[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Preparation and Properties of Hexaaryldisilanes

BY HENRY GILMAN AND G. E. DUNN[1]

An improved procedure for the preparation of hexaphenyldisilane from triphenylchlorosilane, and a new preparation from triphenylsilane are reported. The preparation and reactions of hexa-*p*-biphenylyldisilane and several other *p*-biphenylyl-silicon compounds are described. The evidence against the formation of triarylsilyl radicals is discussed.

It has been known for many years that, under ordinary conditions, hexaaryldisilanes like hexaphenyldisilane[2] and hexa-*p*-tolyldisilane[3] apparently do not dissociate into triarylsilyl radicals analogous to the triarylmethyls. The compounds are too insoluble in organic solvents for molecular weight determinations, and there have been no reports of magnetic susceptibility measurements on disilanes, but Schlenk and co-workers[2] found hexaphenyldisilane to be a very unreactive compound, showing no tendency to take up oxygen, as does hexaphenylethane. We have repeated the preparation and confirmed their conclusions.

$$2(C_6H_5)_3SiCl + 2Na \longrightarrow (C_6H_5)_3SiSi(C_6H_5)_3 + 2NaCl$$

It was found, however, that strict adherence to the published procedure[2] gave yields of only 5–10%, due to the fact that hexaphenyldisilane is only slightly soluble in boiling xylene. If the hot reaction mixture is filtered and the residue discarded as recommended, most of the product is lost. Yields of 85–90%, melting at 361–362°, instead of 355° as previously reported,[2] were obtained when the reaction mixture was worked up as described in the Experimental part. It was also found that hexaphenyldisilane can be prepared in 21% yield from triphenylsilane and lithium metal in diethyl ether.

$$2(C_6H_5)_3SiH + 2Li \longrightarrow (C_6H_5)_3SiSi(C_6H_5)_3 + 2LiH$$

Since the silicon–silicon bond energy (45 kcal./mole[4]) is considerably less than the carbon–carbon bond energy (80 kcal./mole[4]), it might be expected that a homolytic cleavage into radicals would be easier for the disilanes than for the ethanes. The lack of dissociation of hexaphenyldisilane and hexa-*p*-tolyldisilane might be attributed to reduced steric strains in these molecules as compared to the hexaarylethanes, because of the large silicon–silicon and silicon–carbon bond distances (Si–Si, 2.34 Å.[5]; Si–C, 1.93 Å.[6]; C–C, 1.54 Å.[6]). However, attempts to introduce greater strains with bulkier groups have not led to the formation of radicals. When hexachlorodisilane was treated with excess of *o*-tolyllithium, only two chlorines per silicon atom were replaced by organic groups.[7] This suggests that the approach of two silicon atoms, each bearing three *o*-tolyl groups, would meet with sufficient steric interference to make the formation of a stable silicon–silicon bond difficult. In the analogous case involving central carbon atoms, tri-*o*-tolylchloromethane reacts with mercury to give the radical tri-*o*-tolylmethyl,[8] but in the silicon series, neither tri-*o*-tolylchlorosilane[7] nor tri-1-naphthylchlorosilane[9] underwent any reaction with sodium in our modification of Schlenk's procedure. Thus, in a case where steric factors have been shown to be appreciable, but not great enough to prevent radical formation in carbon compounds, triarylsilyl radicals were not formed.

It seems very probable that the non-dissociation of disilanes is due to a small resonance stabilization of the silyl radicals which would be formed. Resonance of the type believed to be of importance in the triarylmethyls[10] would, in the silicon case, require the participation of structures having silicon–carbon double bonds. Contributions from such structures in other silicon compounds appear to be small compared with those from analogous structures in corresponding carbon compounds.[11] The fact that a tri-1-naphthylsilyl radical, in which steric strain and resonance stabilization should both be large, could not be formed seems to support this view. However, it is conceivable that the silicon–chlorine bond in tri-1-naphthylchlorosilane is so shielded that it cannot be attacked by sodium in any fashion. It therefore seemed to be of interest to examine an aryldisilane in which the possibilities for resonance stabilization of a radical would be large, while steric interference would be small enough to permit formation of a silicon–silicon bond. Hexa-*p*-biphenylyldisilane was considered to be such a compound, since the analogous carbon compound, hexa-*p*-biphenylylethane, is reported to be very highly dissociated into radicals even in the solid state.[12]

Hexa-*p*-biphenylyldisilane was prepared and found to be, like hexaphenyldisilane, a very unreactive compound, melting undecomposed at 432–434° (uncor.). It was too insoluble for determinations of molecular weight in solution, but dilute solutions in xylene and chloroform were completely colorless and unaffected by prolonged treatment with oxygen and iodine. These facts make it very unlikely that hexa-*p*-biphenylyldisilane is appreciably dissociated into radicals under ordinary conditions, and further emphasize the smallness of the resonance stabilization to be

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(1) E. I. du Pont de Nemours and Company Fellow, Iowa State College, 1950–1951.

(2) W. Schlenk, J. Renning and G. Rackey, *Ber.*, **44**, 1178 (1911).

(3) W. C. Schumb and C. M. Saffer, THIS JOURNAL, **61**, 363 (1939).

(4) K. S. Pitzer, *ibid.*, **70**, 2140 (1948).

(5) L. O. Brockway and N. R. Davidson, *ibid.*, **63**, 3278 (1941).

(6) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945.

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

(8) W. Theilacker and M. L. Ewald, *Naturwissenschaften*, **31**, 302 (1943).

(9) H. Gilman and C. G. Brannen, unpublished studies.

(10) G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 192 ff.

(11) H. Gilman and G. E. Dunn, THIS JOURNAL, **73**, 3404 (1951); *ibid.*, **72**, 2178 (1950); J. D. Roberts, E. A. McElhill and R. Armstrong, *ibid.*, **71**, 2923 (1949).

(12) W. E. Bachmann in "Organic Chemistry, an Advanced Treatise," H. Gilman, Ed., John Wiley and Sons, Inc., New York, N. Y., 2nd ed., 1943, p. 581 ff.

obtained from structures containing silicon–carbon double bonds. Studies of other hexaaryldisilanes which contain varying proportions of hindering groups and groups with large possibilities for resonance stabilization are in progress.

Experimental

All reactions involving organolithium reagents were run in an atmosphere of dry nitrogen. Melting points were taken in a copper block similar to those described by Morton,[13] and are uncorrected. Silicon analyses were carried out by the procedure recently reported from this Laboratory,[14] and active hydrogens were determined with methyllithium according to a previously published method.[15]

Hexaphenyldisilane from Triphenylchlorosilane.—In accordance with the directions of Schlenk, Renning and Racky, a solution of 6.5 g. (0.022 mole) of triphenylchlorosilane in 125 ml. of xylene was refluxed with 4 g. (0.174 g. atom) of sodium for 3 hours. The suspension developed a deep violet color and a large volume of precipitate appeared. This precipitate was filtered from the hot solution, as specified in the published procedure, and the xylene solution was allowed to cool for 12 hours in the refrigerator. There was obtained as a white precipitate 0.28 g. (5.4% yield) of hexaphenyldisilane melting at 354–355°. Schlenk and coworkers give the melting point as 354° but do not mention the yield.

In a second run the procedure was modified. Fifteen grams (0.051 mole) of triphenylchlorosilane in 75 ml. of xylene was refluxed for 3 hours with 2.1 g. (0.091 g. atom) of sodium. The suspension was allowed to cool to room temperature, then filtered, and the residue was washed with xylene. This solid was placed in 100 ml. of 95% ethanol and stirred until all the excess sodium had reacted. Four volumes of water were then added, and the suspension was filtered. The residue was washed with water and dried to give 11.6 g. (85% yield) of hexaphenyldisilane melting at 361–362°. A check run by the same procedure gave an 87% yield.

Hexaphenyldisilane from Triphenylsilane.—A solution of 5.2 g. (0.02 mole) of triphenylsilane in 100 ml. of dry ether was added slowly to 0.7 g. (0.10 g. atom) of lithium metal cut into small pieces in 50 ml. of ether under an atmosphere of nitrogen. There was no immediate evidence of reaction, so the mixture was refluxed for 24 hours. At the end of this time some white insoluble material had appeared. The suspension was decanted through a stopcock so as to leave the pieces of lithium behind, and poured into 50 ml. of 90% methanol. When the evolution of gas due to decomposition of lithium hydride had ceased, the mixture was filtered. The precipitate weighed 0.40 g. (8% yield), melted at 350–355°, and did not depress the melting point of an authentic sample of hexaphenyldisilane. Removal of solvent from the filtrate and distillation of the residue gave 3.0 g. (58%) of triphenylsilane boiling at 144–145° (0.3 mm.) and 1.7 g. (31%) of triphenylsilanol boiling at 154–200° (0.3 mm.), both identified by mixed melting points with known samples.

A second run using double quantities of reagents in the same volume of ether was refluxed for 6 days. It was worked up exactly as before to give a 21% yield of hexaphenyldisilane, a 22% yield of triphenylsilanol, and a 38% recovery of triphenylsilane.

***p*-Biphenylyllithium.**—Lithium metal, 3.22 g. (0.46 g. atom), was pounded into paper-thin sheets, scrubbed under mineral oil to ensure a bright surface, washed with petroleum ether (b.p. 60–70°), and cut in pieces about 5 mm. square into 200 ml. of dry ether under an atmosphere of nitrogen. Fifty grams (0.214 mole) of *p*-bromobiphenyl in 700 ml. of dry ether was added slowly with good stirring. There was no evidence of reaction and the lithium changed from shiny to black. A few fresh pieces of lithium also turned black when added to the solution. The mixture was refluxed for 5 hours, during which time the lithium was slowly consumed, although it never became bright. The dark brown solution was filtered through glass wool and titrated. The yield was 73%. About a dozen similar runs produced substantially the same results.

Tri-*p*-biphenylylsilanol.—It was first proposed to prepare hexa-*p*-biphenylyldisilane by the series of reactions

$$\mathrm{SiCl_4 + 3C_{12}H_9Li \xrightarrow{H_2O} (C_{12}H_9)_3SiOH + 3LiCl + HCl}$$

$$\mathrm{(C_{12}H_9)_3SiOH + HCl \xrightarrow[ether]{} (C_{12}H_9)_3SiCl + H_2O}$$

$$\mathrm{2(C_{12}H_9)_3SiCl + 2Na \xrightarrow[xylene]{} (C_{12}H_9)_3SiSi(C_{12}H_9)_3 + 2NaCl}$$

The first step, involving the preparation of tri-*p*-biphenylylsilanol, was carried out as follows.

To 6.75 g. (0.040 mole) of silicon tetrachloride in 150 ml. of dry ether was added 0.113 mole of *p*-biphenylyllithium, in accordance with the general directions of Gilman and Clark.[16] The addition was complete in 2 hours, and the reaction mixture was allowed to stand overnight. It was then hydrolyzed with 10% ammonia solution, the solvent was distilled from the ether layer, and the residue was steam distilled to remove 3.5 g. (20%) of biphenyl. Ether extraction of the residue from steam distillation left 1 g. (7%) of insoluble solid, m.p. 200–201°, with gas evolution, which was found to be di-*p*-biphenylylsilanediol.

Anal. Calcd. for $C_{24}H_{20}O_2Si$: Si, 7.62; active H, 2.00. Found: Si, 7.59, 7.69; active H, 1.88, 1.95.

The solvent was distilled from the ether extract and the residue was crystallized from benzene to give 5.6 g. (28%) of tri-*p*-biphenylylsilanol, m.p. 200–201°. This material did not evolve a gas on melting, and a mixed melting point with the di-*p*-biphenylylsilanediol obtained above was depressed about 15°. Subsequent runs gave yields of 32 and 35%.

Anal. Calcd. for $C_{36}H_{28}OSi$: Si, 5.55; active H, 1.00. Found: Si, 5.54, 5.59; active H, 0.94, 0.98.

An attempt was also made to prepare tri-*p*-biphenylylsilanol from silicon tetrachloride using *p*-biphenylyllithium made by halogen-metal interconversion. In order to determine the yield of *p*-biphenylyllithium obtained from the interconversion, 11.65 g. (0.050 mole) of *p*-bromobiphenyl in 50 ml. of dry ether was treated with 0.050 mole of *n*-butyllithium in 100 ml. of ether at 0°. Aliquots were withdrawn and carbonated at intervals of 0, 5, 10, 20 and 40 minutes after mixing. The yields of *p*-phenylbenzoic acid were 62, 60, 60, 60, 57%, respectively. It was therefore concluded that the interconversion mixture could be used immediately after mixing, that its use could be spread over a period of at least 40 minutes, and that the yield would be approximately 60%.

On this basis, 75.6 g. (0.15 mole) of *p*-bromobiphenyl was suspended in 100 ml. of dry ether, and to this was added over a period of 2 minutes 0.15 mole of *n*-butyllithium in 300 ml. of ether at 0°. This solution was added dropwise to 5.1 g. (0.03 mole) of silicon tetrachloride in 100 ml. of dry ether at −10° over a period of 40 minutes. Hydrolysis with 10% ammonia solution gave a solid melting at 200–250° which was insoluble in ether. The ether solution yielded a brown solid melting at 150–180°. Attempts to obtain a pure material from these solids by crystallization were unsuccessful.

Tri-*p*-biphenylylsilanol was successfully prepared from silicon tetrachloride and *p*-biphenylylmagnesium iodide. (*p*-Bromobiphenyl did not react with magnesium.) One and one-half grams (0.060 g. atom) of magnesium turnings were just covered with ether and reaction was started by adding a few crystals of *p*-iodobiphenyl. A solution of 14 g. (0.050 mole) of *p*-iodobiphenyl in 90 ml. of dry ether was added at a rapid drip. Only very gentle reflux occurred, and the solution became dark brown and cloudy. When the addition was complete, the mixture was refluxed for two hours, then filtered and titrated. The yield was 59%. To this Grignard solution (0.030 mole) was added 1.53 g. (0.009 mole) of silicon tetrachloride. The mixture was refluxed until Color Test I[17] became negative (48 hours), then hydrolyzed with 10% hydrochloric acid and filtered. The insoluble material weighed 0.9 g. (20%) and melted at 196–

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[13] A. A. Morton, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1938, pp. 32–34.

[14] H. Gilman, B. Hofferth, H. W. Melvin and G. E. Dunn, THIS JOURNAL, **72**, 5767 (1950). See, also, H. Gilman and L. S. Miller, *ibid.*, **73**, 968 (1951), for a microanalytical procedure for the determination of silicon in organosilicon compounds.

[15] H. Gilman, R. A. Benkeser and G. E. Dunn, *ibid.*, **72**, 1689 (1950).

[16] H. Gilman and R. N. Clark, *ibid.*, **68**, 1675 (1946).

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

199°. This did not depress the melting point of the tri-*p*-biphenylylsilanol reported above.

Attempted Preparation of Tri-*p*-biphenylylchlorosilane.—Three grams (0.006 mole) of tri-*p*-biphenylylsilanol was dissolved in 100 ml. of dry benzene, and dry hydrogen chloride was passed into the solution for 5 hours. There was no heat evolved and no precipitate formed. On distillation of the solvent, a quantitative recovery of tri-*p*-biphenylylsilanol (mixed melting point) was obtained. This method has been very successful for preparing triphenylchlorosilane from triphenylsilanol.[18]

In a second attempt, 2.5 g. (0.005 mole) of tri-*p*-biphenylylsilanol was suspended in 25 ml. of acetyl chloride, and dry hydrogen chloride was passed into the suspension for 12 hours. The solid was then filtered off, washed with petroleum ether (b.p. 28–38°), and found to weigh 2.5 g. (100% recovery) and melt at 200–201°. A mixed melting point with starting material was not depressed. In case the failure of this reaction was due to the insolubility of the silanol in acetyl chloride, the recovered tri-*p*-biphenylylsilanol was dissolved in a slight excess of benzene, and an equal volume of acetyl chloride was added. Dry hydrogen chloride was passed into this solution for 5 hours. Evaporation of the solvent left 2.5 g. of tri-*p*-biphenylsilanol, melting at 197–198°, identified by mixed melting point.

Hexa-*p*-biphenylyldisilane.—Since tri-*p*-biphenylylchlorosilane was not readily available, hexa-*p*-biphenylyldisilane was prepared from hexachlorodisilane and *p*-biphenylyllithium. To 2.69 g. (0.01 mole) of hexachlorodisilane in 100 ml. of ether was added 0.068 mole of *p*-biphenylyllithium in ether. The mixture was refluxed until Color Test I became negative (20 hours), then hydrolyzed with water. The material insoluble in both ether and water was filtered off and dried. It weighed 7.5 g., and melted at 320–370°. This solid was digested with benzene for 4 hours, then filtered and washed with benzene. The benzene, on cooling, deposited 1.5 g. of white solid melting at 260–263°. Recrystallization from benzene gave 1.2 g. (23%) of tetra-*p*-biphenylylsilane melting at 270–272°. The melting point reported in the literature is 274°.[19] The benzene-insoluble residue weighed 3 g. and melted at 400–415°. This material was insoluble in all the organic solvents available with the exception of nitrobenzene. Recrystallization from nitrobenzene gave a product with a lighter color (tan) but the same melting range. It was then discovered that the material was partly soluble in pyridine. After four hours of digestion with hot pyridine, the hot suspension was filtered to give a colorless residue weighing 1.3 g. and melting at 432–434°. The yield is 14%.

Anal. Calcd. for $C_{72}H_{54}Si_2$: Si, 5.75. Found: Si, 5.73, 5.77.

Attempted Reaction of Hexa-*p*-biphenylyldisilane with Oxygen and Iodine.—A suspension of 0.30 g. of hexa-*p*-biphenylyldisilane in 50 ml. of dry xylene was heated to reflux for 48 hours while passing a stream of dry air through the mixture. The xylene was then removed under vacuum. The residue weighed 0.294 g. (98% recovery) and melted at 432–434° alone, or mixed with starting material.

Two 0.30-g. samples of hexa-*p*-biphenylyldisilane were weighed out and suspended, one in 50 ml. of xylene, and the other in 50 ml. of chloroform. To the xylene suspension was added 0.10 g. of iodine and 3 drops of quinoline, and to the chloroform solution was added 1 drop of 0.001 *M* iodine in chloroform. Both solutions were refluxed for 10 hours, then filtered hot. The residue from the xylene suspension weighed 0.252 g. (84%) and that from the chloroform suspension weighed 0.260 g. (87%). Both melted at 432–434° alone or mixed with starting material. The iodine color had not disappeared from either solution, even though it had been very faint in the chloroform solution from the beginning.

Cleavage of Tri-*p*-biphenylylsilanol by Phenyllithium.—Several triarylsilanols have been cleaved to diaryl-*n*-butylsilanols and phenyllithium by treatment with *n*-butyllithium in ether, but up to the present no triarylsilanol has been cleaved by another aryllithium reagent.[15,20] Since the tri-*p*-biphenylylsilanol which was at hand seemed to offer good possibilities of cleavage, it was treated with phenyllithium. Three grams (0.006 mole) of tri-*p*-biphenylylsilanol was refluxed for 48 hours with 0.060 mole of phenyllithium in 175 ml. of dry ether. The mixture was carbonated and worked up as previously described,[15] to give an acid melting at 104–108°. This was extracted with hot water. The material which did not dissolve in hot water melted at 175–190° and, after several crystallizations from aqueous ethanol, it yielded 0.14 g. (12%) of *p*-phenylbenzoic acid, m.p. 227–228°, identified by mixed melting point with an authentic specimen.

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[18] C. A. Kraus and R. Rosen, THIS JOURNAL, **47**, 2739 (1925); H. Gilman, B. Hofferth and H. W. Melvin, *ibid.*, **72**, 3045 (1950).

[19] W. C. Schumb, J. Ackerman, Jr., and C. M. Saffer, Jr., *ibid.*, **60**, 2486 (1938).

[20] See H. Gilman and F. J. Marshall, THIS JOURNAL, **71**, 2066 (1949), for cleavages of organosilicon compounds by acids.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, OSAKA UNIVERSITY]

The Relation between the Geometrical Configurations of Inorganic Complexes and their Absorption Bands. I. The Third Absorption Band of *trans*-Dirhodanato-bis-ethylenediamine-cobalt(III) Chloride

BY YOICHI SHIMURA

The absorption spectra of *cis*- and *trans*-$[Co\,en_2(NCS)_2]Cl\cdot H_2O$, and $[Co\,(NH_3)_5NCS]SO_4$ have been measured. It is concluded that the rhodanato- or nitro-specific absorption bands of *trans*-forms of Co(III) complexes have longer wave lengths than those of the *cis*-forms, and that the *trans*-$[Co\,en_2(NCS)_2]Cl\cdot H_2O$ has the third absorption band at about 108 × 10^{13} sec.$^{-1}$. It had not been found in this complex ion because it is entirely obscured by the larger rhodanato-specific absorption band. The *cis*-form of this salt has no such band. This detection of the third absorption band of *trans*-$[Co\,en_2(NCS)_2]^+$ is in good accord with the Shibata–Tsuchida's hypothesis of the *trans*-pairing of negative groups.

Introduction

There are few relationships of recognized validity concerning the absorption spectra of geometrical isomers of metallic complexes, except the *trans*-anions hypothesis dealing with the occurrence of a third absorption band proposed by Shibata[1] and Tsuchida.[2,3] According to this hypothesis, complex radicals with a pair or pairs of negative groups in *trans*-positions are expected to have these third absorption bands, which are situated almost always in the spectral region 110–120 × 10^{13} sec.$^{-1}$ for Co(III) or Cr(III) complexes. Recently Basolo[4,5] reported that a few Co(III) complexes with two negative ions in *cis*-positions have also the third bands in the region of shorter wave lengths than those of the *trans*-isomers, and that this fact can be

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[1] Y. Shibata, *J. Chem. Soc. Japan*, **36**, 1243 (1915); *J. College Sci., Imp. Univ. Tokyo*, **37**, Art. 2 (1915).

[2] R. Tsuchida, *Bull. Chem. Soc. Japan*, **11**, 721 (1936).

[3] R. Tsuchida, *ibid.*, **13**, 388, 436 (1938).

[4] F. Basolo, THIS JOURNAL, **70**, 2634 (1948).

[5] F. Basolo, *ibid.*, **72**, 4393 (1950).