

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

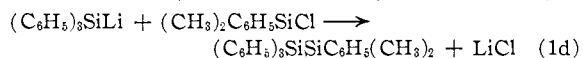
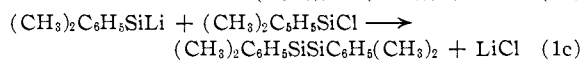
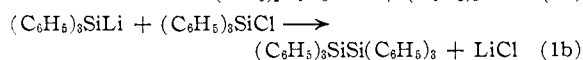
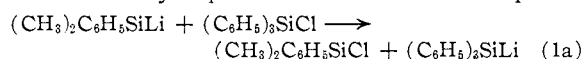
Cleavage Studies of Disilanes by Silyllithium Compounds

BY HENRY GILMAN, GLEN D. LICHTENWALTER AND DIETMAR WITTENBERG

RECEIVED APRIL 22, 1959

Cleavages of hexasubstituted disilanes by silyllithium compounds to give different disilanes and less reactive silyllithium compounds are described. Observations concerning the relative reactivities of silyllithium compounds are reported.

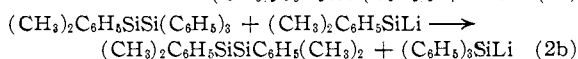
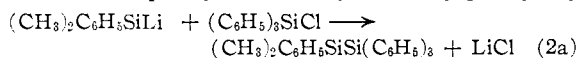
In an earlier paper¹ it was postulated that the formation of hexaphenyldisilane from the reactions of either methylphenylsilyllithium or dimethylphenylsilyllithium with chlorotriphenylsilane was thought to occur *via* a halogen-metal interconversion reaction. For instance, the reaction of dimethylphenylsilyllithium with chlorotriphenylsilane was illustrated by equation 1a. The various possible



coupling reactions could then give rise to hexaphenyldisilane, 1,1,2,2-tetramethyl-1,2-diphenyldisilane and 1,1-dimethyl-1,2,2,2-tetraphenyldisilane (1b, 1c, 1d). The last product was not isolated when the reaction was carried out by addition of chlorotriphenylsilane to dimethylphenylsilyllithium. By reversing the direction of addition, *i.e.*, adding dimethylphenylsilyllithium to chlorotriphenylsilane, good yields of 1,1-dimethyl-1,2,2,2-tetraphenyldisilane were obtained along with a small amount of hexaphenyldisilane.

In a similar manner, addition of methylphenylsilyllithium to chlorotriphenylsilane gave good yields of methylpentaphenyldisilane, whereas reversing the direction of addition gave hexaphenyldisilane, methylpentaphenyldisilane and 1,2-dimethyl-1,1,2,2-tetraphenyldisilane. While the concept of a halogen-metal interconversion reaction explains the formation of the products in these reactions, the importance of the direction of addition is left unanswered. In light of new evidence, an explanation based on the cleavage of disilanes by silylmetallic compounds may be advanced.

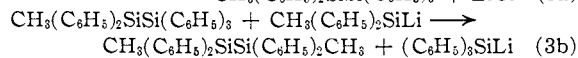
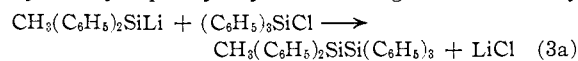
The reaction of dimethylphenylsilyllithium with chlorotriphenylsilane probably involves an initial coupling reaction to give 1,1-dimethyl-1,2,2,2-tetraphenyldisilane (2a), regardless of the direction of addition. In the presence of excess dimethylphenylsilyllithium, a second reaction (2b) takes place involving the cleavage of 1,1-dimethyl-1,2,2,2-tetraphenyldisilane by dimethylphenylsilyl-



lithium to give 1,1,2,2-tetramethyl-1,2-diphenyldisilane and triphenylsilyllithium. Hence, the fail-

ure to isolate 1,1-dimethyl-1,2,2,2-tetraphenyldisilane is not surprising. Hexaphenyldisilane arises through the reaction of triphenylsilyllithium with chlorotriphenylsilane (1b). When dimethylphenylsilyllithium is added to chlorotriphenylsilane, the latter compound is present in excess. The unsymmetrical coupling product, 1,1-dimethyl-1,2,2,2-tetraphenyldisilane, will be isolated from further cleavage and may be obtained in good yields.

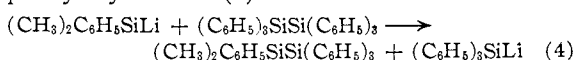
A similar argument may be presented for the formation of the products isolated from the addition of chlorotriphenylsilane to methylphenylsilyllithium. Methylpentaphenyldisilane, formed by an initial coupling reaction (3a), is cleaved further by methylphenylsilyllithium to give 1,2-dimethyl-



1,1,2,2-tetraphenyldisilane and triphenylsilyllithium (3b). In this case, however, some methylpentaphenyldisilane was isolated, which would indicate that cleavage of this compound by methylphenylsilyllithium is kinetically slower than the cleavage of 1,1-dimethyl-1,2,2,2-tetraphenyldisilane by dimethylphenylsilyllithium. This explanation is in line with an activity series for silyllithium compounds, presented later in this paper, in which methylphenylsilyllithium is shown to be less reactive than dimethylphenylsilyllithium. Hexaphenyldisilane is again formed by the reaction of chlorotriphenylsilane with triphenylsilyllithium (1b). Addition of methylphenylsilyllithium to chlorotriphenylsilane gave only the coupling product, methylpentaphenyldisilane.

Support for the hypotheses presented concerning the cleavage of disilanes by silyllithium compounds was obtained by cleavage of pre-formed disilanes with silyllithium compounds.

The addition of dimethylphenylsilyllithium to an equimolar suspension of hexaphenyldisilane in tetrahydrofuran gave a prompt reaction from which the products isolated were 1,1,2,2-tetramethyl-1,2-diphenyldisilane (56%), triphenylsilanol (21%) and hexaphenyldisilane (65% recovery). The formation of these products may be visualized as having occurred through the initial cleavage of hexaphenyldisilane by dimethylphenylsilyllithium to give 1,1-dimethyl-1,2,2,2-tetraphenyldisilane and triphenylsilyllithium (4).



Cleavage of 1,1-dimethyl-1,2,2,2-tetraphenyldisilane by a second molecule of dimethylphenylsilyllithium gives 1,1,2,2-tetramethyl-1,2-diphenyldisilane and triphenylsilyllithium (2b). Failure to iso-

(1) H. Gilman and G. D. Lichtenwalter, *THIS JOURNAL*, **80**, 608 (1958).

late 1,1-dimethyl-1,2,2,2-tetraphenyldisilane from the reaction mixture may be attributed to the difference in solubility of 1,1-dimethyl-1,2,2,2-tetraphenyldisilane and hexaphenyldisilane. The former compound is soluble in tetrahydrofuran and is cleaved as soon as it forms by dimethylphenylsilyllithium in preference to the highly insoluble hexaphenyldisilane.

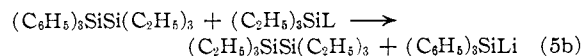
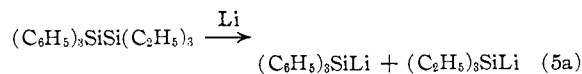
Treatment of 1,1-dimethyl-1,2,2,2-tetraphenyldisilane with one equivalent of dimethylphenylsilyllithium gave, after hydrolysis, triphenylsilanol (22%), 1,1,2,2-tetramethyl-1,2-diphenyldisilane (63%) and 1,1-dimethyl-1,2,2,2-tetraphenyldisilane (26% recovery).

From the reaction of methylphenylsilyllithium with hexaphenyldisilane (2:1 mole ratio), the products isolated were 1,2-dimethyl-1,1,2,2-tetraphenyldisilane (26%), triphenylsilane (59%), hexaphenyldisilane (22% recovery) and *ca.* 29% of a mixture of 1,2-dimethyl-1,1,2,2-tetraphenyldisilane and 1,1-dimethyl-1,2,2,2-tetraphenyldisilane.

Addition of dimethylphenylsilyllithium to 1,2-dimethyl-1,1,2,2-tetraphenyldisilane (2:1 mole ratio) gave, after acid hydrolysis, 1,1,2,2-tetramethyl-1,2-diphenyldisilane (45%) and methylphenylsilyllithium (77%).

Kraus and Nelson² described the preparation of triethylsilyllithium by way of the cleavage of triphenylgermyltriethylsilane with lithium in ethylamine. Recent experiments³ have shown, however, that silylmetallic compounds are instantly ammonolyzed by amines. Attempts to prepare stable solutions of trialkylsilylmetallic compounds have to date been unsuccessful,^{4,5} although a low yield of trimethylphenylsilane was obtained⁶ by the cleavage of 1,1,1-trimethyl-2,2,2-triphenyldisilane with sodium-potassium alloy in diethyl ether, followed by addition of bromobenzene.

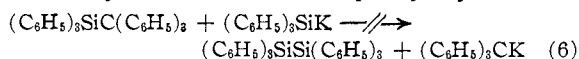
Evidence for the existence of a transient trialkylsilylmetallic compound is afforded by the cleavage of 1,1,1-triethyl-2,2,2-triphenyldisilane by lithium in tetrahydrofuran (5a). The products isolated from this reaction were, after acid hydrolysis, triphenylsilane (92%), triethylsilane (11%) and hexaethylsilane (14%). Isolation of the last compound clearly indicates the formation of triethylsilyllithium which by cleavage of 1,1,1-triethyl-2,2,2-triphenyldisilane gives hexaethylsilane (5b).



Assuming that the silicon-silicon bond strength remains about constant with varying numbers of alkyl and aryl substituents on the silicon atoms, on the basis of the cleavage reactions described, silyllithium compounds may be arranged in a reactivity series. $(\text{C}_6\text{H}_5)_3\text{SiLi} < \text{CH}_3(\text{C}_6\text{H}_5)_2\text{SiLi} < (\text{CH}_3)_2-$

$\text{C}_6\text{H}_5\text{SiLi} \ll (\text{C}_2\text{H}_5)_3\text{SiLi}$. As the number of alkyl groups on the silicon atom of the silyllithium compound increases, the reactivity increases.

It has been reported⁷ that the reaction of triphenylsilylpotassium with chlorotriphenylmethane, followed by carbonation of the reaction mixture, gives hexaphenyldisilane, hexaphenylethane (identified as the peroxide) and triphenylacetic acid. The formation of these products was postulated as having occurred *via* a halogen-metal interconversion reaction, followed by various coupling reactions. It is possible to visualize these products as having arisen by way of a cleavage reaction (6) similar to those described for disilanes. This alternative was tested by the addition of triphenylsilyllithium to



triphenylmethyltriphenylsilane, followed by carbonation of the reaction mixture. Following hydrolysis, no triphenylacetic acid was obtained from the aqueous layer. Recovery of triphenylmethyltriphenylsilane was 90%. It appears, therefore, that the products isolated from the reaction of triphenylsilylpotassium with chlorotriphenylmethane did indeed arise as the result of a halogen-metal interconversion reaction.

It is worthy of note that although disilanes are cleaved readily by silyllithium compounds, they are resistant to cleavage by organolithium compounds. Hexaphenyldisilane is unaffected by either phenyllithium in ether⁸ or *p*-tolyllithium⁹ in tetrahydrofuran.

Experimental¹⁰

Addition of Dimethylphenylsilyllithium to Hexaphenyldisilane.—To a stirred suspension of 9.85 g. (0.019 mole) of hexaphenyldisilane in 50 ml. of tetrahydrofuran (THF) was added 30 ml. of a THF solution of dimethylphenylsilyllithium prepared by the cleavage of 2.57 g. (0.0095 mole) of 1,1,2,2-tetramethyl-1,2-diphenyldisilane with excess lithium. Two hours after the addition was complete, the reaction mixture was hydrolyzed with water. From the organic layer was obtained 6.4 g. (65%) of recovered hexaphenyldisilane, m.p. 365–367° (mixed m.p.). The organic layer was dried and evaporated. The residual oil was treated with petroleum ether (b.p. 60–70°) to give 2.2 g. (21%) of triphenylsilanol, m.p. 154–156° (mixed m.p.). The petroleum ether was stripped off, and distillation of the residue afforded 1.43 g. (56%) of 1,1,2,2-tetramethyl-1,2-diphenyldisilane, b.p. 73° (0.01 mm.). The distillate solidified on seeding with an authentic specimen of 1,1,2,2-tetramethyl-1,2-diphenyldisilane. The infrared spectra were identical.

Addition of Dimethylphenylsilyllithium to 1,1-Dimethyl-1,2,2,2-tetraphenyldisilane.—To a solution of 10.0 g. (0.0254 mole) of 1,1-dimethyl-1,2,2,2-tetraphenyldisilane in 50 ml. of tetrahydrofuran (THF) was added 40 ml. of a THF solution of dimethylphenylsilyllithium prepared from 3.43 g. (0.0127 mole) of 1,1,2,2-tetramethyl-1,2-diphenyldisilane and excess lithium. After stirring overnight, the reaction mixture was hydrolyzed with water. From the dried organic layer was obtained an oil which on treatment with petroleum ether (b.p. 60–70°) gave 1.55 g. (22%) of triphenylsilanol, m.p. 154–156° (mixed m.p.). From the petroleum ether filtrate was obtained an oil which on distillation afforded 4.32 g. (63%) of 1,1,2,2-tetramethyl-1,2-diphenyldisilane, b.p. 76–81° (0.005 mm.), which crystallized

(2) C. A. Kraus and W. K. Nelson, *THIS JOURNAL*, **56**, 195 (1934).

(3) R. A. Benkeser, R. E. Robinson and H. Landesmann, *ibid.*, **74**, 5699 (1952); H. Gilman and G. D. Lichtenwalter, *ibid.*, **81**, 978 (1959).

(4) G. D. Lichtenwalter, unpublished studies.

(5) M. B. Hughes, unpublished studies.

(6) H. Gilman, R. K. Ingham and A. G. Smith, *J. Org. Chem.*, **18**, 1743 (1953).

(7) (a) A. G. Brook, H. Gilman and L. S. Miller, *THIS JOURNAL*, **75**, 4759 (1953); (b) for another case of halogen-metal interconversion in organosilicon chemistry see A. G. Brook and S. Wolfe, *ibid.*, **79**, 1431 (1957).

(8) G. E. Dunn, Doctoral Dissertation, Iowa State College, 1951.

(9) G. D. Lichtenwalter, unpublished studies.

(10) Reactions were carried out under an atmosphere of dry, oxygen-free nitrogen using dry glassware. Melting points are uncorrected.

on seeding with an authentic specimen. The infrared spectra were identical. The distillation residue was treated with ethanol to give 2.6 g. (26%) of recovered 1,1-dimethyl-1,2,2,2-tetraphenylidisilane, m.p. 81.5–83° (mixed m.p.).

Addition of Methylphenylsilyllithium to Hexaphenylidisilane.—To a stirred suspension of 7.9 g. (0.0152 mole) of hexaphenylidisilane in 25 ml. of tetrahydrofuran (THF) was added 80 ml. of a THF solution of methylphenylsilyllithium prepared by the cleavage of 6.0 g. (0.0152 mole) of 1,2-dimethyl-1,1,2,2-tetraphenylidisilane with excess lithium. One hour after the addition was complete, water was added, and filtration of the organic layer gave 1.73 g. (22%) of hexaphenylidisilane, m.p. 365–367° (mixed m.p.). The residue from the dried filtrate was dissolved in hot petroleum ether (b.p. 60–70°) and chromatographed on an alumina column. The petroleum ether fractions were collected. The first was evaporated to dryness and treated with ethanol to give 1.57 g. (26%) of 1,2-dimethyl-1,1,2,2-tetraphenylidisilane, m.p. 142–146°, identified by a mixed melting point with an authentic specimen. A mixed melting point with methylpentaphenylidisilane was depressed. The second petroleum ether fraction was treated similarly with ethanol to give 1.78 g. (ca. 29%) of solid, m. 121–133°. The melting point was not improved by recrystallization. The infrared spectrum indicated that this material was a mixture of 1,2-dimethyl-1,1,2,2-tetraphenylidisilane and methylpentaphenylidisilane, which are very difficult to separate.¹ The ethanol filtrates were combined and evaporated to give an oil. When chilled and seeded with triphenylsilane, the entire mass crystallized. The product weighed 4.7 g. (59.5%), m.p. 43–45°, and was shown by the infrared spectrum and mixed melting point to be triphenylsilane.

Addition of Dimethylphenylsilyllithium to 1,2-Dimethyl-1,1,2,2-tetraphenylidisilane.—To a solution of 11.7 g. (0.0296 mole) of 1,2-dimethyl-1,1,2,2-tetraphenylidisilane in 75 ml. of tetrahydrofuran (THF) was added 70 ml. of a THF solution of dimethylphenylsilyllithium prepared by the cleavage of 8.0 g. (0.0296 mole) of 1,1,2,2-tetramethyl-1,2-diphenylidisilane with excess lithium. Thirty minutes after the addition was complete, the reaction mixture was poured into cold hydrochloric acid. From the dried organic layer was obtained an oil which was distilled to give 9.06 g. (77.5%) of methylphenylsilane, b.p. 79° (0.1 mm.), n_D^{20} 1.5694 (reported b.p. 82° (0.15 mm.), n_D^{20} 1.5747¹¹; b.p. 137–139° (14 mm.), n_D^{20} 1.5724¹²). The identity of the silane was further confirmed by the infrared spectrum which showed a strong Si-H absorption band at 4.7 μ . A second fraction boiling at 96–98° (0.1 mm.), 3.6 g. (45%), crystallized on seeding with 1,1,2,2-tetramethyl-1,2-diphenylidisilane and was shown to be this compound by the infrared spectrum.

- (11) R. A. Benkeser and D. J. Foster, *THIS JOURNAL*, **74**, 5314 (1952).
 (12) R. D. Gorsich, Doctoral Dissertation, Iowa State College, 1957.

Lithium Cleavage of 1,1,1-Triethyl-2,2,2-triphenylidisilane.—One hundred milliliters of tetrahydrofuran was added slowly to a stirred mixture of 15.0 g. (0.040 mole) of 1,1,1-triethyl-2,2,2-triphenylidisilane and 2.5 g. (0.36 g. atom) of finely-cut lithium wire. The reaction started immediately; the deep colored solution gave a positive Color Test I.¹³ During the addition, the flask was cooled in an ice-bath. The reaction mixture was stirred for 45 min. at 0° and allowed to warm to room temperature over a period of 30 min. Subsequent to hydrolysis with dilute acid, addition of some ether, extraction with water, and drying of the organic layer over sodium sulfate, the product was distilled. There was obtained 0.5 g. (11%) of triethylsilane, b.p. 30–35° (15 mm.), identified by the infrared spectrum; 0.65 g. (14%) of hexaethylidisilane, b.p. 103–108° (15 mm.), identified by the infrared spectrum; and 9.45 g. (92%) of slightly impure triphenylsilane, b.p. 142–148° (0.2 mm.). The infrared spectrum of the last compound indicated the presence of an impurity containing aliphatic C—H bonds. Attempts to isolate additional products by use of chromatography or recrystallization failed.

Cleavage of Triphenylmethyltriphenylsilane by Triphenylsilyllithium (Attempted).—To a stirred suspension of 3.0 g. (0.00597 mole) of triphenylmethyltriphenylsilane in 20 ml. of tetrahydrofuran (THF) was added 25 ml. of a THF solution of triphenylsilyllithium prepared by cleavage of 2.08 g. (0.004 mole) of hexaphenylidisilane. After one hour, the reaction mixture was carbonated by pouring jet-wise into a slurry of Dry Ice and ether. The carbonated mixture was allowed to stand for two hours to ensure complete decomposition of lithium triphenylsilanecarboxylate to the lithium salt of triphenylsilanol and carbon monoxide.¹⁴ The mixture was then shaken with 10% sodium hydroxide. Acidification of the aqueous layer gave no acid. From the organic layer was filtered 2.71 g. (90%) of recovered triphenylmethyltriphenylsilane, m.p. 317–325° dec. A mixed melting point with an authentic specimen was not depressed.

Acknowledgment.—This research was supported in part by the United States Air Force under Contract AF 33(616)-3510 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson AFB, Ohio. Infrared spectra were obtained through the courtesy of the Institute for Atomic Research, Iowa State College, and special acknowledgment is made to Mr. R. Knisely for obtaining the spectra.

- (13) H. Gilman and F. Schulze, *THIS JOURNAL*, **47**, 2002 (1925).
 (14) R. A. Benkeser and R. G. Severson, *ibid.*, **73**, 1424 (1951).

AMES, IOWA

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS, THE STATE UNIVERSITY]

A Study of the Induced Decomposition of Benzoyl Peroxide in Diethyl Ether

BY DONALD B. DENNEY AND GERALD FEIG

RECEIVED MARCH 18, 1959

Benzoyl peroxide, labeled with oxygen-18 in the carbonyl oxygens, has been allowed to decompose in a mixture of diethyl ether and sodium hydride. The α -ethoxyethyl benzoate obtained from this reaction was reduced with lithium aluminum hydride to give benzyl alcohol which contained 80% of the excess oxygen-18 originally incorporated in a carbonyl oxygen of the benzoyl peroxide. These results indicate that in the induced decomposition of benzoyl peroxide in ether the α -ethoxyethyl radical attacks predominantly, if not exclusively, on one of the oxygens of the peroxide link.

The reactions of organic peroxides have received much attention in recent years.¹ The products of these reactions are often numerous and vary widely with changes in reaction conditions. These reactions are oftentimes further complicated by in-

duced decompositions in which radicals derived from the solvent or reaction intermediates attack on the peroxide.

A peroxide decomposition that has been studied in some detail is that of benzoyl peroxide (I) in diethyl ether. Cass² has found that this reaction yields 1-ethoxyethyl benzoate (II) and benzoic acid (III)

(1) (a) A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954; (b) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957.

(2) W. E. Cass, *THIS JOURNAL*, **69**, 500 (1947).