ligroin (b.p. 60–70°) gave the product in 64% yield, m.p. 172–174°. A sample recrystallized for analysis melted at 174–175°.

Anal. Calcd. for $C_{14}H_{18}N_2O$: C, 73.01; H, 7.88. Found: C, 73.31; H, 7.82.

DETROIT 32, MICHIGAN

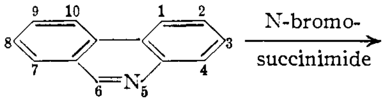
The Bromination of Phenanthridine

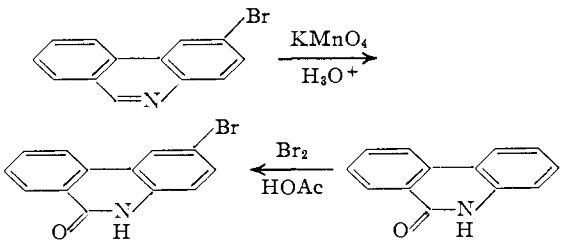
BY HENRY GILMAN AND JOHN EISCH

RECEIVED JULY 5, 1955

In the study of the substitutional chemistry of phenanthridine in relation to other aza-aromatic heterocycles, it was considered of interest to attempt the bromination of this heterocycle. Contrasted with the nitration and sulfonation of quinoline which occur in the benzenoid ring, the bromination of quinoline takes place preferentially in the pyridinoid ring beta to the nitrogen.[1] Since the pyridinoid ring in phenanthridine has no available position beta to the nitrogen, the position assumed by the entering bromine atom might help to elucidate the factors determining the exceptional selectivity of bromination.

As no previous direct bromination of phenanthridine has been reported in the literature, the observation that phenanthridine and N-bromosuccinimide afforded a moderate yield of a monobromophenanthridine is significant. The proof of structure of this compound was accomplished by oxidation with potassium permanganate in acid solution to give the corresponding bromophenanthridone.[2] The latter compound was shown to be identical with 2-bromophenanthridone by a mixed melting point determination and comparison of infrared spectra. The authentic 2-bromophenanthridone was obtained by the bromination of phenanthridone. That phenanthridone yields the 2-isomer upon bromination was recently demonstrated by Mosby[3] and confirmed by independent studies in this Laboratory.[4] These reactions leading to the conclusion that the monobromophenanthridine is the 2-isomer are summarized in the following equations[5]





The bromination of phenanthridine is still under study in order to determine optimal preparative conditions and to search for isomeric bromophenanthridines.[6] However, it can be noted at this stage that bromination of phenanthridine seems more selective than nitration where as many as six mononitrophenanthridines result.[2] It is also probable that the actual bromination of the heterocycle is of an electrophilic nature. If the bromination were to proceed by a free-radical mechanism, one would expect 6-bromophenanthridine to be a major product, by analogy with pyridine and quinoline.[7] In addition, the pyrolysis of phenanthridine hydrobromide perbromide has also resulted in the formation of 2-bromophenanthridine.[8]

Experimental[9]

2-Bromophenanthridone.—This compound was prepared by the bromination of phenanthridone in essential accordance with the directions of Mosby.[3] After two recrystallizations from nitrobenzene the white solid melted at 325.5–326.5°.

2-Bromophenanthridine.—In a 500-ml., 3-necked flask fitted with condenser and sealed stirrer were placed 17.9 g. (0.100 mole) of phenanthridine, 17.8 g. (0.100 mole) of N-bromosuccinimide and 125 ml. of carbon tetrachloride. The contents were stirred under reflux for 41 hours,[10] during which time the original cream-colored suspension changed to a reddish-brown solution and the walls of the flask were coated with an orange gum. An acidified sample still gave a positive blue color test with starch–iodide paper at the end of this period.

After 50 ml. of benzene was added, the reaction mixture was warmed and filtered. The golden orange filtrate was concentrated to 100 ml. and set aside to cool. A cream-colored crop of needles weighing 10.2 g. (40%) was obtained which melted over the range 140–155°. Two recrystallizations from 95% ethanol raised the melting point to 160–162.5°. An analytical sample crystallized as colorless needles from the same solvent, m.p. 162.0–163.0°. It was insoluble in warm sodium hydroxide solution, but soluble in warm, dilute hydrochloric acid.

Anal. Calcd. for $C_{13}H_8BrN$: Br, 30.96; N, 5.43. Found: Br, 30.98, 30.96; N, 5.50, 5.29.

Oxidation of 2-Bromophenanthridine.—2-Bromophenanthridine (2.0 g.), 5 ml. of concentrated sulfuric acid and 55 ml. of water were warmed to attain solution. Over a 30-minute period 3.2 g. of solid potassium permanganate was added portionwise. The color of the permanganate was continuously discharged upon warming the stirred mixture. Effervescence and the odor of free bromine indicated that oxidative degradation of the molecule occurred as a side reaction. After two hours the brown suspension was filtered. When the solid was thoroughly dried, it was ex-

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(1) 3-Bromoquinoline results from heating quinoline with bromine and sulfur (A. Edinger, *J. prakt. Chem.*, [2] **54**, 357 (1896)) or from heating quinoline hydrochloride perbromide (W. LaCoste, *Ber.*, **14**, 915 (1881)). Higher temperatures favor attack at the 2-position; *cf.* reference 6a.

(2) A procedure employed to convert nitrophenanthridines to nitrophenanthridones by A. G. Caldwell and L. P. Walls, *J. Chem. Soc.*, 2156 (1952).

(3) W. L. Mosby, THIS JOURNAL, **76**, 936 (1954).

(4) The authors have found that Walls' "yellow 2-bromophenanthridone" (obtained by dichromate oxidation of 2-bromo-6-methylphenanthridine) is highly impure 2-bromophenanthridone. By careful purification white 2-bromophenanthridone was isolated and found to be identical with the bromination product of phenanthridone. The yellow impurity in Walls' product is a substance melting at 301–303°. Its infrared spectrum has a pronounced carbonyl band at 5.9 μ and lacks an -N-H band in the 2.9–3.1 μ region.

(5) The numbering system for phenanthridine employed in this paper is that of *Chemical Abstracts.*

(6) The reaction of N-bromosuccinimide with acridine was found to give a difficultly separable mixture of bromoacridines and succinimidoacridines. *Cf.* H. Schmidt and W. E. Leutenegger, *Helv. Chim. Acta*, **30**, 1965 (1947).

(7) (a) J. P. Wibaut and H. J. Den Hertog, *Rec. trav. chim.*, **64**, 55 (1945); (b) H. E. Jansen and J. P. Wibaut, *ibid.*, **56**, 699 (1937).

(8) Unpublished studies of this Laboratory.

(9) All melting points were taken in capillaries inserted in an electrically heated copper block and are corrected.

(10) In certain runs a 100-watt bulb was employed to illuminate the reaction mixture, but a subsequent run from which light was rigidly excluded gave comparable results.

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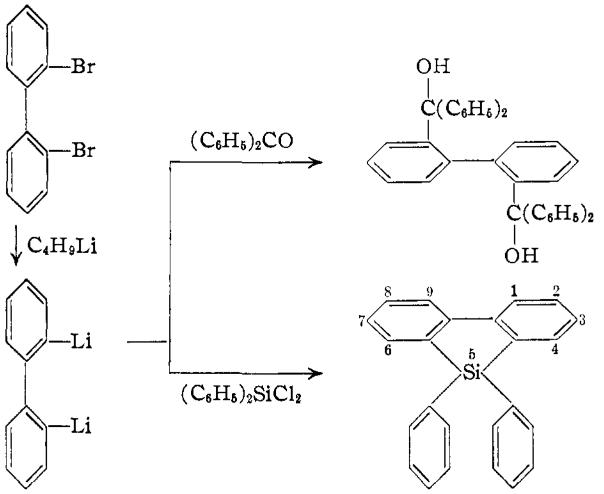
In connection with the preparation of some thermally stable and high boiling tetrasubstituted silanes, it was desirable to investigate new types such as the silicon analog of 9,9-diphenylfluorene. The compound reported here appears to be the first cyclic compound in which silicon is attached to four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