Anal. Calcd. for $C_{14}H_{20}O$: C, 81.50; H, 10.75. Found: C, 81.53; H, 10.84.

Several attempts were made to prepare a 2,4-dinitrophenylhydrazone but none was successful.

Hydrogenation Studies.—The data (see Table VI, p. 1650) describes the hydrogenation on the Paar apparatus at a maximum hydrogen press of 50 p.s.i. at room temperature with a platinum dioxide catalyst. The mixtures were mechanically shaken until no more hydrogen was consumed.

Acknowledgment.—The authors wish to thank Mr. Gregory Gallagher for his invaluable laboratory assistance.

The Preparation of Dodecamethylcyclohexasilane

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Directions are given for an improved method of preparation of dodecamethylcyclohexasilane; a proposed mechanism of catalysis by triphenylsilyllithium in this synthesis is considered.

The reaction of dichlorodimethylsilane with sodium at temperatures above 100° in hydrocarbon solvents has been shown to lead to an insoluble polymer as the principal product, with dodecamethylcyclohexasilane (I) being obtained in a low, unspecified yield.[1] It has been reported recently that the yield of I is only 0.05%, when the reaction mixture was worked up by methanol extraction rather than by the vacuum distillation procedure used by Burkhard, and that the use of lithium and tetrahydrofuran at high temperatures increased the yield to 2.5%.[2] Low yields of I also have been obtained from the treatment of dichlorodimethylsilane with sodium[3] and lithium[4] upon extended refluxing in tetrahydrofuran. In the latter case,[4] the yield of dodecamethylcyclohexasilane was 33%, even when dichlorodimethylsilane was added to the lithium at a slow rate.

If the reaction with lithium in the presence of tetrahydrofuran is allowed to proceed in the presence of silyllithium compounds, we have found that the yields of dodecamethylcyclohexasilane are increased significantly to the range of 60–70%.

Initially, dichlorodimethylsilane in tetrahydrofuran is added to lithium in the presence of a small amount of triphenylsilyllithium. Thereafter, the addition of dichlorodimethylsilane is controlled such that silyllithium compounds are present in the reaction mixture throughout the course of the reaction.

The proposed mechanism of catalysis by triphenylsilyllithium is illustrated in the following equations.

$$(C_6H_5)_3SiLi + ClSi(CH_3)_2R \longrightarrow (C_6H_5)_3Si\text{-}Si(CH_3)_2R \xrightarrow{2Li} (C_6H_5)_3SiLi + \underset{\text{II}}{LiSi(CH_3)_2R}$$

$$(\text{R is Cl, } Si(C_6H_5)_3\text{, or } [Si(CH_3)_2]_nR)$$

Chlorosilanes may then react with either triphenylsilyllithium or with intermediates such as II. Triphenylsilyllithium can also be regenerated by reactions joining dimethylsilylene units, as shown in the following example.[5]

$$R(CH_3)_2Si\text{-}Li + R(CH_3)_2Si\text{-}Si(C_6H_5)_3 \longrightarrow R(CH_3)_2SiSi(CH_3)_2R + (C_6H_5)_3SiLi$$

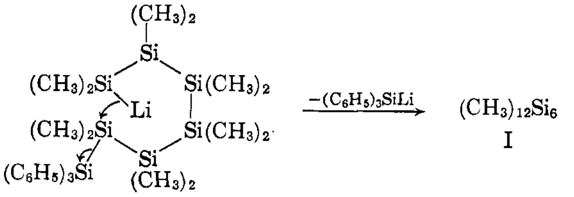
$$(\text{R is Cl, } Si(C_6H_5)_3\text{, or } [Si(CH_3)_2]_nR)$$

These reactions are supported by the observation that 2,2-dimethyl-1,1,1,3,3,3-hexaphenyltrisilane, upon treatment with lithium in tetrahydrofuran, afforded good yields of dodecamethylcyclohexasilane and triphenylsilyllithium, with the latter forming a derivative with chlorotrimethylsilane. In this case, by means of the cleavage reactions shown in the preceding equations, the formation of the observed products may be illustrated by the following mechanistic pathway. The cyclization reaction given here undoubtedly occurs in the reaction involving dichlorodimethylsilane. However, other ring-closure reactions cannot be discounted.

$$6(C_6H_5)_3SiSi(CH_3)_2Si(C_6H_5)_3 + 6Li \xrightarrow{-6(C_6H_5)_3SiLi}$$

$$3(C_6H_5)_3Si[Si(CH_3)_2]_2Si(C_6H_5)_3 \xrightarrow{4Li,\ -4(C_6H_5)_3SiLi}$$

$$(C_6H_5)_3Si[Si(CH_3)_2]_6Si(C_6H_5)_3 \xrightarrow[-(C_6H_5)_3SiLi]{2Li}$$



I

The proposed mechanism of catalysis is further supported by the reaction of five molar equivalents of dichlorodimethylsilane with two equivalents of triphenylsilyllithium in the presence of the calculated amount of lithium. From this reaction, dodecamethylcyclohexasilane was isolated in a 25% yield; there were also obtained crystalline solids which apparently are mixtures of polydimethylsilanes containing terminal triphenylsilyl units. However, only 2,2-dimethyl-1,1,1,3,3,3-hexaphenyltrisilane could be separated in a pure state.

The formation of substituted-dimethylsilylithium intermediates may also occur by the lithium cleavage of tetramethyldisilanyl units. This was demonstrated by allowing the mixture obtained from the triphenyl-

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[1] C. A. Burkhard, *J. Am. Chem. Soc.*, **71**, 963 (1949).

[2] (a) E. Hengge and H. Reuter, *Naturwissenschaften*, **49**, 514 (1962); (b) See, also, the report which just appeared by U. Graf zu Stolberg, *Angew. Chem.*, **75**, 206 (1963).

[3] R. P. Anderson, private communication.

[4] H. Gilman and G. L. Schwebke, unpublished studies.

[5] The formation of hexaethyldisilane upon treatment of 1,1,1-triethyl-2,2,2-triphenyldisilane with lithium in tetrahydrofuran has been proposed to occur by a similar mechanism. See, H. Gilman and H. J. S. Winkler, "Organosilylmetallic Chemistry," in H. Zeiss, Ed., "Organometallic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1960, p. 277; and H. Gilman, G. D. Lichtenwalter, and D. Wittenberg, *J. Am. Chem. Soc.*, **81**, 5320 (1959).

silyllithium-catalyzed reaction of dichlorodimethylsilane to stir with excess lithium. The resulting solution was shown to contain a silyllithium content greater than the amount of triphenylsilyllithium used, by means of a recently developed double-titration technique involving allyl bromide.[6] An attempt to form derivatives of the resulting silyllithium compounds with chlorotriphenylsilane gave no isolable products other than dodecamethylcyclohexasilane in low yield and 14.8% of hexaphenyldisilane. The latter compound evidently was formed by a halogen–metal interconversion reaction, followed by a coupling reaction between the thus formed triphenylsilyllithium and chlorotriphenylsilane. Similar results were obtained from the lithium cleavage of dodecamethylcyclohexasilane. In addition, the insoluble dimethylsilylene polymer[4] reacted with lithium in tetrahydrofuran to give a 32% yield of dodecamethylcyclohexasilane, evidently formed by an intramolecular-cyclization reaction along the polymer chain. Furthermore, this reaction provided a considerable amount of distillable products containing silicon–hydrogen groups, apparently formed by the acid hydrolysis of silyllithium compounds.

Attempts to isolate other cyclic polydimethylsilanes from the catalyzed reaction of dichlorodimethylsilane have not been successful. Waxy solids have been obtained by sublimation which show only dimethylsilyl groups in their infrared spectra. By vapor phase chromatographic analysis, this material was shown to consist principally of three major components. The second fraction to come off of the column was collected and identified as dodecamethylcyclohexasilane. It is believed that the first and third fractions are decamethylcyclopentasilane and tetradecamethylcycloheptasilane, respectively. However, the identities of these materials have not yet been established.

Experimental

All reactions were carried out in oven-dried glassware under atmospheres of oxygen-free, dry nitrogen. Tetrahydrofuran (THF) was dried and purified by refluxing for at least 24 hr. over sodium, followed by distillation into lithium aluminum hydride and redistillation from the hydride immediately before use, *except* in the preparation of dodecamethylcyclohexasilane, where drying by storage over sodium wire was found to give satisfactory results. The temperatures reported are uncorrected.

Preparation of Dodecamethylcyclohexasilane.—A solution of 300 ml. (318 g., 2.5 moles)[7] of dichlorodimethylsilane in 700 ml. of sodium-dried tetrahydrofuran was added in a dropwise fashion to 38 g. (5.45 g.-atoms) of lithium wire (cut into *ca.* 5-mm. pieces), and 0.01 mole of triphenylsilyllithium in 15 ml. of tetrahydrofuran. The rate of addition was carefully controlled such that the reaction mixture maintained a definite light brown coloration.[8] Initially, the reaction was sufficiently exothermic that external heating was not required to maintain reflux. After about one-half of the solution was added, it was necessary to heat the mixture to keep it refluxing. The total addition time was between 24 and 36 hr. A small amount of lithium usually remained, after the completion of the addition, which was separated by decantation through a Büchner funnel.[9] The lithium-free reaction mixture is hydrolyzed in dilute acid. The aqueous layer was separated and extracted three times with *ca.* 100-ml. portions of ether. The combined ether extracts and organic layer was washed with water until neutral to litmus. The organic phase was filtered to remove 1–2% of insoluble polymer. The solvents were removed under reduced pressure and the residue treated with cold acetone and filtered to give 96 g. (67%) of impure dodecamethylcyclohexasilane, m.p. 220–240° (m.p. block preheated to 200°). Recrystallization[10] was accomplished by dissolving the product in 10–20 ml. of petroleum ether (b.p. 60–70°) and adding *ca.* 200 ml. of hot acetone. Upon cooling, there was obtained 86 g. (60%) of pure product, m.p. 250–252° (m.p. block preheated to 240°).[11] The crystal form most frequently observed was diamond-shaped plates. However, feathery needles also were encountered.

Anal. Calcd. for $C_{12}H_{36}Si_6$: mol. wt., 348.9. Found: mol. wt., 349 (vapor pressure osmometer).

The solvents were removed from the original mother liquor and the residue heated to 150° (0.5 mm.), affording 25 g. (*ca.* 17.5%) of volatile material, most of which sublimed and was collected in the side arm of the distillation flask. Attempts to recrystallize this material gave only waxy materials melting in the range 120–190°. Sublimation at 40° (0.005 mm.) did not succeed in separating the components. Vapor phase chromatographic analysis, using a silicone–gum rubber packed column heated to 175°, showed three major peaks, with retention times about 5 min. apart. Infrared spectra on each of the samples collected showed only the presence of dimethylsilylene units. The second fraction was identified as dodecamethylcyclohexasilane, m.p.[11] 250–252° (m.m.p.). The first and third major components were not collected in sufficient amounts to establish their structures, but they are believed to be decamethylcyclopentasilane and tetradecamethylcycloheptasilane. They were waxy solids with indefinite melting points between 160–200°.

Dichlorodimethylsilane and Excess Lithium in the Presence of a Trace of Triphenylsilyllithium.—The reaction was carried out as described in the preparation of dodecamethylcyclohexasilane, using 15.9 g. (0.12 mole) of dichlorodimethylsilane, 2.1 g. (0.3 g.-atom) of lithium and 0.001 mole of triphenylsilyllithium in a total of 97 ml. of tetrahydrofuran. Subsequent to completion of the addition, the reaction mixture was stirred at room temperature for 24 hr. Double titration[6] gave the silyllithium content as 0.033 mole. The reaction mixture was decanted from the remaining lithium and added to 10.3 g. (0.03 mole) of chlorotriphenylsilane. Subsequent to acid hydrolysis, filtration afforded 1.3 g. (14.8%) of hexaphenyldisilane, m.p. 360–365° (m.m.p.). The filtrate was worked up in the usual manner and the solvents were removed. Petroleum ether (b.p. 60–70°) was added to the residue to give 1.4 g. (11.5%) of triphenylsilanol, m.p. 148–155°, identified by its infrared spectrum. The solvent was removed from the mother liquor and the residue heated at 100° (0.2 mm.) to give 0.5 g. (7%) of sublimate, identified as dodecamethylcyclohexasilane, m.p. 248–250° (m.m.p.). Attempts to isolate other compounds were unsuccessful.

Reaction of Dichlorodimethylsilane and Triphenylsilyllithium (5:2 Mole Ratio, Respectively) in the Presence of Lithium.—Triphenylsilyllithium was prepared by the cleavage of 10.4 g. (0.02 mole) of hexaphenyldisilane with 1.4 g. (0.2 g.-atom) of lithium. To the resulting mixture, there was added 12.9 g. (0.1 mole) of dichlorodimethylsilane in 50 ml. of tetrahydrofuran solution at a rate which maintained a light brown coloration in the reaction mixture. The addition required 3 hr. The reaction mixture was decanted from the small amount of remaining lithium and hydrolyzed in dilute acid. Subsequent to the usual work-up and solvent removal, petroleum ether was added to the residue. Filtration afforded 9.7 g. of insoluble material melting over the range 129–180°. By fractional recrystallization from benzene, there was isolated 1.1 g. (9.6%) of 2,2-dimethyl-1,1,1,-3,3,3-hexaphenyltrisilane, m.p. 222–225° (m.m.p.). Attempts to purify the remaining solids gave crystalline solids with wide melting point ranges. The infrared spectra of the various

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[6] H. Gilman and S. Y. Sim, unpublished studies.

[7] Excellent yields also were obtained from runs using from 0.2–1 mole of dichlorodimethylsilane.

[8] The rate of addition is rather sensitive and a too rapid addition nullifies the catalytic action. If the reaction mixture loses the brown coloration, stop the addition of dichlorodimethylsilane. Reinitiation may be accomplished by one or a combination of the following procedures: stir at reflux for an hour or so; add a few pieces of freshly cut lithium; and/or add another portion of triphenylsilyllithium. Repeat if necessary.

[9] The presence of salts tends to make lithium removal difficult.

[10] For smaller quantities of product, acetone alone may be used as the crystallization solvent.

[11] On slow heating from room temperature, dodecamethylcyclohexasilane undergoes numerous crystal transformations and appears to melt partially and resolidify at temperatures below 200°. Sublimation also occurs. When added to the m.p. block at 240°, the material melts at 250–252°, with considerable sintering from 240°.

fractions indicated the presence of silicon–methyl and silicon–phenyl groups. The solvent was removed from the original mother liquor and the residue heated at 100° under a pressure of 0.5 mm. to give 1.5 g. (25.9%) of sublimate, identified as dodecamethylcyclohexasilane, m.p. 250–253° (m.m.p.). Attempts to obtain products from the sublimation residue were unsuccessful.

2,2-Dimethyl-1,1,1,3,3,3-hexaphenyltrisilane. Preparation.—To 2.6 g. (0.02 mole) of dichlorodimethylsilane, there was added 0.04 mole of triphenylsilyllithium in 50 ml. of tetrahydrofuran. The reaction mixture was hydrolyzed in dilute acid and filtered. The solids were washed with water, methanol, and ether, and dried to give 8.2 g. (71.4%) of product, m.p. 222–226°. Two recrystallizations from a mixture of benzene and cyclohexane gave 5.5 g. (47.7%) of pure 2,2-dimethyl-1,1,1,3,3,3-hexaphenyltrisilane, m.p. 223–227°.

Anal. Calcd. for $C_{38}H_{36}Si_3$: Si, 14.60. Found: Si, 14.48, 14.58.

Reaction with Lithium.—A few milliliters of tetrahydrofuran was added to a stirred mixture of 5.8 g. (0.01 mole) of the trisilane and 0.7 g. (0.1 g.-atom) of lithium. The reaction mixture became yellow after 5 min. A total of 25 ml. of tetrahydrofuran was added over a 30-min. period and the reaction mixture was stirred for an additional 3 hr. To the resulting dark green mixture, 3.4 g. (0.03 mole) of chlorotrimethylsilane was added rapidly. The colorless solution was decanted away from the lithium and hydrolyzed in dilute acid. Subsequent to the usual work-up, the solvents were removed and the residue crystallized from ethanol to give 4.3 g. (65.1%) of 1,1,1-trimethyl-2,2,2-triphenyldisilane, m.p. 106–108° (m.m.p.). The solvents were removed from the mother liquor and the residue heated to 100° (12 mm.) to yield 0.4 g. (66%) of impure dodecamethylcyclohexasilane, m.p. 200–230°. Recrystallization from acetone afforded 0.3 g. (50%) of pure product, m.p. 250–252° (m.m.p.).

Cleavage of Dodecamethylcyclohexasilane with Lithium in Tetrahydrofuran.—Triphenylsilyllithium was prepared by the reaction of 0.13 g. (0.00025 mole) of hexaphenyldisilane and 0.7 g. (0.1 g.-atom) of lithium in a small volume of tetrahydrofuran. To this, 5.25 g. (0.015 mole) of dodecamethylcyclohexasilane was added in 25 ml. of tetrahydrofuran.[12] The resulting mixture was stirred at room temperature for 24 hr. Titration of the brown solution showed the silyllithium content to be 0.009 mole.[6] Chlorotriphenylsilane, 3.5 g. (0.012 mole), was added. The colorless solution was hydrolyzed and filtered to give 0.2 g. of hexaphenyldisilane, m.p. 360–365° (m.m.p.). The filtrate was worked up in the usual manner and the solvents were removed. Petroleum ether (b.p. 60–70°) was added to the residue and filtration afforded 1.6 g. (50%) of triphenylsilanol, m.p. 150–155° (m.m.p.). The solvent was removed from the filtrate and the residue crystallized from acetone to give 1.9 g. (36.4%) of recovered dodecamethylcyclohexasilane, m.p. 250–252° (m.m.p.). Attempts to isolate other pure products were unsuccessful.

Reaction of Lithium with the Insoluble Dimethylsilylene Polymer.—About 0.7 g. (0.1 g.-atom) of lithium, which had been used for the preparation of triphenylsilyllithium, and 5.8 g. of the insoluble dimethylsilylene polymer[13] were stirred for 52 hr. in 20 ml. of tetrahydrofuran. The dark brown reaction mixture was hydrolyzed in excess dilute acid and filtered to give 0.7 g. (12%) of recovered polymer. Subsequent to the usual work-up, the solvents were removed and the residue distilled under reduced pressure and afforded a large number of fractions boiling in the range 65° (0.4 mm.) to 100° (0.003 mm.). The total amount of distillable material was 4.5 g. (77.8%). All of these fractions showed strong absorption bands in their infrared spectra for silicon–hydrogen and silicon–methyl groups. One fraction, b.p. 100–105° (0.4 mm.), partially solidified. Recrystallization from acetone afforded 1.8 g. (32%) of dodecamethylcyclohexasilane, m.p. 250–252° (m.m.p.).

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[12] An attempt to cleave dodecamethylcyclohexasilane with untreated lithium in tetrahydrofuran gave no indication of a reaction after 48 hr., and starting material was recovered in a 90% yield.

[13] Obtained from the uncatalyzed reaction of dichlorodimethylsilane with lithium in tetrahydrofuran.[4]

Intramolecular Reactions of Some Cyclic β-Diketones[1]

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The reaction of 3-(4,4-dimethyl-2,6-dioxocyclohexyl)levulinic acid (I) with bromine resulted in an unusual intramolecular reaction. The structure of this product and the reactions of some related model compounds are discussed.

The investigation of the reaction of bromine with ketones has resulted in an understanding of the mechanism of this reaction. It has been shown that the rate of reaction is dependent on the concentration of the ketone and catalyst (acid or base) but is independent of the concentration of the halogen. From this and other data, it is believed that the rate-determining step is the formation of the enol which is then rapidly attacked by halogen.[3] In connection with our structural studies on some cyclic β-diketones,[4] we became interested in the reaction of bromine with certain β-diketones, and this paper describes some novel reactions which we have observed with this system.

When 3-(4,4-dimethyl-2,6-dioxocyclohexyl)levulinic acid (I) was allowed to react with an aqueous solution of bromine, a *neutral product* (II) was obtained which had undergone substitution of a bromine for a hydrogen atom. An examination of the infrared spectrum of the brominated product revealed hydroxyl absorption at 3620 and 3340 cm.$^{-1}$ and carbonyl absorption at 1785 and 1725 cm.$^{-1}$. Furthermore an examination of the ultraviolet spectrum revealed that the β-diketone system was no longer capable of enolization since the characteristic absorption of an enolizable β-diketone was absent; in fact, the only absorption exhibited was at 298 mμ with an ε of 90 which is characteristic of an isolated ketone.[5] In addition, the bromine must be located in this compound in a unique position since when it is allowed to react with sodium hydroxide, a 25% yield of 3-(4,4-dimethyl-2,6-dioxocyclohexyl)levulinic acid (I) is obtained. In order to obtain more

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[1] This investigation was supported generously by research grant CY5527 from the National Cancer Institute, National Institutes of Health, Public Health Service.

[2] The research described in this paper was used in partial fulfillment of the requirements for the Bachelor of Science degree.

[3] A number of reviews on this subject have been published; see, for example, E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p. 372.

[4] For the previous paper of this series, see H. J. Schaeffer and R. Vince, *J. Org. Chem.*, **27**, 4502 (1962).

[5] W. R. Brode, "Chemical Spectroscopy," 2nd Ed., John Wiley and Sons Inc., New York, N. Y., 1943, p. 221-226.