tracted with two 40-ml. portions of boiling pyridine. These filtered extracts upon concentration and cooling gave 0.8 g. (39%) of a light cream-colored solid melting over the range 322–326°. Upon recrystallization from nitrobenzene a white, fluffy solid resulted, m.p. 325.5–326.5°. A mixture with authentic 2-bromophenanthridone melted undepressed. Moreover, the infrared spectrum of this product was identical with that of 2-bromophenanthridone.[11]

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[11] The authors wish to express their thanks to Dr. V. A. Fassel and Mr. Robert McCord of the Institute for Atomic Research for the infrared analyses.

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## A Silicon Analog of 9,9-Diphenylfluorene

BY HENRY GILMAN AND RICHARD D. GORSICH

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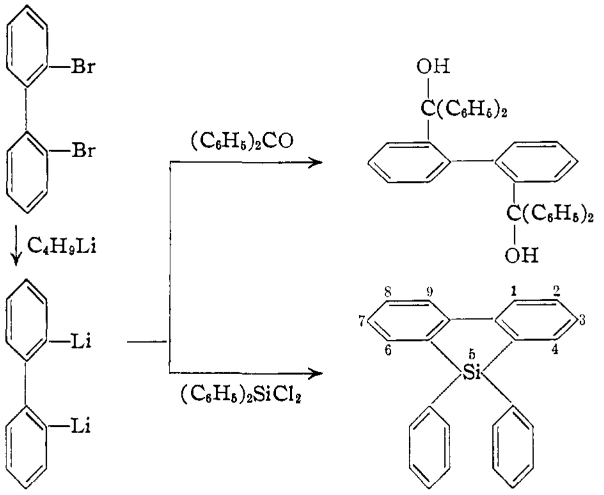
In connection with the preparation of some thermally stable and high boiling tetrasubstituted silanes, it was desirable to investigate new types such as the silicon analog of 9,9-diphenylfluorene. The compound reported here appears to be the first cyclic compound in which silicon is attached to four aromatic nuclei.

Previously several investigators reported some aliphatic cyclic systems containing silicon as the hetero atom. Some of these latter types together with the new type being reported here are highly strained. For example, Sommer and Baum[1] prepared the highly strained 1,1-dimethyl-1-silacyclobutane while West[2] synthesized a similarly strained cyclic compound, 3,3-dicarbethoxy-1,1-dimethyl-1-silacyclobutane. Other less strained aliphatic cyclic silicon compounds including spirane types have been reported.[3–5]

This novel cyclic organosilicon compound which, according to all evidence appears to be 5,5-diphenyldibenzosilole (or diphenyl-2,2′-biphenylenesilane) (I), was prepared by the interaction of 2,2′-dilithiobiphenyl with one equivalent of diphenyldichlorosilane. One of the chlorine atoms appeared to be displaced quite easily by adding the diphenyldichlorosilane to the refluxing ethereal solution of the organolithium compound. To effect ring closure, a reaction temperature higher than that afforded by refluxing ether was employed.

The 2,2′-dilithiobiphenyl was prepared by a halogen–metal interconversion reaction between 2,2′-dibromobiphenyl and two equivalents of *n*-butyllithium. In order to obtain an estimate of the yield of the new organodilithium compound, it was converted to the benzophenone adduct in a yield of about 70%.

Purification of the cyclic silicon compound was somewhat difficult due to the presence of an as yet unidentified silicon-containing compound melting at 228–229°. The evidence thus far indicates that the unknown compound might be one in which six phenyl groups are arranged in some manner about the silicon atom.



I

The Fisher–Hirschfelder–Taylor models indicated that the formation of I would require considerable deformation of the silicon bonds and they further indicated that some other less highly strained types might be formed. However, the formation of a monocyclic silicon compound is compatible with recent evidence indicating that the bond angles at a silicon atom appear to be much more easily deformed than the bond angles at a carbon atom.[2]

5,5-Diphenyldibenzosilole appears to be a fairly thermally stable compound. It volatilizes[6] at about 445° in comparison to tetraphenylsilane which has been reported to boil at 428°.[7] The melting point of the cyclic silicon compound (148°) is considerably lower than that of tetraphenylsilane (233°). It is also interesting to compare this cyclic silicon compound with its carbon analog (9,9-diphenylfluorene). The silicon compound not only melts lower than its carbon analog, but also volatilizes at a higher temperature. The carbon analog melts at 223° and has been found to volatilize at approximately 425°.[6] The cyclic silicon compound showed no change in melting point after being volatilized, indicating that very little decomposition occurred.

### Experimental[8]

**2,2′-Dilithiobiphenyl and Benzophenone.**—To a rapidly stirred solution of 4 g. (0.0129 mole) of 2,2′-dibromobiphenyl in 40 ml. of anhydrous ether was slowly added, over a period of 5 minutes, 26 ml. of an ethereal solution containing 0.028 mole of *n*-butyllithium[9] (determined by the double titration method[10]). The reaction mixture was cooled by an ice-bath during the addition. After stirring the reaction mixture at room temperature for 5 hours, a solution of 4.70 g. (0.0258 mole) of benzophenone in 50 ml. of ether was added in 10-ml. portions until a negative Color Test I[11] was obtained. This occurred when approximately 0.019 mole of the benzophenone solution had been added. The reaction mixture was hydrolyzed with dilute hydrochloric acid

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[1] L. H. Sommer and G. H. Baum, THIS JOURNAL, **76**, 5002 (1954).

[2] R. West, *ibid.*, **77**, 2339 (1955).

[3] R. West, *ibid.*, **76**, 6012 (1954).

[4] A. Bygden, *Ber.*, **48**, 1236 (1915).

[5] G. Grüttner and M. Wiernik, *ibid.*, **48**, 1474 (1915).

[6] The volatilizations were run in a copper melting point block containing three shafts sufficiently large to accommodate melting point capillary tubes.

[7] R. N. Lewis and A. E. Newkirk, THIS JOURNAL, **69**, 701 (1947).

[8] All reactions were carried out in an atmosphere of dry, oxygen-free nitrogen and all melting points are uncorrected.

[9] H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, THIS JOURNAL, **71**, 1499 (1949).

[10] H. Gilman and A. H. Haubein, *ibid.*, **66**, 1515 (1944).

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

and the resulting white, granular, ether-insoluble material was filtered and air-dried to give 4.70 g. (70%) of product melting at 250.5–253°. A crystallization from ethanol gave 4.30 g. (64%) of material melting at 253–255°. Two recrystallizations from the same solvent resulted in a product melting at 255.5–256.5°. The melting point of the benzophenone adduct has been reported by earlier workers to be 253°.[12,13]

**2,2′-Dilithiobiphenyl and Diphenyldichlorosilane.**—To a rapidly stirred solution of 10 g. (0.032 mole) of 2,2′-dibromobiphenyl in 50 ml. of ether was added slowly 47 ml. of a 1.31 *N* *n*-butyllithium solution. The reaction mixture was stirred at room temperature for 4.5 hours after which time Color Test II[14] was negative. To the refluxing organolithium solution was added, over a 15-minute period, a solution of 8.10 g. (0.032 mole) of diphenyldichlorosilane in 35 ml. of ether. Shortly after the addition was begun, a large amount of salt formation was noted. The refluxing was continued for one hour after which time Color Test I was strongly positive. Subsequently, 90 ml. of sodium-dried benzene was added to the reaction mixture and the ether was distilled until a temperature of 59° was reached. After stirring at this temperature for 0.5 hour, more ether was distilled until a temperature of 63° was attained. Subsequent to refluxing 30 minutes at this temperature, Color Test I began to decrease in intensity and in another 30 minutes it was negative. The reaction mixture was hydrolyzed with water and the two resulting phases were separated. After washing the aqueous layer twice with ether, the combined organic layer was dried over anhydrous sodium sulfate, and the solvents removed; upon cooling, the residue solidified. Most of the crude material was dissolved in refluxing petroleum ether (b.p. 60–70°).[15] The material which did not dissolve after several minutes of refluxing was decanted and dried to give 0.50 g. of material melting over the range 210–215°. From the petroleum ether there crystallized 4.33 g. (49%) of slightly impure 5,5-diphenyldibenzosilole melting at 142–145°. The presence of a second compound was quite evident when the mixture was recrystallized from ethanol since from this solvent there were obtained two distinct crystalline types. Two different crystal types were also obtained from petroleum ether but in this case the difference was not so obvious.

Further purification was achieved by dissolving most of the impure cyclic silicon compound in warm but not refluxing petroleum ether. The petroleum ether solution was decanted from the insoluble solid and allowed to cool. The cyclic silicon compound crystallized first and as soon as the second type of crystals began to appear the solution was filtered to give, after drying, 2.10 g. of product melting at 147–148°. Two subsequent recrystallizations from petroleum ether and ethanol, respectively, gave a material melting at 148–149°.

The material melting over the range 210–215° was crystallized twice from ethanol to give white needles melting at 228–229°. More of this same material was obtained by fractionally crystallizing the residue resulting on removal of the solvent from the filtrates of the cyclic silicon compound. The combined residues were first crystallized from ethanol to give a material melting over the range 145–170°. The material was placed in warm petroleum ether and the insoluble needles were filtered. The needles were recrystallized from ethanol to give additional product melting at 229–230°. By repeating this process several times with the impure cyclic silicon compound there was finally obtained a total yield of 0.5 g. of material melting at 229–230° and an additional 1.1 g. of 5,5-diphenyldibenzosilole. The total yield of pure cyclic silicon compound was 3.1 g. (31%).

*Anal.* Calcd. for $C_{24}H_{18}Si$: C, 86.19; H, 5.43; Si, 8.39; mol. wt., 334. Found: C, 86.06, 85.91; H, 5.58, 5.77; Si, 8.38; mol. wt., 318, 326, 315 (Rast), 321 (Signer).

In another run employing *n*-heptane rather than benzene as one of the solvents to obtain an elevated temperature, the yield of 5,5-diphenyldibenzosilole was comparable to the yield mentioned above. In this particular run an attempt was made to separate the high melting compound by chromatographing the material on a column of alumina. This procedure did not result in any clean-cut separation of the two compounds.

*Anal. of the high-melting, silicon-containing compound.* Found: C, 88.68, 88.60; H, 5.53, 5.42; Si, 5.6; mol. wt., 462, 447.

The above analyses together with the molecular weight determinations indicated that the compound might be bis-(2-biphenylyl)-diphenylsilane, a compound which could quite possibly be formed in the reaction. However, the latter compound has been synthesized from 2-biphenylyllithium and diphenyldichlorosilane and has been reported to melt at 137–137.5°.[16] A comparison of the infrared spectra also indicated the compounds to be different. This compound is being investigated further.

**Acknowledgment.**—The authors wish to express their appreciation to the Materials Laboratory, Wright Air Development Center, Wright–Patterson Air Force Base, Ohio, for financial assistance. They also are grateful to the Institute for Atomic Research, Iowa State College, and Dr. V. A. Fassel and R. McCord for assistance in the infrared determinations.

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[12] A. E. Tschitschibabin and P. G. Sergejeff, *Ber.*, **59**, 654 (1926).

[13] G. Wittig and M. Leo, *ibid.*, **64**, 2395 (1931).

[14] H. Gilman and J. Swiss, THIS JOURNAL, **62**, 1847 (1940).

[15] Throughout the remaining text the petroleum ether referred to is that which boils over the range 60–70°.

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

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## Synthesis of Thymine (Methyl-$C^{14}$)[1]

BY ROBERT B. HENDERSON, R. M. FINK AND KAY FINK

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Labeled thymine has been prepared with $N^{15}$ in the 1- and 3-positions[2] and with $C^{14}$ in the 2-position[3] and this note describes the synthesis of thymine (methyl-$C^{14}$). Because this compound was to be used in biological experiments in which filter paper chromatography was the analytical procedure, thymine with a high specific activity was desired in order to facilitate detection of spots representing only a few micrograms of metabolites. To avoid the expedient of diluting the radioactive starting material with inactive compound, a synthesis[4] was adapted for use on a milligram scale to give acceptable yields of radiothymine (5-methyl-$C^{14}$-uracil) starting with sodium propionate-3-$C^{14}$. The propionate, as ethyl propionate, was condensed with diethyl oxalate; the oxalopropionate was hydrogenated to $\beta$-methyl malate; and saponification gave $\beta$-methylmalic acid, which was condensed with urea to produce thymine. In the case of the small scale runs, all reactions from the ester condensation step onward were carried out in one flask with the only purification of reaction products being the pumping off of volatiles.

Using gram quantities of materials and purifying at some steps an over-all yield of about 30% was obtained—governed by the ester condensation and urea–methylmalic acid reactions, which resulted in 60–70% and 50–55% yields, respectively—but on a milligram scale the net yield was only about 10%.

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[1] This investigation was aided by Cancer Research Funds of the University of California and by research grant No. C-1669 from the National Cancer Institute, National Institutes of Health, U. S. P. H. S.

[2] A. A. Plentl and R. Schoenheimer, *J. Biol. Chem.*, **153**, 203 (1944).

[3] L. L. Bennett, Jr., THIS JOURNAL, **74**, 2432 (1952).

[4] (a) D. Davidson and O. Baudisch, *ibid.*, **48**, 2379 (1926); (b) H. M. Scherp, *ibid.*, **68**, 912 (1946).