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CYCLIC ORGANOSILICON AND RELATED COMPOUNDS

by

Ernest Adolph Zuech

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In Charge of Major Work

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Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
of Science and Technology
Ames, Iowa

1960

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INTRODUCTION

Recent developments in the aircraft and missile fields have produced a need for lubricants and hydraulic fluids capable of performing at extreme temperatures. In fact, the stringent and ever-expanding requirements have made many of the existing natural and synthetic compositions inadequate. It is therefore evident that better base stocks and superior additives, such as antioxidants, antiwear agents, and viscosity index improvers, are required to formulate satisfactory materials.

Nitrogen-containing aromatic cyclic silicon compounds, having the 5,10-dihydrophenazasiline nucleus, promise to be of significant value as high temperature antioxidants for certain lubricant compositions. These compounds were first obtained by the extended heating of diphenylsilane with phenothiazine derivatives,[1] but this synthesis suffers from the disadvantages of tedious work-ups, very low yields, and a lack of flexibility. Accordingly, one of the purposes of this investigation has been the development of new procedures for the preparation of 5,10-dihydrophenazasiline compounds. This objective was realized by the reactions of 2,2'-dilithiodiarylamine derivatives with appropriately substituted organo-

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[1] H. Gilman and D. Wittenberg, _J_. _Am_. _Chem_. _Soc_., _79_, 6339 (1957); D. Wittenberg, H. A. McNinch, and H. Gilman, _ibid_., _80_, 5418 (1958).

silicon halides and hydrides. The method is synthetically versatile and has permitted the preparation of a wide variety of interesting compounds, including silicon-hydrogen functional types.

Another purpose of this work has been the synthesis of some monomeric organosilicon compounds for possible use in high temperature lubricant applications. One part of this problem was concerned with the reactions of o-phenylenedilithium with organosilicon compounds. A number of o-phenylene silicon derivatives were prepared, as well as some new cyclic organosilicon compounds. These cyclic compounds are 5,10-dihydrosilanthrene derivatives, silicon analogs of 9,10-dihydroanthracene, and exhibit remarkable thermal stabilities.

Paralleling these studies were related investigations in which a series of non-cyclic aralkyl compounds was synthesized and preliminarily screened for thermal stability, and in which attempts were made to prepare 10H-dibenzosilin derivatives by Friedel-Crafts cyclization reactions.

In addition to the aforesaid purposes, this investigation has been conducted to add to the knowledge of the fundamental chemistry of the organic compounds of silicon.

The names and the numbering systems used herein are in accord with those used and recommended by Chemical Abstracts.

HISTORICAL

The chemistry of cyclic organosilicon compounds has been previously summarized through April, 1957.[2] The purpose of this review is to record the preparations and properties of cyclic organosilicon compounds reported since that time. Chemical Abstracts and Current Chemical Papers have been thoroughly examined through March, 1960. The older literature has also been rechecked in an attempt to achieve completeness in the reviews, and in addition, all cross references contained in individual papers were checked.

For ease in locating pertinent data, this review has been arbitrarily divided into three main sections: preparation of alicyclic organosilicon compounds, preparation of aromatic cyclic organosilicon compounds, and properties of cyclic organosilicon compounds.

It should be noted that the complete chemistry of aromatic cyclic organosilicon compounds will be reported due to their importance to these studies. On the other hand, the numerous studies on the cyclic organosiloxanes and the cyclic organopolysilanes will not be presented in this compilation.

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[2] R. D. Gorsich. Some cyclic organosilicon compounds and derivatives. Unpublished Ph. D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1957.

Preparation of Alicyclic Organosilicon Compounds

Since the preparation of the first cyclic organosilicon compound, 1,1-dichloro-1-silacyclohexane, by Bygden[3] in 1915, a whole new branch of silicon chemistry has evolved. Generally speaking, most of the methods of synthesis for non-cyclic organosilicon compounds are also applicable to the cyclic types. For example, the coupling of Grignard reagents with halosilanes is one of the most important synthetic procedures. Thus, Bygden[3] introduced silicon into a six-membered ring by allowing equal molar amounts of 1,5-pentamethylenedimagnesium dibromide and silicon tetrachloride to interact. Many functional, as well as nonfunctional, alicyclic organosilicon compounds have been prepared by this method and by the analogous reactions involving organolithium reagents.[2]

The reaction of alkyl and aryl halides directly with elementary silicon, in the presence of a suitable catalyst, is widely used industrially for the production of organosilicon halides.[4] When certain aliphatic dihalides are subjected to this reaction, silacycloalkane derivatives are formed. Thus, 1,1-dichloro-1-silacyclopentane was obtained

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[3] A. Bygden, <u>Ber</u>., <u>48</u>, 1236 (1915).

[4] E. G. Rochow. An introduction to the chemistry of the silicones. 2nd ed., p. 36. New York, John Wiley and Sons. 1951.

by the passage of 1,4-dichlorobutane over silicon-copper alloy at 300°.[5,6] An analogous reaction with 3,4-dichloro-1-butene gave 1,1-dichloro-1-sila-3-cyclopentene.[6]

The first derivative in the corresponding silacyclopentadiene series has recently been prepared by Braye and Hübel.[7] The novel strongly fluorescent compound, hexaphenylsilacyclopentadiene, was obtained by treating dichlorodiphenylsilane with $Fe_2(CO)_6(C_6H_5C_2C_6H_5)_2$. The latter substance was formed from diphenylacetylene and iron pentacarbonyl.

As described previously, the most common method for the formation of silacycloalkanes involves coupling of silicon halides with organometallic compounds; however, Wittenberg and Gilman[8] found that certain silicon-containing organolithium compounds would undergo cyclization by displacing a phenyl group. The main products from the reaction of chlorotriphenylsilane and tetramethylenedilithium were 1,1-diphenyl-1-sila-

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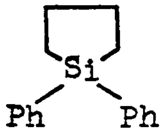
[5] A. D. Petrov, N. P. Smetankiva, and G. I. Niskishin, _Izvest_. _Akad_. _Nauk_ _S.S.S.R._, _Otdel_. _Khim_. _Nauk_, 1468 (1958) [Original available but not translated; abstracted in _C_. _A_., _53_, 8117 (1959)].

[6] G. I. Niskishin, A. D. Petrov, and S. I. Sadykh-Zade, _Khim_. _i_ _Prakt_. _Primenenie_ _Kremneorg_. _Soedinenii_ _Trudy_ _Konf_., No. 1, 68 (1958) [Original not available for examination; abstracted in _C_. _A_., _53_, 17097 (1959)].

[7] E. H. Braye and W. Hübel, _Chem_. _and_ _Ind_. (London), 1250 (1959).

[8] D. Wittenberg and H. Gilman, _J_. _Am_. _Chem_. _Soc_., _80_, 2677 (1958).

cyclopentane and tetraphenylsilane; whereas, the expected

$2\ Ph_3SiCl + Li(CH_2)_4Li \longrightarrow$  $+\ Ph_4Si + Ph_3Si(CH_2)_4SiPh_3$

tetramethylenebis(triphenylsilane) was obtained in a low yield. Similarly, 4-triphenylsilylbutyllithium, prepared from 4-bromobutyltriphenylsilane and lithium, underwent ring closure to give the silacyclopentane derivative and phenyllithium. Extension of this intramolecular cleavage-cyclization reaction to chlorotriphenylsilane and pentamethylenedilithium gave a very low yield of 1,1-diphenyl-1-silacyclohexane.[8]

Benkeser and Bennett[9] prepared a silicon analog of cyclohexanone, 4,4-dimethyl-4-silacyclohexanone, in a four-step synthesis. This involved preparation of di(3-hydroxypropyl)dimethylsilane and subsequent oxidation to the dicarboxylic acid by treatment with alkaline potassium permanganate. The di-carboxylic acid was converted to the thorium salt which afforded the cyclohexanone derivative upon pyrolysis at 350°.

A novel bicyclic silicon-containing compound, 1-chloro-

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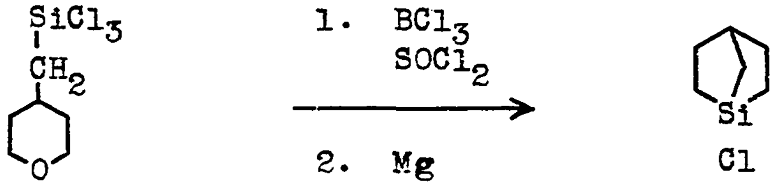
[9] R. A. Benkeser and E. W. Bennett, ibid., 80, 5414 (1958).

1-silabicyclo[2.2.1] heptane (I), has been synthesized by Sommer and Bennett[10] for the purpose of elucidating the stereochemical requirements for substitution at a silicon atom. The elegant multistep synthesis of the bicyclic system involved the following steps: the preparation of the Grignard reagent from 4-bromomethyltetrahydropyran and reaction with silicon tetrachloride to give 4-trichlorosilylmethyltetrahydropyran (II); cleavage of this tetrahydropyran derivative with boron trichloride and subsequent treatment with thionyl chloride to give 1,5-dichloro-3-trichlorosilylmethylpentane; and finally, cyclization of this chloro derivative with magnesium. The corresponding octane derivative, 1-chloro-1-silabicyclo [2.2.2]octane, has been prepared by a similar procedure starting with 4-(2-bromoethyl)tetrahydropyran.[11]



II I

A number of alicyclic systems containing two or more

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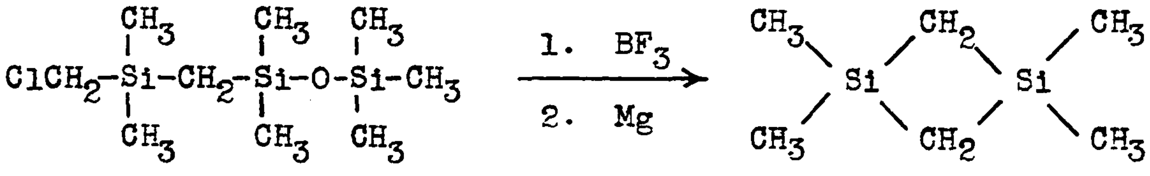
[10] L. H. Sommer and O. F. Bennett, ibid., 79, 1008 (1957).

[11] L. H. Sommer and O. F. Bennett, ibid., 81, 251 (1959).

silicon atoms have been described. Of these, Knoth and Lindsey[12] reported the unique preparation of the smallest ring system, namely a 1,3-disilacyclobutane derivative. Chloromethylpentamethyldisiloxane was converted to the Grignard reagent and then coupled with chloromethyldimethylchlorosilane to give 1-chloro-2,2,4,4,6,6-hexamethyl-5-oxa-2,4,6-trisilaheptane (III). Cleavage of the siloxane linkage by boron trifluoride in ether gave 1-chloro-4-fluoro-2,2,4-trimethyl-2,4-disilapentane which was subsequently cyclized with magnesium to give 1,1,3,3-tetramethyl-1,3-disilacyclobutane (IV) in a 25% over-all yield.



III IV

Silicon hydrides add to alkenes and alkynes to form the respective alkyl and alkenyl silane compounds. This is in effect the addition of silicon and hydrogen to the unsaturated grouping, and is facilitated by peroxides, certain metals or ultraviolet light. Intermolecular addition was found to occur when the silicon contained both hydrogen and an unsaturated

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[12] W. H. Knoth, Jr. and R. V. Lindsey, Jr., *J. Org. Chem.*, **23**, 1392 (1958).

grouping. Thus, Curry[13] prepared and polymerized dimethyl-, diethyl-, diphenyl-, and methylphenylvinylsilane, using platinum suspended on finely divided carbon as the catalyst. In addition to the polymeric materials, there were isolated lesser amounts of low molecular weight products, which were identified as derivatives of the 1,4-disilacyclohexane ring system. Allyldimethylsilane was found to undergo a similar polymerization and cyclization to give a large quantity of polymeric material and a small amount of the cyclic dimer, 1,1,5,5-tetramethyl-1,5-disilacyclooctane.[14]

Fritz and co-workers have reported the synthesis of a number of cyclic derivatives composed of one or more six-membered rings. These compounds were obtained by the thermal decomposition of various organosilicon compounds and are named as derivatives of cyclocarbosilan.[15]

The reaction mixture obtained from the decomposition of chlorotrimethylsilane at 800° affords among other products, a white crystalline compound, $C_9H_{20}Cl_4Si_4$, which was tentatively assigned structure V shown below.[16] The thermal decomposition of tetramethylsilane in static or streaming systems

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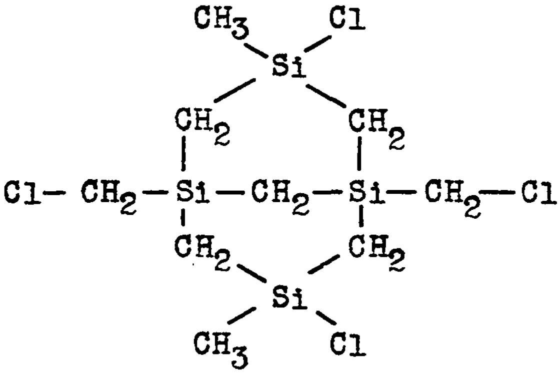
[13] J. W. Curry, J. Am. Chem. Soc., 78, 1686 (1956).

[14] J. W. Curry and G. W. Harrison, Jr., J. Org. Chem., 23, 1219 (1958).

[15] G. Fritz, Angew. Chem., 70, 701 (1958).

[16] G. Fritz, Z. Naturforsch., 12b, 123 (1957).



V

leads to a mixture of gases, liquids and solids.[17] Cyclic compounds with the following empirical formulae were reported to have been isolated: $C_8H_{22}Si_3$, $C_9H_{24}Si_3$, $C_{11}H_{28}Si_4$, $C_{13}H_{34}Si_5$, $C_{14}H_{36}Si_6$, $C_{18}H_{46}Si_7$, $C_{20}H_{50}Si_8$, $C_{24}H_{66}Si_8$, and $C_{27}H_{74}Si_9$. These compounds are viewed as condensed systems of six-membered rings with alternating silicon and carbon atoms. The remaining bonds of the carbon atoms are satisfied by hydrogen, and those of silicon by methyl groups, except that there are one or two silicon-hydrogen groups present in most of the compounds. Fritz and Raabe[17] assigned structures VI and VII to the compounds $C_{18}H_{46}Si_7$ and $C_{20}H_{50}Si_8$, respectively. Using the nomenclature recommended by Fritz[15], compound VI is Si-dodecamethyltricyclocarbosilan and VII is Si-dodecamethyltetracyclocarbosilan.

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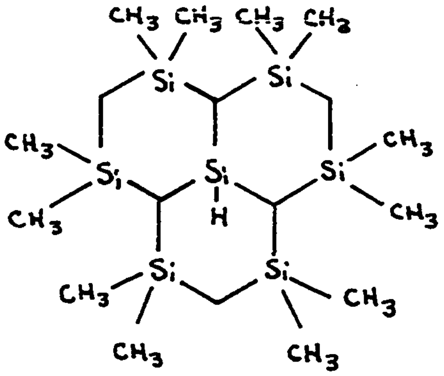
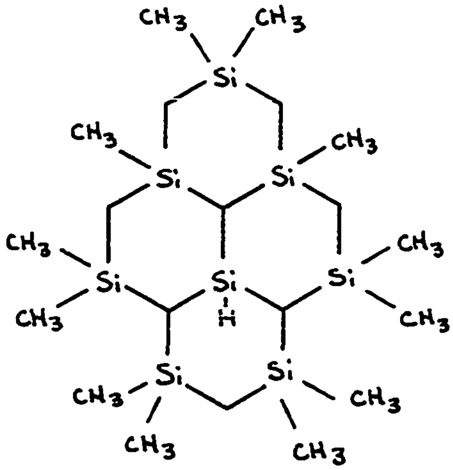
[17] G. Fritz and B. Raabe, _Z_. _anorg_. _u_. _allgem_. _Chem_., _286_, 149 (1956); _299_, 232 (1959).



VI



VII

Decomposition of trichloromethylsilane at 710° gave Si-hexachlorocyclocarbosilan (1,1,3,3,5,5-hexachloro-1,3,5-trisilacyclohexane).[18] In addition, a compound with the empirical formula $C_8H_{13}C_{13}Si_8$ was obtained having the same ring structure as compound VII, but will all of the methyl groups as well as the hydrogen atom attached to silicon replaced by chlorine atoms.

Various synthetic approaches were utilized to prepare several interesting cyclic silicon compounds containing such elements as nitrogen, oxygen, and tin.

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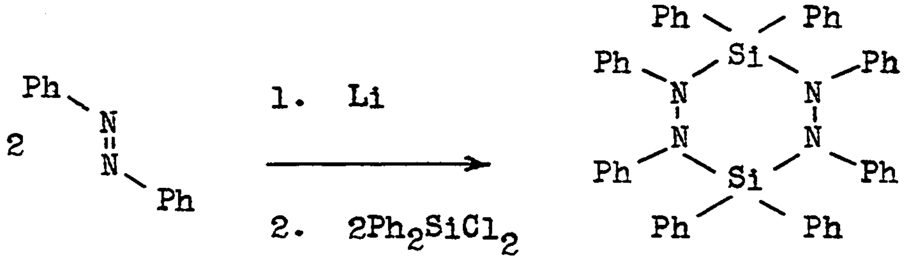
[18] G. Fritz and G. Teichmann, *Angew. Chem.*, *70*, 701 (1958); G. Fritz, D. Habel, K. Kummer, and G. Teichmann, *Z. anorg. u. allgem. Chem.*, *302*, 60 (1959).

George et al.[19] studied a number of reactions of the azobenzene-dilithium adduct with halosilanes. Dichlorodiphenylsilane and dichloromethylphenylsilane gave octaphenyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (VIII) and 1,2,3,4,5,6-hexaphenyl-3,6-dimethyl-1,2,4,5-tetraaza-3,6-disilacyclohexane,



VIII

respectively. Similar experiments with the stilbene-dilithium adduct did not afford any cyclic products.[19] The reaction of dichlorodiphenylsilane and hydrazine yielded a polymeric condensation product, $[-R_2Si(NHNH)-]n$.[20] However, under conditions of high dilution and cooling, the main product was the cyclic dimer, 3,3,6,6-tetraphenyl-1,2,4,5-tetraaza-3,6-disilacyclohexane. An analogous substance was obtained from the reaction of dichlorodimethylsilane and phenylhydrazine.

Knoth and Lindsey[21] synthesized a new class of hetero-

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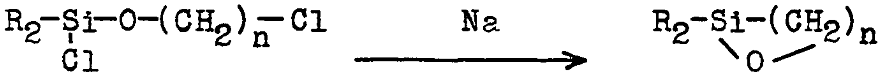
[19] M. V. George, D. Wittenberg, and H. Gilman, J. Am. Chem. Soc., 81, 361 (1959).

[20] U. Wannagat and H. Niederprüm, Angew. Chem., 70, 745 (1958).

[21] W. H. Knoth, Jr. and R. V. Lindsey, Jr., J. Am. Chem. Soc., 80, 4106 (1958).

cycles containing both silicon and oxygen. These 2,2,-disubstituted 1-oxa-2-silacycloalkane (IX) derivatives were obtained by ring closure of the corresponding (chloroalkoxy)-chlorosilanes (X) with lithium or sodium. The dimethyl



X IX

derivatives, where n equals 2, 3, and 4, have been prepared, as well as the diphenyl derivative where n equals 3. The (chloroalkoxy)chlorosilanes (X) were made from dichlorosilanes and α,ω-chlorohydrins or oxacycloalkanes.

A similar oxygen-containing cyclic compound, 1,1,4,4-tetramethyl-1,4-disila-3,6-dioxacyclohexane, was obtained by heating 1,3-di(hydroxymethyl)tetramethyldisiloxane in the presence of calcium oxide.[22] In addition, a linear polymer was also formed.

Merker and Scott[23] have reported the preparation of cyclic systems containing silicon, tin, and oxygen. Hydrolysis of bis(dimethylsilylmethyl)dimethyltin (XI) with ethan-

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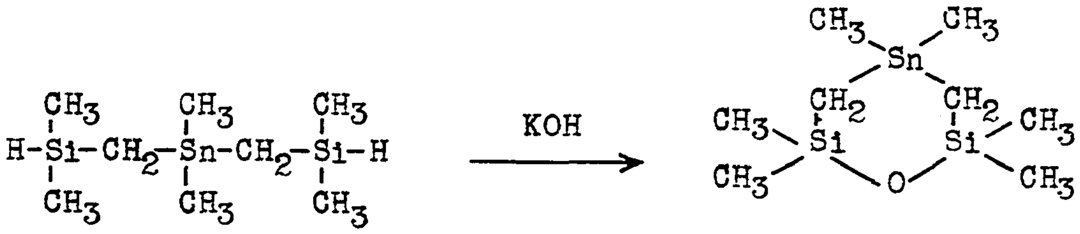
[22] B. A. Eynon, U. S. Patent 2,898,346 (August 4, 1959) [Original not available for examination; abstracted in C. A., 54, 1576 (1960)].

[23] R. L. Merker and M. J. Scott, J. Am. Chem. Soc., 81, 975 (1959).



XI XII

olic potassium hydroxide gave 1,1,3,3,5,5-hexamethyl-1,3-disila-5-stanna-2-oxacyclohexane (XII). The 5,5-dibutyl derivative was similarly prepared from bis(dimethylsilylmethyl)dibutyltin. Attempts to prepare the ten-membered cyclic compound from bis(3-dimethylsilylpropyl)dimethyltin under identical conditions were unsuccessful and yielded only linear polysiloxanes. Thermally cracking the polysiloxanes under alkaline conditions, however, afforded a small yield of the ten-membered cyclic compound.[23]

Recently, a cyclohexane ring system containing both silicon and tin has been synthesized.[24] This was accomplished by an addition reaction involving diphenyltin dihydride and diphenyldivinylsilane to give 1,1,4,4-tetraphenyl-1-sila-4-stannacyclohexane. The similar preparation of cyclic derivatives containing other Group IV-B elements is also reported.

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[24] M. C. Henry and J. G. Noltes, <u>ibid</u>., <u>82</u>, 561 (1960).

Preparation of Aromatic Cyclic Organosilicon Compounds

Aromatic cyclic organosilicon compounds are defined as a class of silicon heterocycles composed of fused bi- or tricyclic systems in which at least one of the rings is an aryl group. The term should not imply that these compounds contain silicon involved in multiple bonding of the ethylenic type. Moreover, it should be noted that there is no evidence for the existence of any organosilicon compound containing this sort of double bond to silicon. Considerable evidence exists, however, for dative multiple bonding in which the silicon d-orbitals are involved in π-bonding with filled p-orbitals of certain covalently linked atoms or groups.[25,26] This "back coordination" may well be the reason for the enhanced stability of some organosilicon compounds.

Gilman and Gorsich[27] reported the preparation of the first cyclic compound in which silicon is attached to four aromatic nuclei. This novel compound was 5,5-diphenyldibenzosilole, a silicon analog of 9,9-diphenylfluorene. The

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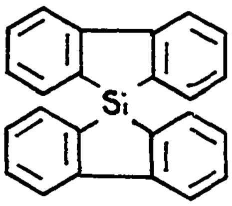
[25] F. G. A. Stone and D. Seyferth, J. Inorg. Nuclear Chem., 1, 112 (1955).

[26] E. R. Rochow, D. T. Hurd, and R. N. Lewis. The chemistry of organometallic compounds. p. 31. New York, John Wiley and Sons. 1957; C. Eaborn. Organosilicon compounds. p. 91. London, Butterworth Scientific Publications. 1960.

[27] H. Gilman and R. D. Gorsich, J. Am. Chem. Soc., 77, 6380 (1955).

synthesis of a number of functional dibenzosilole derivatives, as well as some non-functional types, has subsequently been described.[2,28,29] These heterocycles were obtained by cyclization reactions involving 2,2'-biphenylenedilithium and the appropriately substituted $RSiCl_3$ and R_2SiCl_2 compounds. For example, the dilithium compound was reacted with dichlorodiphenylsilane and with silicon tetrachloride to give 5,5-diphenyldibenzosilole and 5,5'-spirobi-(dibenzosilole) (XIII),



XIII

respectively.[28] Methyl-, n-dodecyl-, and phenyltrichlorosilane all coupled with 2,2'-biphenylenedilithium to give the corresponding 5-methyl-, 5-n-dodecyl-, and 5-phenyl- derivatives of 5-chlorodibenzosilole in excellent yields.[28] 5,5-Dichlorodibenzosilole was obtained by treating a large excess of silicon tetrachloride with the dilithium derivative; however, an appreciable amount of 5,5'-siprobi-(dibenzosilole) was also obtained.[28]

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[28] H. Gilman and R. D. Gorsich, ibid., 80, 1883 (1958).

[29] H. Gilman and R. D. Gorsich, ibid., 80, 3243 (1958).

The scope of this class of compounds has been broadened so as to include cyclic systems containing two hetero atoms, silicon and either oxygen, sulfur, or nitrogen. The first of such derivatives was prepared by Oita and Gilman.[30] Diphenyl ether was dimetalated and subsequently treated with dichlorodiphenylsilane, dichlorodimethylsilane, and silicon tetrachloride to give 10,10-diphenylphenoxasilin, 10,10-dimethylphenoxasilin, and 10,10'-spirobi(phenoxasilin), respectively. 10,10-Dibenzyl- and 10,10-di-n-dodecylphenoxasilin were synthesized in an analogous manner.[31]

Hitchcock et al.[32] found that the diphenyl, dimethyl, and spiro phenoxasilin compounds could be obtained in much improved yields when the 2,2'-dilithiodiphenyl ether was prepared by halogen-metal interconversion of 2,2'-dibromodiphenyl ether with n-butyllithium. The preparation of the 2-methyl-, 3-methyl-, and 2,7-dimethyl derivatives of 10,10-diphenylphenoxasilin was also given. The facile synthesis of 2,8-dimethyl-10,10-diphenylphenoxasilin was recently reported.[33] Treatment of di-p-tolyl ether with two molecular equivalents

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[30] K. Oita and H. Gilman, ibid., 79, 339 (1957).

[31] H. Gilman and D. Miles, J. Org. Chem., 23, 1363 (1958).

[32] C. H. S. Hitchcock, F. G. Mann, and A. Vanterpool, J. Chem. Soc., 4537 (1957).

[33] Tung-Yin Yu, Lin-Yuen Hsu, and Shih-Huei Wu, Hua Hsüch Hsüch Pao, 24, 170 (1958) [Original not available for examination; abstracted in C. A., 53, 6223 (1959)].

of bromine gave 2,2'-dibromodi-p-tolyl ether, which afforded the phenoxasilin derivative, in excellent over-all yield, upon Wurtz-type coupling with dichlorodiphenylsilane and sodium.

Some corresponding sulfur-containing analogs were prepared by the dimetalation of diphenyl sulfone and subsequent coupling with the appropriate chlorosilanes.[34] The 10,10-dimethyl- and 10,10-diphenylphenothiasilin-5,5-dioxide derivatives were readily obtained; however, an attempt to prepare 10,10'-spirobi-(phenothiasilin-5,5-dioxide) from a similar reaction with silicon tetrachloride was unsuccessful.

A novel type of reaction for the formation of cyclic organosilicon compounds has been reported which involves the extended heating of diphenylsilane with sulfur-containing heterocycles.[1] From the crude reaction mixtures, compounds were isolated in which the sulfur is replaced by the diphenylsilylene group. In accordance with this reaction, 10,10-diphenylphenoxasilin, 10,10-diphenylphenothiasilin, 10,10-diphenyl-5,10-dihydrophenazasiline, and 5-ethyl-10,10-diphenyl-5,10-dihydrophenozasiline have been prepared from phenoxathiin, thianthrene, phenothiazine, and 10-ethylphenothiazine, respectively. 5,5-Diphenyl-10*H*-dibenzosilin has reportedly been prepared by a similar procedure from thi-

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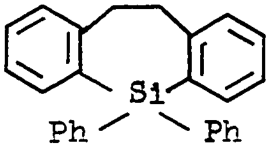
[34] K. Oita and H. Gilman, *J. Org. Chem.*, *22*, 336 (1957).

axanthene.[35]

A unique tricyclic compound containing silicon incorporated in a seven-membered ring has recently been prepared.[2] This substance, 10,11-dihydro-5,5-diphenyldibenzosilepin (XIV), was obtained from the coupling of 2,2'-dilithiobibenzyl and dichlorodiphenylsilane.



XIV

The Friedel-Crafts reaction is one of the most widely used methods of making carbon-carbon bonds and is commonly utilized on an intramolecular basis to synthesize polynuclear compounds. In organosilicon chemistry, interactions with Lewis acids, employed in Friedel-Crafts reactions, usually result in the cleavage of silicon-carbon bonds.[36] However, Wittenberg _et al_.[37] have successfully synthesized some benzosilacyclanone compounds by intramolecular cyclization reac-

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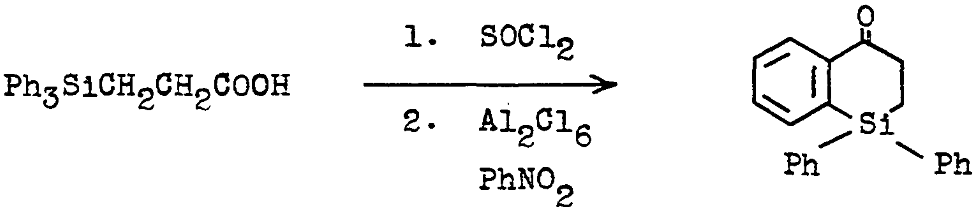
[35] J. W. Diehl. Some organometallic reactions with heterocyclic compounds. Unpublished Ph. D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1959.

[36] H. Gilman and G. E. Dunn, _Chem. Rev._, _52_, 77 (1953).

[37] D. Wittenberg, P. B. Talukdar, and H. Gilman, _J. Am. Chem. Soc._, _82_, in press (1960).

tions. Conversion of 3-triphenylsilylpropionic acid (XV) to the acid chloride with thionyl chloride and subsequent treatment with aluminum chloride in nitrobenzene afforded the cyclic ketone, 2:3-benzo-1,1-diphenyl-1-silacyclohexen-2-one-4 (XVI). The corresponding cyclization of 4-triphenylsilylbutyric acid yielded 2:3-benzo-1,1-diphenyl-1-silacycloheptene-2-one-4. An attempt to cyclize triphenylsilylacetic acid was unsuccessful, as were the attempts to cyclize 3-triphenylsilylpropanol-1 and 3-triphenylsilylpropyl bromide.



XV XVI

Properties of Cyclic Organosilicon Compounds

For the most part, the properties of cyclic organosilicon compounds are analogous to those of the non-cyclic compounds; therefore, this compilation of properties is intended to be illustrative rather than exhaustive.

Benkeser and Bennett[9] measured the dissociation of the cyanohydrin of 4,4-dimethyl-4-silacyclohexanone as well as that of its carbon analog. The dissociation constant of the silicon compound was found to be approximately five times larger than that for the carbon compound and is explained in terms of Brown's I-strain theory.[38] Enlargement of a six-membered ring by the substitution of a silicon atom for a carbon will decrease the symmetry of the ring and hence increase the hydrogen-hydrogen repulsions to some extent. A change in coordination number from four to three, which occurs in the dissociation of the cyanohydrin, will be favored since the preferred angle of a carbonyl group (120°) results in a decrease in internal strain. In other words, the reactivity of the six-membered silicon ring approaches the reactivity of the corresponding seven-membered carbon ring. Additional evidence for the increased ring size of the silicon ketone was obtained from infrared spectra. The frequency of the carbonyl band of 4,4-dimethyl-4-silacyclohexanone was found to be 1702 $cm.^{-1}$ while that for the carbon analog was 1709 $cm.^{-1}$. The value for cycloheptanone is reported to be 1699 $cm.^{-1}$.

Benkeser and Bennett[9] also report the successful reduction of the ketone with lithium aluminum hydride to give 4,4-dimethyl-4-silacyclohexanol.

The bridgehead silicon compound, 1-chloro-1-silabicyclo-[2.2.1] heptane,[10] hydrolyzes rapidly in a stream of moist air or in wet ether to give bis-(1-silabicyclo [2.2.1] heptyl) oxide; while, reduction with lithium aluminum hydride gives an

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[38] H. C. Brown and M. Borkowski, ibid., 74, 1894 (1952).

excellent yield of 1-silabicyclo [2.2.1] heptane.

In light of these facts, Sommer and Bennett[10] made the following postulates regarding substitution at a silicon atom: first, many nucleophilic displacements involve formation of an addition complex with the attacking reagent; second, the geometry of the complex approximates that of a trigonal bipyramid and the bonding is dsp^3; third, the entering group and the group which is ultimately displaced need not occupy the apices of the trigonal bipyramid. It should be noted that only the third postulate is completely new.

Later work on the stereochemistry of hydride displacements[39] from cyclic silicon compounds and on the reactivity of 1-chloro-1-silabicyclo [2.2.2] octane[11] offered additional support to the above postulates.

Silicon-containing cyclobutane ring systems are extremely susceptible to polar reagents readily undergoing ring cleavage. 1,1,4,4-Tetramethyl-1,3-disilacyclobutane[12] decolorizes a carbon tetrachloride solution of bromine slowly, and reduces alcoholic silver nitrate rapidly as evidenced by the formation of a silver mirror. Similar reactivity has previously been observed with the related 1,1-dimethyl-1-silacyclobutane[40] and 3,3-dicarbethoxy-1,1-dimethyl-1-silacyclo-

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[39] L. H. Sommer, O. F. Bennett, P. G. Campbell, and D. R. Weyenberg, <u>ibid</u>., <u>79</u>, 3295 (1957).

[40] L. H. Sommer and G. A. Baum, <u>ibid</u>., <u>76</u>, 5002 (1954).

butane[41] compounds.

Apropos the reactivity of the smaller silacycloalkanes, Smith[42] calculated the bond refractions of the cyclotrimethylene, cyclotetramethylene, and cyclopentamethylene groups bonded to silicon and also the bond dispersions of the last mentioned group. The results show that a ring refraction is present in the four- and five-membered rings but not in the six. Smith states that it is in agreement with the results of an inspection of the molecular models of the three rings and in accord with the unusual reactivity of the silacyclobutane derivatives.[40,41] In comparison it should be noted that in the cyclobutanes, cyclopentanes, and cyclohexanes the latter two are without ring refractions.[43]

A number of reactions have been conducted with functional cyclic organosilicon compounds. Generally speaking, these reactions are analogous to those of the functional non-cyclic types. For example, 1,1,3,3,5,5-hexachloro-1,3,5-trisilacyclohexane,[18] obtained from the thermal decomposition of trichloromethylsilane, was readily reduced with lithium aluminum hydride to give 1,3,5-trisilacyclohexane. This cyclic silicon hydride evolved six moles of hydrogen upon

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[41] R. West, ibid., 77, 2339 (1955).

[42] B. Smith, Acta Chem. Scand., 9, 1286 (1955).

[43] G. H. Jeffery and A. J. Vogel, J. Chem. Soc., 1804 (1948).

treatment with alcoholic alkali.

Fritz and Grobe[44] reported that the silicon-hydrogen bonds in Si-dodecamethyltricyclocarbosilan (VI) and in Si-dodecamethyltetracyclocarbosilan (VII) were resistant to basic hydrolysis. The inertness is attributed to steric effects. However, photochemical chlorination of compound (VI) yields a hexadecachloro compound, $C_{18}H_{30}Cl_{16}Si_7$, which contains one hydrolyzable chlorine. This chlorine is purported to be from a silicon-chlorine group corresponding to the silicon-hydrogen group in the starting material. Fritz and Grobe[45] also reported the measurement of the infrared absorption spectra of some cyclocarbosilanes.

The functional dibenzosilole derivatives have been treated with a variety of organolithium reagents to afford nonfunctional types.[28] For example, treatment of 5-chloro-5-n-dodecyldibenzosilole with 3-biphenylyllithium, phenyllithium, and _n_-hexadecyllithium gave the corresponding 5-(3-biphenylyl), 5-phenyl and 5-_n_-hexadecyl derivatives in good yields. Both 5-chloro-5-phenyldibenzosilole and 5,5-dichlorodibenzosilole, when reacted with phenyllithium, gave 5,5-diphenyldibenzosilole in excellent yields. 5,5-Di-_n_-

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[44] G. Fritz and J. Grobe, _Z. anorg. u. allgem. Chem._, _299_, 302 (1959); _Angew. Chem._, _70_, 701 (1958).

[45] G. Fritz and J. Grobe, _Z. anorg. u. allgem. Chem._, _299_, 316 (1959).

tetradecyldibenzosilole was obtained from the reaction of the 5,5-dichloro compound with n-tetradecyllithium.

Gilman and Gorsich[29] found that 2,2'-dilithiobiphenyl reacts with 5-chloro-5-methyldibenzosilole to give 5,5'-spirobi-(dibenzosilole) and 5,5-dimethyldibenzosilole. The dilithium compound seems first to participate in a reaction with the silicon-chlorine linkage; then, the second anion displaces the methyl group forming the spiro compound and methyllithium. The methyllithium so formed couples with unreacted 5-chloro-5-methyldibenzosilole to give the dimethyl derivative. Unexpectedly, 5,5'-spirobi-(dibenzosilole) was attacked by phenyllithium to give 5-(2-biphenylyl)-5-phenyldibenzosilole. This is essentially the reverse of the process described above.

5-Benzyl-5-chlorodibenzosilole and 5-chloro-5-phenyldibenzosilole were both reduced by lithium aluminum hydride to yield 5-benzyldibenzosilole and 5-phenyldibenzosilole, respectively.[29] The latter compound was reacted with phenyllithium to give a high yield of 5,5-diphenyldibenzosilole.

Two dibenzosilole derivatives containing a silicon-silicon bond, 5,5'-dimethyl-5,5'-bi-(dibenzosilole) and the analogous n-dodecyl derivative, were prepared by sodium condensations of the respective 5-alkyl-5-chlorodibenzosiloles. However, a similar reaction between sodium and 5-chloro-5-phenyldibenzosilole gave only 5,5'-oxybis-(5-phenyldibenzosilole) subsequent to hydrolysis of the reaction mixture.[29]

Treatment of 5,5'-dimethyl-5,5'-bi-(dibenzosilole) with lithium in tetrahydrofuran gave 5-lithio-5-methyldibenzosilole which yielded 5,5-dimethyldibenzosilole upon subsequent reaction with dimethyl sulfate.[29]

Recently, Tamborski and Rosenberg[46] have reported the preparation of eighteen 1,1-disubstituted 1-silacyclohexane derivatives by the reaction of 1,1-dichloro-1-silacyclohexane with alkyl- or aryllithium compounds. The yields were much superior to those from preparative methods employing Grignard reagents.[47] Thus, the advantage of using organolithium compounds in preference to Grignard reagents is clearly demonstrated. It should also be noted that this synthesis involves a two-step process: the preparation of a functional cyclic derivative, and subsequent reaction with an organometallic reagent to give the nonfunctional compound. This process has previously been shown to give higher yields than the direct one-step synthesis.[2,28,47] The advantage of the two-step process lies in the fact that in preparing cyclic organosilicon compounds _via_ a cyclization reaction, the yield of cyclic product increases as the number of chlorine atoms attached to silicon is increased. The higher yield is

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[46] C. Tamborski and H. Rosenberg, _J. Org. Chem._, _25_, 246 (1960).

[47] R. West, _J. Am. Chem. Soc._, _76_, 6012 (1954).

attributed to an increased electrostatic field which would facilitate ring closure.[47]

Since the silicon-carbon bonds in both cyclic and noncyclic organosilicon compounds are extremely sensitive to heterolytic cleavage by polar reagents, few examples of direct substitution are known. Wittenberg et al.[1] obtained 5-benzoyl-10,10-diphenyl-5,10-dihydrophenazasiline by reacting 10,10-diphenyl-5,10-dihydrophenazasiline first with n-butyllithium and then with benzoyl chloride. Reaction of the 5-lithio-10,10-diphenyl-5,10-dihydrophenazasiline intermediate with dimethyl sulfate and with diethyl sulfate gave the 5-methyl and 5-ethyl derivatives, respectively. Also, 10,10-diphenylphenothiasilin was successfully oxidized to 10,10-diphenylphenothiasilin-5,5-dioxide by hydrogen peroxide in acetic acid.[1]

Oita and Gilman[30] found that the ether linkage in certain phenoxasilin derivatives could be cleaved without considerable cleavage of the silicon-carbon bonds. Thus, 10,10-diphenylphenoxasilin and 10,10'-spirobi-(phenoxasilin) upon reaction with lithium in dioxane gave o-hydroxyphenyltriphenylsilane and bis(o-hydroxyphenyl)diphenylsilane, respectively.

Hitchcock et al.[32] point out that if the silicon atom in 10,10-diphenylphenoxasilin has a strong tendency to retain the tetrahedral configuration (C-Si-C angle of 109° 28'), the tricyclic molecule will be folded and, when unsymmetrically substituted, should exist in enantiomeric forms. Attempts were then carried out to verify this experimentally. 2-Methyl-10,10-diphenylphenoxasiline was reacted with N-bromosuccinimide to give the corresponding 2-bromomethyl compound, which they proposed to convert into an acidic or basic derivative for resolution. Unfortunately, the bromomethyl compound would not react with ammonia or with potassium phthalimide and, when reacted with potassium cyanide or diethyl sodiomalonate, gave no definite product.

Somewhat inconclusive evidence for the folded molecule was obtained by comparison of the dipole moment of 10,10-diphenylphenoxasilin with that of the 2,7-dimethyl compound.[32]

Hitchcock <u>et al</u>.[32] also point out that 10,10'-spirobi-(phenoxasilin) will be racemic if the two tricyclic systems are folded. A disubstituted derivative such as the 2,2'-dimethyl compound should therefore exist in two racemic forms. Here again, synthetic shortcomings hampered the confirmation of this proposal. Direct substitution of 10,10'-spirobi-(phenoxasilin) was unsuccessful for the compound did not react with fuming nitric acid in acetic anhydride, with bromine in chloroform, or with N-bromosuccinimide in carbon tetrachloride. Reaction of 2,2'-dilithio-4-methyldiphenyl ether with silicon tetrachloride in an effort to prepare the 2,2'-

dimethyl compound unexpectedly gave a silanol containing one phenoxasilin ring. Consequently, proof of the folding in the phenoxasilin molecule still remains to be obtained.

EXPERIMENTAL

All reactions involving organometallic reagents or other materials sensitive to either oxygen or moisture were carried out in an atmosphere of dry, oxygen-free nitrogen. The apparatus normally consisted of a three-necked flask equipped with a Trubore stirrer, a dropping funnel and either a condenser or a combination thermometer-nitrogen inlet. The flask and attachments were dried in an oven at above 110° and assembled while hot and while flushing the system with nitrogen.

All solvents used with organometallic reagents were commercially available "reagent grade" materials which were stored over sodium wire. The tetrahydrofuran was dried and purified by successively distilling from sodium wire and then from lithium aluminum hydride immediately before use.

The organic halides and the various other compounds used during this investigation were generally commercially available materials. The organosilicon halides, unless otherwise stated, were purchased from Dow Corning Corporation.

The lithium, purchased with a grease coating, was carefully wiped and weighed before use. Magnesium turnings especially prepared for Grignard reagents were utilized. In reactions requiring an excess of either lithium or magnesium, the excess metal was removed by filtering the solution through a glass-wool plug.

The n-butyllithium, employed in many of the reactions, was prepared in accordance with the method of Gilman et al.[48] using, however, a reaction temperature of -40 to -30° during the addition. The titer of the n-butyllithium was determined by the double titration method;[49] while those of the other organometallic reagents were determined by the single acid titration method.[50] Throughout the experimental section, frequent reference is made to Color Tests I and II. Color Test I refers to the qualitative color test of Gilman and Schulze[51] for moderately and highly reactive organometallic compounds. Color Test II corresponds to Test A reported by Gilman and Swiss[52] for highly reactive organometallic reagents.

All melting points and boiling points are uncorrected. The metling points below 200° were taken in an electrically heated silicone oil bath; while those above 200° were taken in an electrically heated copper block.

The infrared spectra cited in this dissertation were

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[48] H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, J. Am. Chem. Soc., 71, 1499 (1949).

[49] H. Gilman and A. H. Haubein, ibid., 66, 1515 (1944).

[50] H. Gilman, P. D. Wilkinson, W. P. Fishel, and C. H. Meyers, ibid., 45, 150 (1923).

[51] H. Gilman and F. Schulze, ibid., 47, 2002 (1925).

[52] H. Gilman and J. Swiss, ibid., 62, 1847 (1940).

obtained on either a Baird, model B, spectrophotometer, property of the Institute for Atomic Research, or on a Perkin-Elmer, model 21, spectrophotometer.

Tetrasubstituted Organosilanes Containing Aralkyl Groups

Benzyltris(*p*-terphenyl-4-yl)silane

A suspension of 27.8 g. (0.09 mole) of 4-bromo-*p*-terphenyl[53] in 200 ml. of ether was treated with 0.09 mole of an ethereal solution of *n*-butyllithium over a period of 15 minutes. After stirring at room temperature for 45 minutes, Color Test II was negative, and 6.31 g. (0.028 mole) of benzyltrichlorosilane[54] in 25 ml. of ether was added dropwise. The reaction mixture was stirred at reflux temperature for 12 hours, and then hydrolyzed. The organic layer was separated and dried over anhydrous sodium sulfate. Distillation of the solvent afforded 20.2 g. of colorless solid, m.p. 125-146°. After numerous recrystallizations from a mixture of toluene and petroleum ether (b.p. 60-70°), 3.9 g. (17.4%) of colorless crystals, m.p. 131-133°, was obtained.

Anal. Calcd. for $C_{61}H_{46}Si$: Si, 3.48. Found: Si, 3.44, 3.39.

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[53] H. Gilman and E. A. Weipert, *J*. *Org*. *Chem*., *22*, 446 446 (1957).

[54] G. Martin and F. S. Kipping, *J*. *Chem*. *Soc*., *95*, 302 (1909).

Dibenzylbis(p-terphenyl-4-yl)silane

An ethereal solution of 0.08 mole of p-terphenyl-4-yllithium,[53] prepared from 24.7 g. (0.08 mole) of 4-bromo-p-terphenyl and 0.08 mole of n-butyllithium as described above, was treated with 10.4 g. (0.037 mole) of dibenzyldichlorosilane[54] in 75 ml. of ether. Color Test I was now negative and hydrolysis was effected with water. Work-up of the reaction mixture in the usual manner gave 21 g. of colorless solid, m.p. 175-195°. This material was recrystallized several times from a mixture of toluene and petroleum ether (b.p. 60-70°) to give 8.45 g. (34%) of colorless solid, m.p. 197-199°.

Anal. Calcd. for $C_{50}H_{40}Si$: Si, 4.19. Found: Si, 4.23, 4.20.

Tribenzyl-p-terphenyl-4-ylsilane

A solution of 3.02 g. (0.01 mole) of tribenzylsilane[55] in 50 ml. of ether was added dropwise to an ethereal solution containing 0.02 mole of p-terphenyl-4-yllithium.[53] After refluxing the reaction mixture overnight, 100 ml. of toluene was added and the ether removed by distillation. Color Test I was negative after refluxing the suspension for 12 hours.

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[55] W. E. Evison and F. S. Kipping, ibid., 2830 (1931).

The reaction mixture was hydrolyzed and worked up as in the preceding experiments to give 3.55 g. of crude material, m.p. 88-115°. Several recrystallizations from a mixture of toluene and petroleum ether (b.p. 60-70°) gave 1.25 g. (24.6%) of colorless crystals, m.p. 125-127°.

Anal. Calcd. for $C_{39}H_{34}Si$: Si, 5.29. Found: Si, 5.28, 5.20.

Tris(beta-phenylethyl)-p-terphenyl-4-ylsilane

A solution of 8.61 g. (0.025 mole) of tris(beta-phenylethyl)silane in 50 ml. of ether was added to an ethereal solution containing 0.02 mole of p-terphenyl-4-yllithium.[53] After refluxing the reaction mixture overnight, 100 ml. of toluene was added and the ether removed by distillation. Color Test I was negative after refluxing the suspension for 22 hours. Hydrolysis and work-up in the usual manner gave 6.55 g. of solid, m.p. 70-78°. Several recrystallizations from a mixture of toluene and petroleum ether (b.p. 60-70°) gave 2.1 g. (18.4%) of colorless solid, m.p. 77-80°.

Anal. Calcd. for $C_{42}H_{40}Si$: Si, 4.92. Found: Si, 5.04, 4.98.

Tris(gamma-phenylpropyl)-p-terphenyl-4-ylsilane

An ethereal solution containing 0.02 mole of p-terphenyl-4-yllithium[53] was treated with 9.7 g. (0.025 mole) of tris-

(*gamma*-phenylpropyl)silane in 25 ml. of ether. After refluxing for 1 hour, 100 ml. of dry toluene was added and the ether removed by distillation. The reaction mixture was refluxed for 20 hours, before Color Test I was negative. Hydrolysis was effected with water and the reaction products were worked up in the usual manner. Efforts to crystallize the resulting oil were unsuccessful. The material was then distilled at reduced pressure to give 3.5 g. (29%) of pale yellow viscous liquid, b.p. 315-317° (0.001 mm.).

Anal. Calcd. for $C_{45}H_{46}Si$: Si, 4.57. Found: Si, 4.64, 4.65.

Dibenzylbis(2-biphenylyl)silane

A solution of 8.44 g. (0.03 mole) of dibenzyldichlorosilane[54] in 50 ml. of ether was treated with 0.074 mole of 2-biphenylyllithium.[56] After heating at reflux for 24 hours, Color Test I was negative. The reaction mixture was then hydrolyzed. Work-up gave an oil, which resisted crystallization and was subsequently distilled at reduced pressure to give 4.76 g. (30.5%) of a pale yellow viscous liquid, b.p. 222-227° (0.001 mm.).

Anal. Calcd. for $C_{38}H_{32}Si$: Si, 5.44. Found: Si, 5.34, 5.38.

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[56] H. Gilman and K. Oita, *J. Org. Chem.*, *20*, 862 (1955).

Dibenzylbis(3-biphenylyl)silane

A solution of 0.036 mole of 3-biphenylyllithium, prepared from 10.9 g. (0.046 mole) of 3-bromobiphenyl in 50 ml. of ether and 0.7 g. (0.1 g. atom) of lithium, was added to 4.22 g. (0.015 mole) of dibenzyldichlorosilane[54] in 50 ml. of ether. The reaction mixture was refluxed for 2 hours, 100 ml. of toluene was added, and the ether removed by distillation. After refluxing for 2 hours, Color Test I was negative and hydrolysis was effected with water. The reaction products were worked up in the usual manner and distilled at reduced pressure to give 5.01 g. (64.2%) of very viscous liquid, b.p. 265-269° (0.003 mm.).

Anal. Calcd. for $C_{38}H_{32}Si$: Si, 5.44. Found: Si, 5.50, 5.51.

Dibenzylbis(4-biphenylyl)silane

n-Butyllithium (0.075 mole) was added to a solution of 17.5 g. (0.075 mole) of 4-bromobiphenyl in 100 ml. of ether, and the reaction mixture was stirred for 30 minutes, before Color Test II was negative. The above solution was treated with 8.44 g. (0.03 mole) of dibenzyldichlorosilane[54] in 50 ml. of ether and refluxed for 24 hours. Color Test I was now negative and hydrolysis was carried out with water. Ether was added and the organic layer separated. After drying the organic solution with anhydrous calcium chloride and distilling, the residue was treated with petroleum ether (b.p. 60-70°) depositing 10.9 g. of solid, m.p. 80-104°. This material was recrystallized three times from a mixture of benzene and absolute ethanol to give 4.05 g. (26.1%) of colorless solid, m.p. 106-108°.

Anal. Calcd. for $C_{38}H_{32}Si$: Si, 5.44. Found: Si, 5.47, 5.48.

Tribenzyl-p-(trimethylsilylphenyl)silane

A solution of 5.26 g. (0.023 mole) of p-bromophenyltrimethylsilane in 50 ml. of ether was added to 0.7 g. (0.1 g. atom) of lithium in 10 ml. of ether. After stirring for 30 minutes, the reaction mixture was filtered through a previously dried glass wool plug. Titration of an aliquot indicated a yield of 0.0178 mole (77.4%). This solution was then added to 6.04 g. (0.02 mole) of tribenzylsilane[55] in 25 ml. of ether, and the mixture heated at reflux for 20 hours. Since Color Test I was positive, toluene was added, and the ether removed by distillation in the usual manner. After refluxing for 3 hours the color test was negative, and the reaction mixture was hydrolyzed. Work-up gave an oil which was distilled at reduced pressure to give 2.55 g. (31.7%) of colorless liquid, b.p. 200-202° (0.005 mm.), n_D^{20} 1.5952, d_{20}^{20} 1.0362.

Anal. Calcd. for $C_{30}H_{34}Si_2$: C, 79.93; H, 7.60; MR_D, 146.85. Found: C, 79.91, 79.90; H, 7.41, 7.30; MR_D, 146.09.

Reactions of Some 2-Triphenylsilylethyl Derivatives

2-Chloroethyltriphenylsilane

Thionyl chloride (8.4 g., 0.07 mole) was added to 10 g. (0.034 mole) of 2-triphenylsilylethanol,[57] and the reaction mixture heated on a steam bath for 30 minutes. The excess thionyl chloride was removed with the aid of a water aspirator. The resulting solid was taken up in hot petroleum ether (b.p. 60-70°), concentrated, and cooled to give 11 g. of colorless solid, m.p. 120-135°. This material was recrystallized twice from petroleum ether to give 7.53 g. (68.6%) of colorless solid, m.p. 128-130°.[58] Another run, using 20 g. of the alcohol, gave an 86.7% yield.

Reaction of 2-chloroethyltriphenylsilane and potassium hydroxide

A mixture of 1.23 g. (0.0038 mole) of 2-chloroethyltriphenylsilane and 0.6 g. of potassium hydroxide in 50 ml. of 95% ethanol was heated at reflux for 20 minutes. After cooling the ethanol was evaporated under an air-jet and the resulting material was taken up in an ether-water mixture. The ethereal solution was separated and worked up in the usual

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[57] H. Gilman, D. Aoki, and D. Wittenberg, _J. Am. Chem. Soc._, _81_, 1107 (1959).

[58] H. Gilman and J. F. Nobis, _ibid._, _72_, 2629 (1950).

manner. The residue was recrystallized two times from cyclohexane to give 0.83 g. (79.8%) of triphenylsilanol, m.p. 151-153°, which was identified by mixed melting point and by comparison of the infrared spectra.

Reaction of 2-chloroethyltriphenylsilane and magnesium

A solution of 10 g. (0.031 mole) of 2-chloroethyltriphenylsilane in 200 ml. of tetrahydrofuran was added to 4.8 g. (0.2 g. atom) of magnesium in 25 ml. of tetrahydrofuran. Attempts to initiate the reaction with iodine and with methyl iodide failed. The reaction mixture was then set at reflux, and after 1 hour Color Test I was positive. The reaction mixture was refluxed an additional 1.5 hours, filtered through a previously dried glass wool plug, and poured onto a Dry Ice-ether slurry. The carbonation mixture was allowed to warm to room temperature and acidified with dilute hydrochloric acid. Ether was added and the organic layer separated. After drying with anhydrous sodium sulfate, the organic layer was evaporated under an air-jet. The resulting solid was treated with 250 ml. of ether and filtered. The solid was recrystallized twice from cyclohexane to give 0.84 g. (9.4%) of colorless crystals, m.p. 213-215°, which was identified as tetramethylenebis(triphenylsilane)[8] by mixed melting point.

The ethereal solution was extracted with 10% sodium hydroxide and the basic aqueous extract acidified. The aqueous solution was then extracted with ether and discarded. After drying, the ether was evaporated and the residue recrystallized from formic acid to give 6.8 g. (66%) of colorless solid, m.p. 139-143°. An additional recrystallization raised the melting point to 142-143.5°. The material was identified as 3-triphenylsilylpropionic acid[37] by mixed melting point.

The ethereal solution was dried and evaporated, and the resulting material chromatographed over alumina with petroleum ether (b.p. 60-70°). From the first eluants, there was obtained a colorless solid which was recrystallized twice from 95% ethanol to give 1.18 g. (13.2%) of ethyltriphenylsilane, m.p. 73-75°, identified by mixed melting point and by infrared spectrum. Using cyclohexane as the eluant, 0.5 g. of colorless solid, m.p. 209-215°, was obtained. This material was recrystallized twice from cyclohexane to give 0.36 g. (4.04%) of tetramethylenebis(triphenylsilane),[8] m.p. 212-215°.

In an analogous run the reaction mixture was heated at reflux for 20 hours; however, the yield of 3-triphenylsilylpropionic acid[37] was only 28.9%.

A mixture of 5 g. of 2-chloroethyltriphenylsilane and 0.7 g. of lithium in 100 ml. of ether were stirred for 20 hours at room temperature. Attempts to initiate the reaction failed and 86% of the 2-chloro derivative was recovered.

2-Bromoethyltriphenylsilane

Phosphorus tribromide (12 g., 0.045 mole) was added dropwise to 20 g. (0.066 mole) of 2-triphenylsilylethanol.[57] After allowing the mixture to stand for 20 minutes, 50 ml. of dry benzene was added and the resulting solution heated at reflux for 15 minutes. Hydrolysis was effected by pouring the reaction mixture into iced water. Ether was added, and the aqueous solution was separated and discarded. After drying the organic solution, the solution was evaporated, and the residue taken up in petroleum ether (b.p. 60-70°) to give 16.9 g. of colorless solid, m.p. 130-140°. This material was recrystallized three times from petroleum ether to give 13.5 g. (51.9%) of colorless solid, m.p. 140-142°. The analytical sample melted at 141-143°.

Anal. Calcd. for $C_{20}H_{19}BrSi$: Si, 7.65. Found: Si, 7.91, 7.84.

In another run using 0.1 mole of 2-triphenylsilylethanol, there was obtained a 58% yield of the 2-bromo derivative.

Reaction of 2-bromoethyltriphenylsilane and magnesium

Twenty ml. of a solution of 5.5 g. (0.015 mole) of 2-bromoethyltriphenylsilane in 100 ml. of tetrahydrofuran was added to 2.4 g. (0.1 g. atom) of magnesium in 10 ml. of tetrahydrofuran. The addition of iodine and methyl iodide failed to initiate the reaction, which was finally started by warming. The rest of the solution was added and the reaction mixture stirred 1 hour at room temperature. Titration of an aliquot indicated the presence of 0.01 mole of base. The reaction mixture was then poured onto a Dry Ice-ether slurry. After warming to room temperature, dilute hydrochloric acid was added. The organic layer was worked up in the usual manner and evaporated to remove the tetrahydrofuran. The residue was treated with 200 ml. of ether and the remaining solid material filtered. The solid was recrystallized from cyclohexane to give 0.19 g. (2.7%) of tetramethylenebis(triphenylsilane),[8] m.p. 212-215°.

The filtrate was extracted with 5% sodium hydroxide and the basic aqueous solution acidified. The resulting solid was filtered and recrystallized from formic acid to give 1.25 g. (25.1%) of 3-triphenylsilylpropionic acid,[37] m.p. 142-144°.

The filtrate was now dried with anhydrous sodium sulfate and evaporated under an air-jet. The resulting material was chromatographed on alumina with petroleum ether (b.p. 60-70°) to give a colorless solid. This material was recrystallized twice from 95% ethanol to give 0.68 g. (15.8%) of ethyltriphenylsilane, m.p. 74-76°. Elution with cyclohexane gave a solid, which was recrystallized from cyclohexane to give 0.46 g. (10.6%) of tetramethylenebis(triphenylsilane),[8] m.p. 213-216°.

In another run, the reaction mixture was allowed to stir for 20 hours at room temperature and gave a 26.7% yield of 3-triphenylsilylpropionic acid.[37]

Reaction of 2-bromoethyltriphenylsilane and lithium

A solution of 5.5 g. (0.015 mole) of 2-bromoethyltriphenylsilane in 100 ml. of ether was added to 1 g. of lithium suspended in 25 ml. of ether. Since there was no apparent reaction, 4 drops of methyl iodide were added. This seemed to initiate the reaction, but Color Test I remained negative. The reaction mixture was stirred for 17 hours at room temperature; the color test remaining negative. The excess lithium was removed by filtration and the reaction mixture was hydrolyzed with dilute acid. The insoluble material was filtered and, after two recrystallizations from cyclohexane, gave 1.08 g. (25.1%) of tetramethylenebis(triphenylsilane),[8] m.p. 213-216°.

The organic layer was evaporated and the residue chromatographed over alumina. Elution with petroleum ether (b.p. 60-70°) gave a solid which was recrystallized twice from absolute ethanol to give 0.71 g. (16.4%) of ethyltriphenylsilane, m.p. 75-77°. Subsequent elution with cyclohexane afforded a solid which was recrystallized twice for cyclohexane to give 0.67 g. (15.6%) of tetramethylenebis(triphenylsilane), m.p. 214-216°.

2-Triphenylsilylethyl p-toluenesulfonate

p-Toluenesulfonyl chloride (11.5 g., 0.06 mole) was added portion-wise over a period of 5 minutes to 15.2 g. (0.05 mole) of 2-triphenylsilylethanol[57] in 50 ml. of dry pyridine, maintained at approximately 10°. The reaction mixture was stirred for 2 hours, while cooling below 20°, and treated with 200 ml. of iced 10% hydrochloric acid. After cooling in an ice-bath, the resulting solid was filtered. This material was recrystallized three times from cyclohexane to give 17.3 g. (75.4%) of colorless crystals, m.p. 110-113°. The analytical sample melted at 112-114°.

Anal. Calcd. for $C_{27}H_{26}O_3SSi$: Si, 6.12. Found: Si, 6.08, 6.13.

Reaction of 2-chloroethyltriphenylsilane and triphenylsilyllithium

Triphenylsilyllithium,[59] prepared from 4.15 g. (0.008 mole) of hexaphenyldisilane and 1.5 g. of lithium in 50 ml. of tetrahydrofuran, was added to 5 g. (0.016 mole) of 2-chloroethyltriphenylsilane in 50 ml. of tetrahydrofuran. After stirring 1 hour at room temperature, Color Test I was negative. The reaction mixture was hydrolyzed with 50 ml. of 5% hydrochloric acid and the resulting solid was filtered.

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[59] H. Gilman and G. D. Lichtenwalter, *ibid*., 80, 608 (1958).

The solid was extracted two times with boiling ethyl acetate leaving 3.07 g. (37%, based on the total silicon) of colorless solid, m.p. 368-370°, which was identified as hexaphenyldisilane by mixed melting point. The combined ethyl acetate solution was evaporated and the resulting material was recrystallized twice from cyclohexane to give 1.01 g. (11.6%) of ethylenebis(triphenylsilane),[60] m.p. 212-214°, identified by mixed melting point.

After the above filtration, the organic layer was separated and worked up in the usual manner. The residue was then chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave a small amount of colorless solid which was recrystallized twice from petroleum ether to give 0.58 g. (11.6%) of recovered 2-chloroethyltriphenylsilane, m.p. 128-130°. Elution with cyclohexane and then with benzene gave a colorless solid. This material was recrystallized twice from cyclohexane to give 1.49 g. (17.6%) of ethylenebis(triphenylsilane), m.p. 210-213°.

Reaction of 2-bromoethyltriphenylsilane and triphenylsilyllithium

A tetrahydrofuran solution containing 0.014 mole of triphenylsilyllithium[59] was added slowly to 5.14 g. (0.014 mole)

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[60] D. Wittenberg, D. Aoki, and H. Gilman, ibid., 80, 5933 (1958).

of 2-bromoethyltriphenylsilane in 50 ml. of tetrahydrofuran. After stirring 3 hours at room temperature, Color Test I was negative. The reaction mixture was hydrolyzed with dilute acid and the resulting solid was filtered. The solid was extracted twice with boiling ethyl acetate leaving 1.72 g. (23.7%) of hexaphenyldisilane, m.p. 368-370°. The combined ethyl acetate solutions were evaporated and the resulting material recrystallized from cyclohexane to give 0.28 g. (3.7%) of ethylenebis(triphenylsilane),[60] m.p. 210-213°.

The organic layer was separated and worked up in the usual manner. The residue was then chromatographed over alumina. The customary techniques gave 0.56 g. (10.9%) of recovered 2-bromoethyltriphenylsilane and 2.23 g. of colorless solid, m.p. 182-190°. This material was recrystallized from various solvents but could not be further purified. The infrared spectrum indicated this material to be a mixture of ethylenebis- and tetramethylenebis(triphenylsilane).

Reaction of 2-triphenylsilylethyl p-toluenesulfonate and triphenylsilyllithium

Triphenylsilyllithium[59] (0.02 mole) was added to 9.16 g. (0.02 mole) of 2-triphenylsilylethyl p-toluenesulfonate in 50 ml. of tetrahydrofuran. The addition caused a slight amount of refluxing and a white precipitate was formed. After stirring for 30 minutes, Color Test I was negative and the reaction mixture was hydrolyzed. Filtration gave 3.3 g.

(31.9%) of hexaphenyldisilane, m.p. 367-370°.

The organic layer was worked up in the usual manner and the residue chromatographed over alumina. Elution with cyclohexane gave a colorless solid, which was recrystallized twice from cyclohexane to give 2.22 g. (20.2%) of ethylenebis(triphenylsilane),[60] m.p. 211-214°. Using benzene and ethyl acetate as the eluants, there was obtained another solid. This material was recrystallized three times from cyclohexane to give 1.14 g. (12.4%) of recovered 2-triphenylsilylethyl p-toluenesulfonate, m.p. 109-112°.

Studies in the 5,10-Dihydrophenazasiline Series

2,2'-Dibromodiphenylamine

The following procedure is that of Jones and Mann[61] with minor revisions. o-Bromobenzanilide (441 g., 1.6 moles) was mixed with 364 g. (1.75 moles) of phosphorus pentachloride. After the spontaneous reaction, the mixture was heated to 100° for 10 minutes, and then allowed to stand at room temperature overnight. The phosphorus oxychloride was removed with the aid of a water aspirator and the remaining material distilled at a lower pressure to give 446.7 g. (94.8%) of N-o-bromophenylbenzimidoyl chloride as a yellow liquid, b.p. 162-164° (1.5 mm.). In two similar runs, the yields were

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[61] E. R. H. Jones and F. G. Mann, J. Chem. Soc., 786 (1956).

90.8% and 96%, respectively.

Sodium ethoxide was prepared by adding 25.3 g. (1.1 g. atoms) of sodium to 700 ml. of absolute ethanol. This solution was cooled in an ice-bath and 200 g. (1.16 moles) of o-bromophenol was added dropwise. With continued cooling of the above reaction mixture, there was then added 304 g. (1.034 moles) of N-o-bromophenylbenzimidoyl chloride in 300 ml. of ether. The reaction mixture was warmed to room temperature and stirred for 11 hours. After the greater part of the ethanol was removed by distillation, the yellow mixture was allowed to cool and poured upon a mixture of ice and water. The resulting pale yellow solid was filtered and recrystallized from absolute ethanol to give 386.7 g. (86.9%) of o-bromophenyl N-o-bromophenylbenzimidoate as pale yellow crystals, m.p. 93-95°. Yields of 81.3 and 85% were obtained in two other runs.

o-Bromophenyl N-o-bromophenylbenzimidoate (200 g., 0.464 mole) was heated from 250-265° for 2.5 hours. The resulting dark brown liquid was allowed to cool and digested with 200 ml. of 95% ethanol. The ethanolic solution was cooled, depositing 130 g. (65%) of impure N-benzoyl-2,2'-dibromodiphenylamine, m.p. 173-177°. The yields from this rearrangement have varied from 55 to 72%.

The 130 g. (0.3 mole) of impure N-benzoyl-2,2'-dibromodiphenylamine from the above reaction was treated with a solution of 200 g. of potassium hydroxide in 200 ml. of water and 800 ml. of 95% ethanol. The reaction mixture was heated at reflux for 16 hours and then reduced in volume by distillation. After cooling, the mixture was hydrolyzed with 1 liter of iced water. The aqueous solution was separated, extracted with a total of 500 ml. of ether, and discarded. The ethereal solution was dried with anhydrous sodium sulfate and distilled. Reduced pressure distillation of the residue gave 84.6 g. (85.7%) of 2,2'-dibromodiphenylamine, b.p. 128-133° (0.008 mm.). A portion was recrystallized from ethanol to give colorless crystals, m.p. 60-62°. The yields from the hydrolysis have ranged from 60 to 88%.

N-Ethyl-2,2'-dibromodiphenylamine

A solution of 10 g. (0.0306 mole) of 2,2'-dibromodiphenylamine cooled in an ice-bath was treated with 0.035 mole of an ethereal solution of methyllithium, and allowed to stir for 30 minutes. Subsequently, 7.7 g. (0.05 mole) of freshly distilled diethyl sulfate in 100 ml. of tetrahydrofuran was added. The ether was removed by distillation until the temperature reached 64°. This solution was heated at reflux for 15 hours, and then hydrolyzed by pouring upon iced water. The organic solution was separated, and the aqueous layer extracted with ether and discarded. After drying with anhydrous sodium sulfate, the solvents were distilled and the resulting material distilled at reduced pressure to give 8.99 g. (83%) of colorless liquid, b.p. 131-133° (0.04 mm.), which solidified upon standing. A portion was recrystallized from petroleum ether (b.p. 60-70°) giving colorless crystals, m.p. 72-74°.

Anal. Calcd. for $C_{14}H_{13}Br_2N$: N, 3.97. Found: N, 4.02, 3.87.

The yields from this ethylation reaction have been consistently in the lower eighty percent range. In one run using 52 g. of 2,2'-dibromodiphenylamine, there was obtained an 81.4% yield of the N-ethyl derivative. Attempts to prepare the compound, by treating 2,2'-dibromodiphenylamine, with either ethylmagnesium bromide or methyllithium and then with ethereal solutions of diethyl sulfate, were unsuccessful. A similar reaction to the above using methyllithium and diethyl sulfate in a toluene-ether solution heated at 65°, the reflux temperature of tetrahydrofuran, gave only partial N-alkylation.

5-Ethyl-10,10-diphenyl-5,10-dihydrophenazasiline

From dichlorodiphenylsilane To 5.05 g. (0.014 mole) of N-ethyl-2,2'-dibromodiphenylamine in 50 ml. of ether cooled in an ice-bath, there was added 0.028 mole of *n*-butyllithium. After stirring under these conditions for 1 hour, Color Test II was negative. The solution was treated with 3.60 g.

(0.014 mole) of dichlorodiphenylsilane in 100 ml. of ether. The reaction mixture was stirred for 28 hours at room temperature, before Color Test I was negative. Hydrolysis was carried out by pouring upon iced water and the organic layer separated. The aqueous layer was extracted with ether and discarded. The combined organic solution was dried with anhydrous sodium sulfate and the ether removed by evaporation under an air-jet. The resulting solid was taken up in petroleum ether (b.p. 60-70°) to give 3.11 g. of colorless crystals, m.p. 118-121°. Recrystallization from the same solvent gave 2.66 g. (49.3%) of 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline, m.p. 121-123°, identified by mixed melting point with an authentic sample and by comparison of the infrared spectra.[1]

From diphenylsilane. A solution of 3.55 g. (0.01 mole) of N-ethyl-2,2'-dibromodiphenylamine in 50 ml. of diethyl ether, cooled in an ice-bath, was treated with 0.02 mole of an ethereal solution of *n*-butyllithium. After stirring for 1 hour, 1.84 g. (0.01 mole) of diphenylsilane[62] dissolved in 50 ml. of dry toluene was added and the reaction mixture heated at reflux for 22 hours. Color Test I was negative and hydrolysis was carried out by pouring upon a dilute sulfuric acid solution. The aqueous layer was separated, extracted

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[62] R. A. Benkeser, H. Landesman, and D. J. Foster, *J. Am. Chem. Soc.*, *74*, 648 (1952).

with ether, and discarded. The combined organic layers were dried and evaporated under an air-jet. The remaining material was taken up in petroleum ether (b.p. 60-70°) to give 1.64 g. of pale yellow crystals, m.p. 109-120°. The crystals were then dissolved in hot petroleum ether (b.p. 60-70°), decolorized with charcoal, and cooled to give 1.36 g. (36.1%) of colorless crystals, m.p. 121-123°, which was identified as 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline by mixed melted point and by comparison of the infrared spectra.

From 5-ethyl-10-phenyl-5,10-dihydrophenazasiline

5-Ethyl-10-phenyl-5,10-dihydrophenazasiline (1.77 g., 0.006 mole) (see below) in 50 ml. of ether was treated with 0.014 mole of an ethereal solution of phenyllithium and the reaction mixture refluxed for 17 hours. After the usual work-up, the resulting material was taken up in petroleum ether (b.p. 60-70°) to give 1.53 g. (68.9%) of colorless crystals, m.p. 119-122°. An additional recrystallization raised the melting point to 121-122°. A mixed melting point with an authentic sample of 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline was undepressed.

5,5'-Diethyl-10,10'-spirobi-(5,10-dihydrophenazasiline)

To a solution of 10.65 g. (0.03 mole) of N-ethyl-2,2'-dibromodiphenylamine in 100 ml. of ether cooled in an ice-bath, there was added 0.06 mole of n-butyllithium over a period of 10 minutes. After stirring for 40 minutes, 2.55 g. (0.015 mole) of freshly distilled silicon tetrachloride in 100 ml. of ether was added, and the reaction mixture stirred for 2.5 hours at room temperature. The ether solution was refluxed for 18 hours, 100 ml. of dry toluene was added, and then the ether distilled. The resulting toluene suspension was refluxed for 2 hours before Color Test I was negative. After hydrolysis by pouring upon cold water, the aqueous layer was separated, extracted with ether, and discarded. The combined organic layer was dried with anhydrous sodium sulfate and evaporated under an air-jet. The resulting material was taken up in ethyl acetate giving 3.19 g. of colorless needles, m.p. 210-214°. After two recrystallizations from the same solvent, there was obtained 2.78 g. (44.4%) of colorless needles, m.p. 215.5-217°.

Anal. Calcd. for $C_{28}H_{26}N_2Si$: Si, 6.71. Found: Si, 6.75, 6.63.

5-Ethyl-10-methyl-10-phenyl-5,10-dihydrophenazasiline

An ethereal solution of 3.82 g. (0.02 mole) of methylphenyldichlorosilane was added to 0.02 mole of N-ethyl-2,2'-dilithiodiphenylamine, prepared from 7.10 g. (0.02 mole) of N-ethyl-2,2'-dibromodiphenylamine and 0.04 mole of n-butyllithium. The reaction mixture was stirred at room temperature for 17 hours and then 2 hours at reflux, before Color Test I was negative. After hydrolysis, the aqueous layer was extracted with ether and discarded. The combined organic layer was dried with anhydrous sodium sulfate and distilled. The residue was distilled at reduced pressure to give 4.54 g. (72%) of pale yellow viscous liquid, b.p. 160-167° (0.01 mm.). The material solidified upon standing and a portion was recrystallized twice from absolute ethanol to give colorless crystals, m.p. 62-64°.

Anal. Calcd. for $C_{21}H_{21}NSi$: Si, 8.90. Found: Si, 8.92, 8.80.

5-Ethyl-10,10-dibenzyl-5,10-dihydrophenazasiline

N-Ethyl-2,2'-dilithiodiphenylamine (0.015 mole) in 70 ml. of ether was treated with 4.22 g. (0.015 mole) of dibenzyldichlorosilane[54] in 50 ml. of ether, while cooling in an ice-bath. The reaction mixture was refluxed for 16 hours, but Color Test I remained positive. Toluene (50 ml.) was added, the ether removed by distillation, and the toluene suspension refluxed for 3 hours at the end of which time Color Test I was negative. After the hydrolysis and the usual work-up, reduced pressure distillation of the residue gave 3.52 g. (57.9%) of viscous liquid, b.p. 204-212° (0.005 mm.). Trituration with absolute ethanol yielded a colorless solid, m.p. 69-72°, which was recrystallized from the same solvent to give long colorless needles, m.p. 71-73°.

Anal. Calcd. for $C_{28}H_{27}NSi$: Si, 6.93. Found: Si, 6.81, 6.83.

5-Ethyl-10-phenyl-5,10-dihydrophenazasiline

A solution of 0.04 mole of N-ethyl-2,2'-dilithiodiphenylamine, prepared from 14.2 g. (0.04 mole) of N-ethyl-2,2'-dibromodiphenylamine and 0.08 mole of n-butyllithium, was added over a period of 1 hour to 5.4 g. (0.05 mole) of phenylsilane[63] in 100 ml. of ether while cooling in an ice-bath. After stirring for 2 hours at room temperature, Color Test I was negative. The reaction mixture was hydrolyzed by pouring upon crushed ice acidified with a small amount of sulfuric acid. The organic layer was separated and dried with anhydrous calcium sulfate, and the ether was removed by distillation. The resulting material was distilled at reduced pressure to give 9.6 g. (79.9%) of a pale yellow viscous oil, b.p. 180-184° (0.014 mm.). The material solidified upon standing to a colorless sticky solid which was extremely difficult to crystallize to a sharp melting point. It was recrystallized finally from petroleum ether (b.p. 60-70°) to give colorless needles, m.p. 75-78°.

Anal. Calcd. for $C_{20}H_{19}NSi$: Si, 9.33. Found: Si, 9.08, 9.16.

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[63] A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach, and H. L. Schlesinger, ibid., 69, 2692 (1947).

In another run employing 0.085 mole of N-ethyl-2,2'-dilithiodiphenylamine and 0.11 mole of phenylsilane, there was obtained a 77.5% yield of 5-ethyl-10-phenyl-5,10-dihydrophenazasiline.

5-Ethyl-10-phenyl-10-p-tolyl-5,10-dihydrophenazasiline

An ethereal solution of p-tolyllithium (0.02 mole) was added to 3.0 g. (0.01 mole) of 5-ethyl-10-phenyl-5,10-dihydrophenazasiline in 50 ml. of ether. The reaction mixture was refluxed for 5 hours and then poured upon crushed ice acidified with sulfuric acid. The organic layer was separated, dried with anhydrous calcium sulfate, and evaporated under an air-jet. The residue was recrystallized from a 1:1 mixture of absolute ethanol and petroleum ether (b.p. 60-70°) affording 2.75 g. (70.4%) of colorless crystals, m.p. 100-103°. An additional recrystallization from the same solvent mixture raised the melting point to 102-103.5°.

Anal. Calcd. for $C_{27}H_{25}NSi$: Si, 7.17. Found: Si, 7.08, 7.06.

5-Ethyl-10-o-biphenylyl-10-phenyl-5,10-dihydrophenazasiline

To a solution of 2.54 g. (0.0085 mole) of 5-ethyl-10-phenyl-5,10-dihydrophenazasiline in 50 ml. of ether, there was added 0.012 mole of o-biphenylyllithium,[56] prepared from o-bromobiphenyl and lithium in ether according to a published procedure. After heating at reflux for 16 hours, the reaction mixture was hydrolyzed by pouring upon crushed ice. Subsequently, ether was added and the organic layer separated. After drying with anhydrous calcium sulfate, the ether was evaporated and the resulting material taken up in 95% ethanol to yield 2.81 g. (72.9%) of colorless crystals, m.p. 121.5-124°. The analytical sample metled at 123-124.5°.

Anal. Calcd. for $C_{32}H_{27}NSi$: Si, 6.19. Found: Si, 6.28, 6.15.

5-Ethyl-10-p-phenoxyphenyl-10-phenyl-5,10-dihydrophenazasiline

A solution of p-phenoxyphenyllithium[64] was prepared by treating 4.98 g. (0.02 mole) of p-bromophenyl phenyl ether in 50 ml. of ether at -15° with 0.02 mole of n-butyllithium. After stirring for 45 minutes 3.0 g. (0.01 mole) of 5-ethyl-10-phenyl-5,10-dihydrophenazasiline in 50 ml. of ether was added and the reaction mixture refluxed for 16 hours. Subsequently, hydrolysis was carried out by pouring upon crushed ice and the organic layer separated. The organic layer was then dried with anhydrous calcium sulfate and evaporated under an air-jet. The resulting material could not be induced to solidify, and therefore, was distilled at reduced pressure to give 1.91 g. (40.6%) of glass-like solid, b.p. 240-245°

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[64] H. Gilman, W. Langham, and F. W. Moore, ibid., 62, 2327 (1940).

(0.005 mm.). Treatment of this material with petroleum ether (b.p. 60-70°) afforded colorless crystals, m.p. 96-98°. The distillation residue was taken up in petroleum ether (b.p. 60-70°) and seeded with some of the crystalline material giving an additional 0.85 g. (18.1%) of similar material, m.p. 96-98°. Successive recrystallizations from petroleum ether (b.p. 60-70°) and then from a 5:1 mixture of absolute ethanol and benzene raised the melting point to 98.5-100°.

Anal. Calcd. for $C_{32}H_{27}NOSi$: Si, 5.98. Found: Si, 6.17, 5.88.

5-Ethyl-10-*p*-bromophenyl-10-phenyl-5,10-dihydrophenazasiline

A solution of 4.52 g. (0.02 mole) of *p*-dibromobenzene[64] in 75 ml. of ether cooled to -20±3° was treated with 0.02 mole of *n*-butyllithium by dropwise addition. After stirring for 2 hours at -20°, 6.0 g. (0.02 mole) of 5-ethyl-10-phenyl-5,10-dihydrophenazasiline in 100 ml. of ether was added, and the reaction mixture allowed to warm to room temperature and stirred for 18 hours. Hydrolysis was carried out by pouring upon crushed ice acidified with sulfuric acid. The aqueous layer was separated, extracted with ether, and discarded. The organic layer was dried and evaporated to yield a tan solid which was taken up in hot petroleum ether (b.p. 60-70°) and cooled to give 6.15 g. of colorless material, m.p. 143-155°. After two recrystallizations from a 1:1 mixture of benzene and petroleum ether (b.p. 60-70°), there was obtained 3.55 g. (38.8%) of colorless crystals, m.p. 158-161°. The analytical sample melted at 159-160.5°.

Anal. Calcd. for $C_{26}H_{22}BrNSi$: Si, 6.15. Found: Si, 6.32, 6.18.

5,5'-Diethyl-10,10'-diphenyl-10,10'-p-biphenylenebis(5,10-dihydrophenazasiline)

A solution of 2.5 g. (0.008 mole) of 4,4'-dibromobiphenyl[64] in 50 ml. of dry benzene was treated with 0.016 mole of n-butyllithium. After refluxing for 2 hours, Color Test II was negative. The insoluble dilithium compound was treated with 5.0 g. (0.0166 mole) of 5-ethyl-10-phenyl-5,10-dihydrophenazasiline in 70 ml. of benzene. Color Test I was negative after refluxing the benzene-ether suspension for 18 hours. The reaction was hydrolyzed by pouring upon crushed ice. Ether was added, and the organic layer separated and dried with anhydrous calcium sulfate. The solvents were evaporated and the resulting oil was induced to crystallize by trituration with a small amount of ethyl acetate giving 3.75 g. of pale yellow material, m.p. 210-230°. The solid was recrystallized twice from a 1:1 mixture of absolute ethanol and benzene to give 2.69 g. (44.8%) of colorless crystals, m.p. 242-246°. The analytical sample melted at 246-248°.

Anal. Calcd. for $C_{52}H_{44}N_2Si_2$: Si, 7.48. Found: Si, 7.24, 7.29.

5-Ethyl-10-n-hexadecyl-5,10-dihydrophenazasiline

A solution of N-ethyl-2,2'-dilithiodiphenylamine, prepared from 17.8 g. (0.05 mole) of N-ethyl-2,2'-dibromodiphenylamine in 200 ml. of ether and 0.1 mole of n-butyllithium, was added over a period of 90 minutes to 14 g. (0.055 mole) of n-hexadecylsilane[65] in 100 ml. of ether; while the reaction flask was being cooled in an ice-bath. The reaction mixture was warmed to room temperature and refluxed for 2 hours before Color Test I was negative. After hydrolyzing by pouring upon crushed ice, ether was added and the organic layer separated. The solvent was distilled and the resulting oil distilled at reduced pressure to give 16.0 g. of turbid liquid, b.p. 193-233° (0.008 mm.). The liquid was then redistilled to give 11.9 gm. (52.9%) of liquid, b.p. 230-235° (0.003 mm.), which solidified upon standing. The solid was recrystallized twice from a 10:1 mixture of methanol and benzene to give colorless crystals, m.p. 51-53°.

Anal. Calcd. for $C_{30}H_{47}NSi$: Si, 6.25. Found: Si, 6.41, 6.29.

5-Ethyl-10-n-hexadecyl-10-phenyl-5,10-dihydrophenazasiline

An ethereal solution containing 0.014 mole of phenyl-

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[65] M. B. Hughes. Some correlations between organosilicon compounds and organogermanium compounds. Unpublished Ph. D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1958.

lithium was added to 2.88 g. (0.0064 mole) of 5-ethyl-10-n-hexadecyl-5,10-dihydrophenazasiline in 50 ml. of ether. The reaction mixture was refluxed for 18 hours and subsequently poured upon crushed ice acidified with sulfuric acid. The aqueous layer was separated, extracted with ether, and discarded. The combined organic layer was dried and evaporated, and the residue distilled at reduced pressure to give 1.67 g. (49.7%) of very viscous liquid, b.p. 227-230° (0.004 mm.). Various attempts to crystallize the material were unsuccessful.

Anal. Calcd. for $C_{36}H_{51}NSi$: Si, 5.34. Found: Si, 5.36, 5.36.

5-Ethyl-10-n-hexadecyl-10-p-tolyl-5,10-dihydrophenazasiline

An ethereal solution of 3.90 g. (0.0087 mole) of 5-ethyl-10-n-hexadecyl-5,10-dihydrophenazasiline was treated with 0.015 mole of p-tolyllithium and heated at reflux for 18 hours. After hydrolysis and the usual work-up, the reaction products were distilled at reduced pressure to give 2.19 g. (46.6%) of a colorless viscous liquid, b.p. 220-225° (0.004 mm.).

Anal. Calcd. for $C_{37}H_{53}NSi$: C, 82.31; H, 9.89, Si, 5.20. Found: C, 82.84, 83.02; H, 9.92, 9.72; Si, 5.22, 5.09.

N-Methyl-2,2'-dibromodiphenylamine

Methyllithium (0.11 mole) was added to 30 g. (0.0918 mole) of 2,2'-dibromodiphenylamine in 100 ml. of ether cooled in an ice-bath. After stirring for 1 hour, a solution of 15.1 g. (0.12 mole) of freshly distilled dimethyl sulfate in 100 ml. of tetrahydrofuran was added, and the ether removed by distillation. The resulting solution was heated at reflux for 18 hours and, after cooling, hydrolyzed with iced water. The aqueous layer was separated, extracted with ether, and discarded. The combined organic layer was dried with anhydrous sodium sulfate and distilled. The reaction products were taken up in petroleum ether (b.p. 60-70°) to give 27.8 g. (88.7%) of colorless crystals, m.p. 106-109°. The analytical sample melted at 106-107°.

Anal. Calcd. for $C_{13}H_{11}Br_2N$: N, 4.11. Found: N, 4.17, 4.10.

5-Methyl-10,10-diphenyl-5,10-dihydrophenazasiline

N-Methyl-2,2'-dibromodiphenylamine (3.41 g., 0.01 mole) in 50 ml. of ether, cooled in an ice-bath, was treated with 0.02 mole of an ethereal solution of n-butyllithium. Color Test II was negative after stirring for 1 hour. A solution of 2.53 g. (0.01 mole) of dichlorodiphenylsilane in 30 ml. of ether was added and the reaction mixture heated at reflux for 17 hours. After hydrolysis and the usual work-up, the residue was taken up in petroleum ether (b.p. 60-70°) to give 2.32 g. (63.9%) of colorless crystals, m.p. 182-184°. Recrystallization from the same solvent raised the melting point to 183-185°. The infrared spectrum of this compound was identical with that of an authentic sample.[1]

5,5'-Dimethyl-10,10'-spirobi-(5,10-dihydrophenazasiline)

An ethereal solution containing 0.03 mole of N-methyl-2,2'-dilithiodiphenylamine, prepared as above, was added to 2.55 g. (0.015 mole) of silicon tetrachloride in 50 ml. of ether over a period of 30 minutes. Color Test I was positive after refluxing for 18 hours; therefore, 50 ml. of dry toluene was added and the ether distilled. The toluene suspension was heated at reflux 1.5 hours before the color test was negative. The reaction mixture was then hydrolyzed, some ether was added, and the insoluble material filtered giving 3.30 g. of colorless solid, m.p. 244-247°. The organic layer was worked up in the usual manner to give 0.63 g. of similar material, m.p. 238-245°. The fractions were combined and recrystallized from ethyl acetate to give 3.35 g. (57.3%) of colorless crystals, m.p. 246-250°. A portion was recrystallized twice from the same solvent to give colorless crystals, m.p. 247-249°.

Anal. Calcd. for $C_{26}H_{22}N_2Si$: Si, 7.19. Found: Si, 7.08, 7.19.

5-Methyl-10,10-dibenzyl-5,10-dihydrophenazasiline

A solution of 5.62 g. (0.02 mole) of dibenzyldichlorosilane[54] in 25 ml. of ether was added to an ethereal solution of 0.02 mole of N-methyl-2,2'-dilithiodiphenylamine, while cooling in an ice-bath. The ethereal solution was heated at reflux for 16 hours, but Color Test I remained positive. The ether was replaced by 50 ml. of toluene, and after refluxing for 3 hours, Color Test I was negative. Subsequently, the reaction mixture was hydrolyzed, and the aqueous layer was separated and extracted with ether. The combined organic layer was dried and evaporated. Treatment of the oily residue with petroleum ether (b.p. 60-70°) gave 3.67 g. of a tan solid, m.p. 113-125°. This material was recrystallized twice from this petroleum ether to give 2.78 g. (35.5%) of colorless needles, m.p. 126-127.5°. An additional recrystallization did not change the melting point.

Anal. Calcd. for $C_{27}H_{25}NSi$: Si, 7.17. Found: Si, 7.23, 7.18.

2,2'-Dibromotriphenylamine

A mixture of 10.24 g. (0.0314 mole) of 2,2'-dibromodiphenylamine, 18.3 g. (0.09 mole) of iodobenzene, 8 g. of anhydrous potassium carbonate, and 0.5 g. of copper-bronze was heated from 175 to 200° for 24 hours. After cooling, the mixture was treated with 200 ml. of ether and filtered. The ether was evaporated and the resulting material dissolved in absolute ethanol. After standing for 5 days, a light brown solid deposited. This was taken up in 95% ethanol, treated with charcoal, and cooled to give 5.37 g. (42.5%) of colorless crystals, m.p. 106-109°. Recrystallization from the same solvent raised the melting point to 108.5-110°.

Anal. Calcd. for $C_{18}H_{13}Br_2N$: N, 3.47. Found: N, 3.47, 3.52.

A similar reaction employing 22.9 g. of 2,2'-dibromodiphenylamine gave only a 27.6% yield of 2,2'-dibromotriphenylamine.

5,10,10-Triphenyl-5,10-dihydrophenazasiline

To a solution of 4.03 g. (0.01 mole) of 2,2'-dibromotriphenylamine in 50 ml. of ether, there was added 0.02 mole of a n-butyllithium solution, while cooling in an ice-bath. This solution was stirred under these conditions for 1 hour and then treated with 2.53 g. (0.01 mole) of dichlorodiphenylsilane in 25 ml. of ether. After refluxing the ethereal solution for 24 hours, Color Test I was still positive; therefore, 50 ml. of dry toluene was added and the ether distilled. The toluene suspension was heated at reflux for 2 hours before the color test was negative. The reaction mixture was hydrolyzed with cold water and worked up in the usual manner. The resulting material was taken up in petroleum ether (b.p. 60-

70°) to give 1.57 g. of solid, m.p. 198-206°. Recrystallization from the same solvent gave 1.37 g. (32.2%) of colorless crystals, m.p. 208-211°. An additional recrystallization raised the melting point to 210-212°.

Anal. Calcd. for $C_{30}H_{23}NSi$: C, 84.66; H, 5.45; N, 3.29; Si, 6.60. Found: C, 85.13; H, 5.52; N, 3.19; Si, 6.29, 6.42.

5,5'-Diphenyl-10,10'-spirobi-(5,10-dihydrophenazasiline)

A solution containing 0.0144 mole of 2,2'-dilithiotriphenylamine, prepared as above, was added to 1.23 g. (0.0072 mole) of silicon tetrachloride in 25 ml. of ether, while cooling in an ice-bath. After heating the ethereal solution at reflux for 18 hours, Color Test I was negative. Subsequently, the reaction mixture was hydrolyzed and the insoluble material filtered. The organic layer was worked up in the usual manner and evaporated under an air-jet. The two fractions were combined and recrystallized from ethyl acetate to give 1.05 g. of a colorless solid, m.p. 309-313°. Recrystallization gave 0.80 g. (24.4%) of colorless needles, m.p. 312-314°. The analytical sample melted at 313-314°.

Anal. Calcd. for $C_{36}H_{26}N_2Si$: Si, 5.46. Found: Si, 5.40, 5.37.

2-Bromo-4-chlorophenyl N-2-bromophenylbenzimidoate

Sodium ethoxide was prepared by reacting 10.3 g. (0.45 g. atom) of sodium with 300 ml. of absolute ethanol. After cooling the solution in an ice-bath, 95 g. (0.46 mole) of 2-bromo-4-chlorophenol in 100 ml. of ether was added, followed by a solution of 133 g. (0.45 mole) of 2-bromophenylbenzimidoyl chloride[61] (see 2,2'-dibromodiphenylamine preparation) in 100 ml. of ether. The reaction mixture was stirred at room temperature for 16 hours, and then concentrated by distillation. Subsequently, hydrolysis was effected by pouring upon crushed ice. The aqueous layer was decanted from the resulting heavy oil. After standing over night, the oil solidified and was recrystallized twice from 95% ethanol to give 148 g. (70.9%) of colorless crystals, m.p. 70-72°. The analytical sample melted at 71-72°.

Anal. Calcd. for $C_{19}H_{12}Br_2ClNO$: C, 49.01; H, 2.60; N, 3.01. Found: C, 49.32, 49.19; H, 2.69, 2.65; N, 3.21, 3.19.

N-Benzoyl-2,2'-dibromo-4-chlorodiphenylamine

2-Bromo-4-chlorophenyl N-2-bromophenylbenzimidoate (15 g., 0.032 mole) was heated from 230 to 240° for 2.5 hours. The resulting black material was dissolved in 50 ml. of absolute ethanol, treated with charcoal twice, and concentrated depositing 6.25 g. (42%) of tan crystals, m.p. 120-

125°. Two additional recrystallizations from the same solvent raised the melting point to 127-128.5°.

Anal. Calcd. for $C_{19}H_{12}Br_2ClNO$: C, 49.01; H, 2.60; N, 3.01. Found: C, 49.09; H, 2.83; N, 2.99.

The yields from two similar runs were 51.8 and 55%, respectively.

2,2'-Dibromo-4-chlorodiphenylamine

A mixture of 18.5 g. (0.0397 mole) of N-benzoyl-2,2'-dibromo-4-chlorodiphenylamine, 20 g. of potassium hydroxide, 20 ml. of water, and 150 ml. of 95% ethanol was heated at reflux for 18 hours. The reaction mixture was concentrated by distilling approximately 150 ml. of solvent and then poured upon crushed ice. After extracting the aqueous solution with ether, the organic solution was dried with anhydrous calcium sulfate and distilled. The residue was taken up in absolute ethanol, treated with charcoal, and reduced in volume to give 11.25 g. (78.5%) of colorless solid, m.p. 81-83°. Recrystallization from the same solvent gave white flakes, m.p. 81-82.5°.

Anal. Calcd. for $C_{12}H_8Br_2ClN$: C, 39.87; H, 2.23; N, 3.88. Found: C, 39.88, H, 2.33; N, 4.00.

In two similar runs, 2,2'-dibromo-4-chlorodiphenylamine was prepared in yields of 71.2 and 73.4%, respectively.

N-Ethyl-2,2'-dibromo-4-chlorodiphenylamine

A solution of 21 g. (0.0582 mole) of 2,2'-dibromo-4-chlorodiphenylamine in 100 ml. of ether was treated with 0.06 mole of methyllithium, while cooling in an ice-bath. After stirring for 1 hour, 9.24 g. (0.06 mole) of freshly distilled diethyl sulfate in 70 ml. of tetrahydrofuran was added and the ether was removed by distillation. The tetrahydrofuran solution was refluxed for 16 hours and then hydrolyzed with 100 ml. of water. The reaction products were worked up in the usual manner and distilled at reduced pressure to give 17.7 g. (78.3%) of pale yellow viscous oil, b.p. 142-146° (0.005 mm.), n_D^{20} 1.6437. Attempts to crystallize the material were unsuccessful.

Anal. Calcd. for $C_{14}H_{12}Br_2ClN$: N, 3.60. Found: N, 3.68, 3.64.

In an analogous run, the ethylated compound was obtained in 81.4% yield.

2-Chloro-5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline

To a solution of 7.78 g. (0.02 mole) of N-ethyl-2,2'-dibromo-4-chlorodiphenylamine in 100 ml. of ether, cooled in an ice-bath, there was added 0.04 mole of an ethereal solution of *n*-butyllithium. Color Test II was negative after stirring for 1 hour. The pale yellow solution was then treated with 5.06 g. (0.02 mole) of dichlorodiphenylsilane in 40 ml. of ether, and the reaction mixture was refluxed for 5 hours, but Color Test I remained positive. Toluene (75 ml.) was added, the ether distilled, and the toluene suspension heated at reflux for 18 hours at the end of which Color Test I was negative. Hydrolysis was effected with water and the organic layer worked up in the usual fashion. The reaction products were treated with petroleum ether (b.p. 60-70°) to give 3.5 g. of yellow solid, m.p. 110-120°. This was taken up in absolute ethanol and treated with charcoal to give 2.25 g. (27.3%) of colorless solid, m.p. 119-121°. Recrystallization from petroleum ether gave colorless crystals, m.p. 121-122°.

Anal. Calcd. for $C_{26}H_{22}ClNSi$: C, 75.79; H, 5.38; Cl, 8.61; Si, 6.82. Found: C, 76.22, 76.04; H, 5.26, 5.41; Cl, 8.47, 8.66; Si, 6.83, 6.70.

2,2'-Dichloro-5,5'-diethyl-10,10'-spirobi-(5,10-dihydrophenazasiline)

A solution of 9.0 g. (0.023 mole) of N-ethyl-2,2'-dibromo-4-chlorodiphenylamine in 100 ml. of ether maintained at approximately -20° was treated with 0.046 mole of an ethereal solution of n-butyllithium. After stirring the reaction mixture from -20 to -10° for 30 minutes, Color Test II was negative. This solution was then added over a period of 1 hour to 1.95 g. (0.011 mole) of silicon tetrachloride in 100 ml. of ether, cooled in an ice-bath. The reaction mixture was allowed to warm to room temperature and stirred for

24 hours. Since Color Test I was positive, 30 ml. of dry toluene was added, the ether distilled, and the toluene suspension refluxed for 1 hour. The color test was then negative and hydrolysis was effected with 150 ml. of water. After the usual work-up, the residue was recrystallized twice from a 1:1 mixture of benzene and petroleum ether (b.p. 60-70°) to give 1.65 g. (29.5%) of colorless crystals, m.p. 188-191°. The analytical sample melted at 189-191°.

Anal. Calcd. for $C_{28}H_{24}Cl_2N_2Si$: C, 68.98; H, 4.96; Si, 5.76. Found: C, 69.04, 69.22; H, 4.79, 4.60; Si, 5.87, 5.80.

3-Bromobiphenyl-4-yl N-2-bromophenylbenzimidoate

A solution of 130 g. (0.56 mole) of 2-bromo-4-phenylphenol was added to 0.55 mole of sodium ethoxide in 700 ml. of absolute ethanol, while cooling in an ice-bath. This solution was then treated with 161 g. (0.55 mole) of 2-bromophenylbenzimidoyl chloride[61] in 100 ml. of ether. After stirring for 16 hours the solution was concentrated by distillation, cooled, and poured upon crushed ice. The aqueous solution was decanted from the resulting sticky solid, which was recrystallized from ethyl acetate to give 208 g. (74.5%) of colorless crystals, m.p. 146-149°. Two recrystallizations of a portion from ethyl acetate raised the melting point to 149-151°.

Anal. Calcd. for $C_{25}H_{17}Br_2NO$: C, 59.19; H, 3.38; N, 2.76. Found: C, 59.76, 59.83; H, 3.40, 3.52; N, 2.56, 2.67.

N-Benzoyl-2,2'-dibromo-4-phenyldiphenylamine

3-Bromobiphenyl-4-yl N-2-bromophenylbenzimidoate (25 g., 0.0493 mole) was heated from 240 to 255° for 2.5 hours. The black reaction mixture was then digested with 50 ml. of ethyl acetate. After cooling, the solution was filtered, reduced in volume (*ca*. 20 ml.), and filtered again. A total of 19.9 g. (79.6%) of tan solid, m.p. 204-208°, was collected. A portion was recrystallized twice from ethyl acetate and then from benzene to give colorless crystals, m.p. 209-211°.

Anal. Calcd. for $C_{25}H_{17}Br_2NO$: N, 2.76. Found: N, 2.73, 2.71.

In two similar runs, the yields of rearrangement product were 68 and 69%, respectively.

2,2'-Dibromo-4-phenyldiphenylamine

A mixture of 27 g. (0.0532 mole) of N-benzoyl-2,2'-dibromo-4-phenyldiphenylamine, 100 g. of potassium hydroxide, and 700 ml. of 95% ethanol was refluxed for 19 hours. The solution was concentrated by distillation and then poured upon crushed ice. The aqueous solution was extracted with ether and discarded. After drying and distilling the organic layer, the residue was taken up in absolute ethanol, treated with charcoal, and reduced in volume to give 16.7 g. (78%) of pale yellow crystals, m.p. 82-83.5°. Recrystallization from the same solvent gave lustrous crystals, m.p. 82-83°.

Anal. Calcd. for $C_{18}H_{13}Br_2N$: C, 53.61; H, 3.25; N, 3.48. Found: C, 54.01, 53.98; H, 3.39, 3.35; N, 3.40, 3.44.

An attempt to hydrolyze 30 g. of the N-benzoyl derivative in 200 ml. of 95% ethanol resulted in a 90% recovery of starting material, possibly due to the low solubility of the compound.

N-Ethyl-2,2'-dibromo-4-phenyldiphenylamine

A solution of 19.9 g. (0.0494 mole) of 2,2'-dibromo-4-phenyldiphenylamine in 100 ml. of ether, cooled in an ice-bath, was treated with 0.05 mole of an ethereal solution of methyllithium. After stirring for 1 hour, 8.5 g. (0.055 mole) of freshly distilled diethyl sulfate in 70 ml. of tetrahydrofuran was added. The ether was removed by distillation and the tetrahydrofuran solution heated at reflux for 16 hours. Hydrolysis was effected with water and the reaction mixture was worked up in the usual manner. The remaining material was treated with a small amount of absolute ethanol and filtered to give 17.6 g. of brown solid, m.p. 90-95°. This material was recrystallized from absolute ethanol to give 15.7 g. (73.7%) of colorless crystals, m.p. 92-95°. The analytical sample melted at 93-95°.

Anal. Calcd. for $C_{20}H_{17}Br_2N$: C, 55.71; H, 3.98; N, 3.25. Found: C, 55.88, 55.95; H, 4.09, 3.96; N, 3.46, 3.36.

In a repeat run, the N-ethyl derivative was obtained in a 72% yield.

5-Ethyl-2,10,10-triphenyl-5,10-dihydrophenazasiline

A solution of 8.62 g. (0.02 mole) of N-ethyl-2,2'-dibromo-4-phenyldiphenylamine in 100 ml. of ether, cooled in an ice-bath, was treated with 0.04 mole of *n*-butyllithium. After stirring for 1 hour, 5.06 g. (0.02 mole) of dichlorodiphenylsilane in 40 ml. of ether was added. The reaction mixture was refluxed for 4 hours, but Color Test I remained positive. Dry toluene (75 ml.) was added, the ether distilled, and the resulting mixture heated at reflux for 19 hours before the color test was negative. After the usual work-up, the residue was recrystallized four times from petroleum ether (b.p. 60-70°) to give 3.11 g. (34.3%) of lustrous crystals, m.p. 145.5-147°.

Anal. Calcd. for $C_{32}H_{27}NSi$: N, 3.09; Si, 6.19. Found: N, 3.20, 2.98; Si, 6.25, 6.22.

5,5'-Diethyl-2,2'-diphenyl-10,10'-spirobi-(5,10-dihydrophenazasiline)

A solution containing 0.02 mole of N-ethyl-2,2'-dilithio-4-phenyldiphenylamine, prepared as above, was added over a period of 1 hour to 1.70 g. (0.01 mole) of silicon tetrachloride in 100 ml. of ether. Since Color Test I was positive after refluxing for 24 hours, 30 ml. of toluene was added, the ether distilled, and the toluene suspension refluxed for 1 hour. Subsequently, the reaction mixture was hydrolyzed and worked up in the usual manner. The remaining material was recrystallized five times from a 1:1 mixture of benzene and petroleum ether (b.p. 60-70°) to give 2.33 g. (40.9%) of colorless crystals, m.p. 234-237°. The analytical sample melted at 235-238°.

Anal. Calcd. for $C_{40}H_{34}N_2Si$: C, 84.16; H, 6.00; Si, 4.92. Found: C, 84.42, 84.62; H, 5.75, 5.96; Si, 4.97, 5.04.

Bromination of 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline

In carbon disulfide at -20° A solution of 11.3 g. (0.03 mole) of 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline in 50 ml. of carbon disulfide, cooled to -20±2°, was treated with 9.6 g. (0.06 mole) of bromine by dropwise addition over a period of 10 minutes. Stirring was continued for 20 minutes at -20°, and then the reaction mixture was poured upon a cold solution of sodium bisulfite. Ether was added and the organic layer separated. After drying and evaporating the organic layer, the residue was chromatographed over alumina. Elution with petroleum ether (b.p. 60-70°) gave a small amount of solid, which was recrystallized three times from petroleum ether to give 0.13 g. of colorless crystals, m.p. 135-137°, identified as N-ethyl-2,2',4,4'-tetrabromodiphenylamine. The infrared spectrum as a carbon disulfide solution showed absorption bands indicative of aromatic and aliphatic C-H and C-N groups. A strong band was present at 12.3 μ characteristic of 1,2,4-trisubstituted benzene.

Anal. Calcd. for $C_{14}H_{11}Br_4N$: C, 32.78; H, 2.16. Found: C, 32.69, 32.59; H, 2.31, 2.34.

Further elution with petroleum ether and then with cyclohexane gave a colorless solid, m.p. 107-115°. After three recrystallizations for petroleum ether (b.p. 60-70°), there was obtained 3.03 g. (26.8%) of recovered 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline, m.p. 118-121°, which was identified by mixed melting point and by comparison of the infrared spectra. Continued elution with cyclohexane, followed by benzene, gave a colorless solid which was recrystallized twice from cyclohexane to give 4.15 g. of colorless solid, m.p. 190-198°. This material was recrystallized twice from ethyl acetate to give 3.37 g. (21%) of colorless crystals, m.p. 197-200°, identified as 5-ethyl-2,8-dibromo-10,10-diphenyl-5,10-dihydrophenazasiline. An additional recrystallization from ethyl acetate raised the melting point to 198-200°. The infrared spectrum of the compound in carbon disulfide exhibited a strong absorption band at 12.4 μ indicative of 1,2,4-trisubstituted benzene. The remainder of the spectrum was similar to that of the other 5,10-dihydrophenazasiline derivatives, except that the ortho-disubstitution band was absent.

Anal. Calcd. for $C_{26}H_{21}Br_2NSi$: C, 58.32; H, 3.95; N, 2.62; Si, 5.25. Found: C, 58.10, 58.32; H, 4.05, 3.87; N, 2.91, 2.97; Si, 5.34, 5.29.

The column was then eluted further with benzene and the product recrystallized twice from petroleum ether (b.p. 60-70°) to give 0.67 g. (3.5%) of colorless flakes, m.p. 138-141°. The analytical sample melted at 138-140°. The material has been tentatively identified as 2-(N-ethyl-2,4-dibromoanilino)-5-bromophenyldiphenylsilanol. The infrared spectrum as a carbon disulfide solution had absorption bands at 2.8, 3.3, 3.4, 9.0, 12.3, and 13.5 μ which are characteristic of the hydroxy, C-H aliphatic, C-H aromatic, silicon-phenyl, 1,2,4-trisubstituted benzene, and monosubstituted phenyl groups, respectively.

Anal. Calcd. for $C_{26}H_{22}Br_3NOSi$: C, 49.38; H, 3.51; N, 2.22; Si, 4.44. Found: C, 49.74, 49.90; H, 3.42, 3.37; N, 2.67, 2.49; Si, 4.54, 4.45.

Another run employing identical reaction conditions and work-up afforded 5-ethyl-2,8-dibromo-10,10-diphenyl-5,10-dihydrophenazasiline in a 21% yield. There was also obtained a 2.3% yield of 2-(N-ethyl-2,4-dibromoanilino)-5-bromophenyldiphenylsilanol, in addition to a 41.9% recovery of 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline.

A slightly improved yield (24.7%) of the dibromo compound was obtained in a third run. The bromine addition was carried out as in the previous runs, but instead of stirring at -20° the reaction mixture was allowed to warm to room temperature, which required 20 minutes, before effecting hydrolysis. However, only 10.6% of the 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline was recovered from this run.

<u>In glacial acetic acid</u> A suspension of 11.3 g. (0.03 mole) of 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline in 100 ml. of glacial acetic acid, cooled in an ice-bath, was treated with 10.5 g. (0.065 mole) of bromine by dropwise addition over a period of 15 minutes. The ice-bath was removed and the reaction mixture stirred for 45 minutes. The orange mixture was then hydrolyzed with a dilute solution of sodium bisulfite. The aqueous solution was filtered and the yellow sticky material was taken up in ether. The ethereal solution was then worked up in the usual manner and the reaction products chromatographed as described in the previous runs. This gave 0.72 g. (4.7%) of N-ethyl-2,2',4,4'-tetrabromodiphenylamine, m.p. 135-137°, which was identified by mixed melting point and by comparison of the infrared spectra, and 0.83 g. (5.2%) of 5-ethyl-2,8-dibromo-10,10-diphenyl-5,10-dihydrophenazasiline. There was also obtained a large amount of a colorless viscous oil which could not be characterized. The infrared spectrum contained large absorption bands indicative of silanols and disiloxanes.

<u>In refluxing glacial acetic acid</u> A solution of 7.54

g. (0.02 mole) of 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline in 100 ml. of glacial acetic acid, cooled in an ice-bath, was treated with 14.4 g. (0.09 mole) of bromine. After warming to room temperature, the reaction mixture was heated at reflux for 1 hour and then hydrolyzed with a dilute solution of sodium bisulfite. The resulting solid material was filtered, air-dried, and chromatographed. Elution with petroleum ether (b.p. 60-70°) and three subsequent recrystallizations from the same solvent afforded 2.27 g. (22.1%) of N-ethyl-2,2',4,4'-tetrabromodiphenylamine, m.p. 134-137°, which was identified by mixed melting point and by comparison of the infrared spectra. Using cyclohexane as the eluant, there was obtained a colorless solid, m.p. 180-186°. This material was recrystallized twice from ethyl acetate to give 3.03 g. (31.2%) of colorless needles, m.p. 185-186.5°, which was identified as 2,2',4,4'-tetrabromodiphenylamine by mixed melting point with an authentic sample.[66]

<u>In glacial acetic acid in the presence of sodium acetate</u> A mixture of 11.3 g. (0.03 mole) of 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline, 6 g. (0.073 mole) of sodium acetate, and 100 ml. of glacial acetic acid was cooled in an ice-bath and treated with 10.5 g. (0.065 mole) of bromine. The ice-bath was removed and the reaction mixture stirred for

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[66] L. A. Elson, C. S. Gibson, and J. D. A. Johnson, *J. Chem. Soc.*, 1080 (1929).

45 minutes. After hydrolysis and the usual work-up, the reaction products were chromatographed. Elution with the various solvents in the customary manner gave 1.53 g. (10%) of N-ethyl-2,2',4,4'-tetrabromodiphenylamine, m.p. 135-137°, 2.42 g. (21.4%) of recovered 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline, and 0.67 g. (4.2%) of 5-ethyl-2,8-dibromo-10,10-diphenyl-5,10-dihydrophenazasiline, m.p. 198-200°. Elution of the column with ethyl acetate gave 7.28 g. of colorless solid, m.p. 136-140°. Recrystallization of this material from a 5:1 mixture of petroleum ether (b.p. 60-70°) and benzene gave a crystalline solid, m.p. 156-160°. An additional recrystallization from the same solvent mixture raised the melting point to 158-160°. This material was found to be identical with 2-(N-ethyl-2,4-dibromoanilino)-5-bromophenyldiphenylsilanol, which has been previously described as colorless flakes, m.p. 138-140°. When the lower melting material was taken up in petroleum ether and seeded with some of the higher melting material, the higher melting crystalline solid was obtained. However, attempts to obtain the lower melting solid by a similar process were unsuccessful affording only a recovery of the higher melting material. The infrared spectra of the two solids as carbon disulfide solutions are identical, but have small absorption differences as potassium

bromide pellets.[67] A total of 6.32 g. (33.4%) of the material was isolated.

2,2',4,4'-Tetrabromodiphenylamine

A solution of 5.1 g. (0.03 mole) of diphenylamine in 200 ml. of glacial acetic acid was treated with 19.2 g. (0.12 mole) of bromine. The reaction mixture was refluxed for 1 hour and subsequently treated with 200 ml. of a dilute solution of sodium bisulfite. The resulting solid was filtered and air-dried. After two recrystallizations from ethyl acetate, there was obtained 12.8 g. (87.9%) of colorless needles, m.p. 184-186° (lit.[66] value, m.p. 186°). A mixed melting point with the previously described material was undepressed.

N-Ethyl-2,2',4,4'-tetrabromodiphenylamine

A suspension of 8.9 g. (0.0183 mole) of 2,2',4,4'-tetrabromodiphenylamine in 200 ml. of ether, cooled in an ice-bath, was treated with 0.027 mole of methyllithium. After stirring for 30 minutes, a solution of 4.2 g. (0.028 mole) of diethyl sulfate in 200 ml. of tetrahydrofuran was added. The ether was removed by distillation and the reaction mixture heated at reflux for 18 hours. After hydrolysis, ether was added

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[67] F. A. Miller. Applications of infrared and ultraviolet spectra to organic chemistry. In H. Gilman, ed. Organic chemistry. Vol. III, p. 139. New York, John Wiley and Sons. 1953.

and the organic layer separated. The ethereal solution was dried with sodium sulfate and evaporated, and the reaction products chromatographed. Elution with petroleum ether (b.p. 60-70°) and two subsequent recrystallizations from the same solvent gave 5.56 g. (59.2%) of colorless crystals, m.p. 133-136°. Another recrystallization raised the melting point to 135-137°. This material was identified as N-ethyl-2,2',4,4'-tetrabromodiphenylamine by mixed melting point and by comparison of the infrared spectra.

Bromination of 2-(N-ethyl-2,4-dibromoanilino)-5-bromophenyldiphenylsilanol

Bromine (1.8 g., 0.011 mole) was added to 4.65 g. (0.00735 mole) of 2-(N-ethyl-2,4-dibromoanilino)-5-bromophenyldiphenylsilanol in 100 ml. of glacial acetic acid, and the reaction mixture stirred at room temperature for 1 hour. After hydrolysis with a dilute solution of sodium bisulfite, the aqueous solution was filtered. The resulting material was air-dried and chromatographed over alumina. Using petroleum ether (b.p. 60-70°) as the eluant, there was obtained a colorless solid, which was recrystallized three times from petroleum ether to give 2.69 g. (71.4%) of colorless crystals, m.p. 133-137°. An additional recrystallization from the same solvent raised the melting point to 135-137°. The material was identified as N-ethyl-2,2',4,4'-tetrabromodiphenylamine by mixed melting point.

Bromination of di-p-tolylamine

Bromine (16 g., 0.1 mole) was added dropwise over a period of 10 minutes to a solution of 10 g. (0.051 mole) of di-p-tolylamine in 100 ml. of glacial acetic acid, while cooling in an ice-bath. The reaction mixture was allowed to warm to room temperature, stirred for 1 hour, and then hydrolyzed with 200 ml. of a dilute solution of sodium bisulfite. The aqueous solution was cooled in an ice-bath and the resulting material was filtered yielding 16.9 g. of pale blue-green solid, m.p. 40-53°. After two recrystallizations from absolute ethanol, there was obtained 11.3 g. (63.5%) of 2,2'-dibromodi-p-tolylamine, m.p. 57-59°. An additional recrystallization of a portion gave colorless needles, m.p. 57.5-59°. The infrared spectrum of the material in carbon disulfide exhibited a strong absorption band at 12.4 μ indicative of 1,2,4-trisubstituted benzene.

Anal. Calcd. for $C_{14}H_{13}Br_2N$: Br, 45.01; N, 3.95. Found: Br, 44.64, 44.59; N, 3.92, 3.76.

A repeat reaction employing 20 g. (0.102 mole) of di-p-tolylamine and 32 g. (0.2 mole) of bromine gave a 59.9% yield of the dibromo compound. When equal molar amounts of bromine and di-p-tolylamine were reacted, 2,2'-dibromodi-p-tolylamine was obtained in 35.3% yield, and 48.9% of the di-p-tolylamine was recovered. None of the mono-bromo compound could be isolated.

N-ethyl-2,2'-dibromodi-p-tolylamine

An ethereal solution containing 0.031 mole of methyllithium was added to 11 g. (0.031 mole) of 2,2'-dibromodi-p-tolylamine in 100 ml. of ether, while cooling in an ice-bath. After stirring for 45 minutes, this solution was treated with 6.16 g. (0.04 mole) of diethyl sulfate in 100 ml. of tetrahydrofuran. The ether was removed by distillation and the resulting tetrahydrofuran solution heated at reflux for 16 hours. After the usual work-up, the reaction products were subsequently taken up in absolute ethanol to give 10.73 g. of pale yellow needles, m.p. 104-111°. This material was recrystallized three times from absolute ethanol to give 9.33 g. (78.6%) of colorless needles, m.p. 109-111°.

Anal. Calcd. for $C_{16}H_{17}Br_2N$: C, 50.15; H, 4.47. Found: C, 50.21, 50.09; H, 4.79, 4.61.

5-Ethyl-2,8-dimethyl-10,10-diphenyl-5,10-dihydrophenazasiline

From N-ethyl-2,2'-dibromodi-p-tolylamine A solution of 5.75 g. (0.015 mole) of N-ethyl-2,2'-dibromodi-p-tolylamine in 50 ml. of ether, cooled in an ice-bath, was treated with 0.03 mole of n-butyllithium. After stirring for 30 minutes, a solution of 3.80 g. (0.015 mole) of dichlorodiphenylsilane in 50 ml. of ether was added and the reaction mixture heated at reflux for 17 hours. Subsequently, 30 ml. of toluene was added and the ether distilled. After refluxing the resulting solution for 2 hours, Color Test I was negative. The reaction mixture was hydrolyzed with 50 ml. of water and worked up in the usual manner. The reaction products were taken up with petroleum ether (b.p. 60-70°) to give 3.76 g. of yellow solid, m.p. 147-158°. This material was taken up again in petroleum ether, treated with charcoal, and concentrated to give 3.27 g. (53.8%) of colorless crystals, m.p. 159-162°. The analytical sample melted at 160.5-162°.

Anal. Calcd. for $C_{28}H_{27}NSi$: C, 82.91; H, 6.71; Si, 6.93. Found: C, 83.23, 83.00; H, 6.89, 6.86; Si, 7.15, 7.01.

From 5-ethyl-2,8-dibromo-10,10-diphenyl-5,10-dihydrophenazasiline An ethereal solution of 0.023 mole of n-butyllithium was added to 4.0 g. (0.0075 mole) of 5-ethyl-2,8-dibromo-10,10-diphenyl-5,10-dihydrophenazasiline in 100 ml. of ether, while cooling in an ice-bath. The reaction mixture was allowed to warm to room temperature and stirred for 45 minutes. A solution of 3.15 g. (0.025 mole) of freshly distilled dimethyl sulfate in 25 ml. of ether was added, and after refluxing for 2 hours Color Test I was negative. Subsequently, the usual work-up and crystallization from petroleum ether (b.p. 60-70°) gave 2.54 g. of colorless solid, m.p. 150-160°. This material was recrystallized twice from petroleum ether to give 1.89 g. (62.2%) of colorless crystals, m.p. 158-160°. An additional recrystallization raised the melting point to 159-161°. The material was identified as

5-ethyl-2,8-dimethyl-10,10-diphenyl-5,10-dihydrophenazasiline by mixed melting point and by comparison of the infrared spectra.

N-Methyldi-p-tolylamine

In accordance with the procedure of Weitz and Schwechten,[68] di-p-tolylamine was reacted with dimethyl sulfate to give the N-methyl derivative in 51.9% yield. Another run was carried out using the modification of Gibson and Vining.[69] A mixture of 40 g. (0.203 mole) of di-p-tolylamine and 37.8 g. (0.3 mole) of dimethyl sulfate was heated on a steam bath for 10 minutes. After cooling to 50°, the rapidly stirred solution was treated with 35 g. of sodium carbonate in 200 ml. of water by dropwise addition over a period of 3 hours. The reaction mixture was allowed to cool and then extracted with ether. The ethereal solution was dried and evaporated, and the resulting material distilled at reduced pressure to give 31.7 g. (74%) of pale yellow liquid, b.p. 118-120° (0.02 mm.), n_D^{20} 1.5997.

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[68] E. Weitz and H. W. Schwechten, Ber., 60, 550 (1927).

[69] C. S. Gibson and D. C. Vining, J. Chem. Soc., 123, 831 (1923).

N-Methyl-2,2'-dibromodi-p-tolylamine

From N-methyldi-p-tolylamine A solution of 5 g. (0.0237 mole) of N-methyldi-p-tolylamine in 50 ml. of glacial acetic acid, cooled in an ice-bath, was treated with 7.58 g. (0.047 mole) of bromine by dropwise addition. After stirring 1 hour at room temperature, the reaction mixture was hydrolyzed with 300 ml. of a dilute solution of sodium bisulfite. The resulting solid material was filtered and recrystallized from absolute ethanol to give 5.8 g. of colorless needles, m.p. 98-104°. Recrystallization from the same solvent gave 5.28 g. (60.4%) of large colorless needles, m.p. 102-104°. The analytical sample melted at 102.5-104°.

Anal. Calcd. for $C_{15}H_{15}Br_2N$: Br, 43.30; N, 3.80. Found: Br, 43.26, 43.06; N, 4.04, 3.86.

The reaction of 31 g. (0.147 mole) of N-methyldi-p-tolylamine and 59 g. (0.37 mole) of bromine under similar conditions gave a 76.5% yield of the dibromo derivative. When equal molar amounts of N-methyldi-p-tolylamine and bromine were reacted in an effort to prepare the mono-bromo compound, N-methyl-2,2'-dibromodi-p-tolylamine was obtained in 31.1% yield. N-Methyldi-p-tolylamine was recovered in 53.4% yield, but none of the mono-bromo compound could be isolated.

From 2,2'-dibromodi-p-tolylamine An ethereal solution of 0.1 mole of methyllithium was reacted with 34 g. (0.0958 mole) of 2,2'-dibromodi-p-tolylamine in 200 ml. of ether, while cooling in an ice-bath. After stirring for 1 hour, 13.9 g. (0.11 mole) of dimethyl sulfate in 150 ml. of tetrahydrofuran was added. The ether was removed by distillation and the resulting solution heated at reflux for 18 hours. Subsequently, the reaction mixture was allowed to cool, hydrolyzed, and worked up in the usual manner. The residue was taken up in absolute ethanol depositing 32.8 g. of colorless crystals, m.p. 98-104°. Recrystallization from the same solvent gave 31.4 g. (88.7%) of colorless needles, m.p. 101-104°. A mixed melting point determination with an authentic sample of N-methyl-2,2'-dibromodi-p-tolylamine was not depressed.

2,5,8-Trimethyl-10,10-diphenyl-5,10-dihydrophenazasiline

By halogen-metal interconversion A solution of 7.38 g. (0.02 mole) of N-methyl-2,2'-dibromodi-p-tolylamine in 100 ml. of ether, cooled in an ice-bath, was treated with 0.04 mole of n-butyllithium. After stirring for 45 minutes, Color Test II was negative and 5.06 g. (0.02 mole) of dichlorodiphenylsilane in 50 ml. of ether was added. The reaction mixture was stirred at room temperature for 18 hours but Color Test I remained positive. Toluene (50 ml.) was added and the ether removed by distillation. The toluene suspension was then refluxed for 4 hours, before the color test was negative.

The reaction mixture was hydrolyzed, ether was added, and the organic layer separated. After drying with anhydrous calcium sulfate, the organic layer was evaporated, and the resulting solid was taken up in petroleum ether (b.p. 60-70°) to give 5.2 g. of pale yellow solid, m.p. 158-167°. After two recrystallizations from petroleum ether, there was obtained 3.87 g. (49.5%) of colorless crystals, m.p. 163-165°. Another recrystallization did not change the melting point.

Anal. Calcd. for $C_{27}H_{25}NSi$: C, 82.81; H, 6.44; N, 3.58; Si, 7.19. Found: C, 82.93, 83.13; H, 6.13, 6.18; N, 3.49, 3.43; Si, 7.30, 7.08.

By direct preparation Ten ml. of a solution of 5.55 g. (0.015 mole) of N-methyl-2,2'-dibromodi-p-tolylamine in 75 ml. of ether was added to 1.4 g. (0.2 g. atom) of lithium in 10 ml. of ether. After adding three drops of methyl iodide, the reaction started and the rest of the dibromo compound was added at such a rate as to maintain a gentle reflux. The reaction mixture was stirred at room temperature for 45 minutes, and filtered through a previously dried glass wool plug. Acid titration of an aliquot indicated the presence of 0.022 mole of organolithium reagent. Assuming this to be all in the form of the dilithium compound, the yield was 73%.

The above solution was added to 3.03 g. (0.012 mole) of dichlorodiphenylsilane in 25 ml. of ether and stirred for 18 hours at room temperature. Color Test I was negative, and the reaction mixture was hydrolyzed. The aqueous solution was separated, extracted with ether, and discarded. After drying and evaporating the combined organic layer, the residue was taken up in petroleum ether (b.p. 60-70°) to give a pale yellow solid, m.p. 145-158°. After two recrystallizations from petroleum ether, there was obtained 2.19 g. (37.3%, based on the N-methyl compound) of colorless crystals, m.p. 162-165°. An additional recrystallization raised the melting point to 163-165°. A mixed melting point determination with an authentic sample of 2,5,8-trimethyl-10,10-diphenyl-5,10-dihydrophenazasiline was not depressed.

2,2',5,5',8,8'-Hexamethyl-10,10'-spirobi-(5,10-dihydrophenazasiline)

A solution of 11.1 g. (0.03 mole) of N-methyl-2,2'-dibromodi-p-tolylamine in 150 ml. of ether, cooled in an ice-bath, was treated with 0.06 mole of n-butyllithium. After stirring for 45 minutes, the solution was transferred to a dropping funnel and added to 2.55 g. (0.015 mole) of silicon tetrachloride in 100 ml. of ether. The reaction mixture was refluxed for 20 hours, but Color Test I remained positive. The ether was then replaced with toluene and the toluene suspension heated at reflux for 2 hours before the color test was negative. After hydrolysis and the usual work-up, the residue was taken up in ethyl acetate to give 3.85 g. of large colorless crystals, m.p. 228-232°. This material was recrystallized twice from ethyl acetate and then twice from cyclohexane to give 2.32 g. (34.7%) of colorless crystals, m.p. 230-233°.

Anal. Calcd. for $C_{30}H_{30}N_2Si$: C, 80.67; H, 6.77; Si, 6.29. Found: C, 80.74, 80.70; H, 6.70, 6.56; Si, 6.32, 6.24.

2,5,8,10,10-Pentamethyl-5,10-dihydrophenazasiline

A solution of 3.9 g. (0.03 mole) of dichlorodimethylsilane in 50 ml. of ether was added to an ethereal solution containing 0.03 mole of N-methyl-2,2'-dilithiodi-*p*-tolylamine, prepared from 0.03 mole of N-methyl-2,2'-dibromodi-*p*-tolylamine and 0.06 mole of *n*-butyllithium. After stirring 20 hours at room temperature, 50 ml. of toluene was added, the ether distilled, and the toluene suspension heated at reflux for 2 hours at the end of which time Color Test I was negative. Subsequently, the reaction mixture was hydrolyzed and worked up in the usual manner. The combined organic layer was distilled and the last traces of solvent were removed with the aid of a water aspirator. Upon treatment with ethanol, there was obtained 4.7 g. of solid, m.p. 96-115°. The material was taken up in absolute ethanol, treated with charcoal, and concentrated to give 3.77 g. (47.1%) of colorless crystals, m.p. 115-118°. The analytical sample melted at 117.5-119°.

Anal. Calcd. for $C_{17}H_{21}NSi$: C, 76.34; H, 7.86; N, 5.24. Found: C, 76.60, 76.42; H, 7.69, 7.76; N, 5.30, 5.20.

2,5,8-Trimethyl-10,10-dibenzyl-5,10-dihydrophenazasiline

An ethereal solution containing 0.015 mole of N-methyl-2,2'-dilithiodi-p-tolylamine, prepared as described above, was treated with 4.55 g. (0.015 mole) of dibenzyldichlorosilane[54] in 50 ml. of ether. The reaction mixture was stirred for 20 hours at room temperature, but Color Test I remained positive. The ether was replaced by dry toluene in the usual manner, and after refluxing for 2 hours the color test was negative. The reaction mixture was then worked up using the customary procedure and the residue recrystallized from petroleum ether (b.p. 60-70°) to give 3.22 g. of pale yellow crystals, m.p. 120-124°. Recrystallization from the same solvent gave 2.67 g. (42.5%) of colorless crystals, m.p. 123-125°. An additional recrystallization raised the melting point to 124-125.5°.

Anal. Calcd. for $C_{29}H_{29}NSi$: Si, 6.69. Found: Si, 6.87, 6.82.

Reaction of N-methyl-2,2'-dilithiodi-p-tolylamine and sym-tetraphenyldisilane

N-Methyl-2,2'-dilithiodi-p-tolylamine, prepared from 5.75 g. (0.015 mole) of N-methyl-2,2'-dibromodi-p-tolylamine and 0.03 mole of n-butyllithium, was added to 5.55 g. (0.015

mole) of sym-tetraphenyldisilane[70] in 100 ml. of ether, and the reaction mixture stirred at room temperature for 24 hours. Toluene was added, the ether removed by distillation, and the resulting solution refluxed for 12 hours before Color Test I was negative. After hydrolysis and the usual work-up, the reaction products were chromatographed over alumina with petroleum ether (b.p. 60-70°). The first fractions gave only traces of oils; however, further elution with the same solvent gave a colorless solid which was recrystallized from petroleum ether to give 3.38 g. (57.6%) of colorless crystals, m.p. 160-165°. An additional recrystallization raised the melting point to 163-165°. This material was identified as 2,5,8-trimethyl-10,10-diphenyl-5,10-dihydrophenazasiline by mixed melting point and by comparison of the infrared spectra. Elution with other solvents gave oils which could not be further purified or identified.

Reaction of N-methyl-2,2'-dilithiodi-p-tolylamine and chlorotriphenylsilane

An ethereal solution containing 0.03 mole of N-methyl-2,2'-dilithiodi-p-tolylamine, prepared by halogen-metal interconversion as described above, was treated with 17.7 g. (0.06 mole) of chlorotriphenylsilane in 150 ml. of ether. The

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[70] H. Gilman and W. Steudel, Chem. and Ind. (London), 1094 (1959).

reaction mixture was stirred 24 hours at room temperature, 50 ml. of toluene was added, and then the ether removed by distillation. After heating the toluene suspension at reflux for 4 hours, Color Test I was negative. The reaction mixture was hydrolyzed with water, ether was added, and the resulting solid material was removed by filtration. After washing with ether, the solid was recrystallized from a 1:1 mixture of benzene and petroleum ether (b.p. 60-70°) to give 5.36 g. of colorless needles, m.p. 236-240°. A portion was recrystallized from ethyl acetate to give needles, m.p. 237.5-239°, which was identified as tetraphenylsilane by mixed melting point and by comparison of the infrared spectra.

The combined organic layer and ether washings were dried and evaporated. The residue was chromatographed over alumina. Elution with petroleum ether (b.p. 60-70°), followed by three recrystallizations from absolute ethanol, gave 1.09 g. (5.7%) of n-butyltriphenylsilane, m.p. 86-88°, identified by mixed melting point. Further elution with petroleum ether gave a colorless solid, which was recrystallized two times from ethyl acetate to give 0.28 g. of tetraphenylsilane, m.p. 235-238°.

After continued elution with petroleum ether and then with cyclohexane, there was obtained a colorless solid, which resisted purification by recrystallization. This solid material was subsequently rechromatographed over alumina. Using petroleum ether as the eluant, there was obtained a trace of solid which was recrystallized from etheyl acetate to give 0.17 g. of tetraphenylsilane. This is a total yield of 5.81 g. (57.6%, based on one-half of the silicon). Further elution with petroleum ether and then with cyclohexane gave a colorless solid. This material was recrystallized three times from petroleum ether to give 4.93 g. (42%) of colorless crystals, m.p. 161-165°. A portion was recrystallized from the same solvent raising the melting point to 163-165°. The material was identified as 2,5,8-trimethyl-10,10-diphenyl-5,10-dihydrophenazasiline by mixed melting point and by comparison of the infrared spectra.

o-Phenylene Silicon Derivatives

Reaction of o-phenylenedilithium and diphenylsilane

First experiment A mixture of 8.28 g. (0.03 mole) of o-phenylene-mercury,[71,72,73] 6 g. of finely cut lithium wire, and 100 ml. of dry ether was placed in a Schlenk tube and agitated on a shaking machine for 4 days. The reaction mixture was filtered through a previously dried glass wool plug giving a reddish-brown solution containing a light gray sus-

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[71] G. Wittig and F. Bickelhaupt, Angew. Chem., 69, 93 (1957).

[72] G. Wittig and F. Bickelhaupt, Ber., 91, 883 (1958).

[73] For convenience the molecular weight of o-phenylenemercury was considered to be 276. The actual value is 1660. See footnote 72.

pension. This material was added over a period of 30 minutes to 5.52 g. (0.03 mole) of diphenylsilane[62] in 50 ml. of ether, while cooling in an ice-bath. After stirring for 24 hours at room temperature, hydrolysis was carried out with 100 ml. of 5% hydrochloric acid. Ether was added and the insoluble gray solid filtered. This solid was then recrystallized from ethyl acetate three times to give 1.64 g. of o-phenylenebis-(diphenylsilane), m.p. 174-176°.

The layers of the filtrate were separated, and the aqueous layer extracted with ether. The combined organic solution was dried with anhydrous calcium sulfate and evaporated under an air-jet. The resulting material was taken up in ethyl acetate and seeded with some of the above solid to afford 0.95 g. of shiny crystals, m.p. 171-174°. This was recrystallized once more to give 0.77 g. of o-phenylenebis-(diphenylsilane), m.p. 174-176°. The total yield was 36.4% (based on the diphenylsilane), and the analytical sample melted at 174.5-176°. The infrared spectrum of the compound in carbon disulfide had characteristic absorption bands at 3.3, 9.0 and 13.3μ, indicative of aromatic C-H, the silicon-phenyl linkage, and *ortho*-disubstitution, respectively. As a carbon tetrachloride solution, the spectrum showed a large Si-H absorption at 4.7μ.

Anal. Calcd. for $C_{30}H_{26}Si_2$: C, 81.39; H, 5.92; Si, 12.69. Found: C, 81.56, 81.38; H, 6.15, 5.98; Si, 12.78, 12.69.

Second experiment. o-Phenylenedilithium, prepared as described above from 10 g. (0.036 mole) of o-phenylene-mercury and 7 g. of lithium, was added dropwise to 14.7 g. (0.08 mole) of diphenylsilane[62] dissolved in 100 ml. of ether. After stirring 16 hours at room temperature, the reaction mixture was poured upon crushed ice containing a small amount of sulfuric acid. Following the same work-up procedure as given in the first experiment, there was obtained 3.71 g. (23.3%, based on the o-phenylene-mercury) of o-phenylenebis(diphenylsilane), m.p. 173-176° (mixed m.p.).

Third experiment A suspension of 10 g. (0.036 mole) of o-phenylene-mercury and 7 g. of lithium in 120 ml. of ether was agitated for 5 days. The reaction mixture was filtered through a sintered glass filter to give a red-brown, suspension-free, solution. A 2-ml. aliquot of the solution was titrated with standard acid indicating the presence of 0.024 mole of o-phenylenedilithium. (An assumption was made that all of the organolithium reagent was o-phenylenedilithium.) This reagent was added over a period of 45 minutes to 11.0 g. (0.06 mole) of diphenylsilane[62] in 150 ml. of ether, while cooling in an ice-bath. After stirring for 16 hours at room temperature, the reaction mixture was poured upon crushed ice containing a small amount of sulfuric acid. Work-up as described previously gave 4.05 g. (38.2%) of o-phenylenebis-

(diphenylsilane) as colorless crystals, m.p. 173-176° (mixed m.p.).

Fourth experiment An ethereal solution containing 0.023 mole of o-phenylenedilithium, filtered and titrated as described in the preceding experiment, was added to 4.23 g. (0.023 mole) of diphenylsilane[62] in 25 ml. of ether. The reaction mixture was stirred at room temperature for 17 hours, 50 ml. of dry toluene was added, and the ether distilled. After refluxing the resulting suspension for 3 hours, Color Test I was negative. Hydrolysis was carried out with 100 ml. of dilute sulfuric acid. The aqueous layer was separated, extracted with ether, and discarded. The combined organic solution was dried and evaporated under an air-jet. The brown oily residue was chromatographed on alumina.

Using petroleum ether (b.p. 60-70°) as an eluant, 0.1 g. of triphenylsilane (mixed m.p.) was obtained. Further elution with the same solvent gave a solid which was recrystallized twice from ethyl acetate to afford 0.21 g. (2.7%) of colorless needles, m.p. 234-237°, identified as tetraphenylsilane by mixed melting point and by comparison of infrared spectra. Subsequently, cyclohexane was used as an eluant and the resulting solid was recrystallized from ethyl acetate to give 1.70 g. of colorless solid, m.p. 170-176°. An additional recrystallization gave 1.58 g. (31.1%) of o-phenylenebis(diphenylsilane), m.p. 175-177° (mixed m.p.). Further elution with cyclohexane, followed by recrystallization from ethyl acetate, afforded 0.68 g. of colorless solid, m.p. 210-216°. After recrystallization from the same solvent, there was obtained 0.54 g. (9.1%) of (o-diphenylsilylphenyl)triphenylsilane, m.p. 214-217°, identified by mixed melting point and by infrared spectrum (see below).

o-Phenylenebis(methyldiphenylsilane)

From o-phenylenedilithium and methyldiphenylchlorosilane

An ethereal solution containing 17.4 g. (0.075 mole) of methyldiphenylchlorosilane was treated with o-phenylenedilithium, prepared from 10 g. (0.036 mole) of o-phenylenemercury and filtered through a glass wool plug, and refluxed for 18 hours. Since Color Test I was positive, 80 ml. of dry toluene was added, the ether removed by distillation, and the resulting mixture heated at reflux for 24 hours. After cooling, the reaction mixture was hydrolyzed and worked up in the usual manner. The oily residue was treated with petroleum ether (b.p. 60-70°) depositing 4.75 g. of colorless crystals, m.p. 140-142°. Recrystallization from petroleum ether gave 4.34 g. (29.3%) of 1,2-dimethyl-1,1,2,2-tetraphenyldisilane, m.p. 141.5-143°, identified by mixed melting point and by comparison of the infrared spectra.

The petroleum ether solution was then concentrated affording 1.6 g. of solid, m.p. 157-165°. After two recrystallizations from petroleum ether (b.p. 60-70°), there was obtained 1.3 g. (7.7%) of colorless crystals, m.p. 172-174°. The analytical sample melted at 173-174°. The infrared spectrum of the material as a carbon disulfide solution showed absorption bands characteristic of aromatic and aliphatic C-H, the silicon-methyl linkage, the silicon-phenyl linkage, and ortho-disubstituted benzene.

Anal. Calcd. for $C_{32}H_{30}Si_2$: C, 81.64; H, 6.42; Si, 11.94. Found: C, 82.10, 81.98; H, 6.31, 6.10; Si, 11.83, 11.55.

Concentration of the mother liquors gave only oils which could not be identified.

From methyllithium and o-phenylenebis(diphenylsilane)

Methyllithium (0.007 mole) was added to 1 g. (0.0023 mole) of o-phenylenebis(diphenylsilane) in 50 ml. of ether. After refluxing for 18 hours, Color Test I was only faintly positive; accordingly an additional 0.003 mole of methyllithium was added. Toluene (40 ml.) was also added, the ether distilled, and the toluene suspension refluxed for 1 hour. After work-up, there was obtained 0.82 g. of colorless solid, m.p. 125-152°. This material was recrystallized six times from petroleum ether (b.p. 60-70°) to give 0.18 g. (16.9%) of o-phenylenebis(methyldiphenylsilane), m.p. 171-173° (mixed m.p. and infrared spectrum). The difficulty in purifying the dimethyl derivative was due to contamination by Si-H containing compounds. An admixture of authentic o-phenylenebis(methyldiphenylsilane) and o-phenylenebis(diphenylsilane) melted over the range 150-165°.

5,5,10,10-Tetraphenyl-5,10-dihydrosilanthrene

From o-phenylenedilithium and dichlorodiphenylsilane

A solution of 7.1 g. (0.028 mole) of dichlorodiphenylsilane in 25 ml. of ether was treated with an ether solution containing 0.028 mole of o-phenylenedilithium, determined by titration after filtering through a sintered glass filter. The reaction mixture was stirred at room temperature for 18 hours, 50 ml. of toluene was added, and the ether removed by distillation. After refluxing the toluene suspension for 6 hours, Color Test I was negative. Subsequently, hydrolysis was carried out with dilute sulfuric acid, and the aqueous layer separated, extracted with ether, and discarded. The combined organic solution was dried and evaporated.

The brown reaction products were chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave a solid which was recrystallized from ethyl acetate to give colorless needles, m.p. 221-228°. Recrystallization from the same solvent gave 0.06 g. (0.6%) of tetraphenylsilane, m.p. 234-237° (mixed m.p.). Using cyclohexane as the eluant, there was obtained a colorless solid, m.p. 210-225°. This material was then recrystallized four times from ethyl acetate to afford 0.76 g. (10.4%) of large colorless crystals, m.p. 234-236°. The infrared spectrum of the compound as a carbon disulfide solution had characteristic absorption bands at 3.3, 9.0, 13.3 and 13.6 μ, indicative of aromatic C-H, the silicon-phenyl linkage, ortho-disubstituted benzene, and monosubstituted benzene, respectively.

Anal. Calcd. for $C_{36}H_{28}Si_2$: C, 83.67; H, 5.46; Si, 10.87; mol. wt., 517. Found: C, 84.05, 84.09; H, 5.57, 5.52; Si, 10.90, 10.88; mol. wt., 508, 487.

The compound volatilized at 540° with slight decomposition.

From o-phenylenedilithium and o-phenylenebis(diphenylsilane) (attempted) An ethereal solution of o-phenylenedilithium, prepared from 4.15 g. (0.015 mole) of o-phenylenemercury and filtered through a glass wool plug, was added to 4.42 g. (0.01 mole) of o-phenylenebis(diphenylsilane) suspended in 100 ml. of dry toluene. The ether was then removed by distillation and the toluene-suspension heated at reflux for 5 hours. After cooling, the reaction mixture was poured upon crushed ice acidified with sulfuric acid. Ether was added and the organic layer worked up as usual. Subsequently the organic solution was evaporated and the resulting oily material treated with ethyl acetate, depositing 1.3 g. of solid, m.p. 165-200°. After two recrystallizations, there was obtained 0.76 g. (14.7%) of colorless crystals, m.p. 212-215°. The analytical sample melted at 214-216°, and the material was identified as (o-diphenylsilylphenyl)triphenylsilane. The infrared spectrum of the compound showed the characteristic absorption bands for aromatic C-H, Si-H, the silicon-phenyl linkage and ortho-disubstituted benzene.

Anal. Calcd. for $C_{36}H_{30}Si_2$: C, 83.34; H, 5.83; Si, 10.83. Found: C, 83.15, 82.96; H, 5.83, 5.82; Si, 10.72, 10.79.

Concentration of the mother liquor gave a resin-like material which could not be crystallized or otherwise purified.

A repeat reaction employing 0.012 mole of o-phenylenebis-(diphenylsilane) and an ethereal solution containing 0.012 mole of o-phenylenedilithium afforded a 22.9% yield of (o-diphenylsilylphenyl)triphenylsilane, plus a 38% recovery of the o-phenylenebis(diphenylsilane).

5,5,10,10-Tetrabenzyl-5,10-dihydrosilanthrene

A solution of 7.3 g. (0.026 mole) of dibenzyldichlorosilane[54] in 75 ml. of ether, cooled in an ice-bath, was treated with an ether solution containing 0.026 mole of o-phenylenedilithium. The reaction mixture was allowed to warm to room temperature and stirred for 16 hours. Since Color Test I was positive, 30 ml. of toluene was added, the ether removed by distillation, and the resulting suspension heated at reflux for 4 hours. Color Test I was now negative and the reaction mixture was hydrolyzed. After the usual work-up, the reaction products were chromatographed on alumina.

Elution with petroleum ether (b.p. 60-70°) and then with cyclohexane gave only traces of oils. Using a 4:1 mixture of cyclohexane and benzene as the eluant, there was obtained 0.51 g. of colorless solid, m.p. 140-170°. This material was recrystallized three times from a 10:1 mixture of petroleum ether and benzene to give 0.21 g. (2.8%) of colorless crystals, m.p. 174.5-176°. The infrared spectrum of this substance in carbon disulfide showed the characteristic absorption bands for aromatic and aliphatic C-H, and monosubstituted and *ortho*-disubstituted benzene, respectively.

Anal. Calcd. for $C_{40}H_{36}Si_2$: C, 83.86; H, 6.33. Found: C, 83.90, 84.07; H, 6.23, 6.30.

The compound volatilized at 510° with decomposition.

o-Phenylenebis(triphenylsilane)

From *o*-phenylenebis(diphenylsilane) and phenyllithium

An ethereal solution containing 0.015 mole of phenyllithium was added to 2.21 g. (0.005 mole) of *o*-phenylenebis(diphenylsilane) in 100 ml. of ether and the reaction mixture was refluxed for 24 hours. After hydrolysis, ether was added and the colorless precipitate filtered. The organic layer was worked up in the usual manner and then evaporated. This material was combined with the solid which had been previously removed by filtration and chromatographed over alumina.

Using cyclohexane as the eluant, there was obtained a colorless solid melting over the range 190-230°. This material was recrystallized five times from ethyl acetate to give 0.62 g. (23.9%) of impure (o-diphenylsilylphenyl)triphenylsilane, m.p. 205-210°, identified by infrared spectrum. Further elution with cyclohexane gave the desired compound which was recrystallized four times from ethyl acetate to afford 0.91 g. (30.6%) of colorless crystals, m.p. 257.5-259°. The infrared spectrum of the compound contained characteristic absorption bands at 9.1, 13.35 and 13.6μ, indicative of the silicon-phenyl linkage, ortho-disubstituted benzene and monosubstituted benzene, respectively.

Anal. Calcd. for $C_{42}H_{34}Si_2$: C, 84.80; H, 5.76; Si, 9.44. Found: C, 85.15, 85.06; H, 5.69, 5.69; Si, 9.49, 9.42.

From (o-diphenylsilylphenyl)triphenylsilane and phenyllithium A solution of 1.35 g. (0.0026 mole) of (o-diphenylsilylphenyl)triphenylsilane in 50 ml. of dry toluene was treated with 0.01 mole of an ethereal solution of phenyllithium. The ether was removed by distillation and the toluene suspension refluxed for 16 hours. Color Test I was only faintly positive; so, an additional 0.003 mole of phenyllithium was added. After refluxing 8 hours longer, the reaction mixture was hydrolyzed with dilute sulfuric acid. The aqueous layer was separated, extracted with ether, and discarded. Subsequently the organic layer was dried and evaporated, and the residue treated with ethyl acetate to give 1.38 g. of colorless solid, m.p. 240-254°. This was recrystallized twice from ethyl acetate to give 1.12 g. (73.2%) of *o*-phenylenebis(triphenylsilane), m.p. 256-259° (mixed m.p.).

From o-phenylenedilithium and chlorotriphenylsilane (attempted) An ethereal solution containing 0.014 mole of *o*-phenylenedilithium was added to 8.23 g. (0.028 mole) of chlorotriphenylsilane in 100 ml. of ether. After adding 75 ml. of toluene, the ether was distilled, and the toluene solution heated at reflux for 24 hours. Work-up employing the usual chromatographic techniques gave an 11.7% yield of tetraphenylsilane, a 14.1% yield of hexaphenyldisiloxane, and a 21.4% yield of triphenylsilanol, plus a resinous brown material.

Studies in the 10*H*-Dibenzosilin Series

Dimethylphenyl-*o*-tolylsilane

An ethereal solution containing 0.62 mole of *o*-tolyllithium was added to 95 g. (0.58 mole) of dimethylphenylchlorosilane in 100 ml. of ether, and the reaction mixture was refluxed for 24 hours. Color Test I remained positive and hydrolysis was effected with dilute hydrochloric acid.

The organic layer was separated and worked up in the usual manner. The residue was distilled at reduced pressure to give 108.6 g. (86.5%) of colorless liquid, b.p. 121-124° (1.5 mm.), n_D^{20} 1.5680, d_{20}^{20} 0.9938.

Anal. Calcd. for $C_{15}H_{18}Si$: Si, 12.41; MR_D, 74.55. Found: Si, 12.29, 12.44; MR_D, 74.53.

o-Dimethylphenylsilylbenzyl bromide

A mixture of 25 g. (0.11 mole) of dimethylphenyl-o-tolylsilane, 19.6 g. (0.11 mole) of N-bromosuccinimide, and 0.15 g. of benzoyl peroxide in 100 ml. of carbon tetrachloride was heated at slight reflux for 3.5 hours. The reaction mixture was cooled in an ice-bath and the succinimide removed by filtration. The solution was then extracted with 100 ml. of 5% sodium hydroxide and dried with anhydrous calcium sulfate. The carbon tetrachloride was removed by distillation and the residue was distilled twice at reduced pressure to give 23 g. (68.6%) of pale yellow liquid, b.p. 131-135° (0.3 mm.), n_D^{20} 1.5987, d_{20}^{20} 1.2827.

Anal. Calcd. for $C_{15}H_{17}BrSi$: Si, 9.20; MR_D, 82.23. Found: Si, 9.15, 9.19; MR_D, 81.31.

5,5-Dimethyl-10H-dibenzosilin (attempted)

A solution of 4.5 g. (0.017 mole) of stannic chloride and 10 ml. of carbon disulfide was added to 7.92 g. (0.026

mole) of o-dimethylphenylsilylbenzyl bromide in 40 ml. of carbon disulfide. The reaction mixture was stirred at room temperature for 16 hours and then at reflux for 2 hours. Hydrolysis was effected by pouring upon crushed ice. The organic layer was worked up in the usual manner and the resulting material distilled at reduced pressure to give 6.6 g. (83%) of recovered bromide, b.p. 134-136° (0.5 mm.), n_D^{20} 1.5940. None of the desired compound could be isolated.

A solution of 8.12 g. (0.027 mole) of o-dimethylphenylsilylbenzyl bromide in 20 ml. of carbon disulfide was added dropwise to 1.7 g. (0.013 mole) of aluminum chloride in 30 ml. of carbon disulfide, while cooling in an ice-bath. The reaction mixture was stirred for 1 hour and then poured upon crushed ice. The reaction products were worked up in the usual manner, but only black tar-like materials were obtained.

o-Dimethylphenylsilylbenzal bromide

A mixture of 22.6 g. (0.1 mole) of dimethylphenyl-o-tolylsilane, 37.4 g. (0.21 mole) of N-bromosuccinimide, and 0.2 g. of benzoyl peroxide in 100 ml. of carbon tetrachloride was heated at reflux for 12 hours. An additional 0.2 g. of benzoyl peroxide was added and refluxing was continued for 30 hours. After cooling in an ice-bath, the reaction mixture was filtered, washed with 5% sodium hydroxide, and dried with anhydrous calcium sulfate. The carbon tetrachloride was distilled and the residue distilled at reduced pressure to give 28.3 g. (73.6%) of pale yellow liquid, b.p. 141-145° (0.01 mm.), n_D^{18} 1.6101.

Anal. Calcd. for $C_{15}H_{16}Br_2Si$: Si, 7.31. Found: Si, 7.34, 7.23.

In a repeat run, the benzal bromide was prepared in 82.5% yield.

o-Dimethylphenylsilylbenzaldehyde

A solution of 25.5 g. (0.15 mole) of silver nitrate in 75 ml. of water was added over a period of 15 minutes to a refluxing solution of 24.8 g. (0.065 mole) of o-dimethylphenylsilylbenzal bromide in 300 ml. of ethylene glycol monomethyl ether, and the reaction mixture was refluxed for 2 hours. After cooling, the precipitated silver bromide was filtered and the solvent removed with the aid of a water aspirator. The resulting material was distilled twice at reduced pressure to give 10.7 g. (69%) of pale yellow liquid, b.p. 131-133° (0.8 mm.), n_D^{20} 1.5865, d_{20}^{20} 1.0713.

Anal. Calcd. for $C_{15}H_{16}OSi$: Si, 11.69; MR_D, 74.55. Found: Si, 11.40, 11.56; MR_D, 75.34.

In another preparation, the benzal bromide was hydrolyzed without isolation. The crude benzal bromide, obtained as described above from 45.2 g. of dimethylphenyl-o-tolylsilane and 75 g. of N-bromosuccinimide, was dissolved in 400 ml. of ethylene glycol monomethyl ether. This solution was heated to reflux and treated with 73 g. (0.43 mole) of silver nitrate in 150 ml. of water. The reaction mixture was refluxed for 2 hours and then poured upon crushed ice. The aqueous solution was extracted with approximately 400 ml. of petroleum ether (b.p. 60-70°) and discarded. After drying and evaporating the petroleum ether solution, the residue was distilled at reduced pressure to give 25.1 g. (52.3%) of o-dimethylphenylsilylbenzaldehyde, b.p. 128-132° (0.8 mm.).

Another run starting with 62 g. of dimethylphenyl-o-tolylsilane gave a 64.3% yield of the aldehyde.

o-Dimethylphenylsilylbenzoic acid

From dimethylphenyl-o-tolylsilane A mixture of 400 ml. of glacial acetic acid, 120 ml. of acetic anhydride, 12 ml. of concentrated sulfuric acid, and 10 g. (0.044 mole) of dimethylphenyl-o-tolylsilane was cooled to 17°. This solution was treated with 44 g. (0.44 mole) of chromium trioxide in three approximately equal portions over a period of 10 minutes. After the addition of the first portion, the temperature of the reaction mixture rose to 22°, but was quickly lowered by cooling in an ice-bath. The reaction mixture was stirred for 10 minutes at 17° and then hydrolyzed by pouring upon crushed ice. The aqueous solution was extracted with ca. 500 ml. of petroleum ether (b.p. 60-70°) and discarded. The petroleum ether was dried with anhydrous sodium sulfate and evaporated. The resulting material was recrystallized twice from petroleum ether to give 1.41 g. (12.5%) of colorless crystals, m.p. 128-130°. The analytical sample melted at 129-131°.

Anal. Calcd. for $C_{15}H_{16}O_2Si$: C, 70.27; H, 6.29; Si, 10.96. Found: C, 70.44, 70.61; H, 6.22, 6.23; Si, 10.69, 11.02.

In another run, 20 g. of dimethylphenyl-o-tolylsilane was oxidized to give the benzoic acid derivative in only 8.7% yield.

From o-dimethylphenylsilylbenzaldehyde   A solution of 4.8 g. (0.02 mole) of o-dimethylphenylsilylbenzaldehyde in 50 ml. of acetone, cooled in an ice-bath, was treated with 3.2 g. (0.02 mole) of potassium permanganate. The reaction mixture was stirred for 1 hour at room temperature. Hydrolysis was effected by pouring upon crushed ice containing sulfuric acid and sodium oxalate. After warming to room temperature, the resulting solid was filtered and recrystallized twice from petroleum ether (b.p. 60-70°) to give 3.46 g. (67.7%) of o-dimethylphenylsilylbenzoic acid, m.p. 128-130°, which was identified by mixed melting point.

An analogous run employing 22 g. of o-dimethylphenylsilylbenzaldehyde gave the acid in 77.8% yield.

5,5-Dimethyl-10*H*-dibenzosilin-10-one (attempted)

Four attempts to cyclize *o*-dimethylphenylsilylbenzoic acid were made using a variety of reagents. Treatment with cold concentrated sulfuric acid for 10 minutes gave only traces of unidentifiable acidic materials. Reaction with polyphosphoric acid at 120° was similarly unsuccessful.

The third and fourth attempts to prepare the cyclic ketone involved prior formation of the acid chloride by treatment with thionyl chloride. The acid chloride was then reacted with stannic chloride in carbon disulfide. Work-up gave a resin-like material which contained a large siloxane absorption band in the infrared spectrum. The acid chloride was also treated with aluminum chloride in nitrobenzene according to the procedure of Wittenberg *et al.*,[37] but again none of the desired compound could be isolated.

DISCUSSION

Tetrasubstituted Organosilanes Containing Aralkyl Groups

The need for high temperature lubricants and related fluids has provided the impetus for many of the studies in organosilicon chemistry. Some of the early work has shown that thermally stable organosilicon monomers can be prepared; but for the most part, the compounds possess relatively high melting points and are therefore unsuitable for these applications. Studies from This Laboratory have dealt with the evaluation or qualitative comparison of organic groups to impart both thermal resistance and a low melting point to various organosilicon derivatives.[2,74,75]

From the standpoint of thermal stability, the most promising groups to incorporate into organosilicon compounds appear to be the aryl and benzyl types.[74,75] Miles[75] observed that the introduction of long-chained _n_-alkyl or aralkyl groups seems to be very effective in lowering the melting points. The _n_-alkyl-containing compounds, however, are more

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[74] J. J. Goodman. Some correlations between structure and thermal stability of organosilicon compounds. Unpublished Ph. D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1955.

[75] D. H. Miles. Low-melting organosilicon monomers of high molecular weight. Unpublished Ph. D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1957.

prone to undergo decomposition at elevated temperatures than aryl or certain aralkyl substituted organosilicon compounds.

Polyphenyl groups, such as the p-terphenyl-4-yl group,[76] attached to silicon show excellent thermal properties, but, in general, the compounds inherently possess a high melting point. In this study, several new organosilicon compounds were synthesized containing aralkyl groups in combinations with the p-terphenyl-4-yl group and with biphenylyl groups. These were prepared in order to obtain high molecular weight, low melting, materials suitable for lubricant applications.

The route to the p-terphenyl compounds involved coupling of p-terphenyl-4-yllithium with the appropriate aralkyl silicon derivatives. Of these, the benzyl and dibenzyl compounds were obtained from the corresponding chlorosilanes; while, the triaralkyl compounds were obtained from tribenzylsilane, tris(beta-phenylethyl)silane and tris(gamma-phenylpropyl)silane, respectively. The biphenylyl compounds were similarly prepared by coupling dibenzyldichlorosilane with the various biphenylyllithium reagents.

The effect of the aralkyl groups on lowering the melting points can readily be noted. For example, p-terphenyl-4-yltriphenylsilane is reported to melt at 216-217°;[76] whereas,

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[76] B. J. Gaj and H. Gilman, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the preparation of p-terphenyl-4-yl silicon compounds. Private communication. 1960.

tribenzyl-p-terphenyl-4-ylsilane melts at 125-127°, and the corresponding tris(gamma-phenylpropyl) derivative is a viscous liquid.

The thermal stabilities for the various compounds prepared in this investigation are recorded in Table 1. These data were obtained in the following manner. A small amount of the compound was inserted into a melting point capillary and subsequently heated in a copper block by means of a Bunsen

Table 1. Thermal stabilities

Compound	M.p., °C	Thermal stability, °C
Benzyltris(p-terphenyl-4-yl)silane	131-133	vol. 525 (light brown distillate)
Dibenzylbis(p-terphenyl-4-yl)silane	197-199	vol. 530-535 (dec.)
Tribenzyl-p-terphenyl-4-ylsilane	125-127	vol. 510-520 (yellow distillate)
Tris(beta-phenylethyl)-p-terphenyl-4-ylsilane	77-80	vol. 440-450 (dec.)
Tris(gamma-phenylpropyl)-p-terphenyl-4-ylsilane	315-317 (0.001)[a]	vol. 435-440 (dec.)
Dibenzylbis(2-biphenylyl)-silane	222-227 (0.001)[a]	vol. 500-505
Dibenzylbis(3-biphenylyl)-silane	265-269 (0.003)[a]	vol. 510-515 (light brown distillate)
Dibenzylbis(4-biphenylyl)-silane	106-108	vol. 510 (pale yellow distillate)
Tribenzyl-p-(trimethylsilylphenyl)silane	200-202 (0.005)[a]	vol. 436-440

[a] B.p., °C (mm.).

burner. A thermometer capable of temperatures to 640° was used. The volatilization point or range was that temperature at which either the compound refluxed freely at the top of the tube or completely disappeared from the bottom.

Recent evidence[75] suggests that the volatilization points of certain organosilicon compounds may actually be decomposition points where the compounds undergo thermal elimination reactions such as that depicted. Therefore, compounds containing

$$RCH_2CH_2SiR'_3 \longrightarrow RCH{=}CH_2 + R'_3SiH$$

beta-phenylethyl and gamma-phenylpropyl groups might exhibit such an elimination, in contrast to benzyl and aryl types. The volatilization points of tris(beta-phenylethyl)-p-terphenyl-4-ylsilane (440-450° dec.) and of tris(gamma-phenylpropyl)-p-terphenyl-4-ylsilane (435-440° dec.) as compared to that of tribenzyl-p-terphenyl-4-ylsilane (510-520°) seem to bear this out. The remainder of the compounds showed good thermal properties volatilizing above 500°, with the exception of tribenzyl-p-(trimethylsilylphenyl)silane which volatilized without decomposition at 436-440°. The two most promising compounds are dibenzylbis(2-biphenylyl)silane and dibenzylbis(3-biphenylyl)silane, both of which are liquids and volatilize at 500-505° and 510-515°, respectively.

Reactions of Some 2-Triphenylsilylethyl Derivatives

Silicon-containing Grignard and organolithium reagents are as synthetically versatile as their organic counterparts, and they are frequently employed to prepare polysilicon-containing compounds and carbon-functional silicon derivatives.[77] Generally, these organometallic reagents are obtained straightforwardly from the reactions of silicon-containing organic halides with magnesium or lithium. Only in the reactions of the 2-haloalkyl silicon compounds is anything unusual encountered.

2-Haloalkyl silicon compounds are unique in that silicon-carbon cleavage occurs in many reactions with the formation of olefinic products. For example, ethylene is evolved in high yield from 2-chloroethyltrichlorosilane upon treatment with dilute alkali.[78] Similarly, methylmagnesium bromide reacts with 2-chloroethyltrichlorosilane[78] and with 2-chloroethyltriethylsilane[79] to give large amounts of ethylene together with tetramethylsilane and methyltriethylsilane, respectively.

Organometallic derivatives derived from 2-haloalkyl

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[77] P. D. George, M. Prober, and J. R. Elliott, Chem. Rev., 56, 1065 (1956).

[78] L. H. Sommer, G. M. Goldberg, E. Dorfman, and F. C. Whitmore, J. Am. Chem. Soc., 68, 1083 (1946).

[79] L. H. Sommer, D. L. Bailey, and F. C. Whitmore, ibid., 70, 2869 (1948).

silicon compounds are unknown. Petrov and Mironov[80] reported the reaction of 2-bromopropyltrimethylsilane with magnesium in ether at 10-15°. Acid hydrolysis gave a small amount of *n*-propyltrimethylsilane, indicating the possible formation of a limited quantity of the Grignard reagent, together with the coupling product and much hexamethyldisiloxane. On the other hand, several reagents are known containing alkali metals. However, these were not formed directly from the 2-haloalkyl silicon compounds, but from the addition of silylmetallic compounds to aryl-containing olefins.[81]

Recently, Gilman *et al.*[82] reported the reaction of triphenylsilyllithium with ethylene oxide to give 2-triphenylsilylethanol. Treatment of this alcohol with thionyl chloride, phosphorus tribromide and *p*-toluenesulfonyl chloride in pyridine has given the respective 2-triphenylsilylethyl derivative in good yields. In light of the reactions of 2-haloalkyl silicon compounds considered previously, it was therefore of interest to investigate certain reactions of these ethyl derivatives.

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[80] A. D. Petrov and V. F. Mironov, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 635 (1952) [Original available but not translated; abstracted in *C. A.*, *47*, 10471 (1953)].

[81] D. Wittenberg and H. Gilman, *Quart. Rev.*, *13*, 116 (1959).

[82] H. Gilman, D. Aoki, and D. Wittenberg, *J. Am. Chem. Soc.*, *81*, 1107 (1959).

The reaction of 2-chloroethyltriphenylsilane with ethanolic potassium hydroxide gave a good yield of the carbon-silicon cleavage product, triphenylsilanol. Similar cleavages by caustic have been previously demonstrated.[77,78]

Treatment of 2-chloroethyltriphenylsilane with magnesium in tetrahydrofuran gave 2-triphenylsilylethylmagnesium chloride, which apparently is the first preparation of such a Grignard reagent. The structure and presence of the Grignard reagent were confirmed by carbonation which afforded the known 2-triphenylsilylpropionic acid.[37] When the reaction was allowed to proceed for 2.5 hours, a 66% yield of acid was obtained. Work-up of the organic layer gave a 13.4% yield of the coupling product, tetramethylenebis(triphenylsilane), and a 13.2% yield of ethyltriphenylsilane.

In another run, the reaction mixture was refluxed for 20 hours before carbonation; however, the yield of 3-triphenylsilylpropionic acid was only 28.9%.

2-Bromoethyltriphenylsilane was similarly found to react with magnesium in tetrahydrofuran to afford the Grignard reagent. In two runs, the yields of acid subsequent to carbonation were 25.1% and 26.7%, respectively.

Whereas 2-chloroethyltriphenylsilane could not be induced to react with lithium in diethyl ether, the 2-bromoethyl compound reacted upon treatment with a small amount of methyl iodide. However, the organolithium compound was not obtained, and only tetramethylenebis(triphenylsilane) (40.7%) and ethyltriphenylsilane (16.4%) were isolated.

As previously described, extensive silicon-carbon cleavage of 2-chloroalkyl silicon compounds occurs upon treatment with Grignard[77,78,79] or organolithium[77] reagents. A similar cleavage was anticipated in these reactions. For example, in the formation of 2-triphenylsilylethylmagnesium chloride from the 2-chloroethyl compound, the Grignard reagent was expected to cleave the unreacted starting material to give ethylenebis(triphenylsilane). However, none of this compound was obtained in these reactions. In connection with possible cleavage, it was therefore of interest to investigate the interactions of the compounds with triphenylsilyllithium.

In these reactions with triphenylsilyllithium, three different modes of interaction have been observed: direct coupling; cleavage of the silicon-carbon bond; and halogen-metal interconversion. 2-Triphenylsilylethyl p-toluenesulfonate gave hexaphenyldisilane and ethylenebis(triphenylsilane) indicating both coupling and cleavage. 2-Chloroethyltriphenylsilane was found to react similarly. The isolation of tetramethylenebis(triphenylsilane) from the reaction of the 2-bromoethyl compound with the silylmetallic appears to suggest that some interaction involving halogen-metal interconversion had occurred. The 2-lithio compound is formed as an intermediate which could then couple with unreacted bromide to give the tetramethylene derivative. The possibility of this intermediate cleaving the bromide to give ethylenebis-(triphenylsilane) also can not be excluded.

The difference in the behavior of primary alkyl chlorides and bromides toward triphenylsilyllithium was previously noted by Gilman and Aoki.[83] The chlorides were found to give the silicon-alkyl coupling products; whereas, hexaphenyldisilane was obtained as the main product from alkyl bromides. The formation of the disilane is due, at least in part, to a halogen-metal interconversion reaction.[83]

Studies in the 5,10-Dihydrophenazasiline Series

5,10-Dihydrophenazasiline derivatives were first prepared by the extended heating of diphenylsilane with phenothiazine compounds. This preparative procedure suffers from the disadvantages of tedious work-ups, very low yields, and a lack of flexibility. Inasmuch as 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline promises to be of significant value as an antioxidant in certain lubricant formulations, it was therefore desirous to develop better methods of synthesis for this and other 5,10-dihydrophenazasiline derivatives.

Aromatic cyclic organosilicon compounds have been prepared, for the most part, by cyclization reactions involving

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[83] H. Gilman and D. Aoki, J. Org. Chem., 24, 426 (1959).

aryl-dilithium derivatives and appropriately substituted silicon halides. 5,5-Diphenyldibenzosilole, for example, was obtained by treating dichlorodiphenylsilane with 2,2'-dilithiobiphenyl.[27,28] Compounds in the phenoxasilin series were similarly prepared by procedures employing 2,2'-dilithiodiaryl ether intermediates.[30,31,32] Accordingly, preparative methods have been developed to synthesize 5,10-dihydrophenazasiline types through the utilization of N-substituted 2,2'-dilithiodiarylamine intermediates.

A search of the literature for suitable starting materials revealed that only one compound, 2,2'-dibromodiphenylamine, had been prepared. The difficulties encountered by Jones and Mann[61] in the synthesis of this compound may, at least in part, explain why more of these amine derivatives are not known. Attempts to prepare the 2,2'-dibromo compound or a precursor by (a) heating _o_-bromoaniline and its hydrochloride at 235-240°, (b) heating _o_-bromophenol with _o_-bromoaniline and zinc chloride at 250°, (c) heating _o_-chloronitrobenzene and _o_-bromoaniline with potassium carbonate and copper-bronze at 170°, and (d) boiling a mixture of _o_-chloronitrobenzene and _o_-bromo-N-sodioacetanilide in xylene all resulted in failure. 2,2'-Dibromodiphenylamine was ultimately prepared, however, by using the Chapman rearrangement.[84]

In the synthesis of this amine,[61] _o_-bromobenzanilide

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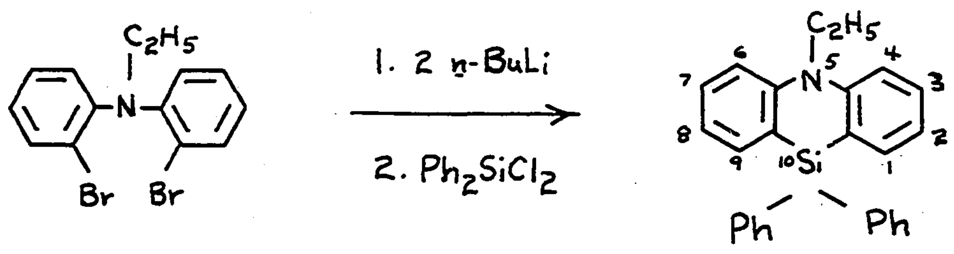
[84] A. W. Chapman, _J_. _Chem_. _Soc_., 1743 (1927); 569 (1929).

was converted by phosphorus pentachloride into N-o-bromophenylbenzimidoyl chloride, which gave o-bromophenyl N-o-bromophenylbenzimidoate upon treatment with sodium o-bromophenoxide. The ester, when suitably heated, rearranged to N-benzoyl-2,2'-dibromodiphenylamine, which on alkaline hydrolysis gave 2,2'-dibromodiphenylamine.

In repeating the above series of reactions, two differences were noted. From the reaction of N-o-bromophenylbenzimidoyl chloride with sodium o-bromophenoxide, Jones and Mann[61] obtained a 48% yield of o-bromophenyl N-o-bromophenylbenzimidoate. The preparation of this compound was conducted three times affording significantly improved yields of 86.9, 81.3, and 85%, respectively. On the other hand, when the ester was rearranged in accordance with the published procedure,[61] that is heating from 155° to 260° for 2.5 hours, very low yields of N-benzoyl-2,2'-dibromodiphenylamine were obtained. However, heating from 250° to 265° for 2.5 hours gave satisfactory yields of this material.

Attempts by Jones and Mann[61] to prepare N-alkyl derivatives of 2,2'-dibromodiphenylamine were unsuccessful. To facilitate N-alkylation, the amine was converted to the N-lithio derivative by treatment with methyllithium and subsequently reacted with an ethereal solution of diethyl sulfate. However, the amine was recovered unaffected, as it also was from a similar reaction employing prior metalation with ethylmagnesium bromide. When the N-lithio derivative was reacted with diethyl sulfate in refluxing tetrahydrofuran (THF), the N-ethyl derivative was obtained in an excellent yield. An analogous reaction employing a toluene-ether solution heated to 65°, the reflux temperature of tetrahydrofuran, afforded only partial ethylation, thus indicating the importance of the tetrahydrofuran.

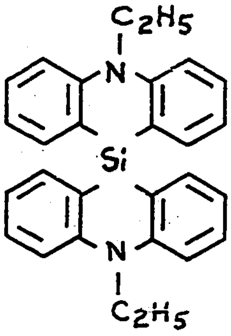
Jones and Mann[61] had previously shown that treatment of 2,2'-dibromodiphenylamine with n-butyllithium at 0° and subsequent carbonation gave an 85% yield of 2,2'-dicarboxydiphenylamine. N-Ethyl-2,2'-dibromodiphenylamine was treated with two equivalents of n-butyllithium in a similar manner, and then with an equal molar quantity of dichlorodiphenylsilane to give a 49.3% yield of 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline (XVII). This compound was shown to be identical with the material obtained from heating 10-ethylphenothiazine and diphenylsilane.[1] It is interesting to compare the work-up simplicity of this cyclization reaction which



XVII

involved only recrystallizations, with that for the sulfur replacement reaction which required distillation, chromatography, and recrystallizations.[1] Another significant advantage of this method can be readily seen from the yields, 49.3% *versus* a maximum of 7.2%.[1]

Thus, with a good method available for obtaining 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline (XVII), procedures for the synthesis of other 5,10-dihydrophenazasiline derivatives were investigated and broadened to include both functional and many nonfunctional types. When dibenzyldichlorosilane and dichloromethylphenylsilane were treated with N-ethyl-2,2'-dilithiodiphenylamine, good yields of 5-ethyl-10,10-dibenzyl- and 5-ethyl-10-methyl-10-phenyl-5,10-dihydrophenazasiline were obtained. Likewise, treatment of silicon tetrachloride with two molar equivalents of the dilithium compound gave a fair yield of 5,5'-diethyl-10,10'-spirobi-(5,10-dihydrophenazasiline) (XVIII).



XVIII

The synthesis of unsymmetrical 5,10-dihydrophenazasiline compounds containing different organic groups attached to silicon is complicated by the inaccessibility of unsymmetrical diorganosilicon halides. Therefore, it was of interest to prepare phenazasiline types having a functional group which could be subsequently reacted with various organolithium reagents. This approach has previously been exploited quite successfully in the synthesis of unsymmetrical dibenzosilole derivatives.[28]

The difficulties encountered in the handling and storing of silicon halides prompted the investigation of organosilicon hydrides[85] in this cyclization reaction with the aim of preparing silicon-hydride functional compounds. In an orienting experiment to determine the course of the reaction, N-ethyl-2,2'-dilithiodiphenylamine was reacted with diphenylsilane. 5-Ethyl-10,10-diphenyl-5,10-dihydrophenazasiline (XVII) was produced in a 36% yield. Accordingly, phenylsilane was treated with the dilithium compound to give a 79.9% yield of the silicon-hydride functional compound, 5-ethyl-10-phenyl-5,10-dihydrophenazasiline. This compound, upon treatment with an ethereal solution of phenyllithium, gave the known derivative XVII, thereby substantiating the proposed struc-

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[85] For reactions of organosilicon hydrides with organometallic compounds, see H. Gilman and E. A. Zuech, J. Am. Chem. Soc., 81, 5925 (1959).

ture. In similar fashion, the compound was reacted with various organolithium reagents to give the unsymmetrically substituted materials in good to excellent yields.

Another functional phenazasiline type, 5-ethyl-10-n-hexadecyl-5,10-dihydrophenazasiline, was prepared by reacting N-ethyl-2,2'-dilithiodiphenylamine with n-hexadecylsilane. Treatment of this substance with organolithium reagents afforded the unsymmetrical derivatives, as described above.

The synthesis of 5-methyl- and 5-phenyl- substituted derivatives of 5,10-dihydrophenazasiline has been accomplished by starting with the corresponding N-methyl and N-phenyl compounds of 2,2'-dibromodiphenylamine.

N-Methyl-2,2'-dibromodiphenylamine was prepared by reacting 2,2'-dibromodiphenylamine with methyllithium and then with a refluxing tetrahydrofuran solution of dimethyl sulfate. Reaction of this compound with n-butyllithium and subsequent treatment with dichlorodiphenylsilane gave the known compound, 5-methyl-10,10-diphenyl-5,10-dihydrophenazasiline.[1] In like manner, the 5-methyl-10,10-dibenzyl-5,10-dihydrophenazasiline and 5,5'-dimethyl-10,10'-spirobi-(5,10-dihydrophenazasiline) derivatives were prepared.

The N-phenyl compound, 2,2'-dibromotriphenylamine, was obtained by heating a mixture of 2,2'-dibromodiphenylamine, iodobenzene, anhydrous potassium carbonate, and copper-bronze. The dilithium compound was then formed by halogen-metal interconversion and reacted with silicon tetrachloride and with dichlorodiphenylsilane to give the respective 5,10-dihydrophenazasiline compounds.

In continuation of this investigation into the synthesis of substituted 5,10-dihydrophenazasiline derivatives, compounds were then prepared containing nuclear substituents in the 2-position. In order to obtain these materials, it was first necessary to synthesize the appropriately substituted diphenylamine intermediates. Here again, the very versatile Chapman rearrangement[84] was utilized. 2-Bromophenylbenzimidoyl chloride was prepared according to the procedure of Jones and Mann,[61] and reacted with the sodium salts of 2-bromo-4-chlorophenol and of 2-bromo-4-phenylphenol. The resulting benzimidoate esters were subsequently thermally rearranged and hydrolyzed to give 2,2'-dibromo-4-chlorodiphenylamine and 2,2'-dibromo-4-phenyldiphenylamine, respectively. The method, previously used to prepare N-ethyl-2,2'-dibromodiphenylamine, was then employed to convert these amines to the corresponding N-ethyl derivatives.

By the usual cyclization techniques, these amines afforded the 2-substituted 5,10-dihydrophenazasiline compounds. 2-Chloro-5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline, for example, was prepared by treating N-ethyl-2,2'-dibromo-4-chlorodiphenylamine with n-butyllithium and then with dichlorodiphenylsilane.

Direct bromination of some aromatic silicon compounds can be accomplished, but in many cases rapid cleavage of carbon-silicon bonds occurs. Treatment of tetraphenylsilane with bromine gives bromobenzene, bromotriphenylsilane, and dibromodiphenylsilane. Similarly,[86] trimethylphenylsilane undergoes cleavage to afford good yields of bromobenzene and bromotrimethylsilane.[87] On the other hand, trichlorophenylsilane may be brominated in the presence of iron to give good yields of the 4-bromo and 2,4-dibromo compounds.[88]

5-Ethyl-10,10-diphenyl-5,10-dihydrophenazasiline (XVII) has been allowed to react with bromine under several different conditions. The addition of bromine to a carbon disulfide solution of the phenazasiline compound, cooled to -20°, gave a 21% yield of 5-ethyl-2,8-dibromo-10,10-diphenyl-5,10-dihydrophenazasiline (XIX). There were also isolated small amounts of cleavage products, N-ethyl-2,2',4,4'-tetrabromodiphenylamine (XX) and a silanol-containing compound tentatively identified as 2-(N-ethyl-2,4-dibromoanilino)-5-bromophenyldiphenylsilanol (XXI), in addition to a 26.8% recovery

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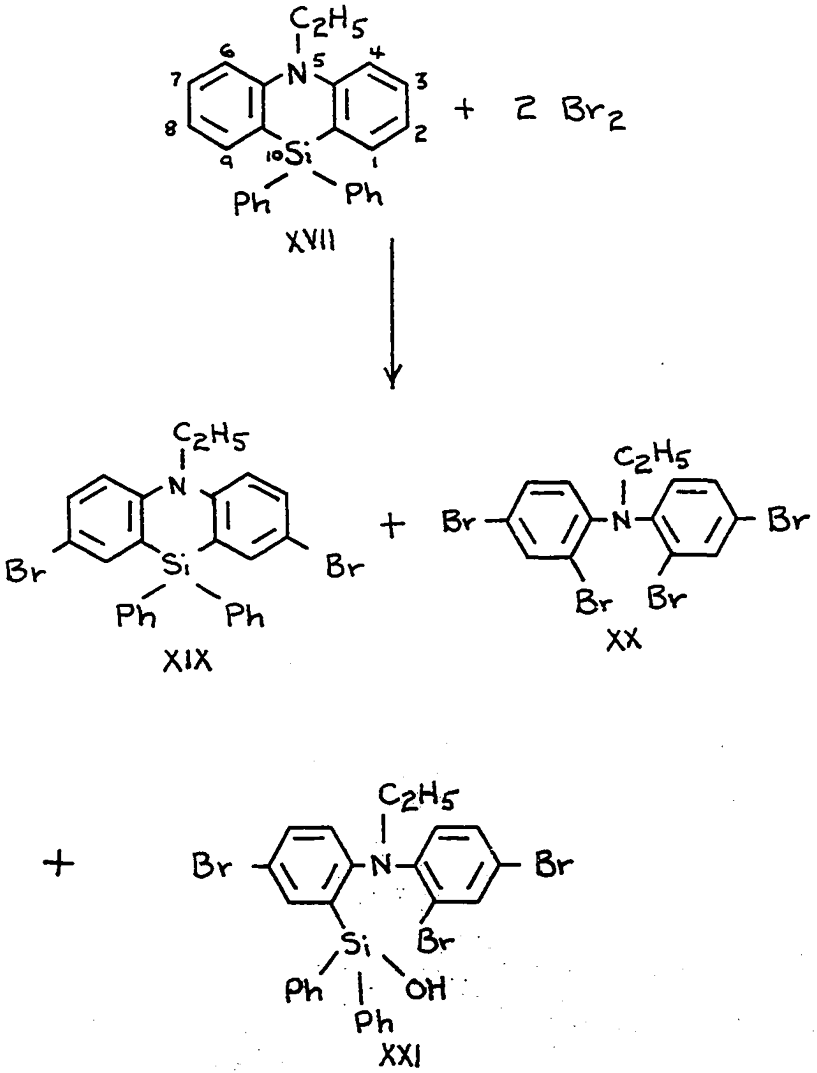
[86] A. Landenburg, Ber., 40, 2274 (1907).

[87] B. O. Pray, L. H. Sommer, G. M. Goldberg, G. T. Kerr, P. D. George, and F. C. Whitmore, J. Am. Chem. Soc., 70, 433 (1948).

[88] A. Y. Yakubovich and G. V. Motsarev, Zhur. Obshchei Khim., 23, 412 (1953) [Original available but not translated; abstracted in C. A., 48, 3286 (1954)].

of starting compound XVII. A slightly improved yield (24.7%) of the 2,8-dibromo phenazasiline compound XIX was obtained, when the reaction mixture was allowed to warm to room temperature, but only 10.6% of the phenazasiline compound XVII was recovered.



When bromine was added to a cold glacial acetic acid solution of the phenazasiline compound, only small amounts of N-ethyl-2,2',4,4'-tetrabromodiphenylamine (XX) and 5-ethyl-2,8-dibromo-10,10-diphenyl-5,10-dihydrophenazasiline (XIX) were isolated. There was also obtained a large amount of a colorless viscous oil which could not be characterized. The infrared spectrum contained large absorption bands indicative of silanols and disiloxanes.

A reaction with excess bromine in refluxing glacial acetic acid gave only silicon-free cleavage products, N-ethyl-2,2',4,4'-tetrabromodiphenylamine (XX) (22.1%) and 2,2',4,4'-tetrabromodiphenylamine (31.2%).

Since acids, such as hydrobromic acid, are known to effect cleavage of silicon-aryl bonds,[89] a reaction between 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline (XVII) and bromine in glacial acetic acid was conducted in the presence of sodium acetate, in an effort to neutralize the hydrogen bromide as it was formed. Work-up gave a 10% yield of the tetrabromo compound XX, a 4.2% yield of the 2,8-dibromo compound XIX, and a 33.4% yield of the silanol XXI. It should be noted that a 21.4% recovery of starting phenazasiline compound XVII was also isolated. None of this material had been recovered in the previous reactions in glacial acetic acid.

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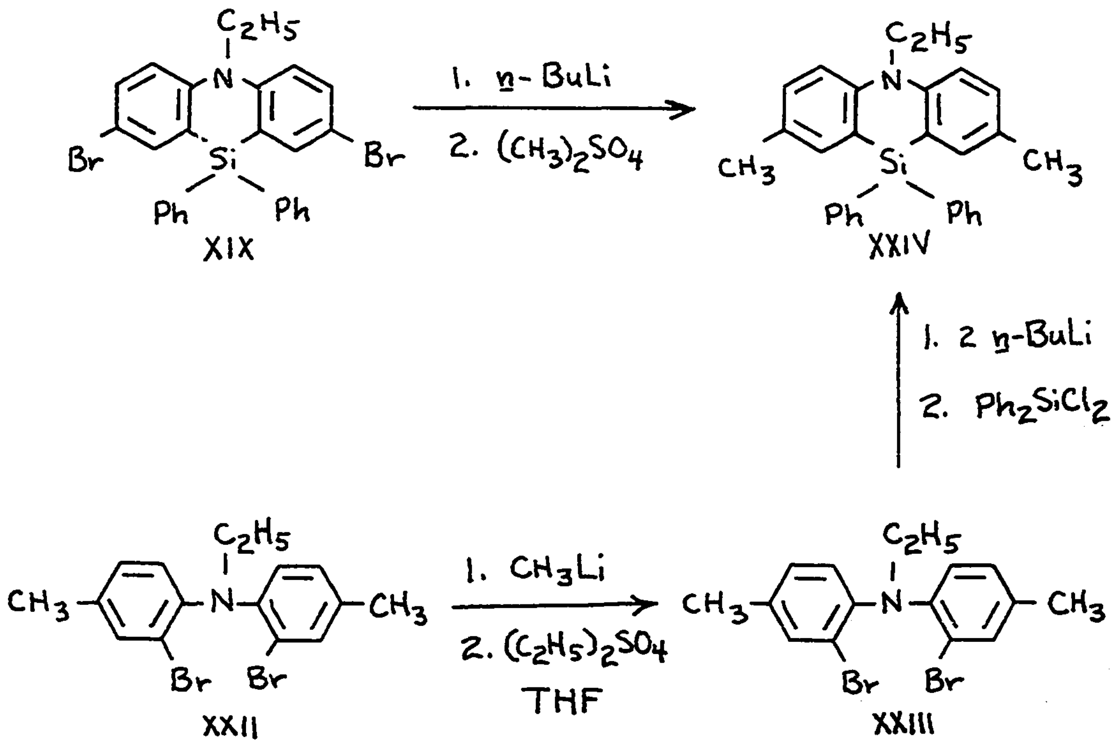
[89] C. Eaborn, *J. Chem. Soc.*, 4859 (1956); F. B. Deans and C. Eaborn, *ibid.*, 2299 (1959).

Thus, it appears that the hydrogen bromide is responsible, in part, for the cleavage of the silicon heterocycle.

The structure of N-ethyl-2,2',4,4'-tetrabromodiphenylamine (XX) was verified by independent synthesis from 2,2',4,4'-tetrabromodiphenylamine using the N-alkylation procedure utilized so successfully on 2,2'-dibromodiphenylamine. The tentative structure assigned to the cleavage product, 2-(N-ethyl-2,4-dibromoanilino)-5-bromophenyldiphenylsilanol (XXI), was based on analytical data, on infrared spectra, and on the fact that treatment with bromine afforded a good yield of N-ethyl-2,2',4,4'-tetrabromodiphenylamine (XX).

To overcome the limited accessibility of 2,2'-dibromodiphenylamine, an investigation of the direct bromination of certain diarylamines was undertaken. Fortunately, one of these dibrominated compounds, namely, 2,2'-dibromodi-p-tolylamine and 5-ethyl-2,8-dibromo-10,10-diphenyl-5,10-dihydrophenazasiline (XIX) could be interrelated by a series of reactions, thus serving to substantiate the structures for the various compounds.

Treatment of di-p-tolylamine in glacial acetic acid with two molar equivalents of bromine gave a 63.5% yield of 2,2'-dibromodi-p-tolylamine (XXII). Compound XXII was then converted to the N-lithio intermediate upon interaction with methyllithium and subsequently reacted with a refluxing tetrahydrofuran solution of diethyl sulfate to give a 78.6% yield of N-ethyl-2,2'-dibromodi-p-tolylamine (XXIII).



The N-ethyl compound XXIII was transformed into the dilithium derivative by halogen-metal interconversion with n-butyllithium and then reacted with dichlorodiphenylsilane to give a good yield of 5-ethyl-2,8-dimethyl-10,10-diphenyl-5,10-dihydrophenazasiline (XXIV). This phenazasiline compound XXIV was also obtained from the 2,8-dibromo compound XIX by treatment first with n-butyllithium and then with dimethyl sulfate.

The general applicability and versatility of the cyclization reaction involving N-alkyl-2,2'-dilithiodiarylamine derivatives for the synthesis of 5,10-dihydrophenazasiline compounds have been demonstrated throughout this investigation. However, this procedure suffers in that the 2,2'-dibromodiarylamines are difficult to prepare and that N-alkylation has only been accomplished by reacting the N-lithio intermediate with a refluxing tetrahydrofuran solution of alkyl sulfate. The previously mentioned preparation of 2,2'-dibromodi-p-tolylamine is a step in the direction of developing simplified procedures for their preparation, which was culminated in the bromination of N-methyldi-p-tolylamine.

A glacial acetic acid solution of N-methyldi-p-tolylamine was treated with two molar equivalents of bromine to give a 60.8% yield of dibromo compound. Reaction of 2,2'-dibromodi-p-tolylamine with methyllithium and then with dimethyl sulfate in tetrahydrofuran afforded the above dibromo compound, proving that the bromines were in the ortho positions. Subsequently, N-methyl-2,2'-dibromodi-p-tolylamine was converted to the dilithium derivative by halogen-metal interconversion with n-butyllithium and then to 2,5,8-trimethyl-10,10-diphenyl-5,10-dihydrophenazasiline by treatment with dichlorodiphenylsilane. Thus, a phenazasiline derivative has been synthesized quite straightforwardly by simple bromination and cyclization.

In an effort to obtain the dilithium compound without the use of n-butyllithium, an ethereal solution of N-methyl-2,2'-dibromodi-p-tolylamine was allowed to react with lithium metal. Treatment of this dilithium compound with dichlorodiphenylsilane gave the 2,5,8-trimethyl phenazasiline compound but in a lower yield. Therefore, the method involving halogen-metal interconversion is preferred.

When two molar equivalents of N-methyl-2,2'-dilithiodi-p-tolylamine was reacted with silicon tetrachloride, 2,2',-5,5',8,8'-hexamethyl-10,10'-spirobi-(5,10-dihydrophenazasiline) was obtained in good yield. Likewise, treatment of the dilithium compound with dichlorodimethylsilane and with dibenzyldichlorosilane gave the corresponding 5,10-dihydrophenazasiline compounds.

In an attempt to prepare a seven-membered heterocyclic system, N-methyl-2,2'-dilithiodi-p-tolylamine was reacted with sym-tetraphenyldisilane. However, scission of the silicon-silicon bond occurred and the only isolable product was 2,5,8-trimethyl-10,10-diphenyl-5,10-dihydrophenazasiline. Similar cleavages of silicon-silicon bonds by organometallic reagents have been demonstrated previously.[90]

The reaction of N-methyl-2,2'-dilithiodi-p-tolylamine with chlorotriphenylsilane unexpectedly gave nearly equimolar amounts of 2,5,8-trimethyl-10,10-diphenyl-5,10-dihydrophenazasiline and tetraphenylsilane. Thus, it appears that one anion of the dilithium compound first displaces the chlorine; then, the second anion cleaves a silicon-phenyl linkage to give the

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[90] For a discussion of the scission of silicon-silicon bonds, see H. Gilman and G. D. Lichtenwalter, J. Org. Chem., 24, 1588 (1959).

silicon heterocycle and phenyllithium which, in turn, couples with chlorotriphenylsilane to give tetraphenylsilane. Similar cleavage-cyclization reactions have been observed in the dibenzosilole[29] and silacyclopentane[8] systems. It should be noted from the latter study[8] that this abnormal cyclization seems to occur preferably when a five-membered cyclic silane is formed. However, in this case, the six-membered phenazasiline compound was formed in a yield comparable to those from the other investigations.

All of the infrared spectra of the 5,10-dihydrophenazasiline compounds showed a split absorption band of weak to medium intensity in the 9.3 to 9.6 μ region. Derivatives containing substituents in the 5- and 10-positions exhibited a band at 13.1-13.2 μ (*ortho*-disubstitution). The derivatives with additional substituents at the 2-position had bands at 13.1-13.2 and 12.3-12.4 μ (1,2,4-trisubstitution); while, those with additional 2,8-disubstitution had only the band at 12.3-12.4 μ. All of 5-ethyl 5,10-dihydrophenazasiline derivatives showed bands at 7.4, 7.6, 7.85, and 8.2 μ. Similarly, the 5-methyl derivatives showed bands at 7.5, 7.85, and 8.1 μ. Also, the absorption bands characteristic of the respective substituent groups appeared in the spectra of the 5,10-dihydrophenazasiline compounds containing these groups.

o-Phenylene Silicon Derivatives

The synthesis of organometallic and organometalloidal derivatives containing the o-phenylene unit has been extremely arduous in some instances due to the inaccessibility of suitable Grignard and organolithium reagents. Grignard reagents, such as o-bromophenylmagnesium bromide,[91,92] and o-bromophenylmagnesium iodide,[93] have been prepared but do not afford a practicable route for the synthesis of o-phenylene derivatives. Similarly, o-bromophenyllithium[94] has been prepared in low yields by the interaction of o-dibromobenzene and n-butyllithium, but is of limited utility as are the other o-halophenyllithium compounds.

Wittig and Bickelhaupt[71,72] have recently prepared o-phenylenedilithium (XXV) providing a new synthetic route to o-phenylene derivatives. The dilithium compound XXV was obtained by the lithium metal cleavage of o-phenylene-mercury, with the identity being confirmed by carbonation furnishing phthalic acid in 69% yield.

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[91] H. Heaney, F. G. Mann, and I. T. Miller, J. Chem. Soc., 4692 (1956).

[92] G. Wittig and L. Pohmer, Ber., 89, 1334 (1956).

[93] H. Heaney, F. G. Mann, and I. T. Miller, J. Chem. Soc., 3930 (1957).

[94] H. Gilman and R. D. Gorsich, J. Am. Chem. Soc., 78, 2217 (1956).

In the course of our studies o-phenlenedilithium (XXV) has been allowed to react with various organosilicon compounds. Preliminary work in This Laboratory[95] on the reaction of the dilithium compound XXV with chlorosilanes showed the interactions to be complex. Contamination of the ethereal solution of the dilithium compound with finely divided lithium metal produced during the cleavage was thought to be the cause of this. After cleavage of the o-phenylene-mercury, the ethereal solution was filtered through a previously dried glass wool plug to give a red-brown solution containing a gray suspension. Acid titration of an aliquot of this solution always indicated base present in excess of 100%. Consequently, in an attempt to reduce the side reactions, the dilithium compound XXV was reacted with an organosilicon hydride, diphenylsilane.

When o-phenylenedilithium (XXV) was allowed to react with diphenylsilane in an effort to synthesize 5,5,10,10-tetraphenyl-5,10-dihydrosilanthrene (XXVI), only o-phenylene-bis(diphenylsilane) (XXVII) was isolated. A reaction with excess diphenylsilane gave an improved yield of the di-silicon hydride XXVII.

Subsequently, a suspension-free ethereal solution of

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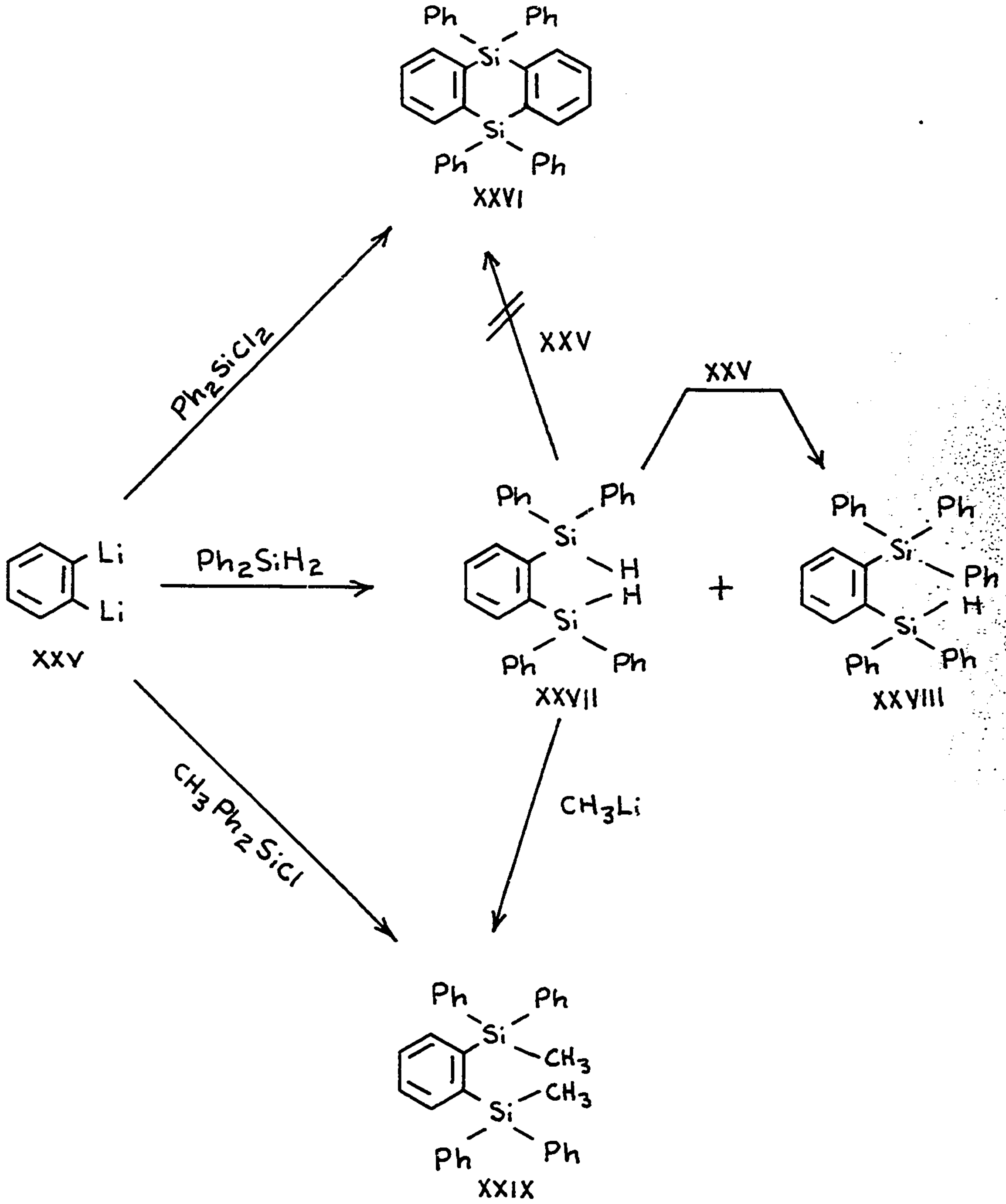
[95] H. Gilman, D. Wittenberg, and M. V. George, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the reactions of o-phenylenedilithium. Private communication. 1959.

o-phenylenedilithium (XXV) was obtained by filtering the cleavage solution through a sintered glass filter. This solution gave acceptable values of base present, upon acid titration of an aliquot, in line with conventional organolithium reagents. When this solution of the dilithium compound XXV was allowed to react with excess diphenylsilane, a good yield of o-phenylenebis(diphenylsilane) (XXVII) was obtained. The reaction of equal molar amounts of the dilithium compound XXV and diphenylsilane, in an attempt to prepare the cyclic derivative XXVI, gave tetraphenylsilane, the di-silicon hydride XXVII, and (o-diphenylsilylphenyl)triphenylsilane (XXVIII).

Treatment of methyldiphenylchlorosilane with a solution of o-phenylenedilithium (XXV) containing a gray suspension afforded o-phenylenebis(methyldiphenylsilane) (XXIX) in low yield along with 1,2-dimethyl-1,1,2,2-tetraphenyldisilane. The formation of the disilane was thought to be due to a coupling reaction effected by the suspended lithium and not to the dilithium compound XXV. The dimethyl derivative XXIX was also obtained from o-phenylenebis(diphenylsilane) (XXVII) and methyllithium. However, the reaction products were contaminated with Si-H containing material and were extremely difficult to purify, indicating incomplete reaction.

Two attempts to prepare the cyclic derivative, 5,5,10,10-tetraphenyl-5,10-dihydrosilanthrene (XXVI), by the reaction


Ph
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XXVI
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Li
Li
XXV
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Si
H
H
Si
Ph
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XXVII
+
Ph
Ph
Si
Ph
H
Si
Ph
Ph
XXVIII
CH3Ph2SiCl
CH3Li
Ph
Ph
Si
CH3
CH3
Si
Ph
Ph
XXIX

of o-phenylenebis(diphenylsilane) (XXVII) and the dilithium compound XXV resulted only in the formation of (o-diphenylsilylphenyl)triphenylsilane (XXVIII). The cyclic derivative XXVII, however, was finally obtained by reacting equal molar amounts of o-phenylenedilithium (XXV) and diphenyldichlorosilane. In a similar fashion, 5,5,10,10-tetrabenzyl-5,10-dihydrosilanthrene was prepared from o-phenylenedilithium (XXV) and dibenzyldichlorosilane.

When o-phenylenebis(diphenylsilane) was treated with an ethereal solution of phenyllithium, nearly equivalent amounts of (o-diphenylsilylphenyl)triphenylsilane (XXVIII) and o-phenylenebis(triphenylsilane) (XXX) were obtained. The silicon-hydride compound XXVIII, on the other hand, was converted in good yield to the fully phenylated derivative by phenyllithium when forced conditions were used. An attempt to prepare o-phenylenebis(triphenylsilane) (XXX) by reacting o-phenylenedilithium with chlorotriphenylsilane was unsuccessful.

Attempts to make the molecular models of the dimethyl derivative XXIX and of the fully phenylated derivative XXX using Stuart and Briegleb atomic models were unsuccessful, indicating a considerable amount of strain in the molecules due to the bulky substituents. This undoubtedly accounts for the slow reactions of methyl- and phenyllithium with o-phenylenebis(diphenylsilane) (XXVII). However, by comparison of the models, the dimethyl derivative XXIX appears to be less strained than the corresponding phenylated derivative XXX, which is in accord with the formation of XXIX, but not of XXX, from the respective reactions of methyldiphenylchlorosilane and of triphenylchlorosilane with the dilithium compound XXV. The molecular models of the other derivatives, including the cyclic silanthrene compounds, can be formed readily.

It is interesting to compare the melting points of the three phenylenebis(triphenylsilane) isomers. The *para*-derivative[79] melts at 360° and the *meta*-derivative[96] at 349°; whereas the sterically hindered *ortho*-derivative melts at 257.5-259°.

Studies in the 10*H*-Dibenzosilin Series

Friedel-Crafts reactions on organosilicon compounds are said to be of little synthetic value due to the susceptibility of the silicon-carbon bond toward cleavage. Tetraphenylsilane upon treatment with aluminum chloride, for example, is cleaved to form silicon tetrachloride in an 80% yield.[97] Similarly, attempts to acylate triethylphenylsilane in the presence of

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[96] D. Wittenberg, T. C. Wu, and H. Gilman, *J. Org. Chem.*, *23*, 1898 (1958).

[97] W. E. Evison and F. S. Kipping, *J. Chem. Soc.*, 2774 (1931).

aluminum chloride gave hexaethyldisiloxane and the corresponding silicon-free phenyl ketone.[98]

Nevertheless a number of syntheses involving acylations are known. Benkeser and Curie[99] found that 2-thienyltrimethylsilane and 2-furyltrimethylsilane could be acetylated, using the mild catalyst iodine. Similarly, successful acylations have been accomplished with the _m_- and _p_-trimethylsilylbenzoyl chlorides employing aluminum chloride and stannic chloride.[100] _o_-Trimethylsilylbenzoyl chloride, however, gave only resinous materials. Also, Szmant and Skendrovich[101] found that acetyl fluoride and benzoyl fluoride would acylate silicon-substituted phenyl compounds in the presence of boron fluoride.

Recently, Wittenberg _et al._[37] have successfully synthesized some benzosilacyclanone derivatives by Friedel-Crafts reactions involving intramolecular acylations. 3-Triphenylsilylpropionic acid was converted to the acid chloride and subsequently treated with aluminum chloride in nitrobenzene to give a 47.9% yield of the heterocycle, 2:3-benzo-1,1-

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[98] B. N. Dolgov and O. K. Panina, _Zhur. Obschei Khim._, _18_, 1293 (1948) [Original available but not translated; abstracted in _C. A._, _48_, 3286 (1954)].

[99] R. A. Benkeser and R. B. Currie, _J. Am. Chem. Soc._, _70_, 1780 (1948).

[100] R. A. Benkeser and H. R. Krysiak, _ibid._, _76_, 599 (1954).

[101] H. H. Szmant and S. Skendrovich, _ibid._, _76_, 2282 (1954).

diphenyl-1-silacyclohexen-2-one-4. The corresponding cyclization of 4-triphenylsilylbutyric acid yielded 2:3-benzo-1,1-diphenyl-1-silacyclohepten-2-one-4.

The success of the latter study prompted this investigation into the possible utilization of Friedel-Crafts type reactions for the preparation of 10H-dibenzosilin derivatives. The first approach involved bromination of dimethylphenyl-o-tolylsilane with N-bromosuccinimide to give o-dimethylphenylsilylbenzyl bromide. This bromide was then allowed to interact with stannic chloride in carbon disulfide and with aluminum chloride in carbon disulfide in an effort to obtain 5,5-dimethyl-10H-dibenzosilin. However, failure attended both reactions. Attempts by Wittenberg et al.[37] to cyclize 3-triphenylsilylpropanol and 3-triphenylsilylpropyl bromide were similarly unsuccessful.

Attention was subsequently turned to the possible cyclization of o-dimethylphenylsilylbenzoic acid or its acid chloride. The synthesis of this acid presented a problem in itself. Benkeser and Krysiak[100] had previously shown that m- and p-tolyltrimethylsilanes could be oxidized to the corresponding acids in good yields, but that only negligible amounts of acid are obtained from the oxidation of o-tolyltrimethylsilane. Oxidations of dimethylphenyl-o-tolylsilane with chromium trioxide according to the procedure of Gilman *et al.*[102] likewise, gave only small amounts of *o*-dimethylphenylsilylbenzoic acid. However, suitable quantities of the acid were finally prepared by a three-step process. *o*-Dimethylphenylsilylbenzal bromide was prepared by treating dimethylphenyl-*o*-tolylsilane with two molar equivalents of N-bromosuccinimide, and then hydrolyzed by dissolving in hot ethylene glycol monomethyl ether and subsequently treating with an aqueous solution of silver nitrate[102] to give *o*-dimethylphenylsilylbenzaldehyde in good over-all yield. Oxidation of the aldehyde with potassium permanganate in acetone afforded *o*-dimethylphenylsilylbenzoic acid in good yield.

In an effort to obtain 5,5-dimethyl-10*H*-dibenzosilin-10-one, attempts were made to cyclize *o*-dimethylphenylsilylbenzoic acid and its acid chloride. Treatment of the acid with cold concentrated sulfuric acid and with polyphosphoric acid at 120° resulted in cleavage, for none of the desired compound or the starting material could be isolated. Next, the acid was converted to the acid chloride and subsequently allowed to interact with stannic chloride in carbon disulfide and with aluminum chloride in nitrobenzene according to the method of Wittenberg *et al.*,[37] but again none of the desired cyclic ketone could be isolated.

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[102] H. Gilman, C. G. Brannen, and R. K. Ingham, *ibid.*, *78*, 1689 (1956).

Suggestions for Further Research

For the purpose of obtaining dibromo derivatives suitable for the preparation of 5,10-dihydrophenazasiline compounds, it might be profitable to investigate the direct bromination of certain diarylamines, such as 4,4'-dichlorodiphenylamine and N-p-tolyl-2-naphthylamine.

It would be of interest to synthesize some 5,10-dihydrophenazasiline compounds containing a silicon-silicon bond. 5,5'-Diethyl-10,10'-diphenyl-10,10'-bi-(5,10-dihydrophenazasiline), for example, might be obtained by the sodium coupling of 5-ethyl-10-chloro-10-phenyl-5,10-dihydrophenazasiline. It would be necessary, of course, to first prepare this silicon-chlorine functional compound, which could be made by treatment of trichlorophenylsilane with N-ethyl-2,2'-dilithiodiphenylamine. The cleavage of these disilanes with lithium in tetrahydrofuran should then be examined and the synthetic utility of the resulting silyllithium intermediates explored.

Studies concerned with the cyclization of o-dimethylphenylsilylbenzoic acid and its acid chloride should be continued. Also, treatment of the acid chloride with phenyllithium would give o-dimethylphenylsilylphenyldiphenylcarbinol which then should undergo facile cyclization. In addition, this study should be extended to the preparation and possible cyclization of o-triphenylsilylbenzoic acid and its acid chloride.

The reactions of dichlorosilanes with the stilbene-dilithium adduct have not given any materials containing the disilacyclohexane ring system but only silicon-containing polymeric substances together with varying amounts of _trans_-stilbene.[19] It would therefore be worthwhile to investigate the reactions of silicon hydrides such as diphenylsilane and dibenzylsilane with the dilithium intermediate. These should afford the disilacyclohexane types.

SUMMARY

The chemistry of cyclic organosilicon compounds has been reviewed for the period April, 1957 to March, 1960.

Several new non-cyclic organosilicon compounds were synthesized which incorporated aralkyl groups in combinations with polyphenyl groups. These were prepared in order to obtain low-melting organosilicon compounds suitable for applications as high temperature lubricants.

Reactions of some 2-triphenylsilylethyl derivatives were investigated. Of particular noteworthiness was the reaction of 2-chloroethyltriphenylsilane with magnesium in tetrahydrofuran to give a good yield of 2-triphenylsilylethylmagnesium chloride, which apparently is the first preparation of such a Grignard reagent.

New procedures have been developed for the preparation of 5,10-dihydrophenazasiline compounds. These procedures involve reactions of 2,2'-dilithiodiarylamine derivatives with appropriately substituted silicon halides and hydrides. Thus, by varying either one or both of the reactants a wide variety of interesting compounds has been prepared. For example, 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline and 5,5'-diethyl-10,10'-spirobi-(5,10-dihydrophenazasiline) were obtained by treating one and two molar equivalents, respectively, of N-ethyl-2,2'-dilithiodiphenylamine with dichlorodiphenylsilane and with silicon tetrachloride.

Two silicon-hydride functional derivatives, 5-ethyl-10-phenyl- and 5-ethyl-10-n-hexadecyl-5,10-dihydrophenazasiline, were prepared by reacting N-ethyl-2,2'-dilithiodiphenylamine with phenylsilane and n-hexadecylsilane, respectively. Treatment of these functional derivatives with various organolithium reagents afforded good yields of the unsymmetrically substituted compounds.

5-Ethyl-10,10-diphenyl-5,10-dihydrophenazasiline has been allowed to react with bromine under several different conditions to give 5-ethyl-2,8-dibromo-10,10-diphenyl-5,10-dihydrophenazasiline, 2-(N-ethyl-2,4-dibromoanilino)-5-bromophenyldiphenylsilanol, N-ethyl-2,2',4,4'-tetrabromodiphenylamine, and 2,2',4,4'-tetrabromodiphenylamine.

Bromination of di-p-tolylamine and N-methyldi-p-tolylamine has given good yields of the respective 2,2'-dibromo compounds. N-Methyl-2,2'-dibromodi-p-tolylamine was converted to the dilithium derivative by halogen-metal interconversion with n-butyllithium, and subsequently to 2,8-dimethyl-5,10-dihydrophenazasiline compounds by treatment with the appropriate silicon halides.

From the reaction of o-phenylenedilithium with dichlorodiphenylsilane and with dibenzyldichlorosilane, 5,5,10,10-tetraphenyl-5,10-dihydrosilanthrene and 5,5,10,10-tetrabenzyl-5,10-dihydrosilanthrene were obtained. The reaction of the dilithium compound with diphenylsilane afforded o-phenylenebis(diphenylsilane), together with other compounds. o-Phenylenebis(diphenylsilane) has been treated with several organolithium reagents to afford some interesting o-phenylene silicon derivatives.

The possibility of synthesizing 10H-dibenzosilin derivatives *via* Friedel-Crafts reactions was investigated. Attempts were made to cyclize o-dimethylphenylsilylbenzyl bromide, o-dimethylphenylsilylbenzoic acid, and its acid chloride, but these reactions resulted in failure. A three-step process was developed for the preparation of o-dimethylphenylsilylbenzoic acid.

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