of 9.5 g. of tri-*n*-hexylbromogermane in 40 ml. of ether. The mixture was refluxed for 4 hr. and was allowed to stand overnight. Unchanged lithium aluminum hydride was then precipitated by the addition of 100 ml. of petroleum ether (b.p. 77–115°) followed by distillation of the ethyl ether. The solution was filtered and then distilled. After a fore-run came over at 95–122° at 0.5 mm., 2.0 g. (26%) of product was collected, b.p. 122–125° at 0.5 mm.

*Anal.* Calcd. for $C_{18}H_{40}Ge$: MR, 97.1. Found: MR, 97.4.

The pure product does not evolve hydrogen at a noticeable rate when treated with dilute alcoholic potassium hydroxide solution, although triphenylgermane reacts readily. The infrared absorption spectrum shows a peak at 1980 cm.$^{-1}$ due to the Ge–H bond.

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA

## Cleavage of the Silicon-Silicon Bond of Hexaphenyldisilane. IV[1]

T. C. WU[2] AND HENRY GILMAN

The silicon-silicon bond of hexaphenyldisilane is much more stable than the carbon-carbon bond of hexaphenylethane. Unlike the carbon analog, hexaphenyldisilane is not cleaved by oxygen,[3,4] iodine,[4] sodium in xylene or dioxane,[1c] or sodium amalgam in ether.[1c] Nevertheless, the silicon-silicon bond of hexaphenyldisilane has been cleaved by sodium-potassium alloy in ether,[1c,5] lithium in tetrahydrofuran,[1a] lithium and sodium in ethylene glycol dimethyl ether,[1b] potassium in di-*n*-butyl ether,[1c] and rubidium or cesium in ether.[5]

In an extension to the studies of the cleavage reactions of the silicon-silicon bond of hexaphenyldisilane, a number of other reagents have been studied. It was found that sodium cleaved the disilane in liquid ammonia. Although iodine does not react with hexaphenyldisilane,[4] bromine was found to effect slow cleavage of the silicon-silicon bond in carbon tetrachloride to give bromotriphenylsilane. For example, 33% of pure bromo-

(1) (a) For Part III of this series see H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.*, **80**, 608 (1958); (b) for Part II see A. G. Brook and H. Gilman, *J. Am. Chem. Soc.*, **76**, 278 (1954); (c) for Part I see H. Gilman and T. C. Wu, *J. Am. Chem. Soc.*, **73**, 4031 (1951).

(2) Present address: E. I. du Pont de Nemours & Co., Inc., Benger Laboratory, Waynesboro, Va.

(3) W. Schlenk, J. Renning, and G. Racky, *Ber.*, **44**, 1178 (1911).

(4) H. Gilman and G. E. Dunn, *J. Am. Chem. Soc.*, **73**, 5077 (1951).

(5) H. Gilman and T. C. Wu, *J. Org. Chem.*, **18**, 753 (1953).

triphenylsilane was isolated in a period of 42 hr., and a 55% yield of bromotriphenylsilane was formed in 6 days. This observation further demonstrates that the silicon-silicon bond of hexaphenyldisilane is more stable than the central carbon-carbon bond of hexaphenylethane since the latter compound reacts readily with iodine due to dissociation.

Hexaphenyldisilane has been treated with a number of oxidizing agents as well as lithium aluminum hydride, but no cleavage reaction of the silicon-silicon bond was observed. In most cases, a nearly quantitative recovery of the starting material was obtained. When chromic acid was employed, some oxidation occurred yielding a sirupy product.

### EXPERIMENTAL[6]

*Reaction of hexaphenyldisilane with bromine.* A suspension containing 10 g. (0.019 mole) of hexaphenyldisilane, 3.4 g. (0.021 mole) of bromine, and 250 ml. of carbon tetrachloride was refluxed with constant stirring for 42 hr. The solvent and the unchanged bromine were removed by distillation to leave a solid residue (10.8 g.) melting at 100° to a turbid liquid. The crude product was boiled with 200 ml. of petroleum ether (b.p. 60–70°), filtered hot, and cooled. The insoluble solid (4.1 g.) melting at 346–354° was recrystallized from dioxane to give 3.6 g. (36%) of hexaphenyldisilane (mixed melting point). The filtrate was concentrated twice to collect 6.2 g. (47%) of solid melting at 115–118°. Two recrystallizations from petroleum ether (b.p. 60–70°) yielded 4.3 g. (33%) of crystals melting at 118–120°. A mixed melting point determination with an authentic specimen of bromotriphenylsilane was not depressed.

In a second experiment, the hexaphenyldisilane was allowed to react with bromine in refluxing carbon tetrachloride for 6 days. The reaction mixture was worked up according to the procedure described in the previous paragraph to give a 19% recovery of hexaphenyldisilane and a 65% yield of crude, and a 55% yield of pure bromotriphenylsilane.

*Reaction of hexaphenyldisilane with sodium in liquid ammonia.* Sodium, 0.35 g. (0.015 g.-atom), was cut into small pieces and dropped into about 50 ml. of liquid ammonia at −50°. To this deep blue solution thus formed there was added 2.6 g. (0.005 mole) of hexaphenyldisilane in one portion. The reaction mixture was stirred for 6 hr. at −50°. It was observed that some brown precipitate had formed although the color was somewhat masked by the deep blue color due to the excess sodium in liquid ammonia. The cooling bath was removed and ammonia was allowed to evaporate as the reaction mixture warmed to room temperature. A small amount of ethanol was added to the pale gray residue to destroy the excess sodium. Water was then added, and the mixture was filtered to give 1.6 g. of solid which softened at 120° but did not melt completely until 360°. This was boiled with a solution of benzene and ethanol and filtered hot. There was obtained, as the insoluble residue, 0.1 g. (4%) of hexaphenyldisilane (mixed melting point) melting at 360–362°. The filtrate was cooled to give 0.8 g. of solid melting at 150–200°. This was shaken with a small amount of cold ethanol and filtered to separate 0.4 g. of solid melting at 230–234°. One recrystallization from benzene raised the melting point to 233–235°. A mixed melting point determination with tetraphenylsilane was not depressed. The yield was 0.3 g. (9%). The ethanolic solution was evaporated to dryness, and the residue was recrystallized from petroleum ether (b.p. 60–70°) to give 0.4 g. (11%) of triphenylsilanol melting at 151–152°. Evaporation of the solvent from the

mother liquor after the removal of 0.8 g. of solid melting at 150–200°, resulted in 0.12 g. of colorless crystals melting at 163–167°. The infrared spectra of this slightly impure product and of hexaphenyldisilazane (the latter prepared by reaction of triphenylsilane with sodium in liquid ammonia[7]) are nearly identical, and a mixed melting point was not depressed.

*Reaction of hexaphenyldisilane with chromic acid.* Chromic acid solution was prepared by dissolving 5.0 g. of chromium trioxide in 5 ml. of water followed by the addition of 10 ml. of glacial acetic acid. This solution was added to 3.0 g. of hexaphenyldisilane, and the mixture was heated at 80–90° for 2 hr. with occasional shaking. The resulting dark green mixture was diluted with 100 ml. of water. Solid sodium carbonate was added to neutralize the reaction product until the addition of a small amount did not cause evolution of gases. Following filtration of the neutralized mixture there was obtained 2.7 g. (90%) of impure hexaphenyldisilane melting at 356–360°. It was boiled with petroleum ether (b.p. 60–70°) and filtered hot to separate 2.5 g. (83%) of purified hexaphenyldisilane. Only a trace of brown solid remained from the distillation of the filtrate.

In a second experiment, twice the amount of chromic acid was used, and the reaction mixture was refluxed for 48 hr. In this run, only a 48% yield of hexaphenyldisilane could be recovered. The aqueous solution was extracted with ether, from which a sirupy residue was obtained. Purification of this residue was unsuccessful.

*Attempted reactions of hexaphenyldisilane with other oxidizing agents, and lithium aluminum hydride.* Hexaphenyldisilane was treated with 30% hydrogen peroxide in refluxing glacial acetic acid for 24 hr. with no sign of reaction. It was also treated separately in refluxing solvent for 48 hr. with selenium dioxide in dioxane, nitric acid in water, periodic acid in benzene, and lead tetraacetate in acetic acid. In all cases no cleavage was observed while more than 90% of the unchanged disilane was recovered. Practically quantitative recoveries of hexaphenyldisilane were also obtained after it had been treated separately for 48 hr. with potassium permanganate in acetone, nitric oxide in ether, or lithium aluminum hydride in refluxing ether.

*Acknowledgment.* The authors are grateful to David H. Miles for general assistance; and to E. M. Layton, Jr., and Dr. V. A. Fassel of the Institute for Atomic Research for the infrared spectra.

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA

(7) H. Reynolds, L. A. Bigelow, and C. A. Kraus, *J. Am. Chem. Soc.*, **51**, 3067 (1929).

## Organoboron Compounds. VII.
## Alkylarylborinates

R. L. LETSINGER AND JOHN R. NAZY[1]

Ethanolamine has proved to be a very useful reagent for the isolation and characterization of

diarylborinic acids.[2] It reacts readily with the borinic acids, even in the presence of water, to yield air stable, sharp melting esters. As the boronic acids (also the boronate esters) and triarylborines do not behave in this manner, the borinates can be separated readily from reaction mixtures containing the three types of substances.

We now find that these techniques involving ethanolamine also provide a convenient means for isolating derivatives of the alkylarylboron-oxygen compounds. The preparation of three representative compounds, aminoethyl benzylphenylborinate (Ia), aminoethyl butylphenylborinate (Ib), and aminoethyl 1-methylheptylphenylborinate (Ic), are described in this note. In all cases the alkyl-boron bond was formed by reaction of the appropriate Grignard reagent with dibutyl benzeneboronate (II). Following hydrolysis the aminoethyl esters were precipitated by addition of ethanolamine. These esters are lower-melting and more soluble in



I　(a) R = C₆H₅CH₂–
　(b) R = C₄H₉–
　(c) R = C₆H₁₃–CH(CH₃)–
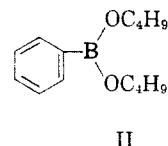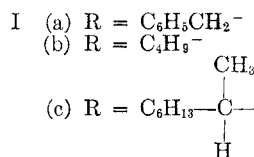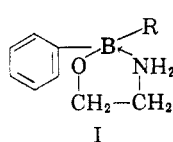
organic solvents than the previously described diarylborinates. The benzyl and butyl derivatives (Ia,b) have stood in vials in air over a year without change; however, the 1-methylheptyl derivative (Ic) is less stable. After a period of several months this compound melted over a range of several degrees at a lower temperature and a strong odor of octanol was noticed. All of the aminoethyl esters hydrolyzed very rapidly in dilute hydrochloric acid to give air sensitive substances (no doubt the free borinic acids since the aminoethyl esters could be regenerated by extraction of the acid with ether and reprecipitation with ethanolamine; however, crystalline borinic acids could not be obtained).

### EXPERIMENTAL

*Aminoethyl benzylphenylborinate.* Benzylmagnesium bromide (55 cc. of 1.81M ether solution) was added over a period of 1 hr. to a stirred solution of 23.4 g. (0.1 mole) of dibutyl benzeneboronate in 175 cc. of ether. The initial temperature of the reaction mixture was −70°; after an hour of stirring the mixture was allowed to warm to room temperature and then hydrolyzed with dilute hydrochloric acid. The ether layer was then separated and to it was added 15 cc. of ethanolamine in 15 cc. of methanol. Up to this point a

(2) R. L. Letsinger and I. H. Skoog, *J. Am. Chem. Soc.*, **77**, 2491, 5176 (1955). R. L. Letsinger and N. Remes, *J. Am. Chem. Soc.*, **77**, 2489 (1955).