

was placed in the freezer (-20°). The crystalline material which separated was collected (3.0 g.) and recrystallized from acetonitrile to yield 2.3 g. (55% yield) of the pure salt. The infrared spectrum was identical to that of an authentic sample of this salt.⁴

B. Tetraethyl Ethylenetetracarboxylate (II).—The following reaction illustrates a typical procedure, and the pertinent data for the other reactions can be found in Table I.

A solution of diethyl dibromomalonate (8.0 g., 0.025 mole) and sodium trichloroacetate (4.7 g., 0.025 mole) in 25 ml. of 1,2-dimethoxyethane was refluxed under a nitrogen atmosphere for 1 hr. The v.p.c. analysis of the mixture using a 12-ft. column of 20% tritolyol phosphate on chromosorb W indicated the presence of 2% carbon tetrachloride and 10% bromotrichloromethane in the solvent (raw data). The precipitated salt was filtered from the hot solution and washed with ether. The solvent was removed *in vacuo* and an ethanol-hexane mixture (20 ml.) was added to the resultant red oil. After standing in the freezer overnight, pale yellow crystals separated. Recrystallization from ethanol-hexane yielded 2.6 g. (66% yield) of the pure product of m.p. $52-53^{\circ}$ (lit.⁹ m.p. $52-53^{\circ}$).

C. Triethyl 1,2,3-Tricyanocyclopropane-1,2,3-tricarboxylate (III).—Ethyl bromocycanoacetate (10 g., 0.05 mole) and sodium trichloroacetate (9.7 g., 0.05 mole) were refluxed in 50 ml. of 1,2-dimethoxyethane under a nitrogen atmosphere for 1 hr. The solid (3.0 g.) was filtered from the hot solution and washed with hot solvent. The filtrate was concentrated to a red oil. Ethanol (15 ml.) was added and the mixture was allowed to stand in the freezer overnight. The crystalline solid was collected (3.5 g., 50% yield) and had m.p. $122-123^{\circ}$ (lit. m.p. $122-123^{\circ}$). The infrared spectrum was identical to that of an independently prepared sample.⁷

The ethyl dibromocycanoacetate run was performed in the same manner using a longer reflux period.

Acknowledgment.—This research was supported in part from a grant from the National Science Foundation (NSF G-19490).

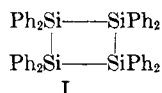
Reaction of Octaphenylcyclotetrasilane with Mercuric Acetate

HENRY GILMAN AND WILLIAM H. ATWELL

Department of Chemistry, Iowa State University, Ames, Iowa

Received May 6, 1963

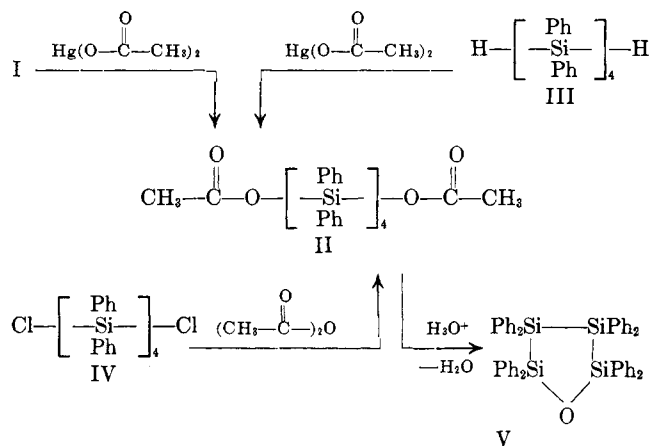
Among the compounds isolated by Kipping from the reaction of dichlorodiphenylsilane with sodium, was a material which he designated as compound "A".¹ In order to explain the high reactivity of this compound in free radical-type reactions, he assigned to Compound "A" a biradical structure ($\dots\text{SiPh}_2\text{SiPh}_2\text{SiPh}_2\text{SiPh}_2\dots$).^{1,2} However, this compound has recently been shown to be octaphenylcyclotetrasilane (I).³ The high reactivity



of I has been attributed to the strained four-membered ring system. For example, I is readily cleaved by certain metal⁴ and nonmetal⁵ halides, halogens,^{3b,6} organometallic compounds,⁷ and by numerous polyhalo-

organic compounds.⁶ In addition, I was found to reduce an ethanolic silver nitrate solution at room temperature.⁵ A similar reduction previously has been reported for the strained ring compounds, 1,1,3,3-tetramethyl-1,3-disilacyclobutane.⁸ Under the same conditions, we obtained no observable reduction with decaphenylcyclopentasilane.⁹

We now wish to report the cleavage of I by mercuric acetate to give 1,4-diacetoxy-1,1,2,2,3,3,4,4-octaphenyltetrasilane (II). An alternate synthesis of II was achieved by heating 1,1,2,2,3,3,4,4-octaphenyltetrasilane (III)¹⁰ and mercuric acetate in glacial acetic acid.¹¹ In addition, II was obtained by refluxing the previously described 1,4-dichloro-1,1,2,2,3,3,4,4-octaphenyltetrasilane (IV)^{2b,3} in acetic anhydride.¹² Further proof of structure was obtained by hydrolysis of II to the monoxide V.¹³



The infrared and n.m.r. spectra of II also were examined and found to be in agreement with the proposed structure.

When either hexaphenyldisilane or decaphenylcyclopentasilane⁹ was treated with mercuric acetate under even more forcing conditions, the starting materials were recovered in good yields. Under such conditions where silicon-silicon bond cleavage is not observed, it may be possible to employ mercuric acetate to effect nuclear substitution.¹⁴

Experimental¹⁵

1,4-Diacetoxy-1,1,2,2,3,3,4,4-octaphenyltetrasilane (II). From Octaphenylcyclotetrasilane (I) and Mercuric Acetate.—Fifteen grams (0.02 mole) of octaphenylcyclotetrasilane and 13.1 g. (0.041 mole) of mercuric acetate in ca. 150 ml. of sodium-dried benzene were heated at reflux for 24 hr. A small amount of mercury was observed on the bottom of the flask. The tan mixture was cooled and filtered. Evaporation of the solvent gave 16.62 g. (95.8%) of a light yellow solid, m.p. $212-234^{\circ}$. Recrystallization from a mixture of benzene and petroleum ether (b.p. $60-70^{\circ}$) gave 13.1 g. (79%) of a white solid, m.p. $233-235^{\circ}$.

(7) A. W. P. Jarvie and H. Gilman, *J. Org. Chem.*, **26**, 1999 (1961).

(8) W. H. Knoth, Jr., and R. V. Lindsey, Jr., *ibid.*, **23**, 1392 (1958).

(9) H. Gilman and G. L. Schwabke, *J. Am. Chem. Soc.*, **85**, 1016 (1963).

(10) H. J. S. Winkler and H. Gilman, *J. Org. Chem.*, **27**, 254 (1962).

(11) For similar reactions of this type see B. N. Polgov, N. P. Khari-tanov, and M. G. Voronkov, *Zh. Obshch. Khim.*, **24**, 861 (1954); *Chem. Abstr.*, **49**, 8094 (1955).

(12) For a general method see N. S. Nametkin, A. V. Topchiev, and F. F. Machus, *Dokl. Akad. Nauk, SSSR*, **87**, 233 (1952); *Chem. Abstr.*, **47**, 12,281 (1953).

(13) A. W. P. Jarvie, H. J. S. Winkler, and H. Gilman, *J. Org. Chem.*, **27**, 614 (1962).

(14) K. A. Kobe and P. F. Lueth, Jr., *Ind. Eng. Chem.*, **34**, 309 (1942).

(15) All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen and all melting points are uncorrected.

(1) F. S. Kipping and J. E. Sands, *J. Chem. Soc.*, **119**, 830, 848 (1921).

(2) (a) F. S. Kipping, *ibid.*, **123**, 2590 (1923); (b) **125**, 2291 (1924).

(3) (a) H. Gilman, D. J. Peterson, A. W. P. Jarvie, and H. J. S. Winkler, *J. Am. Chem. Soc.*, **82**, 2076 (1960); (b) A. W. P. Jarvie, H. J. S. Winkler, D. J. Peterson, and H. Gilman, *ibid.*, **83**, 1921 (1961).

(4) H. Gilman and A. W. P. Jarvie, *Chem. Ind. (London)*, 965 (1960).

(5) W. H. Atwell, unpublished studies.

(6) J. M. Kraemer, unpublished studies.

This material was heated under vacuum at 100° for 1 hr. prior to analysis.

Anal. Calcd. for $C_{22}H_{16}O_4Si_4$: C, 73.79; H, 5.43; Si, 13.26. Found: C, 73.97, 73.98; H, 5.63, 5.54; Si, 13.20, 13.15.

The infrared spectrum showed the bands at 5.8 and 8.2 μ characteristic of the acetate group.¹⁶ The n.m.r. spectrum gave a ratio of aromatic to aliphatic protons of 6.57 (calculated value, 6.67). The methyl groups gave the expected singlet which appeared at 8.28 τ .

From 1,1,2,2,3,3,4,4-Octaphenyltetrasilane (III) and Mercuric Acetate.—A mixture of 3.0 g. (0.0041 mole) of 1,1,2,2,3,3,4,4-octaphenyltetrasilane and 2.58 g. (0.0082 mole) of mercuric acetate in 100 ml. of glacial acetic acid was refluxed for 12 hr. Filtration of the cooled reaction mixture gave 1.3 g. (79%) of mercury and 3.3 g. (95.5%) of a white solid, m.p. 205–230°. Recrystallization of this material from benzene-petroleum ether (b.p. 60–70°) afforded 2.5 g. (72%) of product, m.p. 233–235°. A mixture melting point with an authentic sample of 1,4-diacetoxy-1,1,2,2,3,3,4,4-octaphenyltetrasilane was not depressed and the infrared spectra were superimposable.

From 1,4-Dichloro-1,1,2,2,3,3,4,4-octaphenyltetrasilane (IV) and Acetic Anhydride.—A mixture of 5.0 g. (0.00625 mole) of 1,4-dichloro-1,1,2,2,3,3,4,4-octaphenyltetrasilane in 50 ml. of acetic anhydride was refluxed for 24 hr. Filtration gave 4.0 g. (80%) of unchanged starting material, m.p. 185–187° (m.m.p.). Evaporation of the solvent from the filtrate gave 0.85 g. (16%) of white solid, m.p. 230–235°. Recrystallization from benzene-petroleum ether (b.p. 60–70°) afforded 0.75 g. (14%) of product, m.p. 233–235° (m.m.p.).

Hydrolysis of 1,4-Diacetoxy-1,1,2,2,3,3,4,4-octaphenyltetrasilane (II).—A mixture of 3.0 g. (0.0035 mole) of 1,4-diacetoxy-1,1,2,2,3,3,4,4-octaphenyltetrasilane and 50 ml. of ca. 0.5 N hydrochloric acid was refluxed for 48 hr. Filtration gave 2.5 g. (91.2%) of white solid, m.p. 230–234°. Recrystallization from benzene-petroleum ether (b.p. 60–70°) raised the melting point to 234–236° (87%). A mixture melting point with an authentic sample of monoxide was not depressed. The infrared spectrum showed the strong band at 10.45 μ previously reported for this strained cyclic siloxane.¹³

Reaction of Hexaphenyldisilane with Mercuric Acetate (Attempted).—A mixture of 5.2 g. (0.01 mole) of hexaphenyldisilane and 6.37 g. (0.02 mole) of mercuric acetate in 100 ml. of sodium-dried benzene was refluxed for 72 hr. Filtration gave 8.0 g. of solid, m.p. 270° dec. This material was extracted with hot water and filtered to give 5.0 g. (96%) of recovered starting material, m.p. 365–367° (m.m.p.).

Reaction of Decaphenylcyclopentasilane⁹ with Mercuric Acetate (Attempted).—A mixture of 10.0 g. (0.011 mole) of decaphenylcyclopentasilane and 7.01 g. (0.022 mole) of mercuric acetate in 100 ml. of sodium-dried benzene was refluxed for 72 hr. Filtration gave 11.0 g. of solid, m.p. 275° dec. Extraction of this material with acetone followed by filtration gave 8.5 g. (85%) of recovered starting material, m.p. 456–462° (m.m.p.). No other pure materials could be isolated.

Acknowledgment.—This research was supported by the United States Air Force under contract AF 33(616)-6463 monitored by the Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson AFB, Ohio. The authors are grateful to Dr. Roy King and Mrs. Ikue Ogawa for the n.m.r. and infrared spectral determinations.

(16) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., Methuen and Co., Ltd., London, 1958, pp. 179, 189.

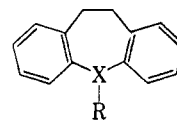
The Preparation of a Di-Grignard Reagent from 2,2'-Dibromodibenzyl

HENRY GILMAN AND WILLIAM H. ATWELL

Chemical Laboratory, Iowa State University, Ames, Iowa

Received April 2, 1963

Incidental to an interesting study concerned with the preparation of 10,11-dihydro-5-phenyldibenz[*b,f*]-



I, X = As, R = C_6H_5-
II, X = P, R = C_6H_5-

arsepin (I) and the analogous phosphepin (II), it was reported¹ that a di-Grignard reagent could not be prepared from 2,2'-dibromodibenzyl (III) in diethyl ether. In view of the subsequently established successes in preparing some Grignard reagents in tetrahydrofuran by the general procedure of H. Normant,² we examined this solvent as a reaction medium in place of diethyl ether.

We now wish to report that III reacts with magnesium in tetrahydrofuran to give a soluble di-Grignard reagent. Carbonation of this di-Grignard compound gave a 68% yield of dibenzyl-2,2'-dicarboxylic acid.³ In addition, reaction of the di-Grignard reagent with dichlorodiphenylsilane yielded the previously described 10,11-dihydro-5,5-diphenyldibenz[*b,f*]silepin (IV).⁴ The yield of IV, although low, was comparable to that obtained employing 2,2'-dilithiodibenzyl³ and dichlorodiphenylsilane.



Experimental⁵

Dibenzyl-2,2'-dicarboxylic Acid.—Five milliliters of a solution of 5 g. (0.0147 mole) of 2,2'-dibromodibenzyl in 50 ml. of tetrahydrofuran was added to 2.43 g. (0.1 g.-atom) of magnesium and 2–3 drops of ethyl iodide. The reaction mixture was refluxed for 5–10 min. at which time a gray color developed and color test I⁶ was positive. The external heat was removed and the addition was continued at a rate sufficient to maintain an exothermic reaction. After dissipation of the heat of reaction, the mixture was stirred for 1 hr., decanted through a glass wool plug into a Dry Ice-ether slurry, and allowed to warm to room temperature. Extraction of the organic layer with dilute base followed by acidification yielded 2.5 g. (68%) of dibenzyl-2,2'-dicarboxylic acid, m.p. 229–231° (lit.³ m.p. 226–228°).

10,11-Dihydro-5,5-diphenyldibenz[*b,f*]silepin.—A tetrahydrofuran solution containing 0.014 mole of the di-Grignard reagent was slowly added to 3.54 g. (0.014 mole) of dichlorodiphenylsilane in 40 ml. of tetrahydrofuran. Color test I⁶ was strongly positive after addition. The reaction mixture was refluxed gently for 24 hr. at which time the color test was negative. Acid hydrolysis followed by the usual work-up gave an oil which was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave 0.51 g. (10%) of product, m.p. 174–175°, after one recrystallization from ethanol-petroleum ether (b.p. 60–70°). A mixture melting point with a known sample⁴ was not depressed and the infrared spectra were identical.

We have found that the n.m.r. spectrum of this compound contains a sharp singlet at 6.83 τ with a relative area consistent with the presence of four benzylic protons. In addition, the aromatic

(1) F. G. Mann, I. T. Millar, and B. B. Smith, *J. Chem. Soc.*, 1130 (1953).

(2) See H. Normant, "Alkenylmagnesium Halides" in "Advances in Organic Chemistry," Vol. II, R. A. Raphael, E. C. Taylor, and H. Wynberg, Eds., Interscience Publishers, Inc., New York, N. Y., 1960, pp. 1–65.

(3) R. C. Fuson, *J. Am. Chem. Soc.*, **48**, 835 (1926).

(4) R. D. Gorsich, Ph.D. thesis, Iowa State University, 1957.

(5) Reactions involving organometallic reagents were carried out under an atmosphere of dry, oxygen-free nitrogen. The tetrahydrofuran was dried over sodium wire and distilled from lithium aluminum hydride immediately before use. All melting points are uncorrected.

(6) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).