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SYNTHESES AND REACTIONS OF SOME CYCLIC ORGANOSILICON COMPOUNDS.

Iowa State University of Science and Technology
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SYNTHESES AND REACTIONS OF SOME CYCLIC ORGANOSILICON COMPOUNDS

by

Oren Lee Marrs

A Dissertation Submitted to the
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Ames, Iowa

1961

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INTRODUCTION

A class of compounds which may be of physiological interest is that of the perhydro-1,2-cyclopentanophenanthrene ring system that has a silicon atom incorporated into the ring. One approach to the preparation of this group of compounds is to begin with tetrahydronaphthalene or α-tetralone derivatives that contain a silicon atom in the aliphatic chain portion and, by classical steroid syntheses, build the molecule to the steroid nucleus.

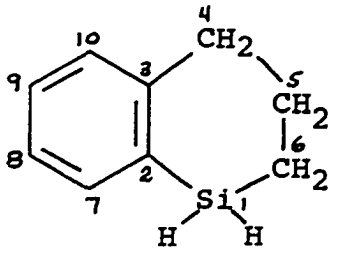
To date, only one silicon-containing tetrahydronaphthalene or α-tetralone derivative is known: 2,3-dihydro-1,1-diphenyl-4*H*-1-silanaphthalen-4-one (2:3-benzo-1,1-diphenyl-1-silacyclohex-2-en-4-one).[1] Therefore, the first efforts of this investigation were directed toward the preparation of these sila-tetrahydronaphthalene (benzosilacyclohexene) derivatives and then to study some of their reactions. To add to the versatility of the possible ensuing compounds, cyclic organosilicon derivatives of 2:3-benzo-1-silacyclopentene, 2:3-benzo-1-silacycloheptene, and 2:3-benzo-1-silacyclooctene have been prepared and studied. The preparation of these cyclic silanes has been accomplished by ring closure of (*o*-chlorophenyl)alkylsilanes and by reactions of the Grignard reagents of

[1] D. Wittenberg, P. B. Talukdar, and H. Gilman, *J. Am. Chem. Soc.*, *82*, 3608 (1960).

(o-bromophenyl)alkyl bromides with the appropriately substituted chlorosilanes. These organomagnesium compounds appear to be the first examples of aralkyl double Grignard reagents.

Incidental to these studies, the promising antioxidant and thermal stability properties of nitrogen-containing organosilicon compounds, and the facile reaction of lithium derivatives of amines with triphenylsilane,[2] prompted the preparation of some N-morpholinylsilanes. Paralleling this study was the reaction of triphenylsilyllithium with quinoline and anthracene.

The nomenclature and the numbering system used herein are those used and recommended by the editorial staff of Chemical Abstracts. For example, the numbering system for 2:3-benzo-1-silacyclohex-2-ene (I) is shown below.



I

[2] H. Gilman, B. Hofferth, H. W. Melvin, and G. E. Dunn, ibid., 72, 5767 (1950).

HISTORICAL

Previous investigations in these Laboratories on cyclic organosilicon compounds have dealt with cyclic derivatives in which the silicon atom was linked to two carbon atoms in the ring system. Gorsich[3] and Zuech[4] have thoroughly reviewed the chemistry of these compounds through March, 1960. The purpose of this review is to summarize the chemistry of this class of compounds since that time. In addition, the chemistry of a class of compounds that has the silicon atom linked to only one carbon atom in the ring system, has been included. These compounds may be considered intermediate between cyclic organosilicon compounds as defined above and cyclic systems having alternating Si-O-Si bonds (cyclosiloxanes), and, hence, they had not been included in the previous compilations.[3,4] Cyclosiloxanes will not be included in this review, as the subject has been consolidated recently.[5]

The literature has been reviewed through May, 1961. Also,

---

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

[4]E. A. Zuech. Cyclic organosilicon and related compounds. Unpublished Ph. D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1960.

[5]C. Eaborn. Organosilicon compounds. p. 227. London, Butterworths Scientific Publications. 1960; W. Noll. Chemie und technologie der silicone. p. 178. Weinheim/Bergstrasse, Verlag Chemie, G.m.b.H. 1960.

the subject has been checked by examination of Current Chemical Papers and Chemical Abstracts to June, 1961. The literature prior to March, 1960, has also been rechecked to insure completeness of the compilation.

For the purpose of clarity, the Historical has been arbitrarily divided into four sections: five-membered, six-membered, seven-membered, and eight-membered ring organosilicon chemistry.

Five-membered Ring Organosilicon Chemistry

A method generally applicable to the formation of silicon-carbon bonds is the addition of silicon hydrides to olefins and acetylenes.[6] The addition of silicon hydrides to vinylsilanes has been considered as taking place in such a manner that the silicon moiety becomes attached to the carbon bearing the greatest number of hydrogen atoms, and, thereby, forming a 1,2-disubstituted ethane derivative. On the basis of this fact and the infrared spectra, Curry[7] concluded that the intermolecular cyclization of various vinyl-substituted silicon hydrides afforded 1,4-disilacyclohexane compounds. However, in a nuclear magnetic resonance reinvestigation of

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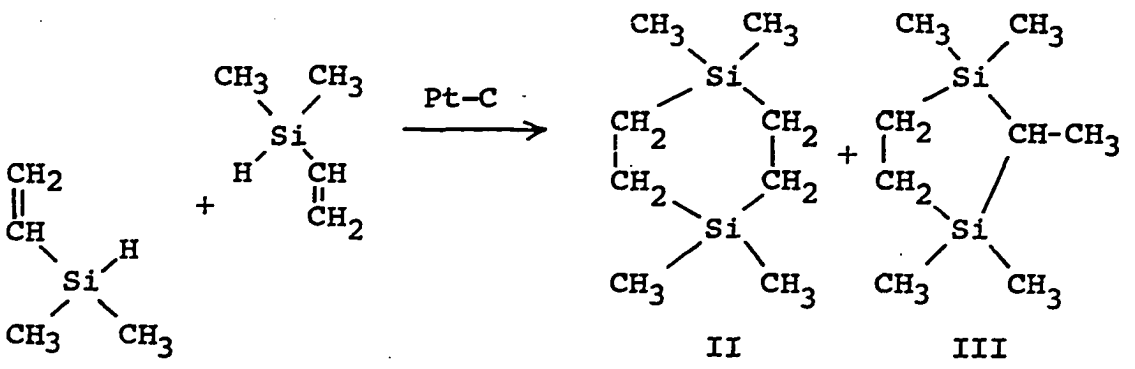
[6] L. H. Sommer, E. W. Pietrusza, and F. C. Whitmore, J. Am. Chem. Soc., 69, 188 (1947).

[7] J. W. Curry, ibid., 78, 1686 (1956).

the reaction products,[8] Curry found that the volatile cyclic product was either a mixture of the 1,3-disilacyclopentane and 1,4-disilacyclohexane or almost exclusively the 1,3-disilacylopentane derivative. Nuclear magnetic resonance analysis showed the presence of a methyl group attached to a tertiary carbon atom. Also, the tertiary hydrogen atom was readily observable. By comparing areas under the methylene bands of the two compounds, the amount of each derivative could be ascertained. For example, the volatile product from the polymerization of dimethylvinylsilane was found to consist of 1,1,4,4-dimethyl-1,4-disilacyclohexane (II) and 1,1,2,3,3-pentamethyl-1,3-disilacyclopentane (III) in a 27:73 ratio.



The mixture from the polymerization of diethylvinylsilane contained a small amount of the silacyclopentane derivative, whereas, diphenylvinylsilane appeared to give exclusively

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[8] J. W. Curry, J. Org. Chem., 26, 1308 (1961).

2-methyl-1,1,3,3-tetraphenyl-1,3-disilacyclopentane. Methylphenylvinylsilane gave a 60:40 mixture of the 5- and 6-membered ring compounts, respectively.

The polymers formed in these reactions were also shown to contain a carbon-methyl group in most cases.

Analysis of the Raman spectrum of the quinoline dehydrohalogenation products of 1,1,3-trichloro-1-silacyclopentane, which had been treated with methylmagnesium chloride, showed that the predominant product was 1,1-dimethyl-1-silacyclopent-2-ene.[9] The carbon-silicon bond cleavage product, 3-butenyltrimethylsilane, was present to extent of ca. 10%. The 1,1,3-trichloro-1-silacyclopentane was prepared by gaseous chlorination of the readily available 1,1-dichloro-1-silacyclopentane, or by heating the silacyclopentane with thionyl chloride in the presence of benzoyl peroxide.[9] However, in a similar study,[10] it has been observed that monochlorination of 1,1-dimethyl-1-silacyclopentane gives primarily the chloromethyl derivative and lesser amounts of the ring-substituted compounds, 2-chloro- and 3-chloro-1,1-dimethyl-1-silacyclopentane. The structures of these three isomers were assigned on the basis of their reactivity toward silver nitrate, re-

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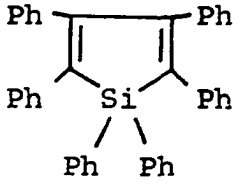
[9] V. F. Mironov and V. V. Nepomnina, Bull. Acad. Sci. U. S. S. R., Div. Chem. Sci., (Eng. trans.), 1188 (1959).

[10] R. Fessenden and F. J. Freenor, J. Org. Chem., 26, 2003 (1961).

action with quinoline, and conversion to known compounds. A 3-olefinic isomer, 1,1-dichloro-1-silacyclopent-3-ene, has been prepared by passage of 3,4-dichloro-1-butene over a silicon-copper alloy at 300°.[11]

Some unique heterocyclopentadiene compounds containing Group IV-A, V-A, and VI-A elements as the hetero atom have recently been reported.[12] These were prepared by reaction of the dilithium compound from the dimerization of diphenylacetylene with metallic (or metalloid) dihalides. Although derivatives of C, Ge, and Sn were readily prepared, silicon dihalides gave ill-defined products for which an explanation could not be given. However, Braye and Hübel[13] reported the preparation of the silicon analog, hexaphenylsilacyclopentadiene (IV) from a phenylacetylene-iron-carbonyl complex and dichlorodiphenylsilane.



IV

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[11] G. I. Niskishin, A. D. Petrov, and S. I. Sodykh-Zade, Khim. i Prakt. Primenenie Kremneorg. Soedinenii, Trudy Konf., Leningrad, No. 1, 68 (1958). [Original not available for examination; abstracted in C. A., 53, 17097 (1959)].

[12] F. C. Leavitt, T. A. Manuel, F. Johnson, L. U. Matternas, and D. S. Lehman, J. Am. Chem. Soc., 82, 5099 (1960).

[13] E. H. Braye and W. Hübel, Chem. and Ind., 1250 (1959).

Although Wittenberg *et al.*[1] used the Friedel-Crafts reaction to effect ring closure of the acid chloride of 3-triphenylsilylpropionic acid (see next section), under the same conditions, triphenylsilylacetic acid failed to cyclize. Triphenylsilanol was the only isolatable product, which suggested ready cleavage of the Si-C bond in this acid perhaps as a consequence of a β-effect.

Benzosilacyclopentene derivatives have, however, been reported.[14] The reaction of α,α'-dichloro-*o*-xylene with magnesium in ether, followed by treatment with silicon tetrachloride, is reported to give 3:4-benzo-1,1,2,5-tetrachloro-1-silacyclopent-3-ene (1,2,2,3-tetrachloro-2-silaindane), subsequent to chlorination of the reaction product with chlorine. Attempts to repeat this reaction using dichlorophenylphosphine failed to give any of the cyclic phosphorus compound.[15]

A modified Wurtz-Fittig type coupling reaction has been of general utility in the synthesis of non-cyclic organosilicon compounds,[16] and the reaction was used successfully, apparently without aliphatic carbon-silcon bond cleavage, in

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[14] J. M. Hersh, U. S. Patent 2,615,033 (October 21, 1952) [Original not available for examination; abstracted in *C. A.*, *47*, 9344 (1953)].

[15] F. G. Mann and F. H. C. Stewart, *J. Chem. Soc.*, 2826 (1954).

[16] H. A. Clark, A. F. Gordon, C. W. Young, and M. J. Hunter, *J. Am. Chem. Soc.*, *73*, 3798 (1951).

the preparation of 1,1-dinaphthyl-1-silacyclopentane derivatives from 1,1-dichloro-1-silacyclopentane, bromonaphthalenes, and finely dispersed sodium or potassium in an inert hydrocarbon.[17]

Incidental to the stability of the five-membered ring, Plate *et al.*,[18] found that 1,1-dimethyl- and 1,1-diethyl-1-silacyclopentane gave 80-94% conversions to 1,3-dibutyltetraalkylsiloxanes by shaking the cyclic silane with concentrated sulfuric acid for 3 hours at room temperature. Under the same conditions, tetraethylsilane exhibited little reaction, giving a small amount of gas, a 4% yield of hexaethyldisiloxane, and a good recovery of starting material.

A group of five-membered ring compounds which also show a considerable amount of strain are those which contain a C-Si-O bond. These have been termed paraffin-siloxanes as the compounds also contain a siloxane linkage. Piccoli and co-workers[19] prepared a series of highly reactive compounds by heating the hydrolysate from the hydrolysis of bis(chlorosilyl)ethanes with base.

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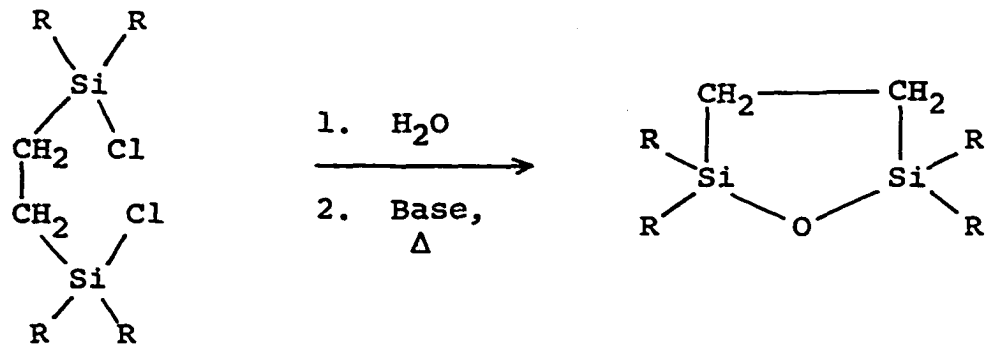
[17] G. E. Schroll, U. S. Patent 2,914,548 (November 24, 1959) [Original not available for examination; abstracted in *C. A.*, *54*, 7651 (1960)].

[18] A. F. Plate, N. A. Belikova, and Yu. B. Egorov, *Doklady Akad. Nauk S. S. S. R.*, *102*, 1131 (1955) [Original not available for examination; abstracted in *C. A.*, *50*, 4911 (1956)].

[19] W. A. Piccoli, G. G. Haberland, and R. L. Merker, *J. Am. Chem. Soc.*, *82*, 1883 (1960).



Several methyl and phenyl derivatives were prepared. The amount of strain in the 5-ring cyclic compound was estimated from the heat of polymerization and was found to be of the order 8-12 kcal/mole. Since the strain energy of cyclopentane is 7 kcal/mole, the replacement of a $-CH_2-CH_2-CH_2-$ unit in cyclopentane with a siloxane linkage, -Si-O-Si-, causes an increase in ring strain. Furthermore, the infrared Si-O-Si stretching vibration was observed to be in the 10.8-11.05μ region for the five-membered ring system, whereas, for linear siloxanes of similar structure, the Si-O-Si absorption band occurs at 9.4μ. This shift to higher wavelengths is indicative of the amount of strain in the ring. It was also noted that as methyl groups are substituted by phenyl groups, the ring strain increased as shown by a shift to higher wavelengths of the Si-O-Si absorption band. It has also been pointed out by Gillespie[20] that due to $p\pi$-$d\pi$ bonding, the normal angle of the Si-O-Si bond is 130-140°. If the angle

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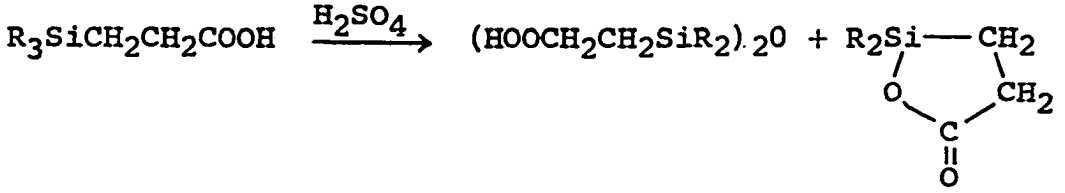
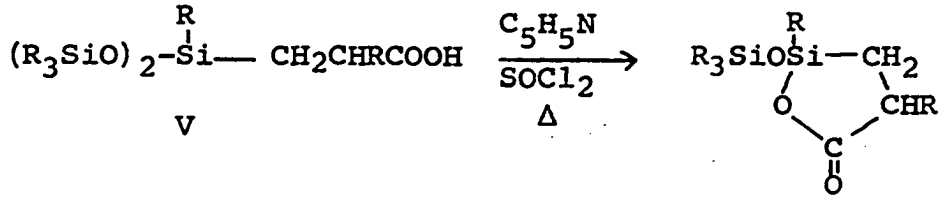
[20] R. J. Gillespie, ibid., 82, 5978 (1960).

becomes less than 130-140°, the reactivity is greatly enhanced.

A similar class of compounds containing the C-Si-O grouping are the silalactones. Treatment of silyl-substituted propionic acids with concentrated sulfuric acid gave a mixture of the diacid and the lactone.[21]



In a later patent, functional lactones VI were described.[22] These were obtained by ring closure of V with pyridine, thionyl chloride and heat.



The trisiloxanes (V) were prepared by a series of reactions beginning with chloromethyldiethoxysilanes and the sodium salt of various malonic acid esters.

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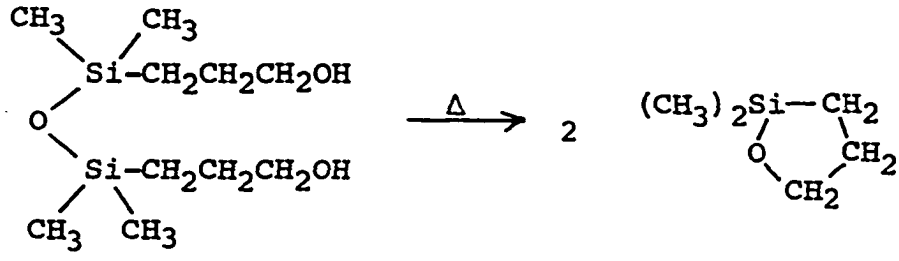
[21] L. H. Sommer, U. S. Patent 2,589,446 (March 18, 1952). [Original not available for examination; abstracted in C. A., 47, 145 (1952)].

[22] L. H. Sommer, U. S. Patent 2,963,500 (December 6, 1960) [Original not available for examination; abstracted in C. A., 55, 10386 (1961)].

A similar compound, 2,2-dimethyl-1-oxa-2-silacyclopentane, has been prepared by dehydration of 1,3-bis(3-hydroxypropyl)-tetramethyldisiloxane.[23]



The ether easily polymerized at room temperature in the presence of small amounts of water.

Six-membered Ring Organosilicon Chemistry

The recent observation that monomeric 1,6-dienes undergo an alternating intramolecular-intermolecular polymerization reaction to give polymers with recurring six-membered rings[24] lead to the investigation of various diallylsilanes. Addition of diallyldimethylsilane to a mixture of triisobutylaluminium and titanium tetrachloride in heptane gave polymers of moderate viscosity to high-melting solids.[25] The absence of un-

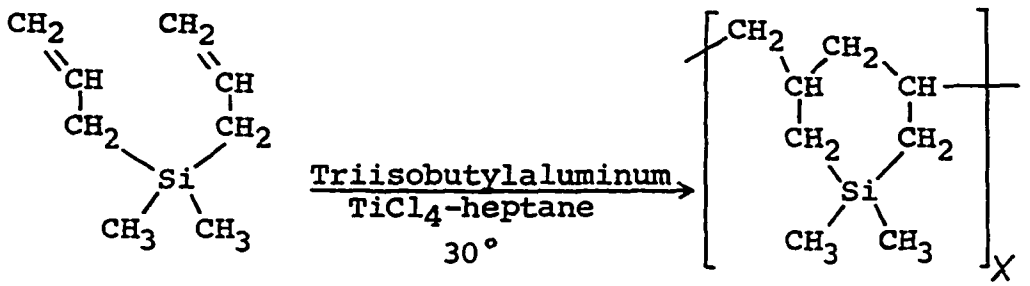
---

[23] J. L. Speier, M. P David, and B. A. Eynon, J. Org. Chem., 25, 1637 (1960).

[24] G. B. Butler, A. Crawshaw, and W. L. Miller, J. Am. Chem. Soc., 80, 3615 (1958).

[25] C. S. Marvel and R. G. Woolford, ibid., 25 1641 (1960).

saturation in the polymer suggested a chain of recurring silacyclohexane units.



Polymerization of diallyldiphenylsilane and diallyldimethylsilane using a triethylaluminum-titanium tetrachloride mixture gave similar results.[26] However, Topchiev and associates[27] report distillable liquids using the same Ziegler catalyst system. These may have been cyclic trimers or tetramers. Significantly, diallyldimethylgermane gave a low molecular weight dimer which was assigned structure VIII.[28]

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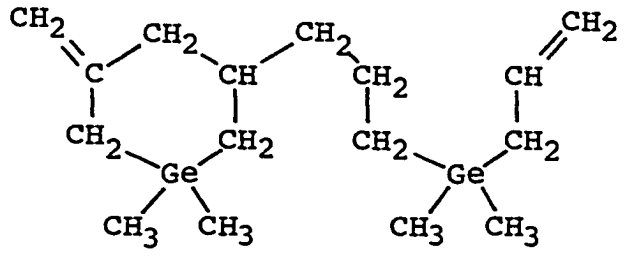
[26] G. B. Butler and R. W. Stackman, ibid., 25, 1643 (1960).

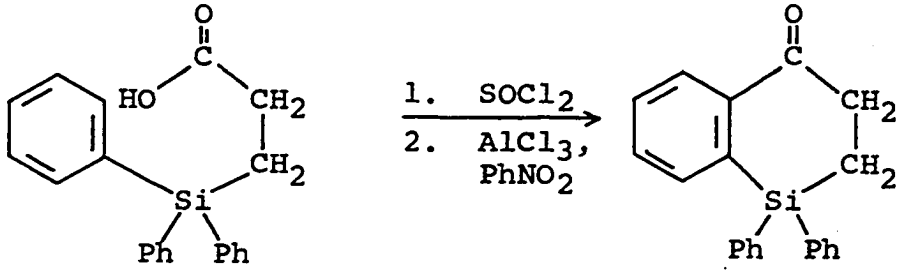
[27] A. V. Topchiev, N. S. Nametkin, S. G. Durgar'yan, and S. S. Dyankov, Khim. i Prakt. Primenenie Kremneorg. Soedinenii, Trudy Konf., Leningrad, No. 2, 118 (1958) [Original not available for examination; abstracted in C. A., 53, 8686 (1959)].

[28] G. S. Kolesnikov, S. L. Davydova, and T. I. Ermolaeva, Makromol. Verb. [Moskau], 1, 1493 (1959) [Original not available for examination; abstracted in Angew. Chem., 73, 197 (1961)].



VIII

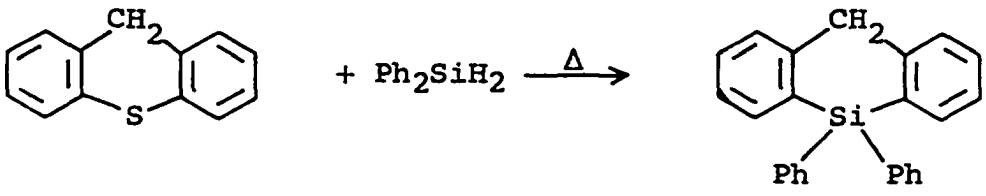
The preparation of another 6-ring system, benzosilacyclohexene, was accomplished by ring closure of the acid chloride of 3-triphenyl-silylpropionic acid with aluminum chloride in nitrobenzene.[1]



Attempts to effect intramolecular alkylation of 3-triphenylsilyl-proponol-1 and 3-triphenylsilylpropyl bromide with Lewis acids were unsuccessful.

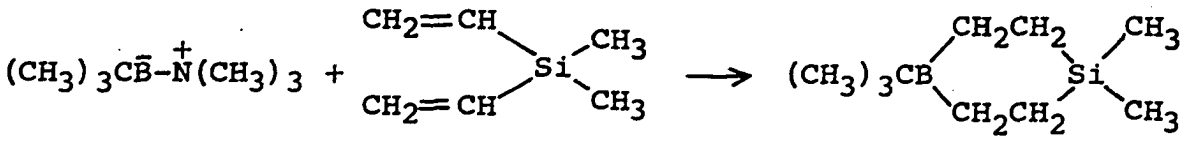
The Friedel-Crafts reaction was also utilized in the attempted preparation of 10H-dibenzosilin-10-one and 10H-dibenzosilin derivatives. Treatment of o-dimethylphenylsilylbenzoic acid or the acid chloride with Lewis acids gave none of the desired ketone. Also, ring closure of o-dimethylphenylsilylbenzyl bromide to give 5,5-dimethyl-10H-dibenzosilin using stannic chloride or aluminum chloride

was unsuccessful. The diphenyl derivative, 5,5-diphenyl-10H-dibenzosilin (X), has been prepared in low yield by the extended heating of thiaxanthene and diphenylsilane.[29]



X

The first cyclic organosilicon compound which contains a boron atom in the ring, 1-bora-1-t-butyl-4,4-dimethyl-4-silacyclohexane, has recently been reported by Hawthrone.[30] The compound was prepared by reaction of trimethylamine-t-butylborane with dimethyldivinylsilane; the borane adding smoothly to the unsaturated groupings.



Another class of cyclic silanes which contain nitrogen as the heteroatom is the 5,10-dihydrophenazasilines. These compounds are silicon analogs of 5,10-dihydroacridine. The first

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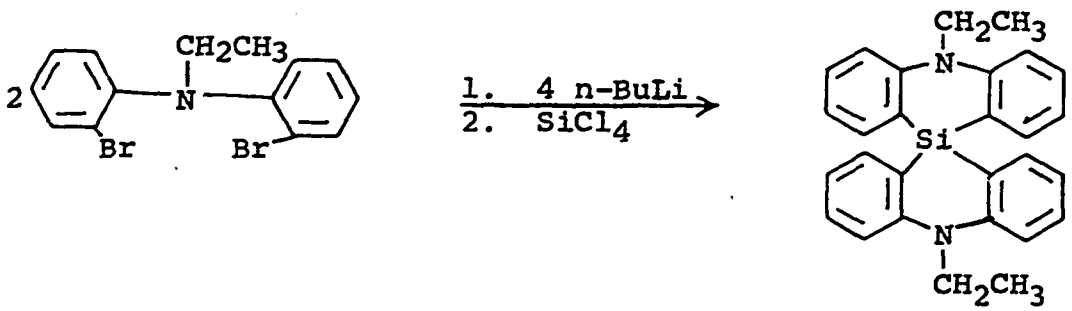
[29] J. W. Diehl. Some organometallic reactions with heterocyclic compounds. Unpublished Ph. D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1959.

[30] M. F. Hawthrone, J. Am. Chem. Soc., 82, 748 (1960).

derivatives were obtained by heating phenothiazine compounds with diphenylsilane for prolonged periods of time.[31] Since these compounds showed promising antioxidant properties, improved methods of syntheses were desirable.[32] This was accomplished by the reaction of 2,2'-dilithiodianylamines with silicon halides and hydrides. For example, 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline was prepared in good yield from N-ethyl-2,2'-dilithiodiphenylamine and dichlorodiphenylsilane. A comparable yield of the spiro compound, 5,5'-diethyl-10,10'-spirobi-(5,10-dihydrophenazasiline), was obtained from the dilithium compound and silicon tetrachloride. Phenylsilane and n-hexadecylsilane reacted with N-ethyl-2,2'-



dilithiodiphenylamine to give the corresponding phenazasiline derivative that contained a silicon-hydrogen group.[33] These compounds could be converted into a variety of phenazasiline

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[31] H. Gilman and D. Wittenberg, ibid., 79, 6339 (1957); D. Wittenberg, H. A. McNinch, and H. Gilman, ibid., 80, 5418 (1958).

[32] H. Gilman and E. A. Zuech, Chem. and Ind., 1227 (1958); J. Am. Chem. Soc., 82, 2522 (1960).

[33] H. Gilman and E. A. Zuech, J. Org. Chem., 26, 2013 (1961).

derivatives by treatment with organolithium reagents.

Since the dibromodiarylamines were of rather limited accessibility, being prepared *via* the Chapman rearrangement,[34] the direct bromination of di-*p*-tolylamine and its N-methyl analogue was investigated.[35] This method was found to give the 2,2'-dibromodiarylamine in good yields. Subsequently, N-methyl-2,2'-dibromodi-*p*-tolylamine was converted to the organolithium reagent with *n*-butyllithium and treated with dichlorodiphenylsilane and silicon tetrachloride to give 2,5,8-trimethyl-10,10-diphenylphenazasiline and 2,2',5,5',8,8'-hexamethyl-10,10'-spirobi-(phenazasiline), respectively.

The scope of the corresponding class of oxygen-containing analogs, phenoxasilins, has been broadened as a consequence of an improved method for the *ortho*-dimetalation of diphenyl ether.[36] Thus, by reaction of 2,2'-dilithiodiphenyl ether with phenylsilane, 5-phenylphenoxasilin (XI) was readily obtained.[37] A number of reactions was conducted with

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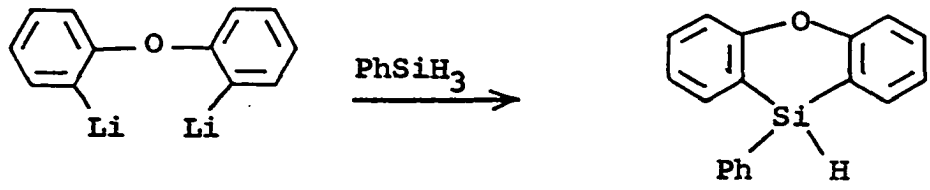
[34] E. R. H. Jones and F. G. Mann, *J. Chem. Soc.*, 786 (1956).

[35] H. Gilman and E. A. Zuech, *J. Org. Chem.*, *24*, 1394 (1959).

[36] H. Gilman and W. J. Trepka, *ibid.*, *26*, in press (1961).

[37] W. J. Trepka. Aryloxy and related organosilicon chemistry. Unpublished Ph. D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1960.



XI

XI: for example, treatment with base gave the silanol which was dehydrated to the disiloxane, and reaction with N-bromosuccinimide gave the cyclic bromosilane.

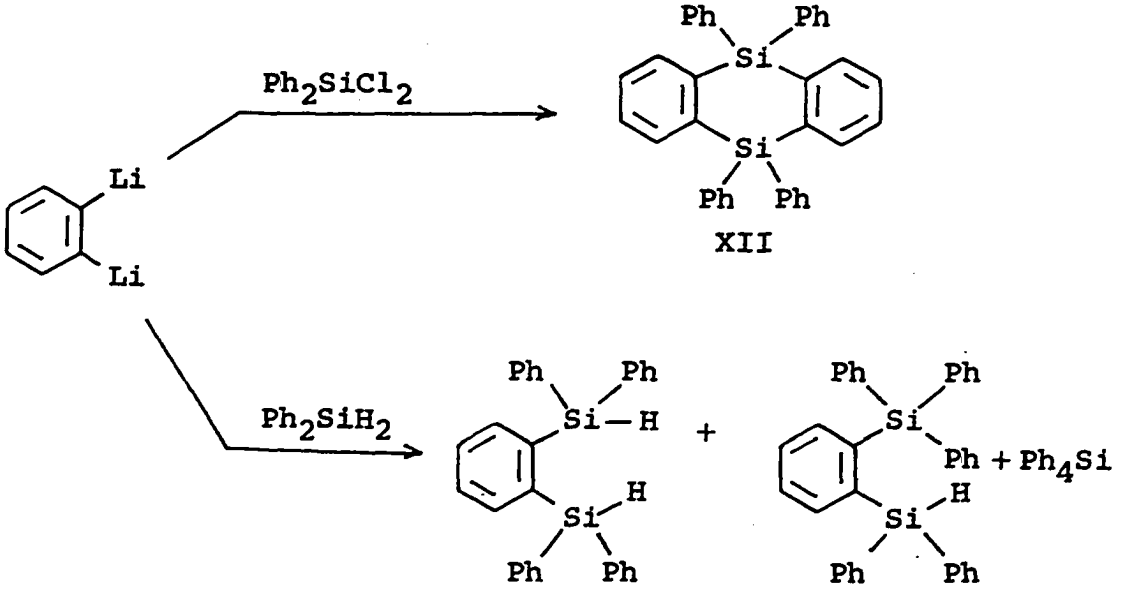
In connection with the reactions of cyclic organosilicon compounds, 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline was reacted with bromine under different conditions.[38] The products isolated were 5-ethyl-2,8-dibromo-10,10-diphenyl-5,10-dihydro-phenazasiline, and the cleavage products N-ethyl-2,2',4,4'-tetrabromodiphenylamine and 2-(N-ethyl-2,4-dibromoanilino)-5,5-bromophenyldiphenylsilanol. The 5-ethyl-2,8-dibromo-10,10-diphenyl-5,10-dihydrophenazasiline compound was treated successively with n-butyllithium and dimethyl sulfate to give 5-ethyl-2,8-dimethyl-10,10-diphenyl-5,10-dihydrophenazasiline.

The successful preparation of o-phenylenedilithium by Wittig and Bickelhaupt[39] provided a method for the preparation

[38] H. Gilman and E. A. Zuech, J. Org. Chem., 26, in press (1961).

[39] G. Wittig and F. Bickelhaupt, Angew. Chem., 69, 93 (1957); Ber., 91, 883 (1958).

of a novel cyclic organosilicon compound, 5,5,10,10-tetraphenyl-5,10-dihydrosilanthrene (XII), a silicon analogue of 9,10-dihydroanthrancene.[40] Treatment of o-phenylenedilithium with dichlorodiphenylsilane and dibenzyldichlorosilane gave the tetraphenyl and tetrabenzyl derivatives of 5,10-dihydrosilanthrene, respectively. In an attempt to reduce side reactions, o-phenylenedilithium was allowed to react with diphenylsilane. However, none of the desired cyclic compound could be isolated. The products were o-phenylenebis-(diphenylsilane) (XIII), (o-diphenylsilylphenyl) triphenylsilane, and tetraphenylsilane.



[40] H. Gilman and E. A. Zuech, Chem. and Ind., 120 (1960); J. Am. Chem. Soc., 82, 3605 (1960).

Preparation of XII from XIII and o-phenylenedilithium was unsuccessful.

Fritz and co-workers[41] have extended their studies in the preparation of six-membered rings with alternating C-Si bonds, termed cyclocarbosilan derivatives, to the thermal decomposition of methyltrichlorosilane and dimethyldichlorosilane. Pyrolysis of either chlorosilane at 700° gave Si-hexachlorocyclocarbosilan. This compound was chlorinated to Si-hexachloro-C-hexachlorocyclocarbosilan, and then hydrolyzed to give theoretical amounts of methylene chloride, ortho-silicic acid, and hydrogen chloride. The latter reaction was used as partial proof of the structure of the pyrolysis product. Furthermore, Si-hexachlorocyclocarbosilan was among the products when methylene chloride was passed over a silicon-copper alloy at 300°.[42] This direct method for the preparation of cyclic organosilicon compounds had been reported by Patnode and Schiessler.[43]

The promising polymers obtained by the polymerization of

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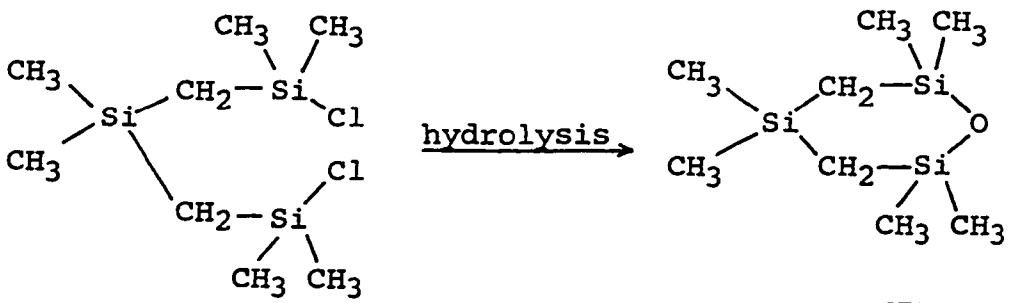
[41] G. Fritz, D. Habel, and G. Teichmann, Z. Anorg. u. allgem. Chem., 303, 85 (1960).

[42] G. Fritz and H. Thielking, ibid., 306, 39 (1960).

[43] W. I. Patnode and W. R. Schiessler, U. S. Patent 2,381,002 (August 7, 1945) [Original not available for examination; abstracted in C. A., 39, 4888 (1945)].

6-ring cyclic siloxanes has lead to the investigation of six-membered ring compounds with C-Si-O structures as monomers. Hydrolysis of 2,6-difluoro-2,6-dimethyl-2,6-disilaheptane with dilute base gave 2,2,6,6-tetramethyl-1-oxa-2,6-disilacyclohexane.[44] A trisilacyclohexane derivative, 2,2,4,4,6,6-hexamethyl-1-oxa-2,4,6-trisilacyclohexane (XIV), was prepared by hydrolysis of 2,6-dichloro- or 2,6-diethoxy-2,4,4,6-tetramethyl-2,4,6-trisilaheptane.[45]



XIV

Recently, cyclohexane ring systems containing the 1,4-dioxa moiety were obtained by dehydration of 1,3-bis-(hydroxyalkyl)tetramethyldisiloxanes.[23] The expected ether, 2,2,6,6-tetramethyl-1,4-dioxa-2,6-disilacyclohexane, was obtained from 1,3-bis(hydroxymethyl)tetramethyldisiloxane with

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[44] M. K. Kumada and A. Habuchi, J. Insti. Polytech., Osaka City Uni., 3, Ser. C, 65 (1952) [Original not available for examination; abstracted in C. A., 48, 9907 (1954)].

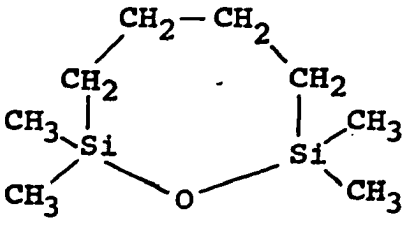
[45] J. T. Goodwin, Jr., W. E. Baldwin, and R. R. McGregor, J. Am. Chem. Soc., 69, 2247 (1947).

sulfuric acid, whereas dehydration with calcium oxide gave a polymer with repeating units of $-OSi(CH_3)_2CH_2-$. A structural isomer to the above cyclohexane, 2,2,5,5-tetramethyl-1,4-dioxa-2,5-disilacyclohexane, was proposed as the intermediate to the polymer.

Seven-membered Ring Organosilicon Chemistry

The only recently reported cyclic organosilicon compound in which silicon is bound to two carbon atoms in the ring system is the cyclic ketone 2:3-benzo-1,1-diphenyl-1-sila-cyclohept-2-ene-4-one.[1] This compound was prepared by treatment of the acid chloride of 4-triphenylsilylbutyric acid with aluminum chloride.

In a study of ring strain in paraffin-siloxanes, Sommer and Ansul[46] observed that the infrared Si-O-Si absorption band of 2,2,7,7-tetramethyl-1-oxa-2,7-disilacycloheptane (XV) occurred at 9.86μ, whereas the linear Si-O-Si absorption band



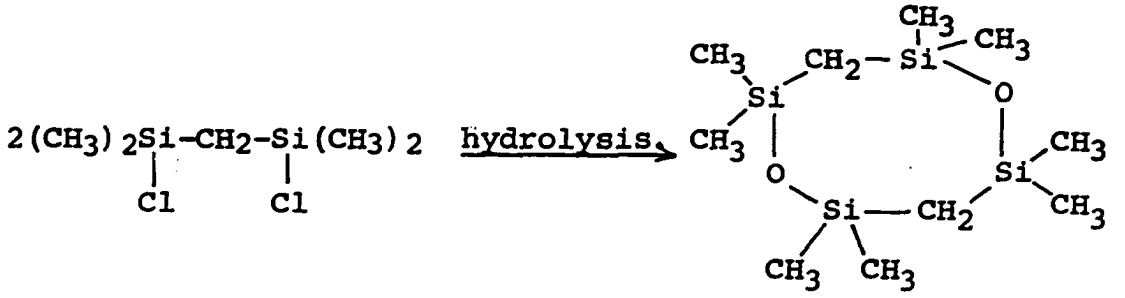
XV

[46]L. H. Sommer and G. R. Ansul, ibid., 77, 2482 (1955).

is observed between 9.4 and 9.5μ. It is to be recalled that the infrared Si-O-Si band in the 5-ring homolog of XV occurs at 10.8-11.05μ.[19] Compound XV was synthesized by ring closure of 2.7-dihydroxy-2,7-dimethyl-2,7-disilaoctane with trifluoroacetic acid in an excellent yield.

Eight-membered Ring Organosilicon Chemistry

The largest ring systems containing silicon, except the polysiloxanes,[5] are the eight-membered cyclic ethers in which silicon is bound to carbon and oxygen. The first of such derivatives was prepared by Goodwin *et al.*[45] by hydrolysis of the chloro or ethoxy derivatives of 2,3-disilapentanes.



This and similar derivatives have been prepared by hydrolysis of the fluoro compound[47] and the silane.[48]

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[47] B. A. Bluestein, *ibid.*, *70*, 3068 (1948).

[48] A. V. Topchiev, N. S. Nametkin, and L. S. Povarov, *Proc. Acad. Sci. U. S. S. R., Sec. Chem.*, (Eng. trans.), *109*, 405 (1956).

EXPERIMENTAL

The solvents used with organometallic reagents were commercially available "reagent grade" materials. These were dried by storing over sodium wire. The tetrahydrofuran was dried by refluxing over sodium wire and lithium aluminum hydride under an atomosphere of nitrogen. The solvent was distilled from the lithium aluminum hydride and used immediately.

Organic halides and other compounds used during the investigation were high quality commercial products. The organosilicon halides were obtained from Dow Corning Corporation unless stated otherwise. Phenylsilane and diphenylsilane were purchased from Andron Chemical Company.

The lithium wire was stored in a desiccator containing anhydrous calcium sulfate. Immediately before use, the wire was wiped free of grease, weighed, and cut into small pieces directly into the reaction flask while flushing with nitrogen. The magnesium was purified turnings. The unreacted metal of many of the reactions was removed by filtration of the organometallic compound through a loose glass-wool plug.

Reactions involving organometallic reagents were carried out under an atmosphere of dry, oxygen-free nitrogen. The reaction apparatus usually consisted of a three-necked flask equipped with a Trubore stirrer, a dropping funnel, and a condenser. The apparatus was dried in an oven maintained

between 110-140° and flushed with nitrogen while hot.

The reduced pressure distillations were carried out in Claisen-type flasks with rotating receivers.

During this investigation frequent use was made of Color Tests I and II. Color Test I[49] is a qualitative color test used to detect the presence of moderately and highly reactive organometallic reagents. Color Test II refers to Test A reported by Gilman and Swiss[50] for highly reactive organometallic compounds such as alkyllithium reagents.

All melting points and boiling points are uncorrected. Compounds melting below 200° were determined in an oil bath, while those melting above 200° were determined using an electrically-heated copper block.

The infrared spectra were obtained on either a Baird, model B, spectrometer or a Perkin-Elmer, model 21, spectrophotometer.

The nuclear magnetic resonance (n.m.r.) spectra were determined using a Varian Associates High Resolution Spectrometer, model HR-60, operated at 60 Mc/sec.

Silicon analyses were performed according to a published procedure.[2]

The titer for organomagnesium and aryllithium reagents

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[49]H. Gilman and F. Schulze, J. Am. Chem. Soc., 47, 2002 (1925).

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

was determined by the single acid titration method,[51] while that of n-butyllithium was found by the double titration method of Gilman and Haubein.[52,53]

Potential Organosilicon Antioxidants or Lubricants

N-Morpholinyltriphenylsilane or 1-(triphenylsilyl)-morpholine

An ether solution containing 0.021 mole of methyllithium was added rapidly to 2.17 g. (0.025 mole) of dry morpholine dissolved in 20 ml. of tetrahydrofuran. Color Test I was negative following complete addition. To the solution was added 5.20 g. (0.02 mole) of triphenylsilane in 50 ml. of tetrahydrofuran. The mixture was stirred 0.5 hour at room temperature and distilled to remove most of the solvent. Ethanol (100 ml.) was added cautiously and subsequently filtered to give 5.13 g. (72.4%) of product, m.p. 177-179°. Recrystallization from a benzene-petroleum ether (b.p. 60-70°) mixture raised the melting point to 178-180°. The melting point was not depressed when admixed with an authentic sample.[54]

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

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

[53] K. C. Eberly, J. Org. Chem., 26, 1309 (1961).

[54] H. Gilman and G. D. Lichtenwalter, J. Am. Chem. Soc., 82, 3319 (1960).

Di-N-morpholinyldiphenylsilane

To a solution containing 0.057 mole of 4-morpholinyllithium, prepared from 0.057 mole of methyllithium in 100 ml. of ether and 5.23 g. (0.06 mole) of morpholine in 60 ml. of tetrahydrofuran, was added 5.16 g. (0.028 mole) of diphenylsilane in 60 ml. of tetrahydrofuran. The mixture was stirred 5 hours at room temperature and distilled to remove the solvent. Ethanol (125 ml.) was added slowly and the resulting solid removed by filtration. Recrystallization from a benzene-petroleum ether (b.p. 60-70°) mixture gave 8.1 g. (81.7%) of white solid, m.p. 151.5-153°. A portion was recrystallized from cyclohexane to give colorless crystals, m.p. 152.5-154°.

Anal. Calcd. for $C_{20}H_{26}N_2O_2Si$: Si, 7.92. Found: Si, 7.81, 7.91.

Tri-N-morpholinylphenylsilane

Morpholine (7.23 g. 0.083 mole) in 90 ml. of tetrahydrofuran was treated with 0.082 mole of methyllithium in ether. The resulting N-morpholinyllithium was added to 2.92 g. (0.027 mole) of phenylsilane dissolved in 40 ml. of the tetrahydrofuran. Subsequent to stirring for 3 hours, the solvent was removed and the residue treated with ethanol. The solid was filtered to give 2.95 g. (30%) of product, m.p. 125-127°.

Recrystallization from cyclohexane raised the melting point to 125.5-127.5°.

Anal. Calcd. for $C_{18}H_{29}N_3O_3Si$: Si, 7.73. Found: Si, 7.81, 7.83.

Dibenzyldi-m-tolylsilane

A solution of dibenzylsilane (4.0 g., 0.019 mole) in 25 ml. of ether was treated with an excess of m-tolyllithium. After refluxing for 3 hours, the reaction mixture was hydrolyzed with dilute hydrochloric acid and worked up in the usual manner. The residue was distilled under reduced pressure to give 3.26 g. (44.1%) of a viscous liquid, b.p. 188-192° (0.008 mm.).

Anal. Calcd. for $C_{28}H_{28}Si$: Si, 7.15. Found: Si, 7.14, 6.92.

Reactions of Triphenylsilyllithium with Polynuclear Hydrocarbons and Heterocycles

Reaction of anthracene with triphenylsilyllithium

Run 1. To a solution of 4.46 g. (0.025 mole) of anthracene in 50 ml. tetrahydrofuran was added 0.025 mole of triphenylsilyllithium,[55] prepared from 6.48 g. (0.0125 mole) of

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

hexaphenyldisilane and 0.7 g. (0.1 g. atom) of lithium in 50 ml. of tetrahydrofuran. The reaction mixture was stirred 2.5 hours at room temperature and hydrolyzed with 2N sulfuric acid. The aqueous layer was separated, extracted with ether and discarded. The organic layer was filtered to give 0.3 g. (4.6%) of hexaphenyldisilane, m.p. 360-362°, identified by a mixed melting point determination. The filtrate was dried with anhydrous sodium sulfate and evaporated. The residue was taken up in petroleum ether (b.p. 60-70°) to give 2.32 g. (53%) of anthracene, m.p. 209-211°. The melting point was not depressed when mixed with an authentic sample. The petroleum ether solution was chromatographed on a column of alumina. Elution with the same solvent gave unreacted anthracene, then 1.8 g. of a compound melting over the range 148-151°. Recrystallization from petroleum ether (b.p. 60-70°) gave 1.36 g. (12.4%) of colorless solid, m.p. 153-155°. The analytical sample melted at 153-154°. The infrared spectrum of the compound in carbon disulfide had characteristic absorption bands at 3.3, 3.5, and 9.06μ, indicative of aromatic C-H, aliphatic C-H, and the silicon-phenyl linkage, respectively. The melting point was not depressed when admixed with an authentic sample of 9,10-dihydro-9-(triphenylsilyl)anthracene (see below).

Anal. Calcd. for $C_{32}H_{26}Si$: Si, 6.40. Found: Si, 6.35, 6.36.

Further elution of the column with benzene and ethyl acetate did not yield any identifiable compounds.

Run 2. A mixture of 0.05 mole of triphenylsilyllithium and 8.92 g. (0.05 mole) of anthracene was stirred 12 hours at room temperature and then hydrolyzed. The aqueous layer was extracted with ether and discarded. The organic layer was filtered to give 6.3 g. of material which was recrystallized from tetralin to give 1.11 g. (8.5%) of hexaphenyldisilane and 4.5 g. (50.4%) of unreacted anthracene.

The filtrate was dried with sodium sulfate and evaporated. The residue was chromatographed on alumina.

Using petroleum ether as the eluant, 7.92 g. of a solid was obtained which melted over a wide range. Fractional crystallization from ethanol gave 3.7 g. (16.9%) of pure 9,10-dihydro-9-(triphenylsilyl)anthracene, m.p. 152-154°, and 0.8 g. of a solid melting over the range 229-233°. Elution of the column with benzene gave 2.86 g. of material which was subsequently treated with hot ethanol to give 0.38 g. of insoluble solid, m.p. 229-233°, and a residual solid melting over the range 100-224°. The two fractions of the high melting solid were combined and treated with a variety of solvents, but the melting point could not be improved. The infrared spectrum was similar to 9,10-dihydro-9-(triphenylsilyl)anthracene, showing absorption bands at 3.37, 3.5, 9.06, and 13.07μ, characteristic of aromatic C-H, aliphatic C-H, the

silicon-phenyl linkage, and ortho-disubstitution, respectively. The solid may be a mixture of 9,10-dihydro-9-triphenylsilyl-10-(9',10'-dihydro-9'-anthryl)anthracenes.

Anal. Calcd. for $C_{46}H_{36}Si$: Si, 4.55. Found: Si, 4.75, 4.85.

9,10-Dihydro-9-(triphenylsilyl)anthracene

9,10-Dihydroanthracene (10.8 g., 0.06 mole), prepared by the method of Wieland,[56] in 100 ml. of ether was metalated with 0.06 mole of n-butyllithium[57] in a manner similar to that previously reported.[58] Color Test I was positive and Color Test II was negative after refluxing the reaction mixture for 12 hours.

The deep red solution was added to 17.69 g. (0.06 mole) of chlorotriphenylsilane suspended in ether. Color Test I was still positive; an additional 5.0 g. of the chlorotriphenylsilane was added and the mixture stirred one hour at room temperature. Color Test I was then negative. Hydrolysis was effected with water and the layers separated. The combined

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[56] H. Wieland, Ber., 45, 484 (1912).

[57] 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).

[58] H. Gilman and R. L. Bebb, ibid., 61, 109 (1939).

organic layer was filtered and dried over anhydrous sodium sulfate. The insoluble material, m.p. 355-358°, (1.06 g., 2.7% based on the chlorotriphenylsilane) was identified as hexaphenyldisilane by mixture melting point.

The organic layer was concentrated and the residue chromatographed on a column of alumina. The first fraction eluted with petroleum ether (b.p. 60-70°) yielded a solid (8.5 g.) which melted over a wide range. The second fraction eluted with the same eluant gave 6.8 g. of material melting over the range 149-153°. Recrystallization from ethanol raised the melting point to 153-154°. A mixed melting point with the 9,10-dihydro-9-(triphenylsilyl)anthracene isolated in the previous experiment was not depressed.

Further elution of the column with petroleum ether gave 4.85 g. of impure 9,10-dihydro-9-(triphenylsilyl)anthracene, m.p. 130-145°. Benzene and methanol elution gave non-identifiable solids melting over wide ranges.

The solid obtained from the first fraction of petroleum ether elution was rechromatographed. There was obtained 4.55 g. of an oily material and 0.92 g. of pure product. The total yield of pure 9,10-dihydro-9-triphenylsilylanthracene was 7.72 g. (29.3%).

Reaction of chlorotriphenylsilane with 9,10-dihydro-9,10-dilithioanthracene

A solution of anthracene (5.35 g., 0.03 mole) in 100 ml. of tetrahydrofuran was added to 0.7 g. (0.1 g. atom) of finely

cut lithium wire. A green color developed immediately. The mixture was stirred 5 hours at room temperature and filtered into a second flask. To the organolithium reagent was added 8.84 g. (0.03 mole) of chlorotriphenylsilane dissolved in 50 ml. of tetrahydrofuran. The color of the solution changed from purple to blue and a solid formed. The suspension was allowed to stir 16 hours at room temperature. Color Test I was weakly positive. Dilute sulfuric acid was added, followed by ether. The layers were separated and the organic layer filtered to remove 3.65 g. (46.9%) of hexaphenyldisilane, m.p. 357-360°, identified by mixed melting point.

The filtrate was dried over anhydrous sodium sulfate and concentrated. The residual solid was taken up in petroleum ether (b.p. 60-70°) and filtered to give 0.9 g. of anthracene. The petroleum ether solution was poured onto alumina and chromatographed. Elution with the same solvent gave 0.2 g. of solid, m.p. 103-110°. Recrystallization from ethanol afforded 80 mg. of solid, m.p. 105-108°, which did not depress the melting point of an authentic sample of 9,10-dihydro-anthracene. Further elution with petroleum ether gave 1.0 g. of anthracene (total yield 1.9 g., 35.5%). When benzene was used as the eluant, traces of anthracene were eluted, followed by 0.8 g. of solid melting at 192-195°. Elution with methanol yielded an additional 0.85 g. of the same solid, m.p. 198-202°. The two fractions were combined and recrystallized from

ethanol to give 1.36 g. (9.07%) of fine needles, m.p. 203-205°. This material has been tentatively identified as 9,10-dihydro-9-(4-hydroxybutyl)-10-(triphenylsilyl)anthracene. The infrared spectrum of the solid contained absorption bands at 2.78, 3.3, 3.47, 9.06, and 13.26μ, indicative of hydroxy, C-H aromatic, C-H aliphatic, and silicon-phenyl linkage, and ortho-disubstitution, respectively. Except for the band at 13.26μ, the infrared spectrum was nearly superimposable with 4-hydroxybutyltriphenylsilane. The n.m.r. spectrum was also compatible with the assigned structure.

Anal. Calcd. for $C_{36}H_{34}OSi$: C, 84.66; H, 6.70; Si, 5.50. Found: C, 84.38, 84.19; H, 6.68, 6.54; Si, 5.54, 5.48.

Reaction of quinoline with triphenylsilyllithium

A tetrahydrofuran solution containing 0.04 mole of triphenylsilyllithium[55] was added to 12.9 g. (0.1 mole) of quinoline. The reaction mixture became red in color, but the color changed to green subsequent to refluxing for one hour. Color Test I was negative. One hundred milliliters of a saturated ammonium chloride solution was added, followed by the addition of ether and separation of the layers. The aqueous layer was extracted with ether and discarded. The combined organic layer was dried and distilled. The residue was refluxed 20 minutes with 20 ml. of nitrobenzene to insure aromatization, and then the nitrobenzene was removed with the

aid of a water aspirator. The red oil was dissolved in a 50:50 mixture of petroleum ether (b.p. 60-70°) and benzene and chromatographed on alumina. Elution with this solvent pair gave at first oily solids which could not be purified. Further elution gave 1.95 g. of solid, m.p. 185-190°. Recrystallization from a methanol-benzene mixture gave 1.55 g. (10%) of colorless crystals, m.p. 202-204°. The analytical sample melted at 205-206°. The infrared spectrum did not contain an N-H absorption band. The compound has been assigned the structure triphenyl-4-quinolylsilane based on its infrared spectrum, elemental analysis, and the fact that the melting point was depressed when mixed with authentic triphenyl-2-quinolylsilane (vide infra). Also, the infrared spectra of the two compounds were quite different.

Anal. Calcd. for $C_{27}H_{21}NSi$: C, 83.68; H, 5.46; N, 3.61; Si, 7.25. Found: C, 83.65, 83.85; H, 5.11, 5.20; N, 3.63, 3.64; Si, 7.35.

The compound formed a picrate, m.p. 226-228° (dec.). A mixture melting point determination with the picrate of triphenyl-2-quinolylsilane was depressed to 180-190° (dec.).

Using benzene and ethyl acetate, hexaphenyldisiloxane (0.27 g.), m.p. 220-226°, and triphenylsilanol (0.79 g.) m.p. 148-151°, were obtained, identified by mixed melting point determinations.

Triphenyl-2-quinolylsilane

To a solution of 2-quinolyllithium,[59] prepared from 5.2 g. (0.025 mole) of 2-bromoquinoline and 0.025 mole of n-butyllithium in ether at -50°, there was added 7.37 g. (0.025 mole) of chlorotriphenylsilane in 60 ml. of tetrahydrofuran at such a rate that the temperature did not rise above -50°. Color Test I was negative after stirring ly hours at this temperature. Water was added and the reaction mixture worked up as described in the previous experiment. The residue was taken up in petroleum ether (b.p. 60-70°) and chromatographed.

Using petroleum ether as the eluant, 0.4 g. of a solid was obtained which was fractionally crystallized with ethyl acetate to give 0.12 g. of hexaphenyldisiloxane, m.p. 223-226°, identified by mixed melting point, and 0.1 g. of a solid, m.p. 127-130°, which proved to be triphenyl-2-quinolylsilane. Elution of the column with benzene gave 1.16 g. of a yellow solid, m.p. 120-124°. The material was dissolved in hot ethyl acetate, decolorized with Norit, and filtered. Cooling of the filtrate gave 0.79 g. (8.2%) of pure product, m.p. 129.5-131.5°. A second recrystallization raised the melting point to 130.8-131.8°.

Anal. Calcd. for $C_{27}H_{21}NSi$: C, 83.68; H, 5.46; N, 3.61; Si, 7.25. Found: C, 84.18, 84.49; H, 5.53, 5.53; N, 3.65,

[59] H. Gilman and T. S. Soddy, J. Org. Chem., 22, 565 (1957).

3.59; Si, 7.05, 6.85.

The picrate of triphenyl-2-quinolylsilane melted at 190-192° with decomposition.

Further elution of the column with ethyl acetate gave 2.81 g. (45.3%) of triphenylsilanol, m.p. 153-155°. The melting point was not depressed when admixed with an authentic sample.

Studies in the Benzosilacycloalkene Series

o-Chlorobenzyldiphenylsilane

A solution of o-chlorobenzylmagnesium chloride,[60] prepared in an 88% yield from 48.31 g. (0.3 mole) of o-chlorobenzyl chloride and 9.73 g. (0.4 g. atom) of magnesium in 300 ml. of ether, was added to an ethereal solution of 57.9 g. (0.265 mole) of chlorodiphenylsilane. After stirring the reaction mixture 12 hours at room temperature, Color Test I was negative. Hydrolysis was effected with dilute sulfuric acid and the layers separated. The organic layer was dried over magnesium sulfate and the solvent evaporated. Distillation under reduced pressure gave 60.5 g. (73.9%) of product, b.p. 158-160° (0.012 mm.), n_D^{20} 1.6141, d_{20}^{20} 1.133.

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[60] P. R. Austin and J. R. Johnson, J. Am. Chem. Soc., 54, 647 (1932).

Anal. Calcd. for $C_{19}H_{17}ClSi$: Si, 9.09; MR_D, 94.78. Found: Si, 9.15, 8.95; MRD, 95.04.

Reaction of o-chlorobenzyldiphenylsilane with sodium

To a refluxing suspension of 6.0 g. (0.26 g. atom) of sodium in 100 ml. of toluene, there was added 29.84 g. (0.13 mole) of o-chlorobenzyldiphenylsilane in 100 ml. of toluene. The brown mixture was refluxed 24 hours and cooled. The suspension was filtered twice through glass-wool plugs to remove unreacted sodium.[61] The toluene solution was poured cautiously into an ice-sulfuric acid mixture. Ether was added and the layers separated. After drying over magnesium sulfate, the ether solution was concentrated and distilled under reduced pressure to give 16.55 g. (55.5%) of unreacted o-chlorobenzyldiphenylsilane, confirmed by comparison of refractive indexes and infrared spectra.

The distillation residue was transferred to a flask and treated with petroleum ether (b.p. 60-70°) to give 0.6 g. of solid, m.p. 280-295°. Recrystallization from a benzene-petroleum ether mixture afforded 0.28 g. of colorless crystals,

[61]In a later experiment, the unreacted sodium and salt mixture ignited while filtering. An improved method of work-up is as follows: The reaction mixture is allowed to stand and the clear liquid carefully withdrawn by means of a pipet. The residual solid is washed 2 or 3 times with dry solvent, withdrawing the washings after the solid is allowed to settle. The decanted liquid is hydrolyzed and the solid is destroyed with ethanol.

m.p. 313-315°. The infrared spectrum of the compound in carbon disulfide showed prominent absorption bands at 3.27, 3.46, 9.05, and 13.07μ, indicative of aromatic C-H, aliphatic C-H, the silicon-phenyl linkage, and ortho-disubstitution. As a carbon tetrachloride solution, the characteristic Si-H absorption band was absent. The compound has been assigned the structure 2:3,6:7-dibenzo-1,1,5,5-tetraphenyl-1,5-disilacyclooöcta-2,6-diene.

Anal. Calcd. for $C_{38}H_{32}Si_2$: C, 83.76; H, 5.92. Found: C, 83.78, 83.99; H, 6.10, 6.17.

o-Bromobenzyldiphenylsilane

To a solution of chlorodiphenylsilane (10.28 g., 0.047 mole) in 15 ml. of ether, there was added an ether solution containing 0.047 mole of o-bromobenzylmagnesium bromide.[62] When the addition was complete, Color Test I was negative. The reaction mixture was hydrolyzed and the organic layer worked up in the usual manner. Distillation of the reaction products under reduced pressure gave 17.61 g. of a pale yellow liquid which was chromatographed over alumina. The petroleum ether (b.p. 60-70°) and cyclohexane eluates were distilled to give 11.42 g. (69.1%) of colorless product, b.p. 148-150° (0.002 mm.), n_D^{20} 1.6268, d_{20}^{20} 1.2814.

[62] M. H. Beeby and F. G. Mann, J. Chem. Soc., 411 (1951).

Anal. Calcd. for $C_{19}H_{17}BrSi$: Si, 7.95; MR_D, 97.62. Found: Si, 7.88, 7.87; MR_D, 97.72.

Reaction of o-bromobenzyldiphenylsilane with sodium

A mixture of o-bromobenzyldiphenylsilane (10.1 g., 0.0286 mole) and sodium metal (1.44 g., 0.06 g. atom) in 130 ml. of toluene was refluxed 6 hours. A 5 ml. aliquot was withdrawn, hydrolyzed, and worked up. The infrared spectrum of the resulting oil contained a strong Si-H absorption band. The refluxing was continued 24 hours at which time the Si-H absorption band did not appear to have decreased in intensity.

The solid was allowed to settle and the clear solution carefully withdrawn and hydrolyzed with dilute sulfuric acid. The solid residue was washed twice with dry toluene and destroyed. Ether was added to the hydrolyzed material and the layers separated. The organic layer was dried and concentrated. The residual oil was treated with petroleum ether (b.p. 60-70°) and allowed to stand. A solid formed slowly. Filtration gave 0.35 g. of material melting over the range 297-303°. Recrystallization from a benzene-petroleum ether mixture raised the melting point to 308-311°. A mixture melting point determination with the 2:3,6:7-dibenzo-1,1,5,5-tetraphenyl-1,5-disilacyclooctadiene previously isolated showed no depression.

The concentrated filtrate was distilled under reduced

pressure to give 1.56 g. (15.5%) of unreacted o-bromobenzyldiphenylsilane, b.p. 116-122° (0.028 mm.), confirmed by an infrared spectra comparison. The infrared spectrum of the viscous distillation residue contained a strong Si-H absorption band.

2-(o-Chlorophenyl)ethanol-1

To a suspension of 24.3 g. (0.64 mole) of lithium aluminum hydride in 600 ml. of ether there was added an ethereal solution of o-chlorophenylacetic acid, prepared by the carbonation of o-chlorobenzylmagnesium chloride.[60] After refluxing 20 minutes, the mixture was poured onto ice and acidified. The aqueous layer was separated and extracted with ether. The combined organic layer was dried and concentrated. Distillation under reduced pressure gave 62.8 g. (80.2%) of liquid, b.p. 128-130° (12.5 mm.), d_{20}^{20} 1.1904, n_D^{20} 1.5515.

Anal. Calcd. for C_8H_9ClO: C, 61.35; H, 5.79; MR_D, 42.17. Found: C, 60.77, 60.98; H, 5.61, 5.77; MR_D, 42.01.

A portion of the alcohol was treated with a slight excess of 1-naphthyl isocyanate to give 2-(o-chlorophenyl)ethyl N-1-naphthylcarbamate, m.p. 121.5-123°, after crystallization from absolute ethanol.

In two repeat runs, the alcohol was obtained in yields of 87.8 and 88.4%, respectively.

2-(o-Chlorophenyl)ethyl bromide

Phosphorus tribromide (54.14 g., 0.2 mole) was added to 62.6 g. (0.397 mole) of 2-(o-chlorophenyl)ethanol-1 cooled to 5°. The mixture was allowed to warm to room temperature, then heated at 100° for 1 hour. After cooling, ice was added and the aqueous layer extracted with ether. The organic layer was washed with water and dried. Removal of the solvent and distillation of the residue afforded 66.43 g. (76.2%) of the bromide, b.p. 110-112° (10 mm.), n_D^{20} 1.5710.

The infrared spectrum of the product was superimposable with a sample prepared by bromination of the silver salt of o-chlorophenylacetic acid.[63]

In a second run, the bromide was prepared in a 56% yield.

3-(o-Chlorophenyl)propionic acid

2-(o-chlorophenyl)ethyl bromide (10 g., 0.046 mole) in 90 ml. of dry ether was added slowly to 1.2 g. (0.05 g. atom) of magnesium turnings suspended in 10 ml. of ether. Subsequent to initiation of the reaction, the mixture was stirred 12 hours at room temperature, refluxed for 1 hour and then carbonated. After the customary work-up, there was isolated 2.64 g. (53%) of acid, m.p. 93-95.5°. Recrystallization from

[63] R. A. Barnes and M. D. Konort, J. Am. Chem. Soc., 75, 303 (1953).

petroleum ether (b.p. 60-70°) afforded a 35% yield of pure product, m.p. 96-98°; reported[63] m.p. 96-97°.

o-Bromobenzyl bromide

The bromide was prepared according to the method of Gorsich[3] from o-bromotoluene and N-bromosuccinimide in yields of 79 and 75%, respectively, b.p. 134-138° (16 mm.). In the second run, ultraviolet light was used to catalyze the reaction.

o-Bromobenzyl cyanide

o-Bromobenzyl bromide (25 g., 0.1 mole) in 25 ml. of 95% ethanol was added to 6.86 g. (0.14 mole) of sodium cyanide dissolved in 10 ml. of warm water and heated 4 hours between 95° and 105°. After cooling and filtering, the filtrate was extracted with ether. The ether extract was dried with anhydrous magnesium sulfate and the solvent evaporated. Distillation of the residual cyanide under reduced pressure gave 14.67 g. (74.8%) of pure product, b.p. 142-144° (14 mm.), n_D^{20} 1.5704; reported[64] b.p. 145-147° (14 mm.).

In a second run, the cyanide was obtained in a 79% yield.

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[64] St. Opolski, L. Czaporowski, and J. Zacharoki, Ber., 49, 2283 (1916).

o-Bromophenylacetic acid

o-Bromobenzyl cyanide (14.0 g., 0.071 mole) was hydrolyzed by refluxing 1 hour in a mixture of water (10 ml.), concentrated sulfuric (10 ml.), and glacial acetic acid (10 ml.). The reaction mixture was poured into an equal volume of water, and the acid filtered and dried. There was obtained 14.3 g. (93.7%) of o-bromophenylacetic acid, m.p. 103-105°; reported[65] 103-104°.

2-(o-Bromophenyl)ethanol-1

To a suspension of 11.4 g. (0.3 mole) of lithium aluminum hydride in 250 ml. of ether, there was added 47 g. (0.218 mole) of o-bromophenylacetic acid dissolved in 250 ml. of the same solvent. The reaction mixture was refluxed 30 minutes and then treated with 20 ml. of ethyl acetate. The gray solution was poured onto crushed ice and the organic layer separated. The aqueous layer was extracted with ether and discarded. The combined organic layer was dried and concentrated. The residual oil was distilled to give 38.61 g. (88.1%) of colorless liquid, b.p. 130-132° (7.5 mm.), n_D^{20} 1.5760, d_{20}^{20} 1.4899.

Anal. Calcd. for C_8H_9BrO: C, 47.79; H, 4.51; MR_D, 45.01. Found: C, 47.95, 47.84; H, 4.56, 4.40; MR_D, 44.67.

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[65] P. P. Bedson, J. Chem. Soc., 37, 90 (1880).

The 1-naphthylcarbamate melted at 139.5-141°, after recrystallization from ethanol.

2-(o-Bromophenyl)ethyl bromide

Phosphorus tribromide (21.66 g., 0.08 mole) was added to 33.85 g. (0.1684 mole) of 2-(o-bromophenyl)ethanol-1 cooled in an ice bath. The mixture was warmed to room temperature and heated at 100° for 1 hour. After hydrolysis, ether was added and the mixture worked up in the usual manner. The reaction products were distilled under reduced pressure to give 34.4 g. (77.5%) of pure product, b.p. 113-115.5° (6 mm.), n_D^{20} 1.5933, d_{20}^{20} 1.7523.

Anal. Calcd. for $C_8H_8Br_2$: C, 36.40; H, 3.06; MR_D, 51.14. Found: C, 36.75, 36.86; H, 3.15, 3.13; MR_D, 51.07.

[2-(o-Chlorophenyl)ethyl]diphenylsilane

A solution of 2-(o-chlorophenyl)ethylmagnesium bromide, prepared in a 71.4% yield from 35.0 g. (0.16 mole) of 2-(o-chlorophenyl)ethyl bromide and 4.8 g. (0.2 g. atom) of magnesium in 150 ml. of ether, was added to 24.96 g. (0.114 mole) of chlorodiphenylsilane dissolved in 50 ml. of ether. After refluxing 1 hour, Color Test I was negative. Acid hydrolysis and the usual work-up gave 19.66 g. (53.4%) of pure product, b.p. 161-163° (0.002 mm.), n_D^{20} 1.6014, d_{20}^{20} 1.1136.

Anal. Calcd. for $C_{20}H_{19}ClSi$: Si, 8.7; MR_D, 99.41.

Found: Si, 8.8, 8.73; MR_D, 99.39.

There was isolated from the forerun by chromatography 1.2 g. (5.4%) of 1,4-bis-(o-chlorophenyl)butane, m.p. 52-53° (reported[63] m.p. 51-52°), and an additional 3.1 g. (8.4%) of the silane.

2:3-Benzo-1,1-diphenyl-1-silacyclopent-2-ene

From [2-(o-chlorophenyl)ethyl]diphenylsilane and sodium

To a refluxing suspension of 2.76 g. (0.12 g. atom) of sodium in 100 ml. of toluene was added 17.5 g. (0.0542 mole) of [2-(o-chlorophenyl)ethyl]diphenylsilane in 125 ml. of toluene. To determine the progress of the reaction, a 5 ml. aliquot was withdrawn and hydrolyzed after 5 hours at reflux. The usual work-up was employed to afford a small amount of oil which slowly crystallized. The infrared spectrum of the solid contained a weak silicon-hydrogen absorption band. The reaction mixture was refluxed an additional 4 hours, cooled and filtered rapidly (see Ref. 61). The insoluble material was added cautiously to absolute ethanol to destroy the excess sodium metal. The filtrate was poured into a cold ammonium chloride solution. The aqueous layer was extracted with ether and discarded. The combined organic layer was dried over anhydrous magnesium sulfate and distilled. The residue crystallized upon seeding to give 12.71 g. of solid, m.p. 55-60°. Two recrystallizations from absolute ethanol, decolorizing

each time with Norit, afforded 9.65 g. (62.1%) of pure product, m.p. 62-63°.

Anal. Calcd. for $C_{20}H_{18}Si$: Si, 9.81. Found: Si, 9.81, 9.63.

From 2-(o-bromophenyl)ethyl bromide and dichlorodiphenylsilane To 2.4 g. (0.1 g. atom) of magnesium in 5 ml. of tetrahydrofuran was added dropwise a solution of 5.28 g. (0.02 mole) of 2-(o-bromophenyl)ethyl bromide in 85 ml. of the same solvent. The reaction started immediately and the addition was completed over a 1 hour period. The mixture was stirred 18 hours at room temperature, refluxed 1 hour and filtered. Titration of an aliquot indicated a 75% yield of the double Grignard reagent. The solution was added to 3.8 g. (0.015 mole) of dichlorodiphenylsilane. The reaction mixture was refluxed 1 hour at which time Color Test I was negative. Subsequent to hydrolysis, the organic layer was dried and distilled. Treatment of the residual oil with petroleum ether (b.p. 60-70°) gave 0.55 g. (17%) of diphenylsilanediol, m.p. 146-148°, identified by mixture melting point. The filtrate was concentrated and treated with absolute ethanol. Filtration gave 2.21 g. (51.5%) of colorless solid, m.p. 61-63°. The solid was identified as 2:3-benzo-1,1-diphenyl-1-silacyclopent-2-ene by a mixture melting point determination and by comparison of the infrared spectra.

From 2:3-benzo-1-phenyl-1-silacyclopent-2-ene Phenyllithium (0.0055 mole) was added to 1.07 g. (0.0051 mole) of 2:3-benzo-1-phenyl-1-silacyclopent-2-ene in 5 ml. of ether and refluxed 18 hours. Hydrolysis and the usual work-up gave 0.6 g. (41.1%) of colorless crystals, m.p. 62-63.5°. A mixed melting point with an authentic sample of 2:3-benzo-1-1-diphenyl-1-silacyclopent-2-ene was not depressed.

[2-(o-Chlorophenyl)ethyl]phenylsilane

2-(o-chlorophenyl)ethylmagnesium bromide was prepared in a 72.8% yield from 39.13 g. (0.178 mole) of 2-(o-chlorophenyl)ethyl bromide and 4.8 g. (0.2 g. atom) of magnesium in 150 ml. of ether and subsequently added to 14.03 g. (0.13 mole) of phenylsilane dissolved in 150 ml. of tetrahydrofuran. After stirring overnight, the ether was distilled and the reaction mixture refluxed for 1.5 hours. After acid hydrolysis and the customary work-up, there was obtained 13.86 g. (43.3%) of pure product, b.p. 138-142° (0.6 mm.), n_D^{20} 1.5756, d_{19}^{19} 1.0913.

Anal. Calcd. for $C_{14}H_{15}ClSi$: C, 68.13; H, 6.13; Si, 11.38; MR_D, 75.22. Found: C, 68.71, 68.69; H, 6.34, 6.53; Si, 10.78; MR_D, 74.75.

2:3-Benzo-1-phenyl-1-silacyclopent-2-ene

[2-(o-chlorophenyl)ethyl]phenylsilane (20.65 g., 0.084 mole) in 100 ml. of dry toluene was added to a refluxing

suspension of 3.86 g. (0.16 g. atom) of sodium in 100 ml. of toluene. The solution became purple soon after the addition was commenced. The addition was completed over a 1.5 hour period. After refluxing three hours, a 5 ml. aliquot was withdrawn and hydrolyzed. After the usual work-up, the infrared spectrum of the residual oil contained a strong absorption band at 12.2μ, characteristic of an Ar_2RSiH system.[66] The band at 10.7μ, characteristic of the $ArRSiH_2$ system, had almost disappeared. The reaction mixture was refluxed an additional 2.5 hours, cooled, and filtered through a previously dried Büchner funnel. During this process it was necessary to change filter paper several times and to work rapidly.[61]

The filtrate was poured into an ice-sulfuric acid mixture. The aqueous layer was extracted with ether and discarded. The organic layer was dried and evaporated. The resulting material was distilled at reduced pressure to give 9.57 g. (54.3%) of colorless liquid, b.p. 125-126° (1.5 mm.), n_D^{20} 1.5998, d_{20}^{20} 1.0587.

Anal. Calcd. for $C_{14}H_{14}Si$: C, 79.94; H, 6.71; MR_D, 68.05. Found: C, 78.70, 78.68; H, 6.83, 6.89; MR_D, 67.97.

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[66] R. N. Kniseley, V. A. Fassel, and E. E. Conrad, Spectrochim. Acta, 13, 651 (1959).

Dibenzyl[2-(o-chlorophenyl)ethyl]silane

A solution of 12.11 g. (0.057 mole) of dibenzylsilane in 50 ml. of tetrahydrofuran was treated with 0.057 mole of 2-(o-chlorophenyl)ethylmagnesium bromide, prepared from 17.6 g. (0.08 mole) of 2-(o-chlorophenyl)ethyl bromide and 2.43 g. (0.1 g. atom) of magnesium in 100 ml. of ether. The ether was distilled and the tetrahydrofuran solution refluxed 17 hours. After acid hydrolysis ether was added and the layers separated. The aqueous layer was extracted with ether and dried. The concentrated organic layer was distilled to give 10.48 g. (52.4%) of product, b.p. 166-168° (0.01 mm.), n_D^{20} 1.5954, d_{20}^{20} 1.0965.

Anal. Calcd. for $C_{22}H_{23}ClSi$: Si, 8.00; MR_D, 108.55. Found: Si, 8.18, 8.18; MR_D, 108.82.

2:3-Benzo-1,1-dibenzyl-1-silacyclopent-2-ene (attempted)

A mixture of 7.81 g. (0.0223 mole) of dibenzyl-[2-(o-chlorophenyl)ethyl]silane and 1.15 g. (0.05 g. atom) of sodium in 100 ml. of toluene was refluxed 48 hours. During this time, there was no evidence of a reaction. The reaction mixture was allowed to cool and the supernatant liquid pipetted from the sodium and hydrolyzed, with caution, by pouring into cold dilute sulfuric acid. Ether was added and the organic layer separated and dried. Distillation gave 5.83 g. (74.6%) recovery of starting material, confirmed by com-

parison of the infrared spectra.

2:3-Benzo-1,1-diphenyl-1-stannacyclopent-2-ene

To a solution of 5.28 g. (.0153 mole) of diphenyltin dichloride in 5 ml. of tetrahydrofuran was added a tetrahydrofuran solution (87 ml.) containing 0.0153 mole of the di-Grignard reagent of 2-(o-bromophenyl)ethyl bromide. After refluxing 2 hours, the reaction mixture was hydrolyzed. The aqueous layer was extracted thoroughly with ether and the combined organic layer dried. Evaporation under an air-jet gave a viscous oil. The oil was taken up in petroleum ether (b.p. 60-70°) and chromatographed over alumina. Elution with the same solvent gave 0.2 g. (2.5%) of colorless crystals, m.p. 73-74.5°, after recrystallization from 95% ethanol. The analytical sample melted at 73.5-74.5°.

Anal. Calcd. for $C_{20}H_{18}Sn$: C, 63.71; H, 4.81. Found: C, 64.07, 64.00; H, 4.70, 4.81.

Further elution of the column gave a yellow oil in several fractions.

o-Chlorobenzylchloromethyldimethylsilane

Chloromethyldimethylchlorosilane (15.73 g., 0.11 mole) in 25 ml. of ether was treated with 0.11 mole of o-chlorobenzylmagnesium chloride suspended in 300 ml. of ether. Color Test I was negative after 4 hours at reflux. The mixture was

poured into dilute hydrochloric acid and worked up in the usual manner. Evaporation of the solvent gave an oil which was distilled under reduced pressure to give 12.94 g. of an oil, boiling over the range 49-135° (11 mm.), and 7.73 g., boiling over the range 135-139° (11 mm.).

The second fraction was redistilled to give 3.0 g. (11.7%) of pure product, b.p. 140-141° (11 mm.), n_D^{20} 1.5355, d_{20}^{20} 1.1303.

Anal. Calcd. for $C_{10}H_{14}Cl_2Si$: C, 51.50; H, 6.05; MR_D, 64.45. Found: C, 51.74, 51.56; H, 6.27, 6.10; MR_D, 64.33.

o,o'-Dichlorobibenzyl, the coupling product of the Grignard reagent, was isolated from some of the fractions.

In a repeat run, the desired product was prepared in a 49.2% yield.

3:4-Benzo-1,1-dimethyl-1-silacyclopent-3-ene (attempted)

Using the method of Read, et al.,[67] o-chlorobenzylchloromethyldimethylsilane (10.79 g., 0.0463 mole) was added slowly to fine pieces of sodium (2.3 g., 0.1 g. atom) covered with ether while maintaining the temperature below 30°. The mixture was allowed to stand 2 days at room temperature with occasional shaking. At the end of this time, the black mixture was diluted with ether and the excess sodium destroyed

[67] R. R. Read, L. S. Foster, A. Russell, and V. L. Simril, Org. Syntheses, 25, 11 (1945).

with ethanol. The aqueous layer was neutralized after hydrolysis, extracted with ether and discarded. The combined organic layer was dried and evaporated. The resulting material was distilled at reduced pressure to give 0.70 g. of colorless liquid, boiling over the range 70-85° (36 mm.), and a large amount of dark distillation residue. The low boiling fractions were vapor phase chromatographed. There appeared to be 3 components, two of which were present in very small amounts. The major component was collected and identified as benzyltrimethylsilane, n_D^{20} 1.4937; reported[68] n_D^{20} 1.4916. The infrared spectrum was identical with that of an authentic sample.

The distillation residue was distilled further, but only 0.46 g. of material boiling over the range 113-140° (20 mm.) could be collected. These were not investigated further.

In a second run using molten sodium in toluene, similar results were obtained.

3:4-Benzo-1,1-diphenyl-1-silacyclopent-3-ene (attempted)

To a suspension of 4.81 g. (0.2 g. atom) of magnesium turnings in 30 ml. of tetrahydrofuran was added dropwise a solution of 26.4 g. (0.1 mole) of α,α'-dibromo-o-xylene and 25.3 g. (0.1 mole) of dichlorodiphenylsilane dissolved in

[68] H. Gilman and F. J. Marshall, J. Am. Chem. Soc., 71, 2066 (1949).

100 ml. of tetrahydrofuran. The reaction began immediately, and the addition was completed over a 2.5 hour period. The mixture was refluxed 1 hour and then stirred overnight at room temperature. Hydrolysis was effected by pouring the suspension into water. Ether was added and the layers separated. The aqueous layer was extracted thoroughly with ether and discarded. The organic layer was filtered to remove 1.67 g. (2.3%) of solid, m.p. 290-310°, identified as octaphenylcyclotetrasilane[69] by mixture melting point and by comparison of the infrared spectra. Recrystallization from benzene raised the melting point to 313-317°.

The filtrate was dried with anhydrous sodium sulfate and concentrated. The oily residue was distilled to give a forerun distilling up to 140° at 0.01 mm., and then 0.97 g. of an oil, boiling over the range 142-175° (0.01 mm.). The forerun, which had solidified, was treated with ethanol and filtered to give 0.5 g. of solid, m.p. 106-109°. Recrystallization from ethanol raised the melting point to 107.5-109°. The infrared spectrum did not contain absorption bands characteristic of the silicon-phenyl linkage. The compound is probably s-dibenzcyclooctadiene; reported[70] m.p. 108.5°. The higher boiling fraction crystallized upon the addition of ethanol.

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[69] A. W. P. Jarvie, H. J. S. Winkler, D. J. Peterson, and H. Gilman, ibid., 83, 1921 (1961).

[70] W. Baker, R. Banks, D. R. Lyon, and F. G. Mann, J. Chem. Soc., 27 (1945).

Recrystallization from the same solvent gave 0.2 g. of solid, m.p. 186-187°. A second recrystallization from petroleum ether (b.p. 60-70°) did not alter the melting point. This compound is thought to be s-tribenzcyclododecatriene; reported[70] m.p. 184.5°. Silicon-phenyl absorption bands were also absent in its infrared spectrum.

The distillation residue was taken up in ether and filtered to give 0.57 g. of a solid, m.p. 210-220°. Recrystallization from a benzene-petroleum ether (b.p. 60-70°) mixture afforded 0.4 g. of a solid melting at 233-236°. The melting point was not depressed when admixed with an authentic sample of octaphenylcyclotetrasilanoxide,[71] and the infrared spectra were identical.

The filtrate was concentrated to give a viscous oil which could not be further purified by chromatography and crystallization techniques.

3-(o-Chlorophenyl)propanol-1

An ethereal solution of o-chlorobenzylmagnesium chloride,[60] prepared from 161 g. (1 mole) of o-chlorobenzyl chloride and 26.75 g. (1.1 g. atoms) of magnesium in 1000 ml. of ether, was cooled in an ice-bath and a two-fold excess of ethylene oxide in 100 ml. of ether added dropwise. A sticky

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[71] A. W. P. Jarvie and H. Gilman, Chem. and Ind., 1271 (1960).

solid slowly separated. When the addition was complete, Color Test I was negative. Dilute sulfuric acid was added slowly, followed by separation of the layers. The aqueous layer was extracted with ether and the combined organic layer dried. The concentrated oil was distilled at 65° (45 mm.) to remove the forerun, then at 12 mm. to give 119.0 g. (67%) of product, b.p. 151-154° (12 mm.), $d_{19.3}^{19.3}$ 1.1569, $n_D^{19.3}$ 1.5440.

Anal. Calcd. for $C_9H_{11}ClO$: C, 63.33; H, 6.50; Cl, 20.77; MR_D, 46.80. Found: C, 62.92, 62.73; H, 6.48, 6.53; Cl, 20.41, 40.45; MR_D, 46.56.

Treatment of a portion of the alcohol with 1-naphthyl isocyanate gave the 1-naphthylcarbamate, m.p. 105.5-107°, after two recrystallizations from petroleum ether (b.p. 60-70°).

In two similar runs, 3-(o-chlorophenyl)propanol-1 was prepared in yields of 80 and 71.4%, respectively.

3-(o-Chlorophenyl)propyl bromide

A flask containing 115.5 g. (0.677 mole) of 3-(o-chlorophenyl)propanol-1 was immersed in an ice-bath and treated with 9.47 g. (0.35 mole) of phosphorus tribromide. The mixture was heated 1 hour at 100°, cooled and poured onto ice. Ether was added and the layers separated. The neutral organic layer was dried and distilled to give 129.7 (82%) of product, b.p. 84-88° (3.5 mm.), d_{20}^{20} 1.4339, n_D^{20} 1.5612.

Anal. Calcd. for $C_9H_{10}BrCl$: C, 46.29; H, 4.32; MR_D, 52.93. Found: C, 46.33, 46.40; H, 4.36, 4.20; MR_D, 52.88.

In two other preparations, the propyl bromide derivative was prepared in yields of 90.3 and 87.2%, respectively.

In some conversions to the bromide, the distillates would become cloudy upon standing. To obtain pure material, the cloudy product was dissolved in petroleum ether (b.p. 60-70°) and chromatographed on alumina. Distillation of the eluates gave the pure product.

4-(o-Chlorophenyl)butyric acid

3-(o-Chlorophenyl)propyl bromide (5.84 g., 0.025 mole) in 45 ml. of ether was added slowly to 0.73 g. (0.03 g. atom) magnesium turnings in 5 ml. of ether. The reaction started immediately, and, subsequent to complete addition, the mixture was refluxed 1 hour. The filtered solution was poured onto a slurry of Dry Ice and ether and worked up as described previously. Extraction of the acidified basic extracts with ether and removal of the ether gave 3.25 g. (65.7%) of acid, m.p. 86-88°. Recrystallization from petroleum ether (b.p. 60-70°) raised the melting point to 89-91°. The analytical sample melted at 90-91°.

Anal. Calcd. for $C_{10}H_{11}ClO_2$: C, 60.46; H, 5.58. Found: C, 60.68, 60.79; H, 5.60, 5.64.

3-(o-Bromophenyl)propanol-1

3-(o-Bromophenyl)propanol-1 was prepared in slightly improved yields of 53 and 57% from the Grignard reagent of o-bromobenzyl bromide and ethylene oxide according to the method of Beeby and Mann[62]; b.p. 115-117° (0.8 mm.), n_D^{20} 1.5699.

In one run, o,o'-dibromobibenzyl, m.p. 83.5-85°, was isolated from the viscous distillation residue. The compound was identified by a mixed melting point determination.

3-(o-Bromophenyl)propyl bromide

3-(o-Bromophenyl)propanol-1 was converted into the bromide by heating with phosphorus tribromide according to published directions[62] in yields of 78.8 and 78.2%, b.p. 128-129° (1.3 mm.), n_D^{20} 1.5830, d_{20}^{20} 1.668.

Anal. Calcd. for $C_9H_{10}Br_2$: C, 38.88; H, 3.63; MR_D, 55.62. Found: C, 39.57, 39.38; H, 3.80, 3.75; MR_D, 55.69.

4-(o-Carboxyphenyl)butyric acid

Five milliliters of a solution of 3-(o-bromophenyl)propyl bromide (6.95 g., 0.025 mole) in 95 ml. of tetrahydrofuran was added to 1.44 g. (0.06 g. atom) of magnesium in 5 ml. of the same solvent. When the exothermic reaction began, the addition was completed over a 1.5 hour period. The mixture was stirred 3 hours at room temperature and heated gently for

1 hour. The yield of the double Grignard reagent, as determined by titration of an aliquot, was 76%. The mixture was carbonated by pouring jet-wise on a slurry of Dry Ice and ether. Subsequent to acid hydrolysis, the aqueous layer was separated, extracted with ether and discarded. The organic layer was extracted with 200 ml. of 5% sodium hydroxide. The basic extract was acidified with concentrated hydrochloric acid and filtered to give 4.02 g. of impure acid, m.p. 128-132°. Recrystallization from an ethyl acetate-heptane mixture yielded 2.65 g. (63.5%) of pure acid, m.p. 138-139°, identified by mixture melting point and by comparison of the infrared spectra.[72]

3-Triphenylsilylpropyl *p*-toluenesulfonate

To a stirred solution of 48.56 g. (0.151 mole) of 3-(triphenylsilyl)propanol-1[73] in 80 ml. of dry pyridine cooled to -10° was added 32.4 g. (.17 mole) of *p*-toluenesulfonyl chloride at such a rate that the temperature did not rise above 20°. After stirring 3 hours below 20°, the reaction mixture was poured into 150 ml. of concentrated hydrochloric acid in 500 ml. of ice water. The solid was removed

[72] P. D. Gardner, *J. Am. Chem. Soc.*, *78*, 3421 (1956). A sample of the acid was kindly furnished by Dr. P. D. Gardner.

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

by filtration and recrystallized from petroleum ether (b.p. 60-70°) to yield 60.9 g. (85.4%) of product, m.p. 102-104.5°. A portion was recrystallized from absolute ethanol to afford an analytical sample melting at 103-104.5°.

Anal. Calcd. for $C_{28}H_{28}O_3SSi$: Si, 5.94. Found: Si, 5.80, 5.87.

[3-(o-Chlorophenyl)propyl]diphenylsilane

A solution of 21.9 g. (0.1 mole) of chlorodiphenylsilane was treated with 0.1 mole of 3-(o-chlorophenyl)propylmagnesium bromide, prepared in an 88% yield from 26.9 g. (0.115 mole) of 3-(o-chlorophenyl)propyl bromide and 3.9 g. (0.16 g. atom) of magnesium turnings in 250 ml. of ether. After refluxing 1 hour, Color Test I was negative. Subsequent to acid hydrolysis, work-up gave 27.82 g. (82.7%) of an oil, b.p. 162-168° (0.005 mm.), n_D^{20} 1.5923, d_{20}^{20} 1.1055.

Anal. Calcd. for $C_{21}H_{21}ClSi$: Si, 8.34. Found: Si, 8.34, 8.18.

2:3-Benzo-1,1-diphenyl-1-silacyclohex-2-ene

From [3-(o-chlorophenyl)propyl]diphenylsilane and sodium

A solution of 25.45 g. (0.0755 mole) of [3-(o-chlorophenyl)-propyl]diphenylsilane in 100 ml. of dry toluene was added to 100 ml. of refluxing toluene containing 4.04 g. (0.18 g. atom) of molten sodium. The brown solution was refluxed 4 hours,

then stirred 12 hours at room temperature. Ethanol was added cautiously and the mixture poured onto ice. Ether was added and the organic layer separated and dried. Distillation gave 14.74 g. of a colorless liquid, boiling over the range 151-174° (0.006 mm.) which crystallized upon standing. Recrystallization from absolute ethanol gave 9.74 g. (43.8%) of pure product, m.p. 76-77.5°.

Anal. Calcd. for $C_{21}H_{20}Si$: C, 83.94; H, 6.71; Si, 9.35; Mol. wt., 300.5. Found: C, 84.09, 84.29; H, 6.64, 6.82; Si, 9.28, 9.22; Mol. wt. (cryoscopic in benzene), 291.

The distillation residue was a viscous oil which could not be further purified.

The reaction was repeated twice to give the cyclic silane in yields of 67.8 and 60.8%. In one reaction, the cyclic silane was isolated without prior distillation. Several recrystallizations were required before pure product was obtained.

From 3-triphenylsilylpropyl p-toluenesulfonate (attempted)

A mixture of 3-triphenylsilylpropyl p-toluenesulfonate (30 g., 0.063 mole) and previously dried sodium formate (5.15 g., 0.076 mole) in 500 ml. of dry formic acid[74] was stirred 10 hours at room temperature. A large quantity of solid remained. The temperature was raised to 70° and the stirring continued for 48 hours. The solid-free solution was then poured into a

[74]S. Winstein and H. Marshall, ibid., 74, 1120 (1952).

large excess of water and extracted with ether. The ether extracts were washed neutral with sodium bicarbonate and dried. The solvent was distilled; the resulting solid was taken up in petroleum ether (b.p. 60-70°) and poured onto a column of alumina.

Elution of the column with petroleum ether gave 0.04 g. of a solid, m.p. 81-82°, after recrystallization from ethanol. Mixed melting points with authentic 2:3-benzo-1,1-diphenyl-1-silacyclohex-2-ene and allyltriphenylsilane were depressed. Further elution with cyclohexane gave 2.04 g. (12.1%) of solid, m.p. 227-229°. The melting point was not depressed when admixed with an authentic sample of hexaphenyldisiloxane and their infrared spectra were superimposable. Benzene elution gave 11.7 g. (57.9%) of 3-triphenylsilylpropanol-1, m.p. 137-139°, identified by mixed melting point. Subsequent to elution with methanol, 0.2 g. of a solid, m.p. 137-143°, was isolated. Recrystallization from cyclohexane raised the melting point to 149-150°. The compound was identified as triphenylsilanol by mixture melting point and by comparison of the infrared spectra.

<u>From 3-(o-bromophenyl)propyl bromide and dichlorodiphenylsilane</u> <u>(a) In an ether-tetrahydrofuran mixture</u> To a suspension of 2.43 g. (0.1 g. atom) of magnesium turnings in 20 ml. of a 1:1 mixture of ether and tetrahydrofuran was added 5.56 g. (0.02 mole) of 3-(o-bromophenyl)propyl bromide

in 30 ml. of the same solvent mixture. When the reaction started the flask was immersed in an ice-bath and the addition completed over a 45 minute period. The mixture was stirred 10 hours at this temperature then allowed to stand 8 hours at room temperature. Dry benzene (50 ml.) was added to the suspension to dissolve the precipitated Grignard reagent and then filtered. Titration of an aliquot indicated a 65% yield of the organomagnesium compound, assuming the base present to be in the form of the di-Grignard derivative. The organomagnesium reagent was added to 3.42 g. (0.0135 mole) of dichlorodiphenysilane dissolved in 20 ml. of ether. When the addition was complete Color Test I was negative. Dilute hydrochloric acid was added and the layers separated. The organic layer was dried and the concentrated oil treated with hot petroleum ether (b.p. 60-70°) to give 0.61 g. (21%) of a solid, m.p. 162.5-163.8°. The melting point was not depressed when mixed with an authentic sample of diphenylsilanediol, and the infrared spectra were superimposable.

Anal. Calcd. for $C_{12}H_{12}O_2Si$: Si, 12.99. Found: Si, 12.90.

The petroleum ether filtrate was concentrated and the oily residue distilled under reduced pressure to give 1.35 g. of an oil, boiling over the range 170-174° (0.007 mm.). The oil partially crystallized and treatment with ethanol gave 0.47 g. (11%) of 2:3-benzo-1,1-diphenyl-1-silacyclohex-2-ene,

m.p. 75-77°, identified by mixed melting point and by comparison of the infrared spectra.

(b) In tetrahydrofuran The double Grignard reagent of 3-(o-bromophenyl)propyl bromide was prepared in an 82% yield by adding 5.56 g. (0.02 mole) of the bromide in 85 ml. of tetrahydrofuran to 1.2 g. (0.05 g. atom) of magnesium and a crystal of iodine in 5 ml. of tetrahydrofuran. The mixture was stirred 18 hours at room temperature, then refluxed 1.5 hours. The filtered organomagnesium compound was added to 3.87 g. (0.0153 mole) of dichlorodiphenylsilane dissolved in 10 ml. of tetrahydrofuran. Color Test I was negative after refluxing 1 hour. After hydrolysis and the work-up as described above, diphenylsilanediol was isolated in a 21.5% yield. The silane was isolated without distillation by removal of the petroleum ether (b.p. 60-70°) and addition of ethanol to the residual oil. The solid was filtered to give 3.66 g. of impure product, m.p. 70-74°. Recrystallization from 95% ethanol afforded 2.29 g. (54.4%) of colorless crystals, m.p. 78-79.5°. There was no depression of the melting point when admixed with an authentic sample.

From 2:3-benzo-1-phenyl-1-silacyclohex-2-ene An ethereal solution containing 0.0043 mole of phenyllithium was added to 0.94 g. (0.0042 mole) of 2:3-benzo-1-phenyl-1-silacyclohex-2-ene in 10 ml. of ether, and the reaction mixture was refluxed 18 hours. After the usual work-up, the

resulting material was treated with hot ethanol to give 0.9 g. (71.4%) of colorless crystals, m.p. 77-79°. A mixed melting point with an authentic sample of 2:3-benzo-1,1-diphenyl-1-silacyclohex-2-ene was undepressed.

From [3-(o-chlorophenyl)propyl]diphenylsilane and lithium

To finely cut lithium wire (0.7 g., 0.1 g. atom) in 50 ml. of tetrahydrofuran was added 30 ml. of a solution of [3-(o-chlorophenyl)propyl]diphenylsilane (14.5 g. 0.043 mole) in 50 ml. of tetrahydrofuran. The mixture was cooled to 0-5° and, after about 20 min., the reaction began with the formation of a green color. The solution became deep red in color while completing the addition of the silane. Color Test I was positive. The reaction mixture was stirred 0.5 hour at 0-5°, and then filtered through a glass-wool plug into a second flask and stirred overnight at room temperature. The tetrahydrofuran was distilled and 100 ml. of dry toluene added. After refluxing 1 hour, the color test was negative. The red solution was poured into iced sulfuric acid. Ether was added and the organic layer separated, dried over magnesium sulfate and distilled. There was obtained 2.62 g. of an oil which slowly crystallized upon standing. Recrystallization from absolute ethanol gave 1.27 g. (9.8%) of the cyclic silane, m.p. 75-77°, identified by mixed melting point and by comparison of the infrared spectra.

The distillation residue was transferred to an Erlenmeyer

flask and treated with various solvents in an attempt to effect a separation. Chromatography of the oil on a column of alumina in the usual manner gave a trace of the cyclic silane with cyclohexane and a pale green oil with benzene and ethyl acetate. Attempts to purify these oils failed.

Reaction of 3-triphenylsilylpropyl *p*-toluenesulfonate with triphenylsilyllithium

Run 1 (1:1) Triphenylsilyllithium (0.015 mole), prepared by lithium cleavage of 3.89 g. (0.0075 mole) of hexaphenyldisilane in 50 ml. of tetrahydrofuran,[55] was added to 7.09 g. (0.015 mole) of 3-triphenylsilylpropyl *p*-toluenesulfonate in 12 ml. of tetrahydrofuran. Heat was evolved and a solid was formed. After the addition was completed, Color Test I was negative. The reaction mixture was hydrolyzed, ether was added and the layers separated. The concentrated organic layer was treated with petroleum ether (b.p. 60-70°) and filtered to give 0.22 g. (5.6%) of hexaphenyldisilane, m.p. 356-359°.

The filtrate was chromatographed over alumina. Elution with petroleum ether and cyclohexane gave 3.44 g. of colorless solid, m.p. 125-195°. Recrystallization from petroleum ether gave 2.86 g. (34%) of 1,3-bis(triphenylsilyl)propane, m.p. 131-132°. A mixed melting point with an authentic sample[75]

[75]H. Gilman, D. Aoki, and D. Wittenberg, *ibid.*, *81*, 1107 (1959).

was not depressed.

Using benzene, a small amount of oil was eluted. Further elution with methanol gave 2.69 g. of material melting 122-132°. Recrystallization from a benzene-petroleum ether mixture gave 2.0 g. (41.6%) of 3-triphenylsilylpropanol-1, m.p. 135-137°, identified by mixture melting point and by comparison of the infrared spectra.

Run 2 (1:2) A tetrahydrofuran solution of triphenylsilyllithium[55] (0.03 mole) was added to 7.09 g. (0.015 mole) of the p-toluenesulfonate dissolved in tetrahydrofuran. Color Test I was negative after three-fourths (0.023 mole) of the organometallic compound had been added. When the addition was complete, the color test was positive. The reaction mixture was stirred 18 hours at room temperature and acid hydrolyzed. The aqueous layer was extracted several times with ether and discarded. The combined organic layer was dried and evaporated. There was no hexaphenyldisilane. The residual material was taken up in petroleum ether (b.p. 60-70°) and chromatographed on alumina. Elution with petroleum ether gave 0.75 g. (9.6%) of triphenylsilane, m.p. 45-47°, which had a sulfur odor. Further elution with the same solvent afforded 0.25 g. (2.5%) of tetraphenylsilane, m.p. 225-228°, after recrystallization from petroleum ether. Using cyclohexane as the eluant, 4.5 g. (53.5%) of 1,3-bis(triphenylsilyl)propane, m.p. 131-132°, was isolated. Continued

elution of the column with ethyl acetate gave 0.45 g. (9.4%) of 3-triphenylsilylpropanol-1, m.p. 133-135°, and then with methanol, 0.42 g. (5.1%) of triphenylsilanol, m.p. 150-152°. All compounds were identified by mixture melting point determinations with authentic samples and by comparison of the infrared spectra.

Reaction of n-butyl p-toluenesulfonate with triphenylsilyllithium

To a solution of n-butyl p-toluenesulfonate (10.96 g., 0.048 mole) in 50 ml. of tetrahydrofuran, there was added 0.096 mole of triphenylsilyllithium, prepared from 24.92 g. (0.048 mole) of hexaphenyldisilane and 1.39 g. (0.2 g. atom) of lithium in 200 ml. of tetrahydrofuran. When the addition was complete, Color Test I was indefinite; the green color of the color test developed very slowly with a large excess of iodine. The mixture was stirred overnight and hydrolyzed. Ether was added and the layers separated. The organic layer was worked up in the usual manner and the residual oil chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 12.04 g. of impure n-butyltriphenylsilane, m.p. 82-86°. Recrystallization from ethanol gave 10.8 g. (71.1%) of pure product, m.p. 85-86.5°, identified by mixed melting point. The ethanol-insoluble material (1.04 g.) was recrystallized from a benzene-petroleum ether mixture to give

0.48 g. (1.5%) of tetraphenylsilane, m.p. 232-234°. The melting point was not depressed when admixed with an authentic sample and their infrared spectra were superimposable. Further elution of the column with benzene and ethyl acetate gave 1.17 g. (4.5%) of crude triphenylsilanol which was not purified further.

[3-(o-Chlorophenyl)propyl]triphenylsilane

From chlorotriphenylsilane (a) Run 1 To a solution of chlorotriphenylsilane (10.3 g., 0.035 mole) in 25 ml. of ether was added an ethereal solution containing 0.035 mole of 3-(o-chlorophenyl)propylmagnesium bromide. The ether was distilled and 75 ml. of dry xylene added. Color Test I was negative after refluxing overnight. The reaction mixture was treated with dilute acid, and the layers separated and dried. Concentration and the addition of petroleum ether (b.p. 60-70°) gave 1.0 g. (10.3%) of triphenylsilanol, m.p. 149-152°, after crystallization from cyclohexane. The petroleum ether filtrate was passed through a column of alumina. Elution with petroleum ether gave an oil which was distilled to give 4.38 g. (30.2%), b.p. 209-211° (0.015 mm.), and 1.23 g. (8.5%), b.p. 222° (0.016 mm.). The latter fraction was analyzed.

Anal. Calcd. for $C_{27}H_{25}ClSi$: Si, 6.80. Found: Si, 6.92, 6.75.

These two fractions crystallized after 3 days to give

long needles, m.p. 77.5-79°, after recrystallization from ethanol. Several months later the material melted over the range 77-87.5°.

(b) Run 2 When the reaction was repeated (18 months later), the petroleum ether filtrate was concentrated and treated with ethanol. Seeding with material melting at 77.5-79° gave 5.03 g. (34%) of solid, m.p. 84-86°. Recrystallization from absolute ethanol raised the melting point to 88-89°.

Anal. Calcd. for $C_{27}H_{25}ClSi$: Si, 6.80. Found: Si, 7.00, 6.98.

The infrared spectrum was superimposable with that of the previously prepared material.

From [3-(o-chlorophenyl)propyl]diphenylsilane An ethereal solution of phenyllithium (0.013 mole) was added to [3-(o-chlorophenyl)propyl]diphenylsilane (4.24 g., 0.013 mole) in 10 ml. of diethyl ether. After refluxing 1 hour, the mixture was poured into a saturated ammonium chloride solution. The organic layer was dried and concentrated to give, upon seeding, 4.66 g. of solid. Recrystallization from methanol and then from ethanol gave 2.3 g. (44.3%) of long flocculent needles, m.p. 77.5-79.5°. A mixture melting point with an authentic sample was not depressed. After 18 months the solid melted at 88.5-90°.

[3-(o-Chlorophenyl)propyl]triphenyltin

An ether solution containing 0.044 mole of 3-(o-chlorophenyl)propylmagnesium chloride was added to 16.77 g. (0.044 mole) of triphenyltin chloride suspended in 50 ml. of ether. Color Test I was negative after 1 hour at reflux. The reaction mixture was hydrolyzed with an ammonium chloride solution and worked up in the usual manner.

The solvent was removed by distillation and the residue poured on a column of alumina. The oil eluted with petroleum ether was distilled under reduced pressure to give 12.08 g. (55.2%) of a colorless, viscous oil, b.p. 208-211° (0.002 mm.).

Anal. Calcd. for $C_{27}H_{25}ClSn$: C, 64.39; H, 5.00. Found: C, 64.62, 64.85; H, 4.99, 5.13.

Reaction of [3-(o-chlorophenyl)propyl]triphenylsilane with magnesium (attempted)

A mixture of 2.67 g. (0.0064 mole) of the silane and 0.48 g. (0.02 g. atom) of magnesium was stirred with catalytic amounts of iodine, ethyl iodide and 1,2-dibromoethane for 2 hours at room temperature, but the reaction could not be initiated. After refluxing 1 hour Color Test I was negative. The reaction mixture was filtered through a glass-wool plug and hydrolyzed. Ether was added, and the organic layer separated and dried. Evaporation of the solvents and seeding

gave an 88% recovery of starting material.

Reaction of [3-(o-chlorophenyl)propyl]triphenylsilane with lithium

In an ether-tetrahydrofuran mixture Color Test I was negative and there was no evidence of a reaction after stirring a mixture of 3.48 g. (0.0084 mole) of 3-(o-chlorophenyl)-propyltriphenylsilane and 0.7 g. (0.1 g. atom) of cut lithium wire in 40 ml. of ether for 30 minutes at room temperature and refluxing 1.5 hours. Tetrahydrofuran (25 ml.) was added and the mixture refluxed 1 hour. Although there appeared to be no reaction, the mixture was filtered and hydrolyzed. Removal of the solvent and the addition of ethanol gave 2.9 g. (83.4%) of a solid, m.p. 84-86°. The infrared spectrum of the solid was superimposable with the starting material which melted at 77.5-79.5°. The melting point of the starting material was not depressed when the two compounds were admixed. An elemental analysis showed the presence of chlorine. The solid was recrystallized twice from absolute ethanol and once from petroleum ether (b.p. 38-45°) to give fine needles, m.p. 84.5-86.5°.

Anal. Calcd. for $C_{27}H_{25}ClSi$: Si, 6.80. Found: Si, 6.86.

The solid melted at 89.5-90° after 18 months.

In tetrahydrofuran A mixture of [3-(o-chlorophenyl)-propyl]triphenylsilane (1.28 g., 0.0031 mole) and lithium (0.07 g., 0.01 g. atom) in 10 ml. of tetrahydrofuran was stirred 50 minutes at room temperature at which time a pink color developed. The flask was immersed in an ice slurry and the stirring continued 1 hour. The black reaction mixture was poured into an ice-sulfuric acid mixture and worked up in the usual manner. The dry organic layer was concentrated to give 1.1 g. of black oil whose infrared spectrum showed a weak Si-H absorption band. The oil was poured onto a column of alumina and chromatographed. Petroleum ether (b.p. 60-70°) and cyclohexane gave traces of oils. Elution with benzene gave a viscous oil, from which no identifiable compounds could be isolated. Ethyl acetate elution also gave an oil which could not be induced to crystallize.

Reaction of [3-(o-chlorophenyl)propyl]triphenylsilane with sodium

To a cold suspension of 0.23 g. (0.01 g. atom) of sodium in 20 ml. toluene was added 1.91 g. (0.0046 mole) of [3-(o-chlorophenyl)propyl]triphenylsilane. Although a pink color developed, the reaction appeared to be slow, therefore, the mixture was refluxed 10 hours. After cooling, ethanol was added and the mixture was poured into iced hydrochloric acid. Ether was added and the organic layer was separated and dried.

Removal of the solvents gave 1.43 g. of a yellow oil which was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 0.45 g. (32.4%) of 2:3-benzo-1,1-diphenyl-1-silacyclohex-2-ene, m.p. 78.5-80°, identified by mixture melting point and by comparison of the infrared spectra. Benzene eluates gave an oil which could not be purified further. The infrared spectrum did not contain absorption bands characteristic of the hydroxyl, silicon-hydrogen or siloxane groupings which may have resulted from silicon-carbon bond cleavage. Elution with ethyl acetate gave a trace of a yellow oil.

Reaction of [3-(o-chlorophenyl)propyl]diphenylsilane with magnesium (attempted)

A mixture of 5 g. (0.0149 mole) of [3-(o-chlorophenyl)-propyl]diphenylsilane and 0.24 g. (0.01 g. atom) of magnesium in 30 ml. of tetrahydrofuran was refluxed a total of 3 hours with intermittent addition of catalytic amounts of iodine and ethyl iodide. There was no evidence of a reaction. Hydrolysis and concentration of the dried organic layer gave 4.27 g. (85.4%) of recovered starting material. The infrared spectra were superimposable.

The recovered oil (4.27 g. 0.013 mole) was treated with 0.0127 mole of phenyllithium and the mixture stirred overnight. Color Test I was negative. The reaction mixture was

hydrolyzed with dilute acid and worked up in the usual manner. Subsequent to concentration of the organic layer and the addition of ethanol, there was obtained 4.28 g. of solid melting at 70-73°. Recrystallization from absolute ethanol gave 2.5 g. (47.7%) of fine needles melting over the range 75-86°. The infrared spectrum was superimposable with the [3-(o-chlorophenyl)propyl]triphenylsilane melting at 77.5-79.5° and 84.5-86.5°.

Anal. Calcd. for $C_{27}H_{25}ClSi$: Si, 6.80. Found: Si, 6.78.

Concentration of the mother liquor gave an additional 1.28 g. (24.4%) of product.

The material that was analyzed (m.p. 75-86°) melted at 89-90° after 18 months.

o-Chloroethylbenzene

o-Chlorobenzylmagnesium chloride (0.3 mole) was alkylated with 75.68 g. (0.6 mole) of dimethyl sulfate in 800 ml. of ether according to a method used to prepare n-propylbenzene.[76] The yield of product boiling at 81-84° (31 mm.) was 70.6%, n_D^{20} 1.5219, d_{20}^{20} 1.0595; reported[77] n_D^{20} 1.5218.

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[76] H. Gilman and W. E. Catlin, Org. Syntheses, Coll. Vol. 1, 471 (1941).

[77] R. R. Dreisbach and R. A. Martin, Ind. and Eng. Chem., 41, 2875 (1949).

Reaction of o-chloroethylbenzene with magnesium

Run 1 A mixture of 10.55 g. (0.075 mole) of o-chloroethylbenzene, 7.2 g. (0.3 g. atom) of magnesium turnings and catalylic amounts of iodine and ethyl iodide in 75 ml. of tetrahydrofuran was refluxed 6.5 hours before Color Test I became positive. After an additional 2 hours at reflux, the reaction products were carbonated by pouring upon a Dry Ice-ether slurry. After the usual work-up, 9.90 g. (88%) of slightly impure o-ethylbenzoic acid, m.p. 59-61.5°, was obtained. Recrystallization from water raised the melting point to 62.5-63.5°; reported[78] m.p. 68°.

A reaction of o-chlorotoluene and magnesium was carried out simultaneously with this run. Under the same conditions, the reaction began after 2.5 hours at reflux. After a total reflux time of 6.5 hours, o-toluic acid was isolated in an 82.6% yield, subsequent to carbonation.

Run 2 In a repeat run using similar quantities of reactants, the reaction could not be initiated. Color Test I was negative after 30 hours at reflux temperature. Carbonation gave no acidic products.

o-Chloropropylbenzene

This compound was prepared in a manner similar to that for the preparation of n-propylbenzene.[76] o-Chlorobenzyl-

[78] S. Gabriel and A. Michael, Ber., 10, 2199 (1877).

magnesium chloride[60] (0.2 mole) and diethyl sulfate (30.84 g., 0.2 mole) reacted to give 23.1 g. (75%) of pure product, b.p. 70-71° (8.5 mm.), n_D^{20} 1.5162, d_{20}^{20} 1.0345.

Anal. Calcd. for $C_9H_{11}Cl$: C, 69.90; H, 7.17; MR_D, 45.25. Found: C, 69.04, 69.22; H, 7.15, 7.17; MR_D, 45.17.

Reactions of o-chloropropylbenzene

With magnesium (attempted) This reaction was carried out under the same conditions that o-chlorotoluene and o-chloroethylbenzene reacted with magnesium. o-Chloropropylbenzene (11.6 g., 0.075 mole) and magnesium (7.2 g., 0.3 g. atom) in 100 ml. of tetrahydrofuran were refluxed 18 hours in the presence of catalytic amounts of iodine and ethyl iodide. Carbonation of the filtered solution and the usual work-up gave no acidic products. The organic layer was dried and distilled to give 7.51 g. (65%) of unreacted o-chloropropylbenzene.

With lithium Nine milliliters of a solution of o-chloropropylbenzene (9.31 g., 0.062 mole) in 80 ml. of tetrahydrofuran was added to cut lithium wire (1.04 g., 0.15 g. atom) in 20 ml. of tetrahydrofuran. After 5 minutes heat was evolved and a green color developed. The mixture was cooled to 5° and the remainder of the o-chloropropylbenzene solution added slowly. The red solution was stirred 5 hours between 0° and 15°. At this time the titration of an aliquot indi-

cated the presence of 0.042 mole of base. The mixture was filtered and carbonated. Basic extraction and acidification of the extracts gave an oil which could not be induced to crystallize. Distillation of the oil gave 1.93 g. (17.3%) of o-propylbenzoic acid, b.p. 164-166° (19 mm.); reported[79] b.p. 164-165° (20 mm.).

The distillate was cooled in ice to give solid o-propylbenzoic acid, m.p. 56-57.5°, after recrystallization from a water-ethanol mixture; reported[79] m.p. 58°.

[3-(o-Chlorophenyl)propyl]phenylsilane

Phenylsilane (10.72 g., 0.099 mole) in 100 ml. of tetrahydrofuran was allowed to react for 24 hours with an ethereal solution of 0.099 mole of 3-(o-chlorophenyl)propylmagnesium bromide at room temperature. The ether was distilled and the resulting tetrahydrofuran solution refluxed 1 hour. Hydrolysis was effected by pouring into an ice-sulfuric acid mixture. The usual work-up gave 20.1 g. (77.9%) of the silane, b.p. 163-165° (2.5 mm.), n_D^{20} 1.5688, d_{20}^{20} 1.075.

Anal. Calcd. for $C_{15}H_{17}ClSi$: Si, 10.77; MR_D, 79.85. Found: Si, 10.48, 10.50; MR_D, 79.48.

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[79] B. B. Elsner, H. E. Strauss, and E. J. Forbes, J. Chem. Soc., 578 (1957).

2:3-Benzo-1-phenyl-1-silacyclohex-2-ene

A mixture of [3-(o-chlorophenyl)propyl]phenylsilane (19.0 g., 0.073 mole) and sodium (3.36 g., 0.15 g. atom) in 200 ml. of toluene was refluxed 5 hours and cooled. The insoluble material was filtered,[61] washed with dry toluene, and destroyed in ethanol. The filtrate was poured onto ice made acidic with sulfuric acid. Work-up in the usual manner gave an oil, which was distilled under reduced pressure to give 12.94 g. (79.2%) of product, b.p. 143-145.5° (2.5 mm.), $n_D^{18.5}$ 1.6000, $d_{18.5}^{18.5}$ 1.0569.

Anal. Calcd. for $C_{15}H_{16}Si$: C, 80.29; H, 7.19; MR_D, 72.68. Found: C, 79.98, 80.05; H, 7.27, 7.38; MR_D, 72.48.

2:3-Benzo-1-methyl-1-silacyclohex-2-ene

3-(o-Bromophenyl)propyl bromide (22.3 g., 0.082 mole) was allowed to react with 4.86 g. (0.2 g. atom) of magnesium in 280 ml. of tetrahydrofuran for 18 hours at room temperature and then filtered. The yield of the double Grignard reagent was 73.5%. This solution was added to 6.79 g. (0.059 mole) of methyldichlorosilane[80] dissolved in 50 ml. of tetrahydrofuran. After refluxing overnight, Color Test I was negative. The mixture was cooled and poured into dilute sulfuric acid. Ether was added and the layers separated. The aqueous layer

[80] Purchased from the Anderson Chemical Div. of the Stauffer Chemical Company.

was extracted several times with ether and discarded. The combined organic layer was dried over magnesium sulfate and evaporated. The oily residue was taken up in petroleum ether (b.p. 60-70°) and passed through a column of alumina. The petroleum ether eluate was concentrated and the oil distilled to give 3.13 g. (33.3%) of product, b.p. 106-106.5° (21 mm.), n_D^{20} 1.5442.

Anal. Calcd. for $C_{10}H_{14}Si$: C, 73.99; H, 8.69. Found: C, 74.53, 74.62; H, 8.60, 8.63.

[3-(o-Chlorophenyl)propyl]phenyl-o-tolylsilane

Phenyl-o-tolylsilane[81] (13.88 g., 0.07 mole) in 60 ml. of tetrahydrofuran was treated with an ethereal solution of 0.07 mole of 3-(o-chlorophenyl)propylmagnesium bromide, prepared in an 88% yield from 18.6% g. (0.08 mole) of 3-(o-chlorophenyl)propyl bromide and 2.19 g. (0.09 g. atom) of magnesium. The ether was distilled and the resulting solution refluxed 16 hours. The reaction mixture was hydrolyzed and worked up in the usual manner. Distillation of the reaction products gave 15.6 g. (63.4%) of colorless product, b.p. 177-180° (0.004 mm.), n_D^{20} 1.5964, d_{20}^{20} 1.1008.

Anal. Calcd. for $C_{22}H_{23}ClSi$: Si, 8.00; MR_D, 108.67. Found: Si, 7.90, 7.87; MR_D, 108.55.

[81] H. Gilman and E. A. Zuech, J. Am. Chem. Soc., 81, 5925 (1959).

2:3-Benzo-1-phenyl-1-o-tolyl-1-silacyclohex-2-ene

A mixture of 15.97 g. (0.0455 mole) of [3-(o-chlorophenyl)-propyl]phenyl-o-tolylsilane and 2.19 g. (0.095 g. atom) of sodium in 200 ml. of dry toluene was refluxed 11.5 hours and cooled. The excess sodium was destroyed with ethanol and the reaction mixture hydrolyzed. After the usual work-up, an oil was obtained which was distilled under reduced pressure to give 11.2 g. of viscous oil, boiling over the range 163-167° (0.003 mm.). The oily fractions were treated with ethanol to give 8.97 g. (62.7%) of product, m.p. 82-85°. Recrystallization of a portion from ethanol raised the melting point to 85-87°.

Anal. Calcd. for $C_{22}H_{22}Si$: Si, 8.93. Found: Si, 9.02, 8.88.

[3-(o-Chlorophenyl)propyl]methylphenylsilane

3-(o-Chlorophenyl)propylmagnesium bromide (0.114 mole) was added to an ethereal solution of 17.8 g. (0.114 mole) of methylphenylchlorosilane. After stirring 1 hour, Color Test I was negative. Hydrolysis and distillation of the dried organic layer gave 25.22 g. (80.6%) of material, b.p. 123-125° (0.002 mm.), n_D^{20} 1.5610, d_{20}^{20} 1.062.

Anal. Calcd. for $C_{16}H_{19}ClSi$: Si, 10.22; MR_D, 84.22. Found: Si, 10.03, 10.09; MR_D, 83.82.

2:3-Benzo-1-methyl-1-phenyl-1-silacyclohex-2-ene

A solution of 25.15 g. (0.092 mole) of [3-(o-chlorophenyl)propyl]methylphenylsilane in 125 ml. of toluene was added to 4.37 g. (0.19 g. atom) of molten sodium in 100 ml. of toluene. The mixture was refluxed 6 hours, cooled, and treated with ethanol to destroy excess sodium. After hydrolysis, the organic layer was worked up in the usual manner. The residue obtained after removal of the solvents was distilled twice under reduced pressure to give 5.2 g. (23.9%) of product, b.p. 110-112° (0.002 mm.), n_D^{20} 1.5862, d_{20}^{20} 1.0362.

Anal. Calcd. for $C_{16}H_{18}Si$: C, 80.61; H, 7.61; MR_D, 77.05. Found: C, 81.45, 81.30; H, 7.91, 7.80; MR_D, 77.24.

Dibenzyl[3-(o-chlorophenyl)propyl]silane

An ether solution (150 ml.) of 3-(o-chlorophenyl)propylmagnesium bromide, prepared in a 91% yield from 25.69 g. (0.11 mole) of 3-(o-chlorophenyl)propyl bromide and 3.12 g. (0.13 g. atom) of magnesium, was added to 21.24 g. (0.1 mole) of dibenzylsilane dissolved in 100 ml. of tetrahydrofuran. The ether was distilled and the tetrahydrofuran solution was refluxed overnight. The reaction mixture was hydrolyzed with a saturated ammonium chloride solution; ether was added and the organic layer was dried and concentrated. Distillation gave 9.2 g. (25.2%) of viscous oil, b.p. 206-211° (0.004 mm.),

n_D^{20} 1.5888, d_{20}^{20} 1.0849.

Anal. Calcd. for $C_{23}H_{25}ClSi$: Si, 7.70; MR_D, 113.18. Found: Si, 7.50, 7.56; MR_D, 113.35.

2:3-Benzo-1,1-dibenzyl-1-silacyclohex-2-ene (attempted)

To a refluxing suspension of 2.76 g. (0.12 g. atom) of molten sodium in 100 ml. of toluene, there was added 21.06 g. (0.0577 mole) of dibenzyl-[3-(o-chlorophenyl)propyl]silane dissolved in 150 ml. of dry toluene. A light brown color slowly developed, but after 24 hours there was no additional change. A 4 ml. aliquot was withdrawn and acid hydrolyzed. Work-up of the aliquot gave an oil whose infrared spectrum was superimposable with the starting material. The mixture was refluxed an additional 24 hours, cooled and filtered.[61] The filtrate was poured cautiously into an ice-hydrochloric acid mixture. Ether was added and the layers separated. Distillation of the organic layer gave 16.9 g. (76.4%) of a viscous oil in several fractions. The infrared spectrum of each fraction was superimposable with the starting material.

In a second run, there was no evidence of a reaction after 48 hours of refluxing, and the starting material was recovered in 79.1% yield.

Dibenzyl[3-(o-chlorophenyl)propyl]phenylsilane

An ether solution containing 0.033 mole of phenyllithium was added to 5.1 g. (0.014 mole) of the recovered dibenzyl-[3-(o-chlorophenyl)propyl]silane dissolved in 10 ml. of ether. The reaction mixture was refluxed 24 hours. After hydrolysis, ether was added and the layers separated. Evaporation of the dried organic layer gave an oil which was distilled to give 3.9 g. (63.2%) of pale yellow viscous liquid, b.p. 196-198° (0.004 mm.), n_D^{20} 1.6065. The infrared spectrum contained an absorption band at 9.05μ, characteristic of the silicon-phenyl linkage, and a band at 13.32μ, indicative of ortho-disubstitution. The silicon-hydrogen absorption band was absent.

Anal. Calcd. for $C_{29}H_{29}ClSi$: Si, 6.37. Found: Si, 6.47, 6.35.

Reaction of benzyltriphenylsilane with sodium (attempted)

A mixture of 3.86 g. (0.011 mole) of benzyltriphenylsilane and 0.18 g. (0.008 g. atom) of sodium in 50 ml. of toluene was refluxed 48 hours. The solution remained colorless and the sodium did not appear to have reacted. The reaction mixture was cooled and trimethyl phosphate (1.54 g. 0.011 mole) was added.[82] There was no apparent reaction. Ethanol

[82]H. Gilman and B. J. Gaj, ibid., 82, 6326 (1960).

was added and then the mixture was poured into dilute sulfuric acid. The usual work-up gave 3.72 g. (96.4%) of recovered starting material, m.p. 96-98°. Recrystallization from ethanol did not alter the melting point.

Ethyldiphenylsilane

To an ethereal solution of 10.28 g. (0.047 mole) of chlorodiphenylsilane was added 0.047 mole of ethylmagnesium bromide. Subsequent to complete addition, Color Test I was negative. After hydrolysis and the usual work-up there was obtained 6.66 g. (66.7%) of a colorless liquid, b.p. 122-122.5° (2.5 mm.), n_D^{20} 1.5677, d_{20}^{20} 0.9894; reported[83] n_D^{20} 1.5674.

Anal. Calcd. for $C_{14}H_{16}Si$: MR_D, 70.18. Found: MR_D, 70.19.

Since the n.m.r. spectrum of this compound was somewhat anomalous (see discussion), the ethyldiphenylsilane was allowed to react with phenyllithium to give the previously reported[84] ethyltriphenylsilane, m.p. 74-76°, identified by mixture melting point and by comparison of the infrared spectra.

[83] V. F. Mironov and A. D. Petrov, Bull. Acad. Sci. U. S. S. R., (Eng. trans.), 391 (1957).

[84] F. J. Marshall. Cleavage and substitution reactions of some organosilanes. Unpublished Ph. D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1948.

Diphenyl-n-propylsilane

An ethereal solution of n-propylmagnesium bromide (0.06 mole) was added to 13.13 g. (0.06 mole) of chlorodiphenylsilane dissolved in ether. Color Test I was negative when the addition was completed. Hydrolysis and the usual work-up afforded an oil which was distilled under reduced pressure to give 8.89 (65.4%) of pure product, b.p. 126-128° (2.5 mm.), n_D^{20} 1.5608, d_{20}^{20} 0.9786.

Anal. Calcd. for $C_{15}H_{18}Si$: C, 79.57; H, 8.01; MR_D, 74.81. Found: C, 80.15, 79.91; H, 7.79, 7.84; MR_D, 74.89.

Reaction of diphenyl-n-propylsilane with sodium in refluxing toluene (attempted)

A mixture of diphenyl-n-propylsilane (2.27 g. 0.01 mole) and sodium (0.46 g. 0.02 g. atom) in 90 ml. of toluene was refluxed 12 hours. There was no apparent reaction. The mixture was allowed to cool and the liquid pipetted and hydrolyzed. Work-up of the organic layer in the customary manner gave an 88.2% recovery of the starting silane, confirmed by comparison of the infrared spectra.

2:3-Benzo-4-bromo-1,1-diphenyl-1-silacyclohex-2-ene

A mixture of N-bromosuccinimide (5.92 g., 0.033 mole), 2:3-benzo-1,1-diphenyl-1-silacyclohex-2-ene (10 g., 0.033 mole), and benzoyl peroxide (0.1 g.) in 200 ml. of carbon

tetrachloride was heated at a gentle reflux for 2.5 hours. Filtration of the cooled suspension gave 3.04 g. (92%) of succinimide, m.p. 124-126°, identified by mixture melting point. The carbon tetrachloride was removed with the aid of an aspirator and petroleum ether (b.p. 60-70°) added to the residue. Slightly impure product (12.4 g.) was obtained by allowing the mixture to stand 3 days at 0°. Two recrystallizations from petroleum ether gave 9.5 g. (76%) of pure product, m.p. 95-97°.

Anal. Calcd. for $C_{21}H_{19}BrSi$: Si, 7.44. Found: Si, 7.35, 7.39.

The n.m.r. spectrum supported the assigned structure, showing a closely coupled tertiary proton peak centered at 4.38 τ, characteristic of a benzylic halide hydrogen, and a multiplet centered at about 8.0 τ for the remaining protons.

In a repeat run the bromo compound was obtained in an 81% yield.

Reaction of 2:3-benzo-4-bromo-1,1-diphenyl-1-silacyclohex-2-ene with magnesium

Run 1 A solution of 1.0 g. (0.00263 mole) of the bromo compound in 15 ml. of tetrahydrofuran was added to 0.1 g. (0.004 g. atom) of magnesium and a crystal of iodine in 5 ml. of tetrahydrofuran. The reaction started immediately and, subsequent to complete addition, the mixture was refluxed 2

hours. The reaction mixture was filtered through a glass-wool plug into an ammonium chloride solution. The layers were separated and the water layer was extracted thoroughly with ether. The combined organic layer was filtered to give 0.25 g. of solid melting at 268-271°. The filtrate was dried over magnesium sulfate and concentrated. An additional 0.11 g. of the high melting solid was obtained. Further concentration gave a viscous yellow oil which could not be purified further.

The two solid fractions were combined and recrystallized from a benzene-petroleum ether (b.p. 60-70°) mixture to give 0.31 g. (39.2%) of fine needles, m.p. 271-273°. The compound has been assigned the structure 4,4'-bi(2:3-benzo-1,1-diphenyl-1-silacyclohex-2-ene) on the basis of elemental and infrared analysis.

Anal. Calcd. for $C_{42}H_{38}Si_2$: C, 84.23; H, 6.39; Si, 9.38; Mol. wt., 598.9. Found: C, 84.61, 84.40; H, 6.43, 6.35; Si, 9.25; Mol. wt. (cryoscopic in benzene), 580.

The infrared spectrum was similar to that of 2:3-benzo-1,1-diphenyl-1-silacyclohex-2-ene, showing prominent bands at 3.28, 3.44, 9.05, and 13.28μ, characteristic of aromatic C-H, aliphatic C-H, the silicon-phenyl linkage, and ortho-disubstitution, respectively.

Run 2 The bromo compound (1.15 g., 0.00303 mole) was allowed to react with 0.1 g. (0.004 g. atom) of magnesium in 20 ml. of tetrahydrofuran as described above, except the

mixture was refluxed 1 hour. Color Test I was negative. The mixture was poured onto a slurry of Dry Ice and ether and subsequently hydrolyzed with dilute acid. Ether was added and the layers separated. The organic layer was filtered to remove 0.15 g. of solid, m.p. 270-273°. The yellow filtrate was transferred to a separatory funnel and extracted with 50 ml. of 5% sodium hydroxide. Acidification of the extracts did not afford any products. The organic layer was washed with dilute acid (solution changed to a reddish color) and dried over magnesium sulfate. Removal of the solvent and the addition of petroleum ether (b.p. 60-70°) gave an additional 0.03 g. of solid, m.p. 257-261°. Further concentration of the petroleum ether filtrate yielded a black oil. Treatment of the oil with acetone gave 0.04 g. of the same solid. The combined solid (0.22 g., 24.2%) was purified by recrystallization from a benzene-petroleum ether mixture and then from chloroform to give a pure product, m.p. 270-273°. A mixed melting point with a sample from the above reaction was not depressed, and their infrared spectra were superimposable.

2:3-Benzo-1,1-diphenyl-1-silacyclohex-2-en-4-one

First experiment A solution of 8.18 g. (0.0216 mole) of 2:3-benzo-4-bromo-1,1-diphenyl-1-silacyclohex-2-ene in 500 ml. of ethylene glycol monomethyl ether was treated with 6.8 g. (0.04 mole) of silver nitrate dissolved in 100 ml. of

water. After refluxing 30 minutes, the silver bromide was filtered and the filtrate extracted with 500 ml. of petroleum ether (b.p. 60-70°). The petroleum ether extract was dried and distilled to give 6.7 g. of a viscous oil. Attempts to obtain crystalline products failed. Distillation of the oil gave 6.23 g. of material, boiling over the range 165-184° (0.005 mm.). After several attempts to purify the oil by crystallization techniques, the oil (6.0 g.) was dissolved in 100 ml. of acetone and cooled to ice-bath temperature. Potassium permangnate (3.0 g., 0.019 mole) was added and the reaction mixture allowed to warm to room temperature. The brown solution was stirred 1 hour, then poured upon crushed ice containing sulfuric acid and sodium oxalate. After warming to room temperature, ether was added, followed by the usual separation, drying, and concentration procedures. The oily residue was treated with petroleum ether and chromatographed on a column of alumina. Elution with petroleum ether and cyclohexane gave only traces of oils. When benzene was used as an eluant, viscous oils were obtained in several fractions which partially crystallized upon standing. Addition of petroleum ether and filtration gave 1.0 g. of a solid, m.p. 95-105°. Recrystallization twice from petroleum ether raised the melting point to 105-108.5°. The reported melting point of this compound is 127-128°.[1] A comparison of the infrared spectrum showed several differences. The

spectrum of the reported material contained medium to strong absorption bands at 7.47, 8.2, 8.53, and 12.33μ, and a broad band at 9.28-9.62μ, which were not present in the spectrum of the isolated material (m.p. 105-108.5°). The broad absorption band at 9.28-9.62μ in the previously reported sample may be attributed to the presence of an Si-O-Si or Si-O-C linkage.[85] The infrared spectrum of the ketone melting at 105-108.5° contained bands at 7.63, 7.85, 12.87, and 13.02μ, which were not present in the other spectrum.

Treatment of the ketone or crude fractions with an ethanolic solution of 2,4-dinitrophenylhydrazine gave the hydrazone as bright red flakes, m.p. 228-230°, after crystallization from ethyl acetate.

Anal. Calcd. for $C_{27}H_{22}N_4O_4Si$: C, 65.57; H, 4.49; N, 11.33. Found: C, 65.55, 65.72; H, 4.43, 4.57; N, 11.29, 11.26.

The reported melting point of this hydrazone is 240° (dec). When the two derivatives were admixed, the melting point was depressed to 221-224°. The infrared spectra were similar but not superimposable.

Second experiment To a solution of 2:3-benzo-4-bromo-1,1-diphenyl-1-silacyclohex-2-ene (1.08 g., 0.00285 mole) in 100 ml. of dioxane was added 2 g. of silver nitrate and 5

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[85] A. Lee Smith, Spectrochim. Acta, 16, 87 (1960).

ml. of water in 20 ml. of dioxane. The mixture was stirred 2 hours at room temperature and filtered. The filtrate was concentrated to about 20 ml. with the aid of an aspirator. Water was added to the residue, followed by extraction with two portions of ether. Concentration of the dried ether solution gave an oil. Addition of petroleum ether (b.p. 60-70°) gave 0.78 g., of a solid melting over the range 45-90°. Concentration of the filtrate gave 0.12 g., m.p. 73-78°. Attempted purification of these solids produced oils. The infrared spectrum showed strong absorption bands at 6.16 and 7.89μ, which were absent in the starting material. These bands are reported[86] to be characteristic of the covalent nitrate grouping.

The impure nitrato compound (0.84 g., 0.0025 mole) was refluxed for 2 hours with 2 g. of potassium hydroxide and 7 ml. of water in 65 ml. of dioxane. After cooling, the reaction mixture was poured into an ice-sulfuric acid mixture. Ether was added and the layers separated. Drying and concentration of the ether solution gave an oil which could not be induced to crystallize. The oil was dissolved in a small amount of ethanol and treated with an ethanolic solution of 2,4-dinitrophenylhydrazine to give 0.02 g. of the hydrazone

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[86] L. J. Bellamy. The infra-red spectra of complex molecules. p. 301. New York, John Wiley and Sons. 1958.

as bright red crystals, m.p. 225-227°. The melting point was not depressed when admixed with a sample from the previous experiment. Also the infrared spectra were superimposable.

Third experiment A mixture of N-bromosuccinimide (5.44 g., 0.0305 mole) and 2:3-benzo-1,1-diphenyl-1-silacyclohex-2-ene (4.58 g., 0.0152 mole) in 100 ml. of carbon tetrachloride was refluxed 2.5 hours while irradiating with ultraviolet light. The reaction appeared to stop if the light source was removed. A red solution was formed and hydrogen bromide was evolved. After cooling, the succinimide (95.4%) was filtered and the carbon tetrachloride distilled. The viscous red residue could not be purified. Also, the red color could not be extracted with a sodium bisulfite solution.

The impure 2:3-benzo-4,4-dibromo-1,1-diphenyl-1-silacyclohex-2-ene (7.3 g.) was dissolved in 100 ml. of ethylene glygol monomethyl ether and heated to reflux. A solution of silver nitrate (5.78 g.) in 30 ml. of water was added slowly and the refluxing continued for 2 hours. A gray gummy solid was removed by filtration. The filtrate was concentrated to about 20 ml. and extracted with ether. The combined organic layer was washed with water and dried. Distillation of the ether afforded 4.5 g. of a red oil. The oil was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 1.96 g. of a colorless viscous oil which could not be purified further. An infrared spectrum of the oil showed

the absence of carbonyl-containing compounds. Using benzene as the eluant, red oils were obtained which partially crystallized subsequent to treatment with petroleum ether. Filtration gave 0.01 g. of solid melting with decomposition at 315°. The petroleum ether filtrate was concentrated, and an ethanolic 2,4-dinitrophenylhydrazine solution was added to the oil. The hydrazone was filtered and recrystallized from ethyl acetate to give 0.4 g. of red flakes, m.p. 225-226°. There was no depression in the melting point when admixed with the 2,4-dinitrophenylhydrazone isolated in the previous experiments. The infrared spectra were superimposable.

Further elution of the column with ethyl acetate gave a trace of a red oil.

2:3-Benzo-1,1-diphenyl-1-stannacyclohex-2-ene

To a solution of diphenyltin dichloride (5.64 g., 0.0164 mole) in 10 ml. of tetrahydrofuran was added 0.0164 mole of the double Grignard reagent, prepared from 6.0 g. (0.022 mole) of 3-(o-bromophenyl)propyl bromide and 1.2 g. of magnesium in 85 ml. of tetrahydrofuran. Color Test I was negative after 2 hours at reflux. The reaction mixture was hydrolyzed with an ammonium chloride solution and worked up in the usual manner. Chromatography of the reaction products over alumina using petroleum ether (b.p. 60-70°) as the eluant gave 0.6 g.

(9.4%) of product, m.p. 70-71°. Recrystallization from ethanol did not alter the melting point.

Anal. Calcd. for $C_{21}H_{20}Sn$: C, 64.50; H, 5.15. Found: C, 64.65, 64.45; H, 5.43, 5.23.

Further elution of the column with benzene and ethyl acetate gave 2.0 g. of an oil which could not be induced to crystallize.

4-(o-Chlorophenyl)butanol-1

o-Chlorobenzylmagnesium chloride[60] (0.1 mole) was treated with 5.81 g. (0.1 mole) of trimethylene oxide dissolved in 100 ml. of ether while cooling with cold water. After stirring overnight, Color Test I was negative. Subsequent to acid hydrolysis and separation of the layers, the organic layer was dried and distilled to give 8.27 g. (44.7%) of pure product, b.p. 107-110.5° (3 mm.), n_D^{20} 1.5385, d_{20}^{20} 1.1282.

Anal. Calcd. for $C_{10}H_{13}ClO$: C, 65.04; H, 7.10; MR_D, 51.43. Found: C, 64.52, 64.50; H, 7.08, 7.08; MR_D, 51.24.

In a second run, a small amount of a solid melting at 65-66°, after recrystallizing from 95% ethanol, sublimed during the initial heating process. The solid is probably 2,2'-dichlorobibenzyl; reported[87] m.p. 65°.

The 1-naphthyl carbamate of the alcohol melted at 91.5-

[87] J. Thiele and O. Holzinger, Ann., 305, 100 (1899).

93°, after successive recrystallizations from petroleum ether (b.p. 60-70°) and ethanol.

4-(o-Chlorophenyl)butyl bromide

4-(o-Chlorophenyl)butanol-1 (39.0 g., 0.0211 mole) and phosphorus tribromide (5.71 g., 0.0211 mole) were heated at 100° for 1 hour as described previously. Work-up of the reaction mixture in the usual manner gave 39.83 g. of a cloudy liquid, b.p. 126-129.5° (3 mm.). The material was taken up in petroleum ether (b.p. 60-70°) and passed through a column of alumina. The eluates were distilled to give 35.56 g. (68%) of pure product, b.p. 122-124° (2 mm.), n_D^{20} 1.5550, d_{20}^{20} 1.3779.

Anal. Calcd. for $C_{10}H_{12}BrCl$: C, 48.51; H, 4.89; MR_D, 57.56. Found: C, 49.27, 49.47; H, 4.86, 5.02; MR_D, 57.67.

5-(o-Chlorophenyl)pentanoic acid

4-(o-Chlorophenyl)butyl bromide (4.95 g., .02 mole) in 30 ml. of ether was allowed to react with 0.5 g. (0.025 g. atom) of magnesium for 18 hours at room temperature. Titration of an aliquot indicated an 89.6% yield of the Grignard reagent. Carbonation with Dry Ice gave 2.8 g. of the acid, m.p. 44-46°. Recrystallization from petroleum ether (b.p. 60-70°) gave 1.75 g. (60%) of 5-(o-chlorophenyl)pentanoic acid, m.p. 46.5-

48°; reported[88] m.p. 46°.

[4-(o-Chlorophenyl)butyl]diphenylsilane

An ethereal solution of 15.68 g. (0.072 mole) of chlorodiphenylsilane was treated with 0.0717 mole of 4-(o-chlorophenyl)butylmagnesium bromide, prepared from 25.4 g. (0.103 mole) of 4-(o-chlorophenyl)butyl bromide and 3.6 g. (0.15 g. atom) of magnesium. Color Test I was negative after stirring overnight at room temperature. The reaction mixture was poured into iced sulfuric acid and worked up in the customary manner. Reduced pressure distillation gave 19.5 g. of liquid boiling over the range 160-178° (0.004 mm.). Redistillation gave 16.83 g. (66.8%) of pure product, b.p. 174-176° (0.002 mm.), n_D^{20} 1.5885.

Anal. Calcd. for $C_{22}H_{23}ClSi$: Si, 8.0. Found: Si, 7.87, 7.80.

2:3-Benzo-1,1-diphenyl-1-silacyclohept-2-ene

A mixture of 2.3 g. (0.1 g. atom) of sodium and 16.8 g. (0.048 mole) of [4-(o-chlorophenyl)butyl]diphenylsilane in 200 ml. of dry toluene was refluxed 7 hours. After cooling, the brown solution was treated with ethanol, and then poured into an ammonium chloride solution. Ether was added and the aqueous layer separated, extracted with ether and discarded.

[88] R. Granger, H. Orzales, and A. Muratelle, Comp. rend., 252, 1478 (1961).

The combined organic layer was dried with anhydrous magnesium sulfate and evaporated under an air-jet. The resulting material was taken up in ethanol to give 10.7 g. of slightly impure product, m.p. 148-151°. Recrystallization from ethanol and petroleum ether (b.p. 60-70°) gave 8.38 g. (55.6%) of pure product, m.p. 151-153°. The analytical sample melted at 151.5-153°.

Anal. Calcd. for $C_{22}H_{22}Si$: Si, 8.93. Found: Si, 8.96, 8.90.

5-(o-Chlorophenyl)pentanol-1

The Grignard reagent of 3-(o-chlorophenyl)propyl bromide, prepared in an 88.4% yield from 39.87 g. (0.171 mole) of the bromide and 4.8 g. (0.2 g. atom) of magnesium, was cooled in an ice-bath and then treated with an excess of ethylene oxide. After stirring overnight, Color Test I was negative. Hydrolysis was effected by pouring into dilute sulfuric acid. Ether was added and the organic layer separated and dried. The ether was evaporated and the residual oil distilled twice under reduced pressure to give 11.89 g. (44.5%) of pure product, b.p. 118-121° (0.4 mm.), n_D^{20} 1.5308, d_{20}^{20} 1.1076.

Anal. Calcd. for $C_{11}H_{15}ClO$: C, 66.49; H, 7.61; MR_D, 56.06. Found: C, 65.66, 65.45; H, 7.47, 7.31; MR_D, 55.51.

5-(o-Chlorophenyl)pentyl bromide

5-(o-Chlorophenyl)pentanol-1 (14.79 g., 0.075 mole) was converted into the bromide by heating with 10.29 g. (0.038 mole) of phosphorus tribromide as described in previous experiments. There was obtained by a reduced pressure distillation 12.2 g. (62.5%) of a colorless liquid, b.p. 104-108° (0.2 mm.), n_D^{20} 1.5468, d_{20}^{20} 1.3383.

Anal. Calcd. for $C_{11}H_{14}BrCl$: C, 50.50; H, 5.39; MR_D, 62.19. Found: C, 49.26, 50.75; H, 5.35, 5.42; MR_D, 61.97.

[5-(o-Chlorophenyl)pentyl]diphenylsilane

5-(o-Chlorophenyl)pentylmagnesium bromide, prepared in a 69% yield from 12.98 g. (0.05 mole) of 5-(o-chlorophenyl)-pentyl bromide and 2.43 g. (0.1 g. atom) of magnesium in 55 ml. of ether, was added to an ethereal solution of 7.22 g. (0.033 mole) of chlorodiphenylsilane. After heating at reflux 6 hours, Color Test I was negative. The reaction mixture was hydrolyzed with dilute acid and the reaction products distilled twice at reduced pressure to give 5.52 g. (45.8%) of viscous oil, b.p. 173-179° (0.004 mm.), n_D^{20} 1.5751.

Anal. Calcd. for $C_{23}H_{25}ClSi$: C, 75.69; H, 6.90. Found: C, 75.35, 74.68; H, 6.98, 6.76.

2:3-Benzo-1,1-diphenyl-1-silacyclooct-2-ene

To a refluxing suspension of 0.71 g. (0.031 g. atom) of sodium in 50 ml. of toluene was added 5.52 g. (0.015 mole) of

[5-(o-chlorophenyl)pentyl]diphenylsilane in 50 ml. of the same solvent. Subsequent to refluxing 12 hours, ethanol was added and the mixture was poured into an ice-sulfuric acid mixture. The aqueous layer was separated, extracted with ether and discarded. The combined organic layer was dried and evaporated.

The residual material was distilled to give 1.58 g. of a viscous oil boiling over the range 144-163° (0.005 mm.). The oils partially crystallized upon standing. Ethanol was added and the solid filtered to yield 0.25 g. (5.04%) of solid, m.p. 154.5-156°, after recrystallization from a petroleum ether (b.p. 60-70°)-ethanol mixture. The analytical sample melted at 154.5-155.5°.

Anal. Calcd. for $C_{23}H_{24}Si$: C, 84.09; H, 7.36. Found: Si, 84.00, 84.19; H, 7.38, 7.28.

The distillation residue (5.02 g.) was a viscous red oil which could not be purified further.

DISCUSSION

Potential Organosilicon Antioxidants or Lubricants

Several organosilicon compounds have been found to be useful in the formulation of high temperature lubricants and related materials. Therefore, a considerable amount of emphasis has been placed on the development of new and better organosilicon type base stocks and antioxidants.

Although compounds containing Si-N bonds have not been investigated for thermal stability and antioxidant properties, nitrogen-containing organosilicon compounds have shown promising antioxidant properties.[32] Therefore, as an extension of previously published studies of the thermal stability of some tribenzylsilane derivatives,[89] compounds containing Si-N bonds were prepared and screened for their thermal stability properties.

These compounds were prepared by reacting the lithium salt of morpholine with triphenylsilane, diphenylsilane, and phenylsilane. The reaction with silicon hydrides was preferred as it had been shown that lithium di-n-butylamide gave much improved yields of the silylamine when the hydride was employed in place of the chlorosilane.[2] The thermal stabilities of the resulting morpholinyl derivatives, along with

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[89] H. Gilman and O. L. Marrs, J. Org. Chem., 25, 1194 (1960).

dibenzyldi-m-tolylsilane for comparison, are shown in Table 1.

Table 1. Thermal stabilities of morpholinylsilanes[a]

Compound	M.p., °C	Thermal stability, °C
N-Morpholinyltriphenylsilane	178-180	Yellow at 380; vol. 295 (condensate black)
Di-N-morpholinyldiphenylsilane	152.5-154	Vol. 380 (condensate black)
Tri-N-morpholinylphenylsilane	125.5-127.5	Yellow at 370; vol. 390 (condensate purple)
Dibenzyldi-m-tolylsilane	191-192(0.008)[b]	Vol. 438

[a]A compound that does not contain the morpholinyl group is included.

[b]B.p., °C (mm.).

The screening data were obtained by heating the compounds in an unsealed capillary tube inserted in a flame-heated copper block. The changes in the sample were noted during the heating process and the volatilization temperature taken as that point where the liquid rapidly disappeared from the capillary tube. The appearance of the condensate was recorded.

It should be noted that as a phenyl group is replaced by a morpholinyl group, the melting point is lowered. However,

the compounds are of about equal thermal stability, but are less than that of dibenzyldi-m-tolylsilane. Also, the latter compound, in addition to good thermal stability, is a high boiling liquid which is also a desirable requisite in high temperature lubricants.

Reactions of Triphenylsilyllithium with Anthracene and Quinoline

The impetus for the development of silylmetallic reagents as intermediates in the preparation of organosilicon compounds was provided by the discovery that these reactive intermediates could be prepared in tetrahydrofuran and were fairly stable in this solvent.[55]

With triphenylsilyllithium, there ensued numerous studies of its reactions with various compounds.[90,91] One of these was the reaction with olefins.[92] In this study, triphenylsilyllithium was found to add to the olefinic linkage of 1,1-diphenylethylene and of triphenylethylene. No addition occurred with tetraphenylethylene or with a variety of aliphatic

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

[91] H. Gilman and H. J. S. Winkler. Organosilylmetallic chemistry. In H. Zeiss, ed. Organometallic chemistry, pp. 270-345. New York, Reinhold Publishing Corporation. 1960.

[92] T. C. Wu, D. Wittenberg, and H. Gilman, J. Org. Chem., 25, 596 (1960).

and alicyclic olefins. In a related study,[93] silylmetallic reagents were postulated to have added to the azomethine linkage of benzophenone anil, followed by rearrangement to the silylamine. With acridine, the expected 9,10-addition occurred to give N-lithio-9-(triphenylsilyl)acridan,[94] as in the case of the analogous alkyl- and aryllithium compounds.[95] Rather than the 1,2-addition that occurs with alkyl- and aryllithium compounds,[95] triphenylsilyllithium underwent addition at the 4-position of pyridine to give triphenyl-4-(1:4-dihydropyridyl)silane after hydrolysis.[96] Selective nucleophiles such as benzylmagnesium chloride[97] and allylmagnesium bromide give 1,4-addition products.[98] With

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[93] D. Wittenberg, M. V. George, T. C. Wu, D. H. Miles, and H. Gilman, J. Am. Chem. Soc., 80, 4532 (1958).

[94] H. Gilman and G. D. Lichtenwalter, J. Org. Chem., 23, 1586 (1958).

[95] K. Ziegler and H. Zeiser, Ber., 63, 1847 (1930); Ann., 485, 175 (1931).

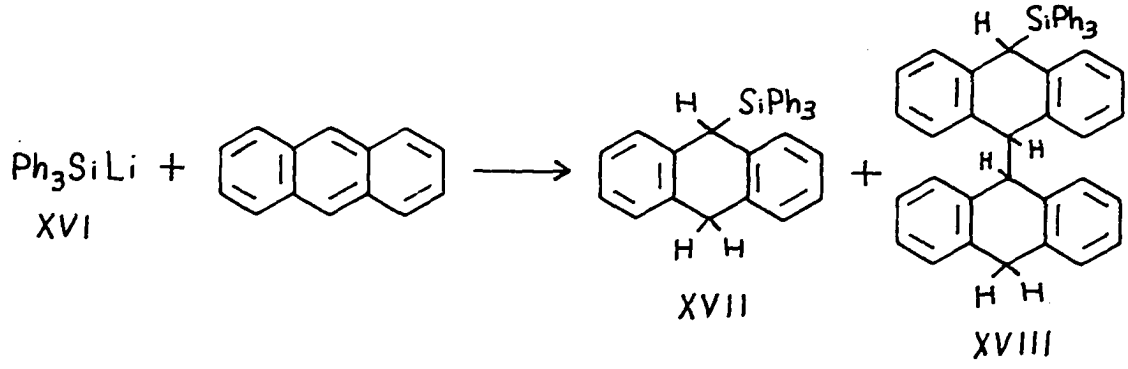
[96] D. Wittenberg and H. Gilman, Chem. and Ind., 390 (1958).

[97] W. L. C. Veer and St. Goldschmidt, Rec. trav. chim., 65, 793 (1946); R. A. Benkeser and D. S. Holton, J. Am. Chem. Soc., 73, 5861 (1951).

[98] H. Gilman, J. Eisch, and T. Soddy, ibid., 79, 1245 (1957).

quinoline, organolithium and most Grignard reagents add predominantly in the two position,[95,99] although benzylmagnesium chloride is reported to give low yields of 4-benzylquinoline and 2,4-dibenzylquinoline, in addition to the 2-isomer.[100] Therefore, it was of interest to study the course of addition of triphenylsilyllithium to anthracene and quinoline.

The reaction of triphenylsilyllithium (XVI) with anthracene was complicated by polymerization reactions and by contamination of the products with unreacted anthracene. There was isolated, however, by chromatography 9,10-dihydro-9-(triphenylsilyl)anthracene (XVII), in addition to unreacted anthracene and a small amount of a solid melting over the range 229-233°. Attempts to purify this material further failed. However, it is believed that this solid is a mixture of the 9,10-dihydro-9-(triphenylsilyl)-10-(9',10'-dihydro-9'-anthryl)anthracenes (XVIII).



[99] H. Gilman, C. G. Stuckwisch, and J. F. Nobis, ibid., 68, 328 (1946).

[100] E. Bergmann and W. Rosenthal, J. prakt. Chem., 135, 267 (1932).

Compound XVII was assigned the dihydro structure and not the fully aromatic compound, 9-(triphenylsilyl)anthracene, on the basis of its infrared spectrum and its alternate synthesis from 9,10-dihydro-9-lithioanthracene and chlorotriphenylsilane. Also, a similar addition to anthracene has been reported with α-cumenylpotassium.[101] In contrast, triphenylmethylpotassium showed little tendency to add.[101]

Compound XVIII is proposed as the reduced bianthracene derivative on the basis of its infrared spectrum, which was similar to the infrared spectrum of XVII, and on the basis of its silicon analysis. The compound may have been formed by the addition of anthracene to the intermediate 9,10-dihydro-10-lithio-9-(triphenylsilyl)anthracene. Schlenk and Bergmann[102] found that in the preparation of the disodium adduct of anthracene with high concentrations of anthracene a similar dimerization occurred as carbonation of the reaction mixture gave 9,9',10,10'-tetrahydro-9,9'-bianthryl-10,10'-dicarboxylic acid. Similarly, polymerization reactions have been suggested as interfering in the normal course of the reaction of 9,10-dihydro-9,10-disodioanthracene with alkyl halides.[103]

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[101] K. Ziegler and K. Bähr, Ber., 61, 253 (1928).

[102] W. Schlenk and E. Bergmann, Ann., 463, 98 (1928).

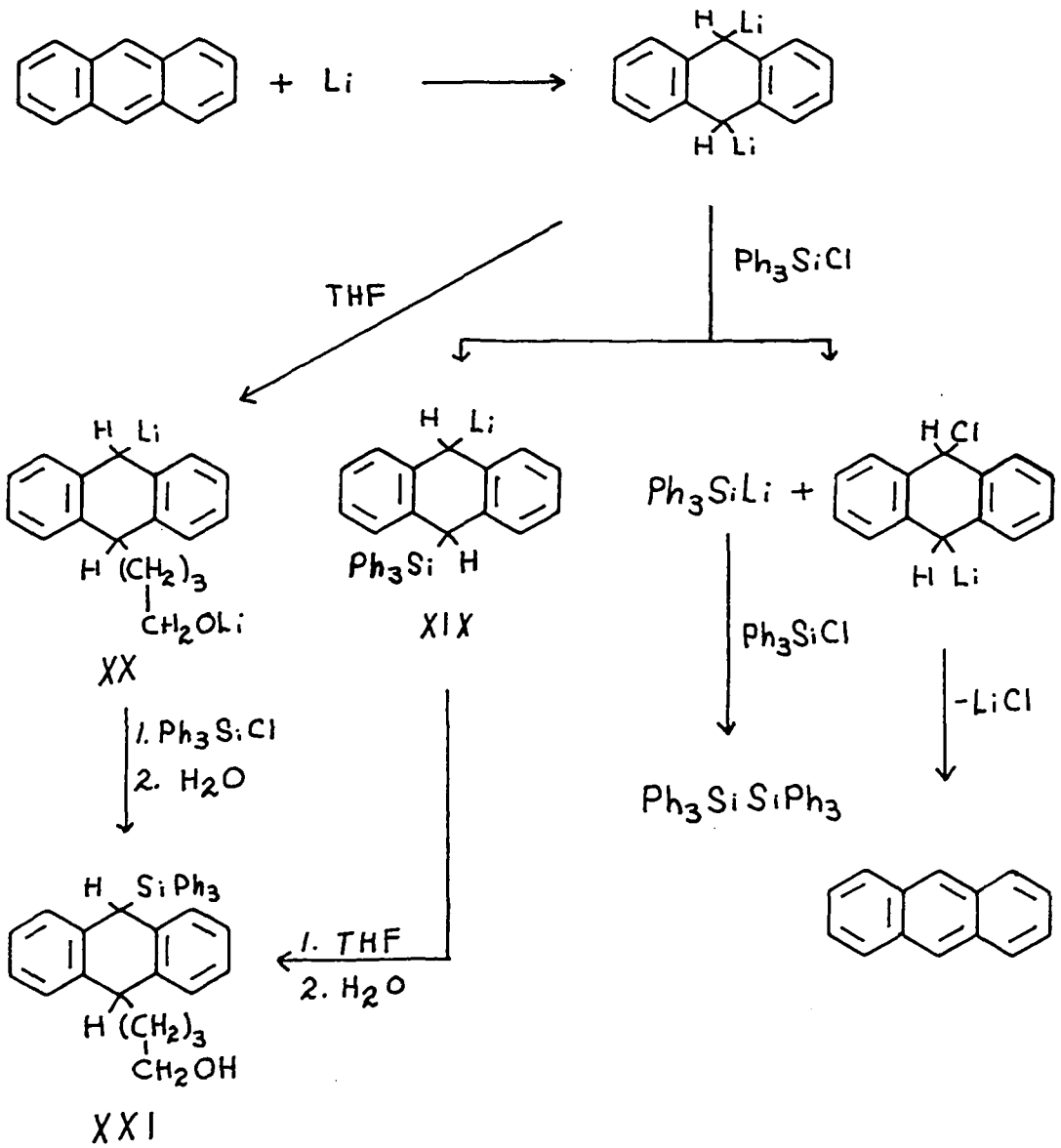
[103] B. M. Mikhailov and A. N. Blokhina, Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk, 164 (1947) [Original not available for examination; abstracted in C. A., 44, 2962 (1950)].

In the alternate synthesis of 9,10-dihydro-9-(triphenylsilyl)anthracene (XVII) from 9,10-dihydro-9-lithioanthracene and chlorotriphenylsilane, hexaphenyldisilane was also isolated. This product probably results from halogen-metal interconversion between the chlorosilane and the organolithium reagent to give triphenylsilyllithium and 9,10-dihydro-9-chloroanthracene. Reaction of the triphenylsilyllithium with chlorotriphenylsilane would give the hexaphenyldisilane. The fate of the chloroanthracene was not established, although unidentifiable mixtures were isolated. Halogen-metal interconversion between chlorotriphenylsilane and triphenylmethylsodium or -lithium has been reported with the resulting hexaphenyldisilane being identified only by its X-ray diffraction pattern.[104] The usual mode of reaction between chlorosilanes and organolithium reagents is coupling.[5]

The recently reported successful synthesis of 9,10-dihydro-9-(trimethylsilyl)anthracene from the dilithium adduct of anthracene and chlorotrimethylsilane[105] encouraged an attempt to prepared XVII *via* this method. However, when a tetrahydrofuran solution of the dilithium adduct was allowed to react with chlorotriphenylsilane, the only products isolated were anthracene, 9,10-dihydroanthracene, hexaphenyl-

[104] A. G. Brook, H. Gilman, and L. S. Miller, *J. Am. Chem. Soc.*, *75*, 4759 (1953).

[105] M. Maienthal, M. Hellman, C. P. Haber, L. A. Hymo, S. Carpenter, and A. J. Carr, *ibid.*, *76*, 6392 (1954).



disilane, and a compound which has tentatively been identified as 9,10-dihydro-10-(4-hydroxybutyl)-9-(triphenylsilyl)-anthracene (XXI).

The anthracene and hexaphenyldisilane would arise as a consequence of halogen-metal interconversion, and XXI would result from cleavage of the solvent, tetrahydrofuran (THF).

Although other mechanisms may be envisioned, compound XXI may be formed either by cleavage of the solvent by the intermediate 9,10-dihydro-10-lithio-9-(triphenylsilyl)anthracene (XIX) or by cleavage of the THF by the dilithium adduct, followed by reaction of the resulting intermediate (XX) with chlorotriphenylsilane. The alkoxylsilane that would be produced in this latter step would be hydrolyzed in the work-up.

Analogous halogen-metal interconversion reactions were observed when the dilithium or disodium adduct of anthracene was reacted with alkyl halides.[103] For example, with chlorotriphenylmethane, anthracene was recovered in a 66.7% yield. The preparation of the dilithium adduct proceeds to over 95% conversion,[106] hence, the recovered anthracene was not unreacted starting material.

The structure assigned to XXI was based on its infrared and n.m.r. spectra and elemental analysis. Furthermore, it has been shown that the dilithium adduct readily cleaves other cyclic ethers.[107] In addition, Gilman and Gaj[108] have found that organolithium reagents are unstable in tetrahydrofuran, perhaps decomposing by cleavage of the solvent. Cleavage of

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[106]B. M. Mikhailov and A. N. Blokhina, Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk, 279 (1949) [Original not available for examination; abstracted in C. A., 44, 2963 (1950)].

[107]C. S. Rondestvedt, Jr. and I. Nicholson, J. Org. Chem., 20, 346 (1955).

[108]H. Gilman and B. J. Gaj, ibid., 22, 1165 (1957).

tetrahydrofuran was observed with triphenylmethylmagnesium halide[109] and triphenylsilyllithium[3,73] to give good yields of the alcohol.

The reaction of triphenylsilyllithium with quinoline proved to be complicated by unreacted quinoline and viscous resinous materials. There was obtained, however, a low yield of the fully aromatic triphenyl-4-quinolylsilane.

The adduct was shown to be the 4-isomer and not the 2-isomer by the preparation of triphenyl-2-quinolylsilane from 2-quinolyllithium and chlorotriphenylsilane. The melting point of the 2-isomer, 129.5-131.5°, was depressed when admixed with the 4-isomer, m.p. 205-206°. Also the infrared spectra were different.

Although the formation of the 2-quinolyl derivative cannot be excluded in the reaction of triphenylsilyllithium with quinoline, due to the low yield of the 4-quinolyl compound, the course of the reaction does proceed with some 1,4-addition.

Studies in the Benzosilacycloalkene Series

The physiological effects of organosilicon compounds have not been extensively studied to permit generalizations, but of the compounds studied they appear to be less toxic than their

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[109] F. R. Jensen and R. L. Bedard, ibid., 24, 874 (1959).

carbon analogues.[110] However, compounds that are easily hydrolyzed, such as chlorosilanes, are quite toxic due to their hydrolysis products.

Although physiological activity of many drugs is not clearly understood, their effects may be a consequence of their close resemblance to metabolic compounds. Since the silicon atom is larger than the carbon atom, the incorporation of a silicon atom into a carbon ring system should alter the shape of the system without greatly changing the basic structure. The subsequent physiological effect of such an alteration in the perhydro-1,2-cyclopentanophenanthrene system should prove interesting.

One approach to the preparation of these cyclic silanes would be to begin with tetrahydronaphthalene or α-tetralone compounds in which a silicon atom has replaced a carbon atom in the aliphatic portion and subsequently build the molecule to the steroid nucleus. One example of a cyclic silane having the α-tetralone structure and one example of the next higher homolog have been reported.[1] Since this method of preparation is limited to the availability of the acid derivatives that are obtained from silylmetallic reagents, the purpose of this investigation was to develop better methods for the preparation of this class of cyclic silanes and to study some of

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[110] H. Gilman and G. E. Dunn, Chem. Rev., 52, 77 (1953).

their reactions. These compounds will be referred to as benzosilacycloalkenes.

The method which appeared to be the most promising for their preparation was an intramolecular cyclization reaction of (o-chlorophenyl)alkyl-substituted silicon hydrides with sodium metal in an inert solvent. The silicon hydrides, rather than the chlorosilanes, were preferred due to ease of handling, and sodium was the metal of choice since Benkeser and Foster[111] had shown that the metal did not react with silicon hydrides, even at elevated temperatures. Also, Benkeser and Foster have observed quantitative reactions of phenylsodium with silicon hydrides.[111]

The first benzosilacycloalkene, 2:3-benzo-1,1-diphenyl-1-silacyclohex-2-ene (XXIIId), was obtained in good yield by ring closure of [3-(o-chlorophenyl)propyl]diphenylsilane (XXIId) with sodium metal in toluene. The silane was prepared from chlorodiphenylsilane and 3-(o-chlorophenyl)propylmagnesium bromide. The Grignard reagent was partially characterized by carbonation to the corresponding acid. The precursors to the organomagnesium compound were obtained using classical preparative methods.

To illustrate the versatility of this method and to make available other precursory benzosilacycloalkenes, the five-

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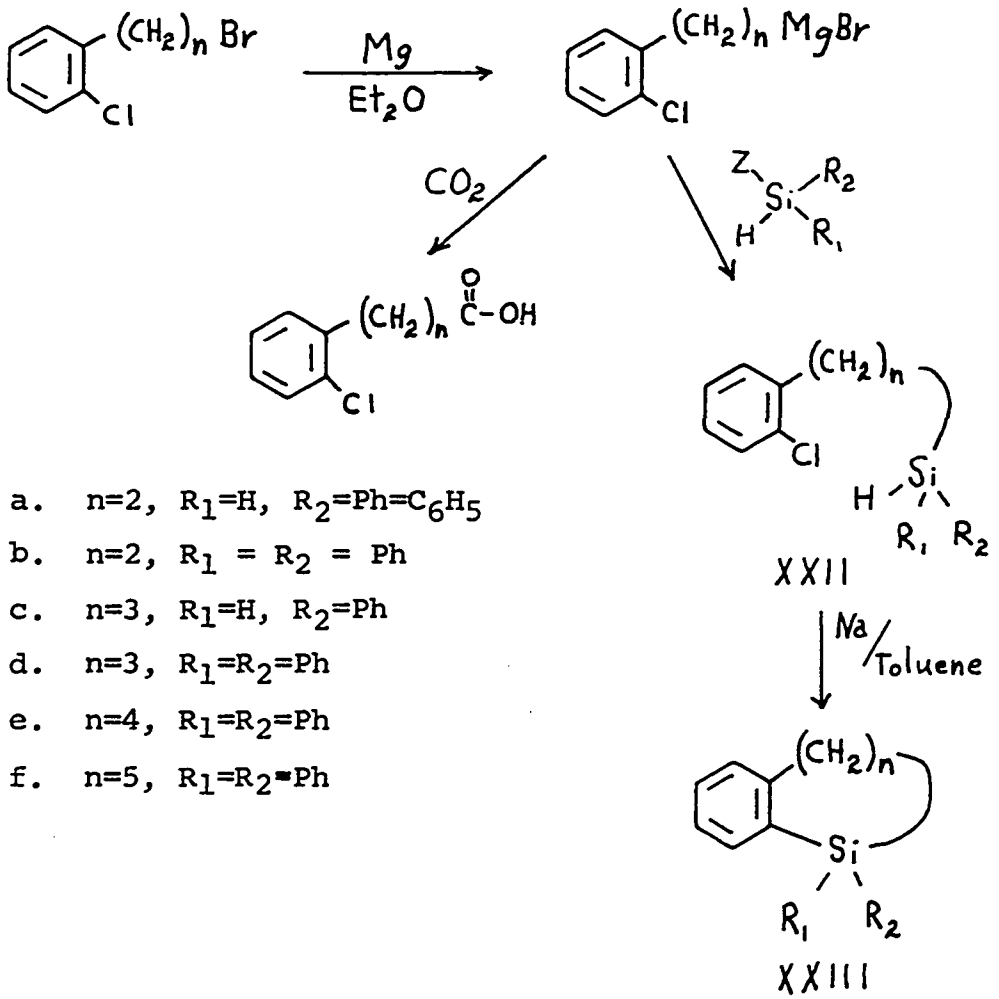
[111] R. A. Benkeser and D. J. Foster, J. Am. Chem. Soc., 74, 5314 (1952).



a. n=2, R_1=H, R_2=Ph=C_6H_5

b. n=2, R_1 = R_2 = Ph

c. n=3, R_1=H, R_2=Ph

d. n=3, R_1=R_2=Ph

e. n=4, R_1=R_2=Ph

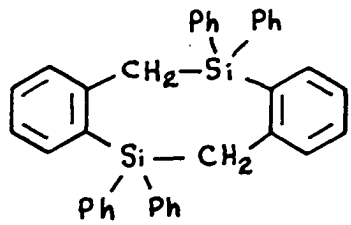
f. n=5, R_1=R_2=Ph

membered (XXIIIb) and the seven-membered (XXIIIe) ring compounds were prepared in good yields. The eight-membered homolog (XXIIIf) was similarily synthesized but in a low yield.

By varying R_1 and R_2, the method proved to be applicable for the preparation of other functional and non-functional derivatives. Thus, by treating phenylsilane with the appropriate organomagnesium compound, and subsequently effecting ring closure, 2:3-benzo-1-phenyl-1-silacyclopent-2-ene (XXIIIa) and 2:3-benzo-1-phenyl-1-silacyclohex-2-ene (XXIIIc) were

obtained in good yields. These Si-H-containing compounds were converted into the fully-phenylated derivatives by reaction with phenyllithium. Conceivably, other derivatives can be prepared by utilizing various organolithium reagents.

Benzosilacycloalkenes which should prove of interest due to the inherent ring strain are the benzosilacyclobutenes. However, the existence of the strain may deter their synthesis. In an effort to prepare such a derivative, o-chlorobenzyldiphenylsilane was reacted with sodium under the conditions used to prepare the higher homologs. The reaction appeared to be slow and, after 24 hours at reflux, a 55.5% recovery of starting material was obtained. A solid material, m.p. 313-315°, was isolated which has been assigned the structure 2:3,6:7-dibenzo-1,1,5,5-tetraphenyl-1,5-disilacyclooocta-2,6-diene (XXIV), based on its high melting point, elemental analysis, and infrared spectrum. A Rast molecular weight determination gave erratic results, possibly due to its insolubility. Compound XXIV would result from an intermolecular cyclization reation. An analogous intermolecular cyclization reaction has been employed to prepare 5,10-di-



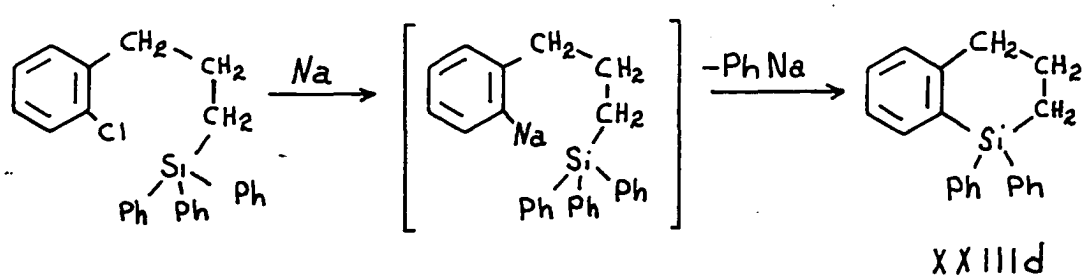
XXIV

hydrosilanthrene derivatives from o-chlorophenylsilanes.[112] To improve the yield of XXIV, o-bromobenzyldiphenylsilane was prepared and treated similarly. The yield of the cyclic compound was still low, but the starting material was recovered in only a 15.5% yield. The reaction that appeared to be enhanced was the competing intermolecular polymerization reaction as the distillation residue consisted of an immobile liquid containing Si-H groupings.

To further broaden the scope of this cyclization reaction, dibenzyl[2-(o-chlorophenyl)ethyl]silane and dibenzyl-[3-(o-chlorophenyl)propyl]silane were prepared and reacted with molten sodium. However, there was no apparent reaction and the starting material was recovered unchanged in each case. Treatment of the recovered propyl derivative with phenyllithium gave dibenzyl[2-(o-chlorophenyl)propyl]-phenylsilane. The reason for the anamolous results of the benzyl compound is, at present, unknown. Metalation of the methylene carbon is a possibility, but benzyltriphenylsilane showed no reaction with sodium metal. Furthermore, the course of the cyclization reaction was verified by the lack of a reaction between sodium and diphenyl-n-propylsilane, and by the facile reaction between sodium and [3-(o-chlorophenyl)propyl]triphenylsilane.

[112]E. A. Zuech, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the preparation of cyclic organosilicon compounds. Private communication. 1960.

The reaction of sodium with [3-(o-chlorophenyl)propyl]-triphenylsilane had another interesting aspect. The product of the reaction was the previously prepared 2:3-benzo-1,1-diphenyl-1-silacyclohex-2-ene (XXIIId), rather than the expected triphenyl-(γ-phenylpropyl)silane. In all probability, [3-(o-sodiophenyl)propyl]triphenylsilane is formed which subsequently cyclizes with the displacement of a phenyl group as phenylsodium.



Other cleavage-cyclization reactions have been reported,[113,114] but these appear to occur when a five-membered cyclic silane was the product. However, Gilman and Zuech[112] observed the formation of a six-membered cyclic silane when N-methyl-2,2'-dilithiodi-p-tolylamine was allowed to react with chlorotriphenylsilane. In this case phenyllithium is displaced.

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[113]H. Gilman and R. D. Gorsich, J. Am. Chem. Soc., 80, 1883 (1958).

[114]D. Wittenberg and H. Gilman, ibid., 80, 2677 (1958).

The low reactivity of o-chlorobenzyl-, dibenzyl[2-(o-chlorophenyl)ethyl]-, and dibenzyl[3-(o-chlorophenyl)propyl]-diphenylsilane encouraged further investigation into the reactivity of o-chlorophenyl-substituted derivatives. Ramsden et al.,[115] reported that no difficulties were encountered in the initiation of the reaction between various aryl chlorides and magnesium in tetrahydrofuran, although o-chloroalkylbenzene derivatives, other than o-chlorotoluene, were not studied. One exception was 2-chloro-p-xylene in which the initiation was difficult. Also, the reaction between o-chlorophenylphenylsilane and magnesium could not be initiated.[112] In this study, several silicon-containing and non-silicon-containing compounds were allowed to react with magnesium and lithium in tetrahydrofuran, and in one case in an ether-tetrahydrofuran mixture. The results are summarized in Table 2.

The chloro derivatives reacted with lithium in tetrahydrofuran with ease. A red color developed when the reaction had started, indicative of an organolithium reagent,[108] but with silicon-containing compounds, the solution rapidly became black in color. This is probably due to silicon-carbon bond cleavage that Gorsich[3] observed with lithium and organosilicon compounds in tetrahydrofuran. The only successful reactions

[115] H. E. Ramsden, A. E. Balint, W. R. Whitford, J. J. Walburn, and R. Cserr, J. Org. Chem., 22, 1202 (1957).

Table 2. Reaction of o-chlorophenyl-substituted compounds with lithium and magnesium

Compounds	Metal	Solvent[a]	Remarks
[3-(o-Chlorophenyl)propyl]-triphenylsilane	Mg	THF	No reaction.
[3-(o-Chlorophenyl)propyl]-triphenylsilane	Li	Ether/ THF	No apparent reaction.[b]
[3-(o-Chlorophenyl)propyl]-triphenylsilane	Li	THF	Reaction. Products were oils.
[3-(o-Chlorophenyl)propyl]-diphenylsilane	Mg	THF	No reaction
[3-(o-Chlorophenyl)propyl]-diphenylsilane	Li	THF	Reaction. Products were cyclic silane and oils.
o-Chlorotoluene	Mg	THF	Reaction. Carbonation gave o-toluic acid.
o-Chloroethylbenzene	Mg	THF	Reaction. Carbonation gave o-ethylbenzoic acid.
o-Chloroethylbenzene	Mg	THF	No reaction.
o-Chloropropylbenzene	Mg	THF	No reaction.
o-Chloropropylbenzene	Li	THF	Reaction. Carbonation gave o-propylbenzoic acid.

[a]THF = tetrahydrofuran.

[b]The recovered material melted 7° above that of the starting material. See Experimental.

with magnesium were with o-chlorotoluene, and in one run, o-ethylbenzene. However, the ethyl derivative appeared to react somewhat slower than the o-chlorotoluene, and o-chloropropylbenzene did not react. Although it is not completely conclusive, the longer-chained alkyl groups ortho to the chloro group appear to retard the formation of the Grignard reagent. A similar retarding effect of ortho-alkyl groups was observed in the esterification of o-methyl-, o-ethyl-, and o-propylbenzoic acid.[116]

The reaction of [3-(o-chlorophenyl)propyl]triphenylsilane with lithium in an ether-tetrahydrofuran mixture gave unexpected results. There was no evidence of a reaction, but the recovered solid melted at 84.5-86.5°, whereas the starting material melted at 77.5-79°. The infrared spectra of the recovered material and the starting silane were superimposable. The starting material, [3-(o-chlorophenyl)propyl]triphenylsilane, had been prepared by two routes; from chlorotriphenylsilane and 3-(o-chlorophenyl)propylmagnesium bromide and from [3-(o-chlorophenyl)propyl]diphenylsilane and phenyllithium, and was observed to melt at 77.5-79.5°. Several months later, the chlorotriphenylsilane and 3-(o-chlorophenyl)propylmagnesium bromide reaction was repeated to give a product melting at 88-89°. The infrared spectrum of this material was super-

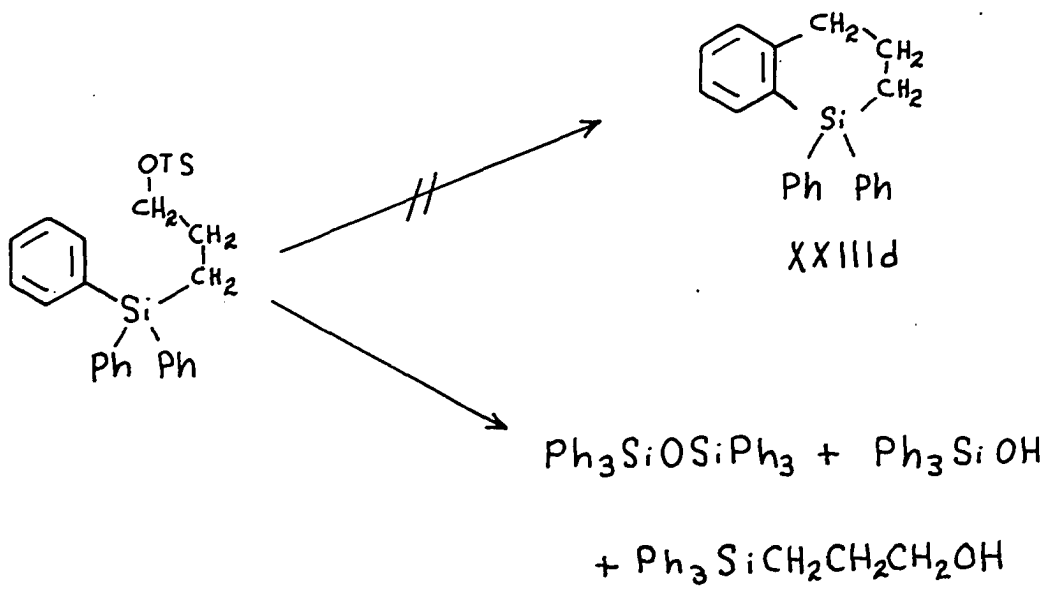
[116] J. J. Sudborough and M. K. Turner, J. Chem. Soc., 101, 237 (1912).

imposable with the infrared spectra of the previously isolated derivatives that melted at 77.5-79.5° and 84.5-86.5°. The melting points of the latter were rechecked and were found to melt at 88-90°. In addition, material previously observed to melt over the range 75-86° melted at 89-90°. This appears to be a case of polymorphism in which there is a slow transition from the lower melting compound to the higher melting compound. Attempts to reverse this process were unsuccessful. Polymorphism has recently been observed with methoxytriphenylsilane,[54] p-tolyltriphenylsilane,[117] and 2-(N-ethyl-2,4-dibromoanilino)-5-bromophenyldiphenylsilanol.[38] In two of these cases,[38,54] attempts to convert the higher melting solid to the lower melting solid were also unsuccessful.

The reactions of [3-(o-chlorophenyl)propyl]diphenylsilane with lithium in tetrahydrofuran did afford a low yield of the cyclic silane, 2:3-benzo-1,1-diphenyl-1-silacyclohex-2-ene (XXIIId). The reaction was complicated by side reactions involving cleavage of the Si-H bond or Si-C bonds. Gorsich[3] has shown that silicon hydrides and tetraphenylsilane readily react with lithium in tetrahydrofuran, and, therefore, this cyclization method appears to be of little preparative value.

[117] B. J. Gaj. Reactions of triphenylsilyllithium with compounds containing Group VB elements. Unpublished Ph. D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1960.

In the early stages of this investigation, an independent synthesis of these benzosilacycloalkene compounds was sought. Heck and Winstein[118] had shown that solvolysis of 4-phenylbutyl benzenesulfonates gave tetralin, and, therefore, it was envisioned that perhaps solvolysis of 3-triphenylsilylpropyl p-toluenesulfonate would afford the desired cyclic silane. However, formolysis of 3-triphenylsilylpropyl p-toluenesulfonate yielded hexaphenyldisiloxane, triphenylsilanol, and 3-triphenylsilylpropanol-1. In addition, a trace of a solid melting at 81-82° was isolated, but this was not the desired cyclic derivative or allyltriphenylsilane.



[118]R. Heck and S. Winstein, J. Am. Chem. Soc., 79, 3105 (1957).

The 3-triphenylsilylpropanol-1 would arise from hydrolysis of the formate ester formed in the solvolysis, whereas the hexaphenyldisiloxane and triphenylsilanol would result from a γ-elimination reaction in which the silicon atom is attacked by base to give triphenylsilyl formate, cyclopropane, and p-toluenesulfonic acid. The triphenylsilyl formate would subsequently be converted into hexaphenyldisiloxane or triphenylsilanol.

To test the possibility of γ-elimination, triphenylsilyllithium was allowed to react with 3-triphenylsilylpropyl p-toluenesulfonate. It was postulated that if a γ-elimination reaction was occurring the silylmetallic reagent would attack the silicon atom of the sulfonate to give the highly insoluble hexaphenyldisilane as one of the products. When the reaction was carried out in a 1:1 molar ratio, a solid was formed during the addition of triphenylsilyllithium, and hexaphenyldisilane was subsequently isolated, but in low yield (5.6%). There were also obtained 1,3-bis(triphenylsilyl)propane (34%), and 3-triphenylsilylpropanol-1 (41.6%). The 1,3-bis(triphenylsilyl)propane would result from a normal S_N2 reaction at the carbon atom bearing the p-toluenesulfonate by the silylmetallic reagent, and the alcohol may be formed by hydrolysis of the starting material during the work-up or during chromatography. However, in a separate experiment, the p-toluenesulfonate was only partially converted into

alcohol by passing through a column of alumina, and the sulfonate appears to be rather resistant to acid hydrolysis (see preparation).

To throw more light on the reaction, 3-triphenylsilylpropyl p-toluenesulfonate was treated with two equivalents of triphenylsilyllithium. The reaction products were triphenylsilane (9.6%), tetraphenylsilane (2.5%), 1,3-bis(triphenylsilyl)propane (53.5%), 3-triphenylsilylpropanol-1 (9.4%), and triphenylsilanol (5.1%). Hexaphenyldisilane was not formed. Also, the triphenylsilane had a sulfur odor. Similarly, when triphenylsilyllithium was reacted with n-butyl p-toluenesulfonate in a 2:1 molar ratio, tetraphenylsilane (1.5%) and the expected n-butyltriphenylsilane were isolated. The mode of formation of these compounds can only be speculative. The preferred reaction is formation of 1,3-bis(triphenylsilyl)propane by a S_N2 displacement reaction. In completing reactions, hexaphenyldisilane could be formed via a γ-elimination reaction, and the propanol is formed by cleavage of the alcohol sulfur-oxygen bond. An E_2 elimination with triphenylsilyllithium acting as the base, and a subsequent reaction of the resulting triphenylsilane with triphenylsilyllithium would explain the formation of tetraphenylsilane.[3, 119] In support of these suggested mechanisms,

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[119] A. G. Brook and H. Gilman, ibid., 76, 2333 (1954).

Sommer and co-workers[120] found that 3-bromopropyltrimethylsilane underwent a γ-elimination reaction with aluminum halides to give a 92% yield of cyclopropane, together with an 82% yield of bromotrimethylsilane. Furthermore, 3-chloropropyldiethylmethylsilane undergoes γ-elimination during distillation.[121] Cleavage of the alcohol sulfur-oxygen bond has been reported as a side reaction of n-butyl p-toluenesulfonate and phenylmagnesium bromide,[122] and similar addition cleavage reactions were observed with diphenyl sulfone and triphenylsilyllithium.[123]

An independent synthesis of the benzosilacycloalkenes was accomplished by treatment of the double Grignard reagents of 2-(o-bromophenyl)ethyl bromide and 3-(o-bromophenyl)propyl bromide with the appropriate dichlorosilane. For example, 3-(o-bromophenyl)propyl bromide reacted with magnesium in tetrahydrofuran to give a homogeneous solution of the di-Grignard reagent. When the preparation was carried out in an

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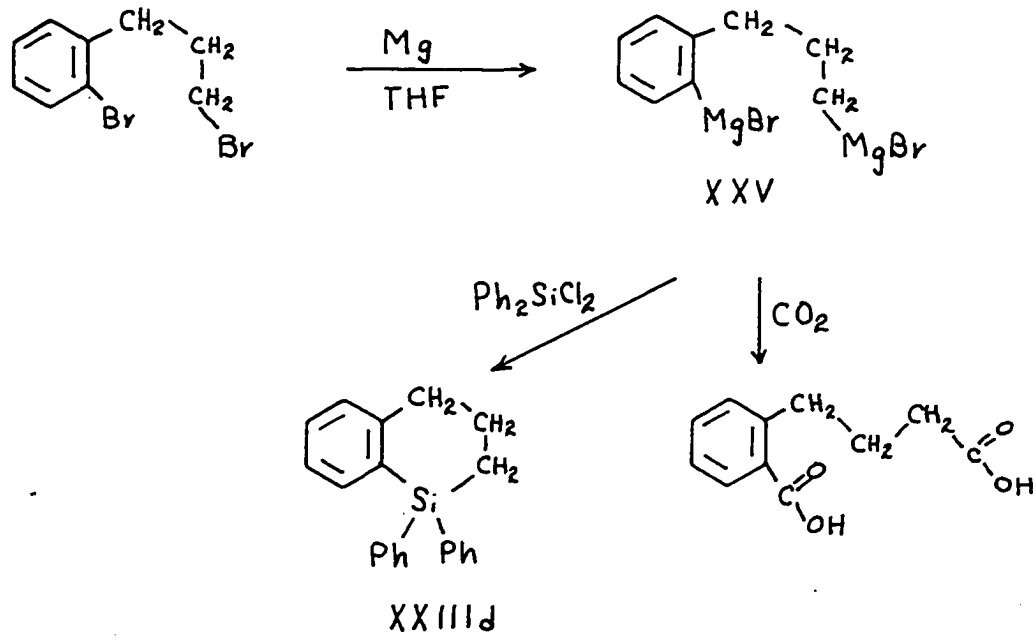
[120] L. H. Sommer, R. E. Van Strien, and F. C. Whitmore, *ibid.*, *71*, 3056 (1949).

[121] V. A. Ponomarenko, B. A. Sokolov, Kh. M. Minachev, and A. D. Petrov, *Proc. Acad. Sci. U. S. S. R., Sec. Chem.*, (Eng. trans.), *106*, 17 (1956).

[122] H. Gilman and L. L. Heck, *J. Am. Chem. Soc.*, *50*, 2223 (1928).

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

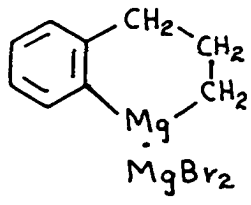
ether-tetrahydrofuran mixture a heterogeneous solution resulted, and the yield of the di-Grignard reagent was decreased. Carbonation of the tetrahydrofuran solution gave a good yield of 4-(o-carboxyphenyl)butyric acid. Addition of the di-Grignard reagent to dichlorodiphenylsilane gave 2:3-benzo-1,1-diphenyl-1-silacyclohex-2-ene (XXIIId).



In addition to the alternate synthesis of XXIIId and the five-membered homolog XXIIIb, the di-Grignard reagent was successfully employed to prepare two tin analogues, 2:3-benzo-1,1-diphenyl-1-stannacyclopent-2-ene and 2:3-benzo-1,1-diphenyl-1-stannacyclohex-2-ene, and a cyclic silicon hydride 2:3-benzo-1-methyl-1-silacyclohex-2-ene.

The actual composition of the double Grignard reagent

(XXV) is probably not that as shown. In view of the fact that magnesium bromide may be precipitated from Grignard solutions by the addition of dioxane, and the recent proposal[124] that Grignard reagents are better represented by the complex $R_2Mg \cdot MgX_2$, XXV may have the structure



Also, this appears to be the first known example of an aryl-alkyl di-Grignard reagent.[125]

Two attempts were made to prepare isomeric benzosilacyclopentenes. An intramolecular Wurtz-Fittig reaction with o-chlorobenzylchloromethyldimethylsilane gave only the doubly reduced compound benzyltrimethylsilane. None of the expected 3:4-benzo-1,1-dimethyl-1-silacyclopent-3-ene could be isolated. Similarly, 3:4-benzo-1,1-diphenyl-1-silacyclopent-2-ene could not be isolated from the reaction of α,α'-dibromo-o-xylene and dichlorodiphenylsilane in the presence of magnesium. The products isolated were octaphenylcyclotetra-

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[124] R. E. Dessy and G. S. Handler, J. Am. Chem. Soc., 80, 5824 (1958).

[125] I. T. Millar and H. Heaney, Quart. Rev., 11, 109 (1957).

silane,[69] octaphenylcyclotetrasilanoxide,[71] s-dibenzycyclo-octadiene,[70] s-tribenzcyclododecatriene,[70] and polymeric material. Although Wilson and Hutzel[126] recently coupled α,α'-dibromo-o-xylene and chlorotrimethylsilane with magnesium to give α,α'-di(trimethylsilyl)-o-xylene, the above reaction is complicated by the reaction of dichlorodiphenylsilane with magnesium to give octaphenylcyclotetrasilane.[127] Octaphenylcyclotetrasilane is easily oxidized to octaphenylcyclotetrasilanoxide[127] or it may have been formed from the 1,4-dichloro compound during work-up of the reaction.[71] The two non-organosilicon compounds probably are formed by dimerization and trimerization of the intermediate o-qunio-dimethane which results from the reaction of α,α'-dibromo-o-xylene with magnesium.[70] Mann and Stewart[15] were also unsuccessful in preparing the analogous phosphorus compound from α,α'-dichloro-o-xylene, magnesium, and dichlorophenylphosphine.

Since the precursory properties of benzosilacycloalkenes will depend largely on the presence of functional groups on the ring, either on the benzo portion or the aliphatic chain, it was of interest to investigate some of the reactions of

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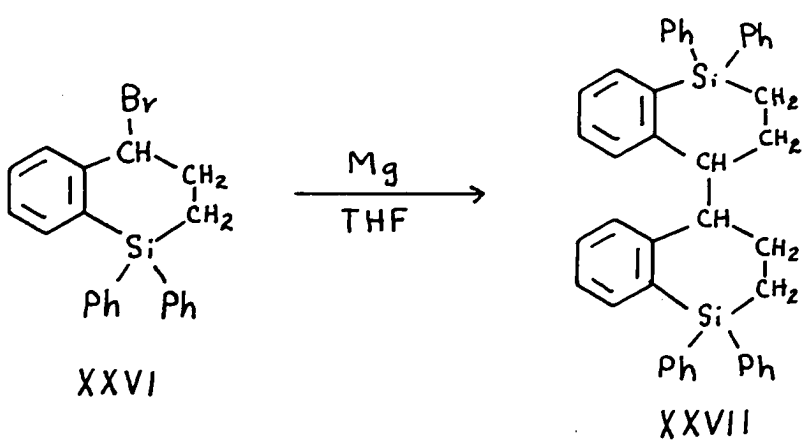
[126] G. R. Wilson and G. M. Hutzel, J. Org. Chem., 24, 1791 (1959).

[127] D. J. Peterson, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the reaction of dichlorodiphenylsilane with various metals. Private communication. 1961.

these cyclic silanes, particularly 2:3-benzo-1,1-diphenyl-1-silacyclohex-2-ene. This compound underwent smooth bromination with N-bromosuccinimide to give good yields of asymmetric 2:3-benzo-4-bromo-1,1-diphenyl-1-silacyclohex-2-ene (XXVI). The bromination was established as occurring at the expected 4-position by a proton magnetic resonance study of the compound. The single tertiary proton peak occurred at 4.38τ, which can be assigned to a benzylic hydrogen. If the bromination had occurred at the 5- or 6-position, a higher shielding value would have been observed for the tertiary hydrogen.

In an effort to convert the bromo compound (XXVI) into other functional derivatives, the compound was reacted with magnesium and carbonated. The only identifiable product was 4,4'-bi(2:3-benzo-1,1-diphenyl-1-silacyclohex-2-ene) (XXVII). The structure was assigned on the basis of its infrared spectrum, elemental analysis, and molecular weight.



XXVI XXVII

The same material was obtained upon hydrolysis of the reaction mixture. Evidently, the Wurtz reaction which normally competes with the formation of the Grignard reagent is the predominant reaction. Normant[128] stipulates that Wurtz-type reactions are enhanced when tetrahydrofuran is used as the solvent in the preparation of benzylic and allylic Grignard reagents.

In an attempt to prepare the ketone, 2:3-benzo-1,1-diphenyl-1-silacyclohex-2-en-4-one, that had been obtained by cyclization of the acid chloride of 3-triphenylsilylpropionic acid,[1] the bromo compound was hydrolyzed with aqueous silver nitrate according to the method of Gilman et al.[129] The resulting alcohol could not be purified, possibly due to some dehydrobromination and/or γ-elimination reactions. The infrared spectrum was similar to other six-membered ring compounds (see Table 3). The crude alcohol was oxidized with potassium permangnate in acetone to give a low yield of a ketonic product, m.p. 105-108.5°. The 2,4-dinitrophenylhydrazone was bright red flakes, m.p. 228-230°, and gave good elemental analysis for the proposed 2,4-dinitrophenylhydrazone of 2:3-benzo-1,1-diphenyl-1-silacyclohex-2-en-4-one. The

[128] H. Normant. Alkenylmagnesium halides. In R. A. Raphael, E. C. Taylor, and H. Wynberg, eds. Advances in organic chemistry, Vol. 2, pp. 1-65. New York, Interscience Publishers, Inc. 1960.

[129] H. Gilman, C. G. Brannen, and R. K. Ingham, J. Am. Chem. Soc., 78, 1689 (1956).

reported[1] melting points of these two derivatives are 127-128° and 240° (dec.), respectively. The infrared spectra of the two ketones were quite different; that of the ketone isolated in this investigation (m.p. 105-108.5°) was similar to other benzosilacyclohexenes (see Table 3), whereas, the previously prepared ketone[1] (m.p. 127-128°) showed a strong band between 9.28 and 9.62μ, indicative of an Si-O-Si or Si-O-C linkage.[85]

The ketone was obtained (isolated as the 2,4-dinitrophenylhydrazone), but in low yield, by two other methods. The bromo compound was converted into an impure nitrato compound and subsequently hydrolyzed to the ketone with base. This method had been used recently to convert a benzyl bromide derivative into an aldehyde in good yield.[130] A third method involved the treatment of 2:3-benzo-1,1-diphenyl-1-silacyclohex-2-ene with two equivalents of N-bromosuccinimide, followed by hydrolysis of the crude dibromo compound to the ketone with aqueous silver nitrate.[129]

In these experiments, the desired ketone could not be isolated as the pure material due to contamination by oily products believed to arise from dehydrobromination and/or γ-elimination reactions. The easy dehydrobromination of tetralin-type compounds is well-established,[131,132] and in some

[130] R. L. Letsinger and J. D. Jamison, ibid., 83, 193 (1961).

[131] R. A. Barnes, ibid., 70, 145 (1948).

[132] L. Horner and E. H. Winkelmann, Angew. Chem., 71, 349 (1959).

cases the elimination of HX occurs spontaneously. γ-Elimination reactions have been discussed previously, and in this case, the bromo compound XXVI may be particularly prone toward this type of elimination since the bromo group is benzylic in character.

The infrared spectra of the benzosilacycloalkenes and their precursors in carbon disulfide or carbon tetrachloride, or as a liquid film showed the expected aromatic C-H, aliphatic C-H, and ortho-disubstitution absorption bands at 3.3, 3.4, and 13.0-13.6μ, respectively. When OH, Si-H, Si-CH_3, or Si-O-Si groups were present in the compounds, the characteristic bands at 2.7, 4.75, 8.0, and 9.5μ, respectively, were observed in the spectra. The region in which the silicon-phenyl linkage band is normally observed (8.7-9.55μ) appeared to exhibit certain regularities, and these are summarized in Table 3.

The five-membered ring compounds contained a strong single peak at 8.99μ, whereas the six-membered ring homologs with at least one phenyl group attached to the silicon atom consistently showed three medium to strong bands between 8.75 and 9.07μ. The bands at 8.8 and 8.9μ became weaker as the ring size increased and disappeared in ethyldiphenylsilane. The absorption band at 8.8μ may be associated with ortho-disubstitution as shown by the presence of a very weak band at about 8.8μ in the o-chlorophenyl derivatives. However,

Table 3. Infrared data of benzosilacycloalkenes[a]

Compound (medium)	Bands in 8.7-9.55μ	region[b]
2:3-Benzo-1-phenyl-1-silacyclopent-2-ene(liq.)	8.98(s)	9.51(m)
2:3-Benzo-1,1-diphenyl-1-silacyclopent-2-ene(CS_2)	8.99(s)	9.48(m)
2:3-Benzo-1-methyl-1-silacyclohex-2-ene(liq.)	8.8(s),8.9(s)	9.35(s)
2:3-Benzo-1-phenyl-1-silacyclohex-2-ene(liq.)	8.8(s),8.92(s),9.03(s)	9.35(m)
2:3-Benzo-1,1-diphenyl-1-silacyclohex-2-ene(CS_2)	8.81(s),8.92(s),9.07(s)	9.34(m)
2:3-Benzo-4-hydroxy-1,1-diphenyl-1-silacyclohex-2-ene(CS_2)[c]	8.8(m),8.92(s),9.07(s)	9.34(m)
2:3-Benzo-1,1-diphenyl-1-silacyclohex-2-en-4-one (CS_2)	8.75(m),8.92(s),9.0(s)	9.32(m)
2:3-Benzo-1,1-diphenyl-1-silacyclohept-2-ene(CS_2)	8.8(w),8.89(m),9.04(s)	9.4(m)
2:3-Benzo-1,1-diphenyl-1-silacyclooct-2-ene(CS_2)	8.75(w),8.99(m),9.06(s)	9.37(w)
[3-(o-Chlorophenyl)propyl]-triphenylsilane(CS_2)	8.82(w) 9.05(s)	9.55(m)
Ethyldiphenylsilane(liq.)	9.01-9.05(s)[d]	9.45(w)

[a]Two non-cyclic compounds are included.

[b]Letter in parenthesis represents intensity of band: s = strong, m = medium, and w = weak.

[c]Impure.

[d]Broad band slightly split.

this band is much more intense in the cyclic compounds. Therefore, it appears that the 1-aryl-substituted benzosilacyclohexenes can be identified, in part, by the presence of three strong absorption bands at ca. 8.8, 8.9, and 9.0μ. A band at 9.35μ may also be characteristic of the system.

The proton magnetic resonance (n.m.r.) data of the benzosilacycloalkenes are shown in Table 4. For the purpose of correlating the cyclic silanes with the open-chained analogues and other derivatives, particularly compounds containing the Si-H grouping, the proton magnetic resonance spectra of some representative derivatives were determined.[133] These data are given in Table 5. The data were obtained relative to tetramethylsilane and the shielding values are expressed as τ values as described by Tiers.[134] The position of each peak is accurate to ± 0.5 cycle/sec. The numbering system in Table 4 corresponds to the numbering system of the benzosilacycloalkenes.[135] The aromatic proton shielding values are not included as the protons were represented by a multiplet in most cases.

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[133]For a correlation of some silicon hydrides with their carbon analogues, see D. E. Webster, J. Chem. Soc., 5132 (1960).

[134]G. V. D. Tiers, J. Phys. Chem., 62, 1151 (1958).

[135]See page 2 of this dissertation.

Table 4. Proton magnetic resonance data of cyclic silanes[a]

Compound (solvent)	Si-H[b]	C_4-H[b]	C_5-H[b]	C_6-H[b]
2:3-Benzo-1-phenyl-1-silacyclopent-2-ene (CCl_4)	4.85(3)	6.83(3)	8.69(m)	
2:3-Benzo-1,1-diphenyl-1-silacyclopent-2-ene (CCl_4)		6.85(3)	8.57(3)	
2:3-Benzo-1-phenyl-1-silacyclohex-2-ene (CCl_4)	5.13(3)	7.16(3)	7.98(6)	8.81(7)
2:3-Benzo-1,1-diphenyl-1-silacyclohex-2-ene ($CDCl_3$)		7.13(3)	7.97(m)	8.63(4)
2:3-Benzo-4-bromo-1,1-diphenyl-1-silacyclohex-2-ene($CDCl_3$)		4.38(4)	m	m
2:3-Benzo-1,1-diphenyl-1-silacyclohex-2-en-4-one(CCl_4)			7.19(5)	8.56(4)
2:3-Benzo-1,1-diphenyl-1-silacyclohept-2-ene ($CDCl_3$)		7.26(3)	m	m
2:3-Benzo-1,1-diphenyl-1-silacyclooct-2-ene ($CDCl_3$)		7.23(3)	m	m

[a]Run at 60 mc.

[b]Values are given in τ units. Number in parenthesis represents peak multiplicity. m signifies a multiplet, where the number of peaks could not be counted accurately.

Table 5. Proton magnetic resonance data of non-cyclic silanes[a]

Compound	Si-H[b]	Si-C[b] (H)	Aromatic methyl
Diphenylsilane	5.12(1)		
Methyldiphenylsilane	5.10(4)	9.41(2)	
Ethyldiphenylsilane	5.21(m)	8.92(1)[c]	
Diphenyl-n-propylsilane	5.16(3)	m[c]	
Diphenyl(phenylethynyl)-silane	4.75(1)		
Tri-p-tolylsilane	4.58(1)		7.76(1)
Triphenylsilane	4.56(1)		
Chlorodiphenylsilane	4.32(1)		
Tri-o-tolylsilane	4.27(1)		7.68(1)
Trichlorosilane	3.84(1)		

[a]Run at 60 mc. in carbon tetrachloride.

[b]Values are given in τ units. Number in parenthesis represents peak multiplicity. m signifies a multiplet.

[c]Methylene and methyl groups were not resolved.

The shielding value of the proton attached to the silicon atom is particularly noteworthy. In the five-membered ring cyclic hydride, the τ value is approximately 0.3 less than the six-membered ring homolog. However, the shielding value of the six-membered ring derivative was about the same as that of the non-cyclic compounds methyl-, ethyl-, and n-propyldiphenylsilane. Also the shielding value of the C_4-protons (C_4-H), which are benzylic hydrogens, in the five-membered ring is about 0.3 less than the corresponding C_4-protons of the six-membered ring, and 0.4 less than the seven- or eight-membered ring compounds. Whether these chemical shifts are due to ring strain and/or particular conformations of the rings cannot be deduced without additional data.

Ethyldiphenylsilane proved to be somewhat anomalous. Although the methyl group of methyldiphenylsilane exhibited the expected doublet in the n.m.r. spectrum, the ethyl group occurred as a single peak (two shoulders), rather than the expected resolved methylene and methyl groups, commonly observed for ethyl groups. This appears to be related to the electronegativity of the group attached to the ethyl group and has also been observed with dichlorodiethylsilane[136] and tetraethyllead.[137]

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[136] P. T. Narasimhan and M. T. Rogers, J. Am. Chem. Soc., 82, 5983 (1960).

[137] E. B. Baker, J. Chem. Phys., 26, 960 (1957).

Suggestions for Further Research

The reactions of silicon hydrides with the lithium salts of nitrogen bases should be extended to piperidine, pyrrole, and piperazine. Non-symmetrical and symmetrical silanes that have a silicon-nitrogen bond may prove interesting. In this connection, a comparison of the chemistry of these compounds with halosilanes would be worthwhile.

A study of the reactions of other silylmetallic reagents with anthracene should be carried out. The adducts could be dehydrogenated to the aromatic derivatives. For example, methyldiphenylsilyllithium should afford 9,10-dihydro-9-(methyldiphenylsilyl)anthracene. Subsequent aromatization with N-bromosuccinimide or chlornil should give 9-(methyldiphenylsilyl)anthracene. These compounds could also be obtained by the reaction of 9-lithioanthracene with the appropriate chlorosilane, although possibly in lower yields. The reaction of silylmetallic compounds with these silyl-substituted anthracene derivatives should provide a method for the preparation of di-substituted anthracene compounds. However, silicon-carbon bond cleavage may be appreciable in this latter reaction. The preparation of a series of silyl-substituted anthracene derivatives for scintillation studies may be profitable.

Since the dilithium adduct of anthracene is conveniently prepared, the reactions of this reagent with various silicon

hydrides may provide new functional derivatives.

The studies in the benzosilacycloalkene series should be extended to the preparation of the isomeric analogues of those reported in this investigation. The di-Grignard reagents of o-(2-bromoethyl)benzyl bromide and 2-[o-(2-bromoethyl)phenyl]-ethyl bromide should provide a convenient method for the preparation of six-membered and seven-membered ring compounds. Considerable coupling may be observed, however, with the benzyl bromide derivative.

Another interesting series of compounds would be the benzo-1,4-disilacycloalkenes. These should be obtained from the reaction of o-phenylenedilithium[39] with various bis-(chlorosilyl)-ethanes.[19]

The dehydrohalogenation of 2:3-benzo-4-bromo-1-silacyclohex-2-ene should be studied further, as isolation of the cyclic olefin would provide an interesting functional derivative.

Catalytic and Birch reductions of the benzosilacycloalkenes, particularly the 1,1-dimethyl derivative, should be worthwhile.

For the purpose of synthesizing a perhydrophenanthrene compound having a silicon atom incorporated in the ring system, 2:3-benzo-9 -methoxy-1,1-diphenyl-1-silacyclohex-2-ene, prepared from 2-chloro-5-methoxybenzyl bromide,[138] may be a useful precursor.

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[138] R. G. Wilkinson, T. L. Fields, and J. H. Boothe, J. Org. Chem., 26, 637 (1961).

SUMMARY

A review of the chemistry of cyclic organosilicon compounds since March, 1960, has been presented. Included in this review is the chemistry of cyclic compounds in which the silicon atom is linked to only one carbon atom in the ring system.

The reaction of the lithium salt of morpholine with silicon hydrides was extended to diphenylsilane and phenylsilane. The N-morpholinylsilanes may serve as antioxidants.

Triphenylsilyllithium has been found to add to anthracene and quinoline. These reactions were complicated by the formation of polymeric materials.

For the purpose of subsequently preparing the perhydro-1,2-cyclopentanophenanthrene ring system with a silicon atom incorporated into the ring, procedures have been developed for the preparation of benzosilacycloalkenes which may act as precursors to this steroid nucleus. By intramolecular cyclization of [(o-chlorophenyl)alkyl]diphenylsilanes, five-, six-, seven-, and eight-membered ring compounds were prepared. This method was also applicable for the preparation of two derivatives which contain the silicon-hydrogen grouping: 2:3-benzo-1-phenyl-1-silacyclopent-2-ene and 2:3-benzo-1-phenyl-1-silacyclohex-2-ene. These were obtained by ring closure of [2-(o-chlorophenyl)ethyl]phenylsilane and [3-(o-chlorophenyl)propyl]phenylsilane, respectively. The two

cyclic compounds gave the fully phenylated derivatives upon treatment with phenyllithium.

The benzosilacycloalkenes were also prepared from the di-Grignard reagents of 2-(o-bromophenyl)ethyl bromide and 3-(o-bromophenyl)propyl bromide and the appropriate dichlorosilanes. One silicon-hydride functional derivate, 2:3-benzo-1-methyl-1-silacyclohex-2-ene, was prepared by this method.

2:3-Benzo-1,1-diphenyl-1-silacyclohex-2-ene was readily brominated with N-bromosuccinimide to give good yields of 2:3-benzo-4-bromo-1,1-diphenyl-1-silacyclohex-2-ene. This compound coupled when allowed to react with magnesium. The bromo derivative was converted into a ketone by treatment with silver nitrate and subsequent oxidation with potassium permangnate.

The preparation of these cyclic silanes necessitated the synthesis of several new organic halides and non-cyclic silanes.

An attempt has been made to correlate the proton magnetic resonance spectra of the benzosilacycloalkenes with their open-chain analogues and various other organosilicon compounds.

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