

Directorate of Laboratories, Wright Air Development Center, Wright-Patterson AFB, Ohio. The authors are grateful to Dr. R. King for determination of the

n.m.r. spectra and to G. L. Schwebke and F. K. Cartledge for assistance during the course of this investigation.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

Reactions and Structure of Decaphenylcyclopentasilane

BY HENRY GILMAN AND GERALD L. SCHWEBKE

RECEIVED FEBRUARY 8, 1964

One of the perphenylated cyclosilanes obtained from the reaction of dichlorodiphenylsilane with lithium in tetrahydrofuran, previously proposed to be dodecaphenylcyclohexasilane, has been shown to be decaphenylcyclopentasilane. This cyclosilane is cleaved fairly specifically by bromine in benzene and by lithium in tetrahydrofuran to give the respective 1,5-disubstituted derivatives in high yields. Molecular weight determinations on decaphenylcyclopentasilane by three different methods give results which are consistent with the present proposal.

Introduction

Prior to 1960, few organosilanes containing silicon atom chains of greater length than three were known. Organic-substituted cyclosilanes derived from the reaction of sodium with dichlorodiphenylsilane and some straight chain polysilanes were first investigated by Kipping and Sands about 40 years ago.¹ More recently,² Burkhard prepared dodecamethylcyclohexasilane in low yield from dichlorodimethylsilane and sodium. A dimethylsilylene polymer was also obtained from this reaction. Octaphenyltrisilane³ and decaphenyltetrasilane,⁴ as well as the corresponding permethylated compounds,^{4b,c} have been prepared and studied.

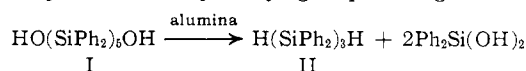
The reason for the dearth of polysilanes has in the past³ been attributed to the low energy of the Si-Si bond. However, recent evidence indicates that the dissociation energy of the Si-Si bond in disilane ($\text{H}_3\text{Si-SiH}_3$) is 81.3 kcal. mole⁻¹, similar to that of the carbon-carbon bond in ethane (83 kcal. mole⁻¹), in contrast to earlier values of about 50 kcal. mole⁻¹.⁵ Assuming this to be true, it would appear that the reason for the small number of polysilanes is due to a lack of synthetic methods and to the greater chemical reactivity of compounds containing the Si-Si bond rather than to a low order of intrinsic stability of the bond.

With a view of preparing various polysilanes, the work of Kipping was reinvestigated. From the reaction of dichlorodiphenylsilane with sodium in refluxing toluene or xylene^{1a} Kipping had obtained several distinctly crystalline compounds.^{1a,c} One compound, designated as Compound A, was considered to contain four diphenylsilylene units in a straight chain with terminal tervalent silicon atoms. The reasons for this proposal were based on the unusual reactivity of the compound and upon the fact that molecular weight determinations indicated that a second crystalline compound (Compound B) was also an octaphenyltetrasilane. Compound B is much less reactive than

"A" and therefore was considered to have a closed chain (octaphenylcyclotetrasilane).

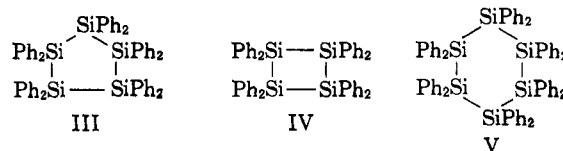
However, since that time Compound A has been shown to be octaphenylcyclotetrasilane⁶ and Compound B has been proposed to be dodecaphenylcyclohexasilane.⁷ Derivatives obtained from this latter compound were therefore assigned the structure of hexasilanes.⁷⁻⁹ The basis for these assignments was mainly molecular weight determinations.⁷ No conclusive evidence was gained through independent synthesis of derivatives.

A recent study¹⁰ indicated that the dihydroxy compound obtained from hydrolysis of the α,ω -dichloro derivative of Compound B is actually decaphenylpentasilane-1,5-diol (I). The reaction involved in this inference is the selective cleavage of a silicon-silicon bond adjacent to a hydroxyl group during chromatog-



raphy on basic alumina to give 1,1,2,2,3,3-hexaphenyltrisilane (II). This reaction has been shown to occur with the related compounds 1,4-dihydroxyoctaphenyltetrasilane and 1,1,2,2,3,3,4,4-octaphenyltetrasilan-1-ol, resulting in the expected cleavage products.¹⁰

Therefore, it was necessary to reinvestigate the lithium and bromine cleavages of Compound B. Preliminary evidence^{10,11} indicates that its derivatives are pentasilanes and, barring unexpected secondary reactions, that Compound B is decaphenylcyclopentasilane (III), and not, as previously proposed, octaphenylcyclotetrasilane (IV)^{1a,b} or dodecaphenylcyclohexasilane (V).⁷ The utility of the 1,5-dilithiododecaphenyl-



(1) (a) F. S. Kipping and J. E. Sands, *J. Chem. Soc.*, **119**, 830 (1921); (b) F. S. Kipping, *ibid.*, **123**, 2590 (1923); (c) F. S. Kipping, *ibid.*, **125**, 2291 (1924); (d) F. S. Kipping, *ibid.*, 2719 (1927).

(2) C. A. Burkhard, *J. Am. Chem. Soc.*, **71**, 963 (1949).

(3) H. Gilman, T. C. Wu, H. A. Hartzfeld, G. A. Guter, A. G. Smith, J. J. Goodman, and S. H. Eidt, *ibid.*, **74**, 561 (1952).

(4) (a) D. Wittenberg, M. V. George, and H. Gilman, *ibid.*, **81**, 4812 (1959); (b) G. R. Wilson and A. G. Smith, *J. Org. Chem.*, **26**, 557 (1961); (c) U. G. zu Stolberg, *Angew. Chem.*, **74**, 696 (1962).

(5) W. C. Steele and F. G. A. Stone, *J. Am. Chem. Soc.*, **84**, 3599 (1962).

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

(7) (a) H. Gilman, D. J. Peterson, A. W. Jarvie, and H. J. S. Winkler, *Tetrahedron Letters*, **23**, 5 (1960); (b) H. J. S. Winkler, A. W. P. Jarvie, D. J. Peterson, and H. Gilman, *J. Am. Chem. Soc.*, **83**, 4089 (1961).

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

(9) A. W. P. Jarvie, H. J. S. Winkler, and H. Gilman, *ibid.*, **27**, 614 (1962).

(10) G. R. Chainani, S. Cooper, and H. Gilman, *ibid.*, **28**, 2146 (1963).

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

pentasilane for preparing other organic-substituted polysilanes was also investigated. Finally, it was imperative that a satisfactory molecular weight determination be carried out.

Experimental¹²

Preparation and Purification of Decaphenylcyclopentasilane.—Decaphenylcyclopentasilane was prepared by a modified procedure¹³ from dichlorodiphenylsilane and lithium in sodium-dried tetrahydrofuran in nearly quantitative crude yields. Purification of this material was accomplished by adding sufficient benzene (about 2 l. per 175 g.) to dissolve the decaphenylcyclopentasilane at room temperature. After standing for several days, the insoluble material was removed by filtration and the benzene solution concentrated to about 300 ml. Addition of this hot solution to 1 l. of hot petroleum ether (b.p. 60–70°) gave, after cooling to room temperature, 70–75% yields of pure decaphenylcyclopentasilane which melted at 466–470° (mixture m.p.) when placed in a melting point block at 400° or at 472–474° when inserted at 460°. Further recrystallizations from benzene–petroleum ether (b.p. 60–70°), cyclohexane, or ethyl acetate did not alter its melting point characteristics.

1,5-Dibromodecaphenylpentasilane.—To 10.00 g. (0.011 mole) of decaphenylcyclopentasilane dissolved in 100 ml. of sodium-dried benzene, cooled to ice-bath temperature, was added dropwise a solution of 1.76 g. (0.011 mole) of bromine in 300 ml. of benzene. The addition took 1 hr. After stirring for an additional 6 hr. at room temperature, the pale yellow solution was distilled to remove the solvent, the final traces being removed at reduced pressure. There was obtained a sticky froth which solidified when digested with petroleum ether (b.p. 60–70°). Removal of the crystalline solid by filtration provided 10.90 g. (94.4%) of 1,5-dibromodecaphenylpentasilane, m.p. 202–207°. Recrystallization from cyclohexane–benzene raised the m.p. to 207–209° (mixture m.p.).

Decaphenylpentasilane-1,5-diol.—One-hundred milliliters of 1 *N* hydrochloric acid was added to 30.0 g. (0.028 mole) of 1,5-dibromodecaphenylpentasilane dissolved in 200 ml. of tetrahydrofuran. The two-phase reaction mixture was stirred overnight at room temperature.

The organic layer was separated from the aqueous layer, which was also extracted with several portions of diethyl ether. The combined organic layers were dried (sodium sulfate) and the solvents were evaporated. The residue was dissolved in boiling cyclohexane and upon cooling there precipitated 25.35 g. (95.7%) of decaphenylpentasilane-1,5-diol, m.p. 172–174° (mixture m.p.).

1,1,2,2,3,3-Hexaphenyltrisilane.—Decaphenylpentasilane-1,5-diol was prepared as described above from 29.5 g. (0.0275 mole) of 1,5-dibromodecaphenylpentasilane. The crude reaction product was dissolved in benzene and chromatographed on a 5 × 50 cm. basic alumina column (Alcoa activated alumina F-20). Elution of the column with about 12 l. of benzene over a period of 4 days yielded 11.92 g. (79.0%) of crude 1,1,2,2,3,3-hexaphenyltrisilane.

Recrystallization of this material from benzene–ethanol provided 10.76 g. (71.3%) of pure 1,1,2,2,3,3-hexaphenyltrisilane, m.p. 95.5–97° (mixture m.p.). Stripping the column with a mixture of acetic acid and tetrahydrofuran (1:5) provided viscous phenylsiloxane polymer from which was isolated some diphenylsilanediol, m.p. 148–153° dec., and a trace of hexaphenylcyclotrisiloxane, m.p. 187–189° (mixture m.p.).

1,1,2,2,3,3-Hexaphenyltrisilane with N-Bromosuccinimide in Carbon Tetrachloride.—A stirred mixture of 6.00 g. (0.0109 mole) of 1,1,2,2,3,3-hexaphenyltrisilane, 3.90 g. (0.0219 mole) of N-bromosuccinimide, and 100 ml. of carbon tetrachloride was subjected to ultraviolet light (G.E. sunlamp) for 30 min. At this time a flocculent precipitate was floating in the clear reaction solution.

Filtration of the mixture gave 2.17 g. (100%) of succinimide, m.p. 121–124° (mixture m.p.). The filtrate, which became red in contact with air, was evaporated and the residue recrystallized

from sodium-dried petroleum ether (b.p. 60–70°). There was obtained 4.70 g. (65%) of a product, m.p. 137–138°.

Anal. Calcd. for $C_{36}H_{30}Br_2Si_3$: Si, 11.92. Calcd. for $C_{36}H_{30}BrClSi_3$: Si, 12.71. Found: Si, 12.54, 12.45.

The infrared spectrum of this material indicated the presence of only Si–phenyl and not SiOH or SiOSi. It is possible that chlorine from the solvent is in some manner incorporated into the compound.

A repeat of this reaction was carried out completely under nitrogen, including crystallization and filtration of the pure product and resulted in the same product, m.p. 137–138° (mixture m.p.).

Anal. Found: Si, 12.37, 12.52.

1,3-Dibromohexaphenyltrisilane.—To 4.00 g. (0.00728 mole) of 1,1,2,2,3,3-hexaphenyltrisilane dissolved in 50 ml. of sodium-dried benzene, cooled to ice-bath temperature, was added slowly a solution of 2.34 g. (0.0146 mole) of bromine in 50 ml. of benzene. The bromine decolorized immediately upon addition. A light red-brown color persisted after the addition was complete. An aspirator vacuum was applied to remove excess bromine and hydrogen bromide which had formed and then the benzene was removed by distillation at atmospheric pressure. The residue was digested with 20 ml. of sodium-dried petroleum ether (b.p. 60–70°) and then allowed to cool to room temperature. Up to this point all steps had been carried out under a nitrogen atmosphere.

Filtration provided 3.72 g. (72.5%) of gray crystalline material, m.p. 151–152°. A mixture melting point of this product with 1,2-dibromotetraphenylidisilane, m.p. 153–154.5°, was depressed to 128–140°. Purification of the compound was accomplished by dissolving it under nitrogen in benzene, adding charcoal, and filtering after warming for a few minutes. The solution thus obtained was distilled to remove most of the benzene and then 20 ml. of petroleum ether was added to give white crystalline pure 1,3-dibromohexaphenyltrisilane, m.p. 153–154°.

Anal. Calcd. for $C_{36}H_{30}Br_2Si_3$: Br, 22.6. Found: Br, 22.3, 22.4 (hydrolysis).

1,5-Dibromodecaphenylpentasilane with Lithium Aluminum Hydride.—To 4.00 g. (0.0037 mole) of 1,5-dibromodecaphenylpentasilane suspended in 50 ml. of diethyl ether was added 0.30 g. (0.0075 mole) of lithium aluminum hydride. After 10 min. of stirring, the dibromo compound also appeared to be dissolving. However, upon continued stirring a heavy white precipitate began to form. After refluxing the reaction mixture gently for 2.5 hr., hydrolysis was effected by addition to ice–water which was acidified with hydrochloric acid. The insoluble material was removed by filtration and this, along with some material recovered from the ether solution, provided 3.24 g. (95.3%) of 1,1,2,2,3,3,4,4,5,5-decaphenylpentasilane, m.p. 147–149°. Recrystallization of this material from acetone raised the melting point to 151–151.5°. The mixture m.p. and infrared spectrum of this material were consistent with the compound obtained by acid hydrolysis of the dithio derivative of Compound B.⁸

1,5-Dilithiodecaphenylcyclopentasilane.—To a stirred mixture of 14.6 g. (0.016 mole) of decaphenylcyclopentasilane and 1.1 g. (0.16 g.-atom) of cut lithium wire was added ca. 10 ml. of tetrahydrofuran. Within 1 min. the reaction mixture became yellow and 150 ml. of tetrahydrofuran was added dropwise over a period of 45 min. The mixture was stirred for an additional 75 min. at room temperature and then filtered through glass wool into an addition funnel. Analysis of the solution (166 ml.) by the double titration technique using allyl bromide¹⁴ indicated the presence of 0.0321 mole (100%) of silyllithium content. This method of preparation of 1,5-dilithiodecaphenylpentasilane was used to prepare several polysilanes. Shorter reaction times led to recovered decaphenylcyclopentasilane, while longer times gave lower yields of 1,5-disubstituted derivatives and increased quantities of shorter chained cleavage products.

1,5-Di-*n*-butyldecaphenylpentasilane.—Eighty milliliters of a tetrahydrofuran solution of 1,5-dilithiodecaphenylpentasilane (0.0155 mole of SiLi) obtained from the lithium cleavage of decaphenylcyclopentasilane was added rapidly to 4.40 g. (0.0165 mole) of tri-*n*-butyl phosphate dissolved in 20 ml. of tetrahydrofuran. Within 15 min. the reaction mixture was practically colorless and Color Test I¹⁵ was negative. Hydrolysis was effected by addition to 200 ml. of 1 *N* hydrochloric acid. The

(12) All melting points are uncorrected. Reactions involving organometallic or silylmetallic reagents were carried out under an atmosphere of dry, oxygen-free nitrogen. Unless otherwise indicated, tetrahydrofuran was purified by refluxing over sodium, followed by distillation from lithium aluminum hydride. Anhydrous ether was stored over sodium wire.

(13) H. Gilman and J. Kraemer, unpublished studies.

(14) H. Gilman, F. K. Cartledge, and S. Y. Sim, *J. Organometal. Chem.*, **1**, 8 (1963).

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

usual work-up, followed by removal of the solvents by distillation, provided the crude reaction product, which was digested with ethanol. Removal of the insoluble material by filtration gave 5.82 g. (73.2%) of crude 1,5-di-*n*-butyldecaphenylpentasilane, melting over the range 153–161°. Recrystallization from benzene-petroleum ether (b.p. 60–70°) raised its melting point to 162.5–164°.

Anal. Calcd. for $C_{48}H_{48}Si_5$: Si, 13.70; arom. H/aliph. H, 50/18. Found: Si, 13.66, 13.61; arom. H/aliph. H, 51.5/18 (n.m.r.).

The remainder of the reaction residue was chromatographed on alumina to give 0.035 g. (0.9%) of 1,2-di-*n*-butyltetraphenyldisilane, which melted at 101–102° (mixture m.p.) after recrystallization from ethanol, and 0.115 g. (2.2%) of 1,3-di-*n*-butylhexaphenyltrisilane, which melted at 147–149° after recrystallization from petroleum ether.

Anal. Calcd. for $C_{44}H_{48}Si_3$: Si, 12.75; arom. H/aliph. H, 30/18. Found: Si, 12.60, 12.72; arom. H/aliph. H, 30.0/18.

There was also isolated 0.62 g. (7.9%) of 1,5-di-*n*-butyldecaphenylpentasilane, m.p. 160–162°, and 0.14 g. (2.0%) of decaphenylcyclopentasilane, m.p. 430–445° (mixture m.p.).

1,2-Di-*n*-butyltetraphenyldisilane.—*n*-Butylmagnesium bromide was prepared in 94.4% yield from 3.42 g. (0.025 mole) of *n*-butyl bromide and 2.43 g. (0.10 g.-atom) of magnesium metal in 50 ml. of tetrahydrofuran; 44 ml. of this solution, containing 0.020 mole of Grignard reagent, was added to 5.24 g. (0.010 mole) of 1,2-dibromotetraphenyldisilane dissolved in 50 ml. of tetrahydrofuran. After stirring at room temperature for 24 hr. Color Test I was negative. Hydrolysis and the usual work-up gave 4.9 g. of an oil which was chromatographed on an alumina column. There was isolated 0.94 g. (19.6%) of 1,2-di-*n*-butyltetraphenyldisilane, which melted at 101–102° after recrystallization from ethanol.

Anal. Calcd. for $C_{32}H_{38}Si_2$: Si, 11.72. Found: Si, 11.74, 11.54.

1,4-Di-*n*-butyloctaphenyltetrasilane (Attempted).—To 8.00 g. (0.010 mole) of 1,4-dichlorooctaphenyltetrasilane dissolved in 50 ml. of tetrahydrofuran was added 0.040 mole of *n*-butylmagnesium bromide in 104 ml. of tetrahydrofuran solution. The resulting mixture was stirred for 24 hr. at the reflux temperature. Color Test I was negative at the end of this time. Hydrolysis was effected with 200 ml. of 1 *N* hydrochloric acid and the usual work-up was employed.

There was isolated in three fractions 5.72 g. (75%) of octaphenyltetrasilane-1,4-diol,¹⁰ m.p. 213–215 (mixture m.p.). No other products were isolated from the residue.

1,5-Dimethyldecaphenylpentasilane. A. From 1,5-Dilithiodecaphenylpentasilane and Trimethyl Phosphate.—To 2.30 g. (0.0165 mole) of trimethyl phosphate dissolved in 20 ml. of tetrahydrofuran was added rapidly 0.0075 mole of 1,5-dilithiodecaphenylpentasilane in 80 ml. of tetrahydrofuran solution. The red-brown color of silyllithium disappeared immediately, and heat evolution caused quite vigorous refluxing of the reaction mixture. Color Test I was negative and, after stirring for 15 min., the mixture was hydrolyzed with 200 ml. of 1 *N* hydrochloric acid.

Following the usual work-up, 5.50 g. (75.5%) of crude product, m.p. 183.5–188°, was isolated. Recrystallization from benzene-petroleum ether (b.p. 60–70°) raised the melting point to 189–190° (mixture m.p.).

Anal. Calcd. for $C_{62}H_{56}Si_5$: arom. H/aliph. H, 50/6; mol. wt., 941.5. Found: arom. H/aliph. H, 51.5/6, 52/6; mol. wt., 938 (vapor pressure osmometer in benzene with decaphenylcyclopentasilane as standard).

B. From 1,5-Dibromodecaphenylpentasilane and Methylmagnesium Iodide.—Methylmagnesium iodide was prepared in the conventional way from 28.4 g. (0.20 mole) of methyl iodide and 10.0 g. (0.41 g.-atom) of magnesium metal in 250 ml. of diethyl ether in 97% yield; 20 ml. of this solution, containing 0.073 mole of methylmagnesium iodide, was added to 8.90 g. (0.0831 mole) of 1,5-dibromodecaphenylpentasilane dissolved in 150 ml. of tetrahydrofuran. Color Test I was negative after 3 hr. A second 20 ml. of the Grignard reagent was added to the reaction mixture which was then stirred overnight at room temperature and for 4 hr. at the reflux temperature. Color Test I remained positive.

Work-up was effected by hydrolysis with 1 *N* hydrochloric acid, followed by the usual extractive procedure. Removal of the ether and tetrahydrofuran resulted in a residue which, after treatment with cyclohexane, provided 7.52 g. (96.2%) of crude

product, m.p. 180–185°. Recrystallization from benzene-petroleum ether (b.p. 60–70°) gave pure 1,5-dimethyldecaphenylpentasilane, m.p. 186–188° (mixture m.p.).

An attempt to prepare 1,5-dimethyldecaphenylpentasilane by this method employing the dibromo compound and the Grignard reagent in a 1:2 mole ratio at room temperature failed. There was isolated after hydrolysis 75.4% of decaphenylpentasilane-1,5-diol and, by chromatography of the mother liquor, a trace of 1-methyl-1,1,2,2,3,3,4,4-octaphenyltetrasilane, m.p. 171–174° (mixture m.p.).

C. From 1-Lithio-2-methyltetraphenyldisilane and Dichlorodiphenylsilane.—1-Lithio-2-methyltetraphenyldisilane was prepared according to a published procedure^{7b} from 4.19 g. (0.0046 mole) of decaphenylcyclopentasilane dissolved in 40 ml. of tetrahydrofuran and 0.0231 mole of methyltriphenylsilyllithium in 59 ml. of tetrahydrofuran solution. After stirring for 48 hr., analysis by double titration (allyl bromide) indicated that the silyllithium content of the solution had decreased only about 4%.

Eighty-eight milliliters of this solution, containing 0.0195 mole of silyllithium compounds and 0.0254 mole of total base, was added to 3.21 g. (0.0127 mole) of dichlorodiphenylsilane. Within 1 hr. after the addition was complete, Color Test I was negative. Acid hydrolysis and the usual work-up resulted in an oil which resisted crystallization from petroleum ether or from ethanol.

However, there was isolated by fractional crystallization from ethyl acetate and alumina chromatography 3.10 g. (28.6%) of crude 1,5-dimethyldecaphenylpentasilane, which melted at 188–189° (mixture m.p.) after recrystallization from ethyl acetate.

1,1,1,7,7,7-Hexamethyldecaphenylheptasilane.—To 3.42 g. (0.0316 mole) of chlorotrimethylsilane dissolved in 50 ml. of tetrahydrofuran was added over a period of 15 min. 0.0075 mole of 1,5-dilithiodecaphenylpentasilane in 83 ml. of tetrahydrofuran solution. Fifteen minutes after completion of the addition the reaction mixture was clear and colorless. Hydrolysis was effected with ice water, and after work-up there was isolated 6.77 g. (83%) of crude product, m.p. 194–198°.

Recrystallization from petroleum ether (b.p. 60–70°) gave pure 1,1,1,7,7,7-hexamethyldecaphenylheptasilane, m.p. 197–199°. The n.m.r. spectrum of this compound showed absorption for phenyl and methyl (10.4 τ) protons in a ratio of 49.5/18 (calcd. 50/18).

Anal. Calcd. for $C_{66}H_{68}Si_7$: C, 74.96; H, 6.48. Found: C, 74.84, 74.87; H, 6.32, 6.40.

1,1,2,2,3,3,4,4,5,5,6,6,7,7-Tetradecaphenylheptasilane.—To 10.1 g. (0.045 mole) of rapidly stirred chlorodiphenylsilane at room temperature was added in a dropwise fashion 0.0152 mole of 1,5-dilithiodecaphenylpentasilane in 170 ml. of tetrahydrofuran. The red silyllithium color disappeared immediately upon mixing. Color Test I was negative upon completion of the addition.

Acid hydrolysis and work-up gave an oily solid which was digested with boiling petroleum ether (b.p. 60–70°). Filtration of the hot petroleum ether suspension afforded 15.72 g. (82.0%) of white powder, m.p. 195–200°. When this material was recrystallized from benzene-propanol and from benzene-cyclohexane there was obtained pure 1,1,2,2,3,3,4,4,5,5,6,6,7,7-tetradecaphenylheptasilane, m.p. 203–204°.

Anal. Calcd. for $C_{84}H_{72}Si_7$: Si, 15.39. Found: Si, 15.31, 15.39.

1,1-Dimethyldecaphenylcyclohexasilane.—To 2.15 g. (0.015 mole) of dichlorodimethylsilane dissolved in 200 ml. of tetrahydrofuran was added dropwise 0.0144 mole of 1,5-dilithiodecaphenylpentasilane in 166 ml. of tetrahydrofuran. After about 120 ml. of this solution had been added, the silyllithium color began to persist. The final 50 ml. was added slowly. The solution became clear on continued stirring.

Hydrolysis with acidified ice water caused the precipitation of 0.55 g. (5.2%) of octaphenylcyclohexasilane, m.p. 318–324°. The tetrahydrofuran-soluble material was crystallized from benzene-petroleum ether (b.p. 60–70°) to give 5.0 g. (37%) of 1,1-dimethyldecaphenylcyclohexasilane, m.p. 472–476°. Recrystallization from benzene did not alter the melting point.

The compound obtained in this manner retained benzene as shown by the fact that refluxing a sample of the compound with carbon tetrachloride and distilling the resulting solution gave benzene in the distillate (ultraviolet spectrum). There was indicated to be more than 2 moles of benzene per mole of 1,1-dimethyldecaphenylcyclohexasilane by this method. The elemental analysis also indicates this fact.

Anal. Calcd. for $C_{62}H_{56}Si_6$: C, 76.80; H, 5.82; Si, 17.38. Found: C, 79.60, 79.39; H, 6.07, 6.06; Si, 14.55, 14.56.

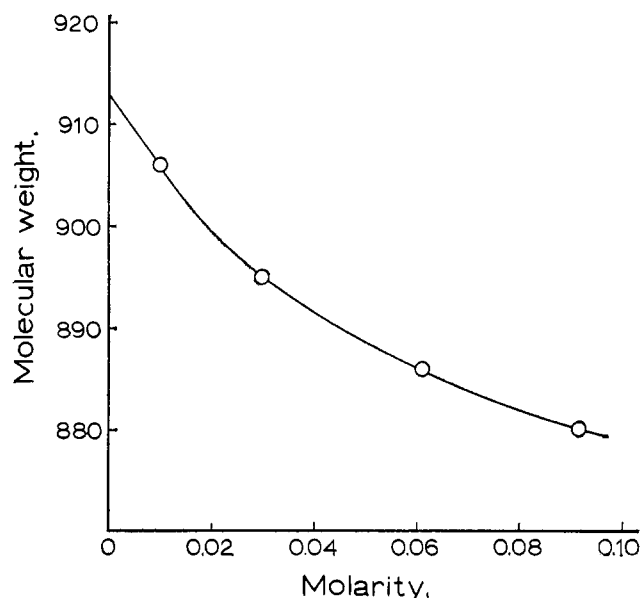


Fig. 1.—Extrapolation of the molecular weight of decaphenylcyclopentasilane (911.4) to infinite dilution.

The n.m.r. spectrum of the compound possessed absorption for methyl (9.46 τ) and for aromatic protons in a ratio of about 74/6. In addition to the usual monosubstituted phenyl absorptions, the infrared spectrum contained bands at 8.07, 11.95, and 12.53 μ characteristic for dimethylsilane compounds as well as absorption at 9.68 and 14.90 μ indicative of the presence of benzene.

Lithium Cleavage of Decaphenylcyclopentasilane in the Presence of Chlorotrimethylsilane.—Twenty milliliters of tetrahydrofuran was added to 14.6 g. (0.016 mole) of decaphenylcyclopentasilane and 1.6 g. (0.23 g.-atom) of lithium metal. After 5 min. of stirring, 4.32 g. (0.0398 mole) of chlorotrimethylsilane dissolved in 140 ml. of tetrahydrofuran was added over a period of 30 min. The silyllithium color remained throughout the addition and began to darken perceptibly after the addition was complete. Therefore, the filtered reaction mixture was added to 2.60 g. (0.0239 mole) of chlorotrimethylsilane. The color discharged immediately.

Acid hydrolysis and the usual work-up gave a residue from which was isolated by treatment with benzene-petroleum ether (b.p. 60–70°) 4.2 g. (29%) of decaphenylcyclopentasilane, m.p. 470–474° (mixture m.p.). The soluble portion was chromatographed on alumina. Elution of the column with petroleum ether gave first an oil from which there was isolated by distillation 1.47 g. (14.1%) of 1,1,1,2,2,2-hexamethyldiphenyltrisilane, b.p. 131–133° (0.55 mm.), n_D^{20} 1.5717. Redistillation of this material gave the pure product, b.p. 105.5–106° (0.2 mm.), n_D^{20} 1.5736.

Anal. Calcd. for $C_{18}H_{38}Si_3$: C, 65.78; H, 8.59. Found: C, 65.94, 65.97; H, 8.32, 8.30.

Secondly, there was obtained 1.04 g. (6.4%) of crude 1,1,1,4,4,4-hexamethyltetraphenyltetrasilane, m.p. 255–260°. Recrystallization from ethanol gave the analytical sample, m.p. 261.5–263°.

Anal. Calcd. for $C_{30}H_{58}Si_4$: C, 70.50; H, 7.49. Found: C, 70.42, 70.30; H, 7.26, 7.14.

Continued elution with petroleum ether gave 1.98 g. (17.9%) of a third compound, m.p. 289–297°. Recrystallization of this material from ethyl acetate and from benzene-ethanol gave pure 1,1,1,5,5,5-hexamethylhexaphenylpentasilane, m.p. 315–320°.

Anal. Calcd. for $C_{42}H_{84}Si_5$: C, 72.76; H, 6.98. Found: C, 72.98, 73.05; H, 6.67, 6.82.

With cyclohexane there was isolated from the column 0.72 g. (5.1%) of crude 1,1,1,6,6,6-hexamethyloctaphenylhexasilane, m.p. 285–290°, which melted at 293–296° (mixture m.p.) after recrystallization from benzene-petroleum ether. Carbon tetrachloride eluted 3.66 g. (21.6%) of crude 1,1,1,7,7,7-hexamethyldecaphenylheptasilane. Recrystallization from ethyl acetate gave the pure compound, m.p. 197–198° (mixture m.p.).

1,5-Dithiodidecaphenylpentasilane with Dichlorodiphenylsilane.—To 4.04 g. (0.0159 mole) of dichlorodiphenylsilane dissolved in 200 ml. of tetrahydrofuran was added dropwise 166 ml. of a

tetrahydrofuran solution containing 0.0157 mole of 1,5-dithiodidecaphenylpentasilane. After about three-fourths of this solution had been added, the silyllithium color began to persist in the reaction mixture. Therefore, an additional 1.21 g. (0.0048 mole) of dichlorodiphenylsilane was introduced and the addition of silyllithium solution completed. A slight orange-yellow color remained at the end of the addition. After stirring overnight, the reaction mixture was colorless.

Hydrolysis with 1 *N* hydrochloric acid caused the precipitation of 1.50 g. (13.1%) of octaphenylcyclopentasilane, m.p. 307–317° (mixture m.p.). The usual work-up provided a residue which was treated with benzene to give 0.4 g. (2.7%) of crude Compound C, melting with decomposition over the range 470–500°. Recrystallization from tetralin raised its melting point to 500° (mixture m.p.).

Concentration of the benzene-soluble portion of the reaction residue and addition of petroleum ether (b.p. 60–70°) provided 3.50 g. (24.5%) of decaphenylcyclopentasilane, m.p. 435–445°.

Discussion of Results. Molecular Weight Determination.—Previous proposals for the structure of Compound B have been based in the main on molecular weight determinations. Determinations made cryoscopically in benzene and in camphor by Kipping gave values very close to the theoretical 729 for an octaphenyltetrasilane. The problem of the molecular weight and structure of Compound B was investigated in this laboratory after the structure octaphenylcyclopentasilane had been assigned to Compound A. The molecular weight of B was determined cryoscopically in perylene and by isothermal distillation methods.⁷ By the perylene method a range of 830 to 1270 was obtained in seven determinations with an average value of 1085. This molecular weight indicated that Compound B was dodecaphenylcyclohexasilane (1094). The isothermal distillation method also indicated a cyclohexasilane with values of 1025, 1120, and 1225 being obtained. However, later chemical evidence indicated that some derivatives of Compound B were pentasilanes which, barring secondary cleavage reactions, implied that the compound was decaphenylcyclopentasilane.

Molecular weight determinations by three different and quite independent methods have now been obtained and agree excellently with the structure decaphenylcyclopentasilane for Compound B.

Using a vapor pressure osmometer¹⁶ the molecular weight of decaphenylcyclopentasilane in benzene, with benzil as the standard, was determined at several concentrations (Table I). The measured molecular

TABLE I
MOLECULAR WEIGHT OF DECAPHENYLCYCLOPENTASILANE IN BENZENE AT 37.0° (VAPOR PRESSURE OSMOMETER)^a

Concentration		
G./l.	M. obsd.	Mol. wt.
9.056	0.0100	906
26.58	.0296	895
54.04	.0610	886
80.57	.0915	880

^a Benzil as standard.

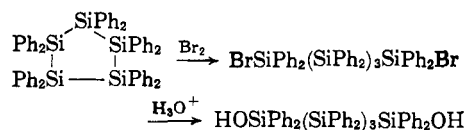
weights of the compound at higher concentrations are low; however, not so low as to indicate a tetrasilane. The molecular weights at lower concentrations approach the calculated value of 911.4 for decaphenylcyclopentasilane. Graphical extrapolation (Fig. 1) of the data to infinite dilution gives a value of 912 which is in excellent agreement with the theoretical value.

(16) Manufactured by Mechrolab, Inc., Mountain View, Calif.

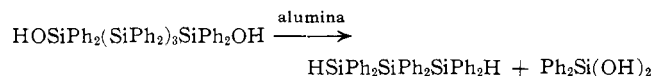
The molecular weight of decaphenylcyclopentasilane has also been determined for us ebullioscopically in toluene¹⁷ using octaphenylcyclotetrasilane as a standard to give a value of 921 (average of four values).¹⁸ An X-ray diffraction study and density determination¹⁹ of crystalline decaphenylcyclopentasilane provided a value of 983. The crystal used was grown from a mixture of benzene and ethanol from which decaphenylcyclopentasilane crystallizes with one molecule of benzene per $\text{Si}_5\text{Ph}_{10}$ unit to give a theoretical molecular weight of 989.

These molecular weight determinations, obtained by methods which generally give quite accurate data, point definitely to the fact that Compound B is decaphenylcyclopentasilane. In this light the chemistry of the compound was reviewed and extended to investigate its use in the synthesis of polysilane compounds.

Cleavage of Decaphenylcyclopentasilane with Bromine.—The cleavage of Compound B with bromine had been reported previously at a time when the compound was thought to be dodecaphenylcyclohexasilane. In view of the present corrected structure, the bromination was repeated to give 1,5-dibromodecaphenylpentasilane in 94% yield. This dibromo compound was hydrolyzed easily with 1 *N* hydrochloric acid to the corresponding decaphenylpentasilane-1,5-



diol in a manner similar to that employed in the hydrolysis of 1,5-dichlorodecaphenylpentasilane.¹⁰ Chromatography of the diol on basic alumina provided 79% of 1,1,2,2,3,3-hexaphenyltrisilane. Stripping of the alumina column with acetic acid provided a viscous

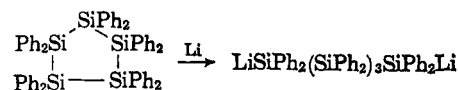


siloxane polymer from which was isolated some diphenylsilanediol and hexaphenylcyclotrisiloxane.

This chromatographic method provides the best route to phenylated trisilanes. An attempt to prepare 1,3-dibromohexaphenyltrisilane by treatment of 1,1,2,2,3,3-hexaphenyltrisilane with *N*-bromosuccinimide in carbon tetrachloride presents an interesting problem. This method has been reported in the past for the bromination of silicon hydrides.^{20,21} In this case reaction did occur; however, apparently chlorine atoms from the solvent are incorporated in the halogenated product. In two separate preparations a product, containing close to equal numbers of chlorine and bromine atoms, was obtained. Whether this product was a single compound or a mixture of the three possible compounds was not determined. In any case it appears that silyl radicals²² are formed in the reaction which are capable of abstracting chlorine atoms from the sol-

vent. 1,3-Dibromohexaphenyltrisilane was prepared by the treatment of 1,1,2,2,3,3-hexaphenyltrisilane with bromine in benzene, and was found to be different from the product obtained from the halogenation with *N*-bromosuccinimide.

Cleavage of Decaphenylcyclopentasilane with Lithium.—The cleavage of the silicon-silicon bond by lithium in tetrahydrofuran and the reactions of the silyllithium compounds thus obtained have been studied in detail.²³ Decaphenylcyclopentasilane undergoes ready reaction with lithium metal in tetrahydrofuran to give a high yield of 1,5-dilithiodecaphenylpentasilane. Titration of an aliquot using the allyl bromide double titration method¹⁴ after a 2-hr. reaction time indicated complete cleavage of decaphenylcyclopentasilane to 1,5-dilithiodecaphenylpentasilane. Treatment of this solution with tri-*n*-butyl phosphate provided 81% of 1,5-di-*n*-butyldecaphenylpentasilane, in

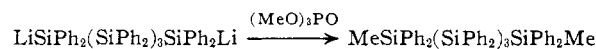


addition to 1,2-di-*n*-butyltetraphenylidisilane (0.9%), 1,3-di-*n*-butylhexaphenyltrisilane (2.2%), and recovered decaphenylcyclopentasilane (2%). Evidently a secondary cleavage of the 1,5-dilithiodecaphenylpentasilane had taken place. Shorter cleavage times led to larger amounts of recovered decaphenylcyclo-

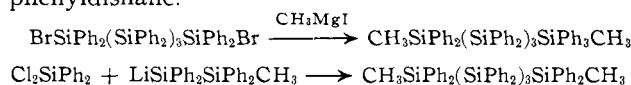


pentasilane, and longer times provided more of the secondary cleavage products.

Treatment of 1,5-dilithiodecaphenylpentasilane with trimethyl phosphate gives a high yield of 1,5-dimethyldecaphenylpentasilane. This compound was also pre-



pared by treatment of 1,5-dibromodecaphenylpentasilane with methylmagnesium iodide and by reaction of dichlorodiphenylsilane with 1-lithio-2-methyltetraphenylidisilane.



1,5-Dilithiodecaphenylpentasilane was also used to prepare higher polysilanes. A preparation of a nonasilane has been reported using this intermediate.²⁴ It has also been used to prepare 1,1,1,7,7,7-hexamethyldecaphenylheptasilane as well as 1,1,2,2,3,3,4,4,5,5,6,6,7,7-tetradecaphenylheptasilane in high yields. Also, 1,1-dimethyldecaphenylcyclohexasilane was prepared by the treatment of dichlorodimethylsilane with 1,5-dilithiodecaphenylpentasilane.

In an effort to prepare dodecaphenylcyclohexasilane, dichlorodiphenylsilane was treated with 1,5-dilithiodecaphenylpentasilane. There was isolated octaphenylcyclotetrasilane (13%), decaphenylcyclopentasilane (24.5%), and 3% of a compound which is apparently identical with Kipping's Compound C.^{1c} It is now felt that Compound C is dodecaphenylcyclo-

(17) C. A. Glover and R. R. Stanley, *Anal. Chem.*, **33**, 447 (1961).

(18) Determined by Dr. C. A. Glover, Tennessee Eastman Co. Research Laboratories.

(19) Determined by Dr. H. W. Patton, Tennessee Eastman Co. Research Laboratories.

(20) H. Gilman and W. J. Trepka, *J. Org. Chem.*, **27**, 1418 (1962).

(21) H. Hartmann and C. Sarafidis, *Naturwissenschaften*, **21**, 494 (1962).

(22) J. Curtice, H. Gilman, and G. S. Hammond, *J. Am. Chem. Soc.*, **79**, 4754 (1957).

(23) See H. Gilman and H. J. S. Winkler, in H. Zeiss, Ed., "Organometallic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1960.

(24) H. Gilman and R. A. Tomasi, *Chem. Ind. (London)*, 954 (1963).

Fig. 2.—Infrared spectra of octaphenylcyclotetrasilane (A) from 700 to 200 cm^{-1} (Nujol) and of decaphenylcyclopentasilane (B) from 2 to 10.5 μ (CCl_4), from 10.5 to 15 μ (CS_2), and from 700 to 200 cm^{-1} (Nujol). In the 2 to 15 μ range spectra were obtained with a Perkin-Elmer 21, while in the 700 to 200 cm^{-1} range they were obtained with a Beckman IR-7 using cesium iodide optics.

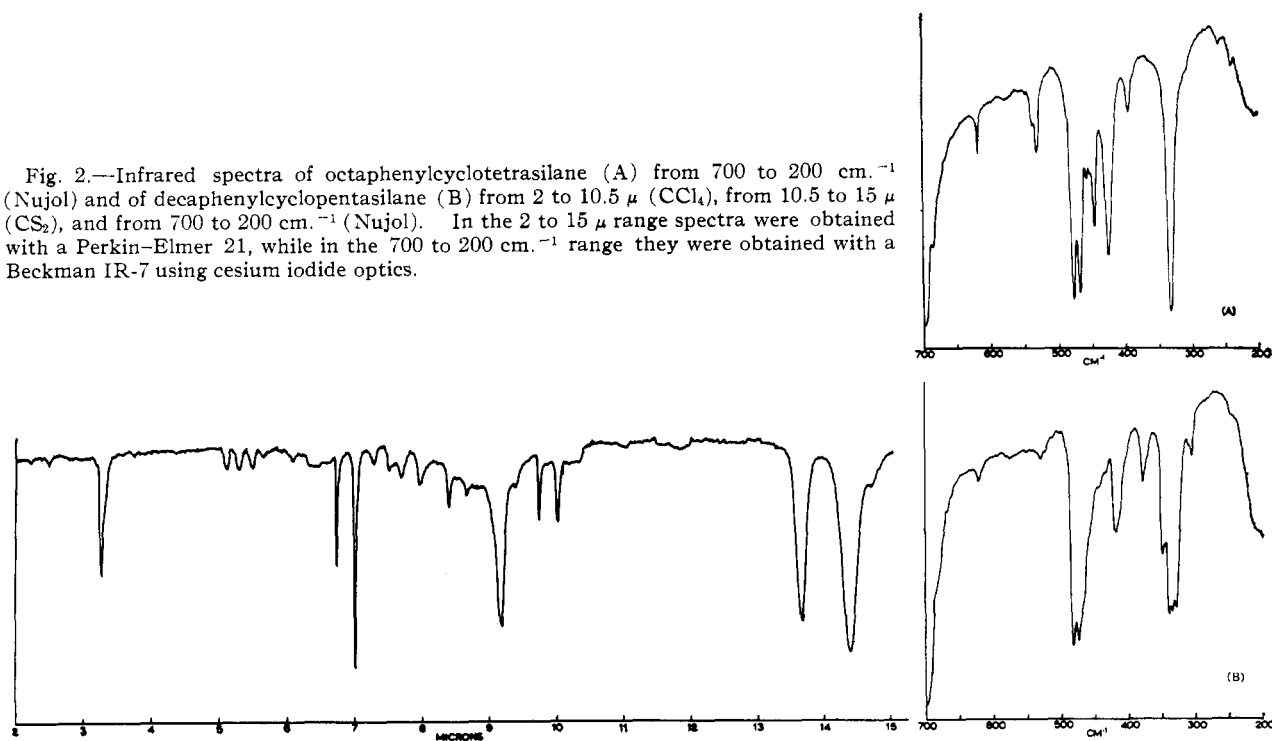
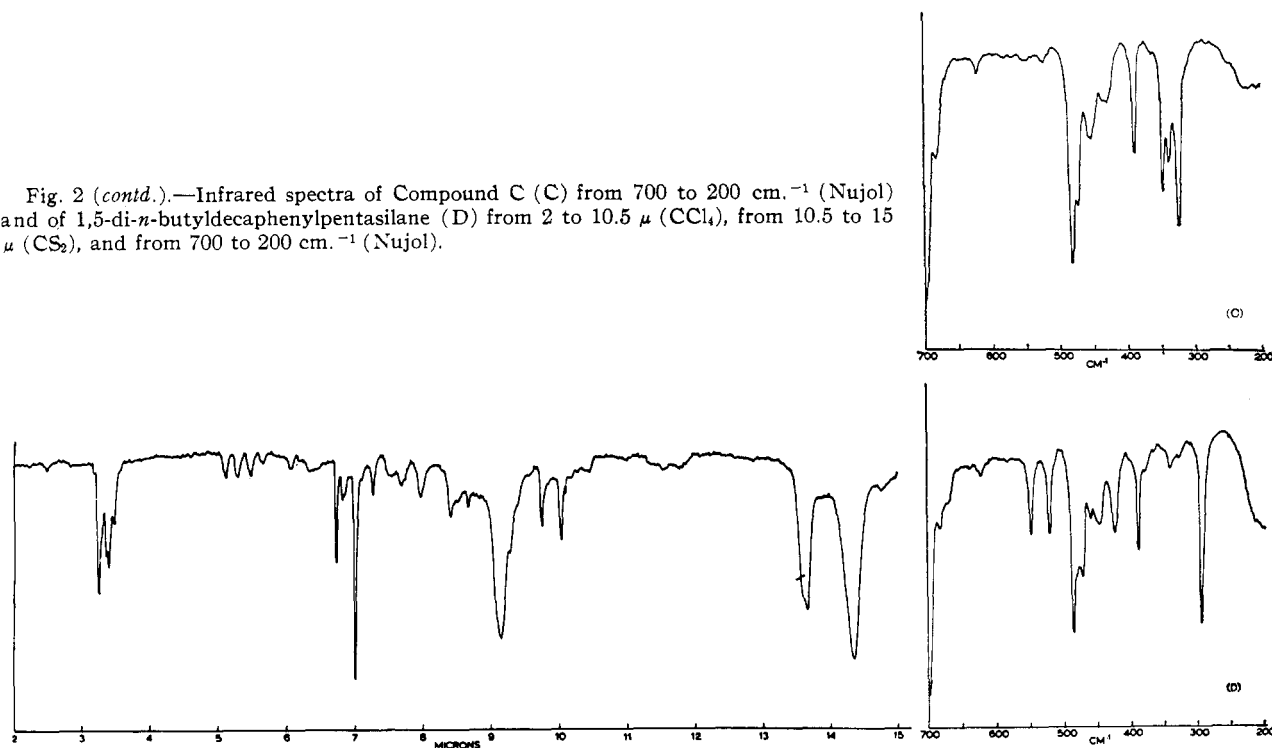
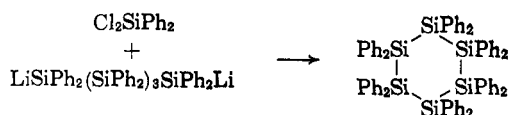


Fig. 2 (contd.).—Infrared spectra of Compound C (C) from 700 to 200 cm^{-1} (Nujol) and of 1,5-di-*n*-butyldecaphenylpentasilane (D) from 2 to 10.5 μ (CCl_4), from 10.5 to 15 μ (CS_2), and from 700 to 200 cm^{-1} (Nujol).



hexasilane. Further proof of this hypothesis will be offered at a later date.



Comparison of Decaphenylcyclopentasilane with Octaphenylcyclotetrasilane.—These two cyclosilanes show a remarkable difference in reactivity although they are quite closely related structurally. While octaphenylcyclotetrasilane reacts readily with oxidizing agents, iodine, and *sym*-tetrachloroethane, deca-

phenylcyclopentasilane is stable under similar conditions. Both react with bromine; however, octaphenylcyclotetrasilane reacts so rapidly that it might



possibly be titrated with the halogen, while with decaphenylcyclopentasilane care must be taken to provide a slow addition of bromine.

Cleavage of both cyclosilanes is effected by lithium in tetrahydrofuran to give 1,4-dilithiooctaphenyltetrasilane and 1,5-dilithiodecaphenylpentasilane, respec-

tively. However, treatment with an alkylating agent such as trimethyl phosphate provides only about 30% of 1,4-dimethyloctaphenyltetrasilane in the first case, while yields in excess of 80% of 1,5-dimethyldecaphenylpentasilane can be obtained in the latter case. This can be accounted for by the fact that octaphenylcyclotetrasilane is more susceptible to cleavage by silyllithium compounds than is decaphenylcyclopentasilane.²⁵ The greatly enhanced reactivity of octaphenylcyclotetrasilane over that of decaphenylcyclopentasilane can be accounted for by the relative ease of formation of a pentacovalent intermediate.²⁶

The infrared spectra of octaphenylcyclotetrasilane, decaphenylcyclopentasilane, Compound C, and 1,5-di-*n*-butyldecaphenylpentasilane were obtained (Fig. 2). The first three which are phenylated cyclosilanes have

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

(26) H. Gilman and G. L. Schwebke, in F. G. A. Stone and R. West, Ed., "Advances in Organometallic Chemistry," Academic Press, Inc., New York, N. Y., 1964.

almost identical spectra in the 5000–700 cm^{-1} range. However, in the 700–200 cm^{-1} region significant differences in the spectra are evident. The three cyclosilanes have absorptions centered at 333 cm^{-1} . In 1,5-di-*n*-butyldecaphenylpentasilane absorption at this point is lacking; however, a new strong absorption band appears at 294 cm^{-1} . Absorption in this region has been attributed, in the case of hexaphenyldisilane, to axial deformation of the two silicon atoms.²⁷ Whether absorptions for these more complex molecules can be attributed to the same linkage cannot, of course, be certain.

Acknowledgment.—This research was supported in part by the United States Air Force under Contract AF 33(616)-6463 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson AFB, Ohio.

(27) L. A. Harrah, M. T. Ryan, and C. Tamborski, *Spectrochim. Acta*, **18**, 21 (1962).

[CONTRIBUTION FROM THE THOMPSON CHEMICAL LABORATORY, WILLIAMS COLLEGE, WILLIAMSTOWN, MASS.]

Rearrangement of Aromatic N-Oxides. II. Rates and Mechanism for the Reaction of Acridine N-Oxide with Acetic Anhydride^{1a}

By J. HODGE MARKGRAF AND MYONG-KU AHN^{1b}

RECEIVED FEBRUARY 5, 1964

The kinetics of the rearrangement of acridine N-oxide with excess acetic anhydride to form acridone have been studied over the temperature range 0–25° by spectrophotometric and conductometric methods. Four possible reaction courses were considered: intramolecular, intermolecular, ion pair, and free radical. All runs, which were followed to at least 60% completion, exhibited pseudo-first-order kinetics; the value of *k* was constant over a fivefold change in concentration. A free radical chain mechanism was excluded by the absence of gaseous decomposition products commensurate with such a process. The intramolecular rearrangement of a free cation was excluded by the kinetic data. Additional runs with added sodium perchlorate and tetra-*n*-butylammonium acetate permitted a choice to be made between pathways involving free ions and ion pairs. The stoichiometry of the rate enhancement observed with added perchlorate ion was consistent with an external ion pair as the significant intermediate. This interpretation was supported by the values of the activation parameters.

Recently there has been interest in the mechanisms by which picoline N-oxides can undergo rearrangements with acid anhydrides.^{2–6} In a previous report from this laboratory results of a kinetic study of the rearrangement of pyridine N-oxide with acetic anhydride were presented.⁶ It was shown that under the conditions studied a free radical chain process was not operative. Since the reaction was pseudo-first order in excess acetic anhydride, the rate-determining step did not involve an intramolecular rearrangement of the free cation (N-acetoxypyridinium ion) to product (2-acetoxypyridine, isolated as 2-pyridone). No distinction was possible between intermolecular and ion pair pathways.

In the present study rates and products have been determined for the rearrangement of acridine N-oxide

with acetic anhydride. This represents the first systematic study of such a rearrangement in which both α -positions of the aromatic N-oxide are blocked. It is arresting that in no study of the rearrangement of pyridine N-oxide with acetic anhydride has 4-pyridone ever been detected as product. The only report of the reaction of acridine N-oxide with acetic anhydride stated that acridone was obtained when the reactants were heated.⁷ It was anticipated, therefore, that the latter reaction may proceed by a different mechanism. Accordingly, a kinetic study of this system was undertaken.

Experimental⁸

Materials.—Acridine N-oxide was prepared by the method of Acheson, *et al.*⁹ The crude product (42% yield, m.p. 164–165°) was chromatographed in dichloromethane on alumina, and the recovered yellow crystals were dehydrated over phosphorus pentoxide under vacuum in an Abderhalden apparatus warmed by refluxing acetone. The final yield was 22%, m.p. 168.0–169.0° (lit.⁹ m.p. 169°). The bright yellow crystalline product was stored in the dark under nitrogen. Acridone (Eastman

(1) (a) This work was supported by a grant from the National Science Foundation; (b) based on the Honors Thesis of M.-K. Ahn, 1963.

(2) (a) S. Oae, T. Kitao, and Y. Kitaoka, *J. Am. Chem. Soc.*, **84**, 3359 (1962); (b) *ibid.*, **84**, 3362 (1962).

(3) (a) V. J. Traynelis and R. F. Martello, *ibid.*, **80**, 6590 (1958); (b) *ibid.*, **82**, 2744 (1960); (c) V. J. Traynelis, A. I. Gallagher, and R. F. Martello, *J. Org. Chem.*, **26**, 4365 (1961).

(4) (a) V. Boekelheide and D. L. Harrington, *Chem. Ind. (London)*, 1423 (1955); (b) V. Boekelheide and W. J. Linn, *J. Am. Chem. Soc.*, **76**, 1286 (1954).

(5) J. A. Berson and T. Cohen, *ibid.*, **77**, 1281 (1955).

(6) J. H. Markgraf, H., B. Brown, Jr., S. C. Mohr, and R. G. Peterson, *ibid.*, **85**, 958 (1963); considered as paper I in this series.

(7) A. Kliegel and A. Fehrlé, *Ber.*, **47**, 1629 (1914).

(8) Melting points and boiling points are uncorrected. Infrared spectra were obtained as mineral oil mulls with a Perkin-Elmer Infracord spectrophotometer, Model 137.

(9) R. M. Acheson, B. Adcock, G. M. Glover, and L. E. Sutton, *J. Chem. Soc.*, 3367 (1960).