 hours, 42.3 g. (51%) of tri-2-biphenylylchlorosilane melting sharply at 241° was obtained.

Tri-2-biphenylylsilanol. (a) Methanolic potassium hydroxide. To a 1-liter flask containing a warm solution of 20 g. (0.038 mole) of tri-2-biphenylylchlorosilane in 650 ml. of benzene was added 200 ml. of 1.2 *N* methanolic potassium hydroxide. This solution was digested on a steam plate for 24 hours, cooled, and the volume reduced by distillation. The reaction mixture was vigorously stirred with 200 ml. of water, filtered, and air-dried to give 9.7 g. of a product melting over the range 194–205°. This crude material was dissolved in benzene and chromatographed on 80–200 mesh alumina with benzene as an eluant. The two main fractions obtained were: 8.71 g. (m.p. 217–218°) and 0.32 g. (m.p. 187–188°). The chromatogram was extracted with methanol in a Soxhlet extraction apparatus. The methanolic solution when cooled yielded 7.63 g. of tri-2-biphenylylsilanol melting at 186.5–187°. From the filtrate 0.90 g. of a product melting at 184.5–186° was recovered. The total yield was 8.85 g. (41%).

Anal. Calc'd for $C_{36}H_{28}OSi$: Si, 5.57. Found: Si, 5.70, 5.56.

The infrared spectrum of this compound as a carbon disulfide solution had a sharp hydroxyl band at 2.77 μ. The presence of a hydroxyl group is also indicated by the fact that it was only sparingly eluted from alumina with benzene.

The volatilization temperature of tri-2-biphenylylsilanol was 460°. Above 460° a considerable evolution of bubbles began and at 470° only a very small amount of colorless liquid residue remained.

The compound melting at 217–218° is as yet unidentified but further studies on this compound are being pursued.

(b) N,N-Dimethylformamide. This run was patterned after that reported by Rochow and Gingold (17) for converting chlorosilanes to siloxanes with dimethylformamide. The amount of dimethylformamide employed in this run was just sufficient to dissolve the tri-2-biphenylylchlorosilane used, at the reflux temperature of dimethylformamide.

A solution of 5.23 g. (0.01 mole) of tri-2-biphenylylchlorosilane in 15 ml. of dimethylformamide was refluxed under nitrogen atmosphere for 72 hours. The product which crystallized on cooling was filtered, then washed with petroleum ether, water and ethanol, respectively, to yield 4.35 g. (83% recovery) of tri-2-biphenylylchlorosilane melting at 237.5–238.5°. A mixture melting point determination and an infrared spectrum confirmed its identity.

Tri-2-biphenylylsilanol (0.46 g., 9.1%) precipitated on diluting the mother liquor with water. This material melted at 184–185.5° and was identified by a mixture melting point determination.

(c) Tri-2-biphenylylsilane and potassium hydroxide in piperidine. To a solution of 1.8 g. of potassium hydroxide in 60 ml. of piperidine and 5 ml. of water was added 1 g. (0.0021 mole) of tri-2-biphenylylsilane. The solution obtained on heating was refluxed for 24 hours under a nitrogen atmosphere. Some evolution of gas was noted. The residue on distilling the solvent was acidified with 100 ml. of 1 *N* hydrochloric acid, filtered, then washed with absolute ethanol and air-dried. The white product obtained weighed 1.04 g. and melted over the range 172–220°. This material was chromatographed on 80–200 mesh alumina using benzene as a solvent and eluant. From the eluate 0.87 g. (87% recovery) of tri-2-biphenylylsilane melting at 171–172° was obtained. The chromatogram was extracted with methanol in a Soxhlet extraction apparatus. The removal of most of the methanol from the extract gave 0.1 g. (9.6%) of tri-2-biphenylylsilanol melting at 186–187° which was identified by a mixture melting point with tri-2-biphenylylsilanol (m.p. 187–188°).

Tri-2-biphenylylsilane. (a) Ethylene glycol dimethyl ether. A slurry of 26.7 g. (0.051 mole) of tri-2-biphenylylchlorosilane in 60 ml. of purified ethylene glycol dimethyl ether[8] was

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[8] Ethylene glycol dimethyl ether was purified by stirring it at a reflux temperature over sodium. When the solvent became anhydrous, benzophenone, added as an indicator, reacted

added to a flask containing a suspension of 2.0 g. (0.053 mole) of lithium aluminum hydride in 15 ml. of ethylene glycol dimethyl ether over a period of 10 minutes. The reaction mixture was stirred at a reflux temperature under nitrogen atmosphere for 15 hours, cooled, and the excess lithium aluminum hydride was destroyed with 30 ml. of ethyl acetate. The mixture was filtered and the product obtained was extracted in a Soxhlet extraction apparatus with acetone. The precipitate which formed on cooling the acetone solution weighed 20.5 g. and melted at 169.5–172°. When the mother liquor was reduced in volume and cooled, 1.54 g. of product melting at 168–169° was recovered. The two products were combined and recrystallized from a mixture of acetone and benzene to give 17.6 g. (71%) of tri-2-biphenylylsilane melting at 169.5–170.5°.

Anal. Calc'd for $C_{36}H_{28}Si$: Si, 5.74. Found: Si, 5.80, 5.80.

The infrared spectrum of this compound as a Nujol mull showed a Si—H stretching band at 4.6 μ and a Si—H bending band at 12.34 μ (24).

Tri-2-biphenylylsilane melted at 169.5–170.5° forming a light yellow liquid. The volatilization temperature was 450° although some microbubbles appeared above 430°. At 460° only a very small amount of yellow liquid residue remained.

(*b*) *Tetrahydrofuran.* To a flask containing a slurry of 2 g. (0.053 mole) of lithium aluminum hydride in 15 ml. of purified tetrahydrofuran[9] was added a suspension of 26.7 g. (0.051 mole) of tri-2-biphenylylchlorosilane in 30 ml. of tetrahydrofuran over a period of 1.5 hours. After completion of the addition, the reaction mixture was refluxed and stirred under a nitrogen atmosphere for 8 hours. The unreacted lithium aluminum hydride was decomposed with ethyl acetate and the reaction mixture was filtered, washed with water, and air-dried to give a product melting over the range 160–210°. This material was extracted with acetone to give 7.45 g. of a product melting at 161–162°. Recrystallization from a mixture of acetone and benzene yielded 5.31 g. (21%) of tri-2-biphenylylsilane melting at 170–171°. Another recrystallization from the same solvent did not affect the melting point.

The residue from the extraction was recrystallized from benzene to give 7.75 g. (30% recovery) of tri-2-biphenylylchlorosilane melting at 242°. A mixture melting point with the analyzed sample was not depressed.

(*c*) *Diethyl ether.* The procedure used in this run was essentially that used by Gilman and Brannen (5) in preparing tri-1-naphthylsilane in a 95% yield from tri-1-naphthylchlorosilane.

To a slurry of 2.0 g. (0.053 mole) of lithium aluminum hydride in 15 ml. of ether was added a suspension of 26.7 g. (0.051 mole) of tri-2-biphenylylchlorosilane in 30 ml. of ether over a period of 1.5 hours. After the mixture was stirred at a reflux temperature for 1.5 hours, 15 ml. of ethyl acetate was added. The reaction mixture was filtered, digested with 100 ml. of 1 *N* hydrochloric acid, filtered, and air-dried to give a quantitative recovery of tri-2-biphenylylchlorosilane melting at 240–242°.

Attempted preparation of hexa-2-biphenylyldisilane. (*a*) *Tri-2-biphenylylchlorosilane and sodium.* This run was carried out according to the procedure for preparing hexaphenyldisilane from triphenylchlorosilane and sodium as reported by Schlenk (25) and modified by Gilman and Dunn (15).

A mixture of 10.5 g. (0.02 mole) of tri-2-biphenylylchlorosilane and 4.60 g. (0.02 g.-atom) of sodium in 50 ml. of xylene was stirred at a reflux temperature for 24 hours. The unreacted sodium was decomposed with absolute ethanol; then 100 ml. of water was added and the xylene layer was separated from the aqueous layer. The product obtained on concentrating the xylene layer was digested with petroleum ether and then recrystallized twice from xylene to give 0.63 g. (12.6% assuming the stoichiometric ratio of sodium to tri-2-biphenyl-

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with sodium to form sodium ketyl which gave a bluish-green color to the solution. After the appearance of the bluish color the ethylene glycol dimethyl ether was distilled and stored over sodium in a dark bottle.

[9] Tetrahydrofuran was purified by stirring for 24 hours at a reflux temperature over sodium. The solvent was distilled and stored in a dark bottle.

ylsilane as being 2:1) of tri-2-biphenylylsilane melting at 169–170°. The identification of this compound was confirmed by comparing its spectrum with that of tri-2-biphenylylsilane prepared by reducing tri-2-biphenylylchlorosilane with lithium aluminum hydride and by a mixture melting point determination.

(*b*) *Hexachlorodisilane and 2-biphenylyllithium.* To a dry flask cooled by an ice-bath and containing 8.07 g. (0.03 mole) of hexachlorodisilane was added 257 ml. of an ethereal solution containing 0.25 mole of 2-biphenylyllithium. After stirring the mixture for 12 hours most of the ether was removed by distillation and the concentrated suspension was stirred for another 24 hours. Color Test I was still positive. The remaining ether was removed under water-aspirator vacuum and the syrupy residue was baked at 160° for 4 hours. Color Test I was still positive. After 5 more hours of baking at the same temperature the test was negative.

The reaction mixture was cooled, stirred thoroughly with 100 ml. of benzene, and carefully hydrolyzed with 100 ml. of 2 *N* hydrochloric acid. The residue obtained from the benzene layer on distillation of the benzene was digested with petroleum ether to give 3.29 g. of a material melting over the range 200–210°. This product was digested with hot water and then was recrystallized twice from xylene to yield 1.21 g. of tetra-2-biphenylyldichlorodisilane melting at 221–222°.

Anal. Calc'd for $C_{48}H_{36}Cl_2Si_2$: Si, 7.58. Found: Si, 7.57, 7.62.

The volatilization temperature of this compound was 440° although microbubbles were observed above 380°. At 440° volatilization was complete.

SUMMARY

1. 2-Biphenylyllithium has been prepared in excellent yields from the reaction of 2-bromobiphenyl and lithium ribbon.

2. Seven new aromatic silicon compounds containing one or more 2-biphenylyl groups have been prepared. These are 2-biphenylyltriphenylsilane, di-2-biphenylyldiphenylsilane, tri-2-biphenylylphenylsilane, di-2-biphenylylphenylsilanol, tri-2-biphenylylchlorosilane, tri-2-biphenylylsilanol, and tri-2-biphenylylsilane.

3. The relatively drastic conditions required to prepare these compounds (compared to analogous phenyl-substituted compounds) and the failure to prepare hexa-2-biphenylyldisilane and hexa-2-biphenylyldisiloxane are attributed to steric factors.

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