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REACTIONS OF TRIPHENYLSILYLLITHIUM WITH COMPOUNDS CONTAINING GROUP VB ELEMENTS

by

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I. INTRODUCTION

The application of organosilylmetallic compounds in the realm of synthetic organic chemistry blossomed into maturity with the advent of convenient and relatively stable solutions of organosilyllithium compounds in tetrahydrofuran.[1,2] Prior to this, research along these lines was limited to reactions involving suspensions of triphenylsilylpotassium in ethers,[3,4] or unstable solutions of organosilylpotassium compounds in ethylene glycol dimethyl ether.[5] The use of tetrahydrofuran as a solvent for the preparation and reactions of these versatile intermediates provided an incentive to initiate a broad and intensive study of their utility in the synthesis of a wide variety of so-called "custom-made" organosilicon compounds.[6]

Particularly noteworthy among the more recent endeavors

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[1] H. Gilman and G. D. Lichtenwalter, J. Am. Chem. Soc., 80, 608 (1958).

[2] H. Gilman, D. J. Peterson and D. Wittenberg, Chemistry and Industry, 1479 (1958).

[3] R. A. Benkeser and R. G. Severson, J. Am. Chem. Soc., 73, 1424 (1951).

[4] H. Gilman and T. C. Wu, ibid., 73, 4031 (1951).

[5] A. G. Brook and H. Gilman, ibid., 76, 278 (1954).

[6] For an interesting and informative review on organosilylmetallic compounds, see D. Wittenberg and H. Gilman, Quart. Rev., 13, 116 (1959).

in this field is the elegant study[7] by Lichtenwalter, pertaining to the chemistry of organosilyllithium compounds. Of even greater importance, however, is the voluminous literature, dealing with reactions of organosilylmetallic compounds, which has been summarized in the excellent review by Wittenberg and Gilman.[6] The recent expansion in this field, together with the interest in organosilicon compounds as possible high-temperature lubricants and anti-oxidants helped to stimulate the inauguration of this investigation.

In the present study, the reactions of triphenylsilyllithium with a variety of compounds containing group VB elements have been investigated. Thus, triphenylsilyllithium has been shown to: (1) react with trialkyl phosphates to give good yields of alkaltriphenylsilanes; (2) react with triaryl phosphates to displace aryloxy groups; (3) cleave triphenyl derivatives of the more metallic group VB elements; (4) form silicon-containing amines when reacted with N,N-disubstituted amides; and (5) react with N-substituted phthalimides to form *o*-formyl-N-substituted benzamides, with the concomitant formation of hexaphenyldisilane.

The products isolated from the reactions involving phosphate esters, imides and N,N-disubstituted amides were un-

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[7] G. D. Lichtenwalter. Organosilylmetallic compounds and derivations. Unpublished Ph.D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1958.

expected on the basis of the corresponding reactions with Grignard reagents and organolithium compounds. An attempt has been made to explain their formation.

Incidental to this research, two unprecedented reactions of organolithium compounds were discovered: namely, their alkylation with trialkyl phosphate esters, and the cleavage by them of the silicon-silicon bond in hexaphenyldisilane. The former reaction was found to be applicable to some Grignard reagents.

Efforts during the past few years have contributed considerably toward an understanding of organosilylmetallic chemistry. However, the possibilities for future research in this field appear to be unlimited; much interesting and challenging work remains to be done.

II. HISTORICAL

In 1924, Kraus and Nelson[8] reported the isolation of triethylsilane from the reaction of lithium with triethylsilyltriphelylgermane in ethylamine. This was the first indication for the existence of an organosilylmetallic compound as a reaction intermediate. Comparatively little was done in the field of organosilylmetallic chemistry in the subsequent years until triphenylsilylpotassium[3,4] and organosilyllithium[1,2] compounds became available as research tools. The ready accessibility of these reagents has brought about an extremely rapid growth in this area during the past nine years. The recent review[6] testifies to the importance of this field in the chemical world today.

Although progress during the present decade has been marked, a search through the literature yielded only two references to reactions of organosilylmetallic compounds with reactants closely related to those used in this investigation. One of these[9] represents work done in connection with the present research, and describes the reaction of triphenylsilyllithium with tri-n-butyl phosphate. The other[7] reports two unsuccessful attempts to prepare triphenylsilylaldehyde

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[8] C. A. Kraus and W. H. Nelson, J. Am. Chem. Soc., 56, 195 (1924).

[9] M. V. George, B. J. Gaj and H. Gilman, J. Org. Chem., 24, 624 (1959).

from triphenylsilyllithium and N,N-dimethylformamide; the only product isolated being triphenylsilanol.

Because of the absence of previous work in these directions, the Historical section covers the corresponding reactions of organolithium compounds and Grignard reagents with substances related to those used in this investigation. No attempt, however, has been made to include the very large number of references to reactions of the amide group with organometallic compounds; only a few representative examples of this reaction have been discussed.

A. Reactions of Grignard Reagents and Organolithium Compounds

1. With phosphate, phosphite, phosphonate and related esters

In 1915, Michaelis and Wegner[10] reported the isolation of triphenylphosphine oxide from the reaction of phenylmagnesium bromide with phenyl dichlorophosphinate in diethyl ether. This unexpected displacement of a phenoxide group from phosphorus by a Grignard reagent was the first of numerous displacements of this type to be reported. Gilman and Vernon[11] isolated the same product from the reaction of phenyl-

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[10] A. Michaelis and F. Wegner, Ber., 48, 316 (1915).

[11] H. Gilman and C. C. Vernon, J. Am. Chem. Soc., 48, 1063 (1926).

magnesium bromide with triphenyl- and tri-p-tolyl phosphate in yields of 17 and 50 percent, respectively; whereas, the use of triphenyl phosphite resulted in the isolation of triphenylphosphine, in 60 percent yield. These investigators failed to identify the phosphorous-containing products from the reactions of n-propylmagnesium bromide and triphenyl phosphate, or from benzylmagnesium chloride and tri-p-tolyl phosphate, although phenol and p-cresol were obtained in yields of 49 and 28 percent, respectively, from these reactions.

In 1929,[12] the reaction was extended to trialkyl phosphates and phosphites, with the hope of observing alkylation of the Grignard reagent; however, similar displacements were observed. For example, the action of three equivalents of phenylmagnesium bromide on trimethyl phosphite resulted in the formation of methyldiphenylphosphine oxide; a rearrangement of methyl diphenylphosphinate to the isolated product was used to explain its formation. When triethyl phosphite was used in a similar reaction, the only product isolated was triphenylphosphine oxide; however, triethyl phosphate gave diethyl benzenephosphonate and diphenylphosphinic acid in meagre yields. Similarly, no toluene could be detected from the reaction of phenylmagnesium bromide with trimethyl phosphate.

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[12] H. Gilman and J. Robinson, Rec. trav. chim., 48, 328 (1929).

The first reaction of a phosphonate ester with a Grignard reagent was reported by Kosolapoff[13] in 1950; diphenylphosphinic acid was prepared from phenylmagnesium bromide and diethyl benzenephosphonate, in a study concerned with methods for preparing phosphinic acids.

Burger and Dawson[14] reported the preparation of seven aromatic phosphonic acids and six triarylphosphine oxides by using dialkyl phosphorochloridates and Grignard reagents or organolithium compounds. In this publication, the importance of mode of addition and steric hindrance were discussed. Thus, esters of aromatic phosphonic acids result from the addition of unhindered Grignard reagents to one equivalent of a dialkyl phosphorochloridate, or when the ester is added to a solution of an _ortho_-substituted Grignard reagent. However, the addition of the phosphorochloridate ester to an unhindered Grignard reagent in a one to three mole ratio resulted in the formation of a triarylphosphine oxide. Based on the reactions of _ortho_- and _para_-tolyllithium with diethyl phosphorochloridate, the authors concluded that organolithium compounds behaved similarly to Grignard reagents in these reactions.

During the same year, Kosolapoff and Watson[15] obtained

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[13] G. M. Kosolapoff, _J. Am. Chem. Soc._, _72_, 5508 (1950).

[14] A. Burger and N. D Dawson, _J. Org. Chem._, _16_, 1250 (1951).

[15] G. M. Kosolapoff and R. M. Watson, _J. Am. Chem. Soc._, _73_, 4101 (1951).

di-n-propyl and di-n-butyl phosphinic acid from diethyl phosphite and the appropriate Grignard reagent subsequent to peroxide oxidation. Morgan and Herr[16] obtained triphenyl- and tri-p-tolylphosphine, in yields of less than 50 percent, from the reactions of trialkyl phosphites with Grignard reagents, while attempting to prepare alkyldiarylphosphine oxides via a previously reported[12] reaction. These investigators were unable to isolate the desired compounds.

Williams and Hamilton[17] succeeded in preparing di-n-octyl- and di-n-octadecylphosphine oxide by reacting three equivalents of the appropriate Grignard reagent with di-n-butyl phosphite in diethyl ether. The yields were reported to be 70 and 26 percent, respectively.

In 1953, the earlier work[14] of Burger and Dawson was extended to determine the relative amount of bulk necessary in the ortho-position of the Grignard reagent to prevent the occurrence of di- and trisubstitution in their reactions with dialkyl phosphorochloridates.[18] They reported that o-anisylmagnesium bromide gave a 65.4 percent yield of the dialkyl phosphonate ester; whereas, o-fluorophenylmagnesium bromide

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[16] P. W. Morgan and B. C. Herr, ibid., 74, 4526 (1952).

[17] R. H. Williams and L. A. Hamilton, ibid., 74, 5418 (1952).

[18] N. D. Dawson and A. Burger, J. Org. Chem., 18, 207 (1953).

afforded only 5.7 percent of o-fluorobenzenephosphonic acid, subsequent to hydrolysis with hydrochloric acid. The latter reaction gave a large amount of neutral material, but the investigators were unable to establish its structure. In connection with this study, diethyl benzenephosphonate was reacted with magnesium bromide, then with phenylmagnesium bromide to help elucidate the mechanism of the reactions forming triarylphosphine oxides.

The equimolar reaction of diethyl phosphite with ethylmagnesium bromide has been studied by Gawron and co-workers.[19] In this case, the alkoxy groups were not affected by the Grignard reagent, but instead, the ester was metalated. These workers were able to prepare diethyl 2-hydroxypropane-2-phosphonate and the corresponding toluene derivative by treating the metalated ester with acetone and benzaldehyde, respectively.

In 1955, Maguire and Shaw[20] treated triethyl phosphite with one equivalent of phenylmagnesium bromide, and obtained a mixture of triphenylphosphine oxide, diphenylphosphinic acid and phenylphosphonous acid, together with biphenyl and recovered triethyl phosphite. These products were also obtained when two equivalents of the ester were used. During the same

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[19] O. Gawron, C. Grelecki, Wm. Reilly and J. Sands, _J. Am. Chem. Soc._, _75_, 3591 (1953).

[20] M. H. Maguire and G. Shaw, _J. Chem. Soc._ (London), 2039 (1955).

year, Williams and Hamilton extended their previously reported reaction[17] to synthesize the series of di-*n*-alkylphosphine oxides which included the di-*n*-amyl to the di-*n*-octadecyl derivatives, with the exception of the tridecyl compound.[21] In these preparations, yields from 12 to 70 percent were obtained when di-*n*-butyl phosphite was allowed to react with three or, in some cases, six equivalents of the appropriate Grignard reagent. This procedure has been applied in the synthesis of dibenzyl-[22,23] and di-*n*-octylphosphine[23] oxide in connection with an investigation of their addition reactions with carbonyl-containing compounds and *alpha*,*beta*-unsaturated nitriles. The reaction was also used by Hunt and Saunders[24] to prepare diphenylphosphine oxide from the corresponding diethyl ester. These workers were able to demonstrate, at least in aqueous solution, an equilibrium between the phosphine oxide and diphenylphosphinous acid.

The equimolar reaction of diphenyl phosphorochloridite with a variety of Grignard reagents has been reported by

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[21] R. H. Williams and L. A. Hamilton, *J. Am. Chem. Soc.*, *77*, 3411 (1955).

[22] R. C. Miller, J. S. Bradley and L. A. Hamilton, *ibid.*, *78*, 5299 (1956).

[23] R. C. Miller, C. D. Miller, Wm. Rogers, Jr. and L. A. Hamilton, *ibid.*, *79*, 424 (1957).

[24] B. B. Hunt and B. C. Saunders, *J. Chem. Soc.* (London), 2413 (1957).

Kamaǐ and Gerasimova.[25] In these reactions, only the chlorine atom was displaced by the Grignard reagent.

A comprehensive study on the use of organolithium compounds in reactions of this type was reported by Willans[26] in 1957; however, details are lacking. Phenyllithium was reacted with diethyl phosphorochloridate, in a three to one mole ratio, to give 80 percent of triphenylphosphine oxide. Analogous reactions using triethyl phosphite or trialkyl phosphates produced equally good yields of triphenylphosphine, or triphenylphosphine oxide, respectively. Diaryl phosphinic acids were also prepared in satisfactory yields from di-*n*-butyl phosphite and aryllithium compounds, subsequent to perioxide oxidation.

In 1959, Janczewski[27] obtained similar results from the reactions of phenyllithium with diethyl phosphorochloridate and diethyl benzenephosphonate. A high yield of triphenylphosphine oxide was obtained in each case.

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[25] G. Kamaǐ and E. A. Gerasimova, *Trudy Kazan. Khim. Tekhrol. Inst. im. S. M. Kirova*, *1950*, No. 15, 26 (1951). (Original not available for examination; abstracted in *C. A.*, *51*, 11273 (1957)).

[26] J. L. Willans, *Chemistry and Industry*, 235 (1957).

[27] M. Janczewski, *Roczniki Chem.*, *33*, 185 (1959). (In Polish, French summary, p. 188).

2. With the amide group

The first report of ketone formation from the reaction of a Grignard reagent with an acid amide appeared in 1903.[28] At that time, Béis reported the synthesis of six ketones in yields of 20 to 50 percent from the reactions of methylmagnesium iodide or ethylmagnesium bromide with acetamide, propionamide, butyramide, isovaleramide or benzamide. He also found that the reaction was not applicable to formamide. Almost simultaneously, however, Bouveault[29] succeeded in preparing a number of aldehydes by employing N,N-disbustituted formamides in an analogous synthesis. The latter reaction, commonly referred to as the "Bouveault aldehyde synthesis", is one of the seemingly ever-increasing number of "name reactions" of organic chemistry. Although aldehydes and ketones generally result from reactions of Grignard reagents with amides, a number of investigators have observed several other transformations, among which are conversions to amines, imines, nitriles and phthalides, to name only a few.[30]

Shortly after the discovery of this reaction by Béis,

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[28] C. Béis, Compt. rend., 137, 575 (1903).

[29] L. Bouveault, ibid., 137, 987 (1903).

[30] For a comprehensive discussion and accompanying bibliography on reactions of the amide group with Grignard reagents, see M. S. Kharasch and O. Reinmuth. Grignard reactions of nonmetallic substances. New York, N. Y., Prentice-Hall, Inc. 1954. pp. 870-908.

several 3-substituted isoindolinones were prepared from phthalimide and the Grignard reagents derived from ethyl, isobutyl and isoamyl halides.[31] During the same year, Sachs and Ludwig[32] succeeded in preparing 2-ethyl-3-methyl-3-hydroxyisoindolinone, as well as the 3-ethyl- and 3-phenyl- derivatives, from N-ethylphthalimide and the appropriate Grignard reagent. These workers also reported the occurrence of ring opening when N-ethylsaccharin was treated with ethyl- or phenylmagnesium bromide; the products isolated were o-(N-ethylsfulfonamido)diethylphenylcarbinol and o-(N-ethylsulfonamido)triphenylcarbinol, respectively.

An interesting case of reductive alkylation was observed by Viguier in 1911.[33] In this study, the author reported the isolation of 4-(diethylamino)heptadiine-2,5 from the equimolar reaction of propynylmagnesium bromide with N,N-diethylformamide. Numerous other references to reactions of this type can be found scattered throughout the literature.[30] In all of the reported cases, however, N,N-disubstituted amides were involved, and in no instance was this type of reaction observed when organolithium compounds were used.

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[31] C. Béis, Compt. rend., 138, 987 (1904).

[32] F. Sachs and A. Ludwig, Ber., 37, 385 (1904).

[33] P. L. Viguier, Compt. rend., 153, 955 (1911).

Imides of aliphatic dicarboxylic acids have also been employed in reactions with Grignard reagents. From the interaction of phenylmagnesium bromide with N-methylsuccinimide, 2-hydroxy-2-phenyl-1-methylpyrrolid-2-one and 2,5-diphenyl-1-methylpyrrole were obtained.[34] In contrast, Ellingboe and Fuson[35] reported the occurrence of ring opening when N-phenyl-1,2-cyclobutanedicarboxamide was reacted with either one or two equivalents of the same Grignard reagent; the products isolated were cis-2-benzoylcyclobutanecarboxanilide and 2-(alpha-hydroxybenzhydryl)cyclobutanecarboxanilide, respectively.

Maxim and Mavrodineanu[36,37] observed the formation of tertiary amines, together with small amounts of aldehydes, from reactions of N,N-disubstituted formamides with Grignard reagents. The same products were isolated when either one, two or three equivalents of the Grignard reagents were employed.

Treatment of N-methylglutarimide with a series of Grig-

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[34] R. Lukeš and V. Prelog, Chem. Listy, 22, 244 (1928). (Original available but not translated; abstracted in C. A., 23, 1408 (1929)).

[35] E. Ellingboe and R. C. Fuson, J. Am. Chem. Soc., 56, 1777 (1934).

[36] N. Maxim and R. Mavrodineanu, Bull. soc. chim., [5], 2, 591 (1935).

[37] N. Maxim and R. Mavrodineanu, ibid., [5], 3, 1084 (1936).

nard reagents resulted in the isolation of six 1-methyl-6-alkyl-6-hydroxypiperid-2-ones.[38] In this series, the alkyl groups varied from methyl to *n*-hexyl.

In 1951, Kuffner and Polke[39] observed results similar to those of Maxim and Mavrodineanu.[36,37] These workers also reported the isolation of tertiary amines together with aldehydes from the reactions of ethyl-, *n*-propyl- and *n*-butylmagnesium bromide with N,N-diisopropylformamide. The yield of 5-(diisopropylamino)nonane from the reaction involving the *n*-butyl compound was 67 percent.

One year later, Lukeš and Bláha[40] extended the reaction of N-methylglutarimide with Grignard reagents, to obtain mixtures of *alpha*,*omega*-bis(1-methyl-2-hydroxy-6-oxo-2-piperidyl)-alkanes and 1-methyl-2-alkyl-2-hydroxy-6-piperidones by using Grignard reagents derived from *alpha*,*omega*-dihaloalkanes. The Grignard reagents contained from five to ten methylene units.

In contrast, N-phenylsulfonylphthalimide and N-phenylsulfonyl-1,2-benzisothiazol-3-one were observed to undergo ring opening when treated with phenylmagnesium bromide, giving

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[38] R. Lukeš and J. Gorocholinskij, *Collection Czech. Chem. Communs.*, *8*, 223 (1936).

[39] F. Kuffner and E. Polke, *Monatsh.*, *82*, 330 (1951).

[40] R. Lukeš and K. Bláha, *Chem. Listy*, *46*, 726 (1952). (Original available but not translated; abstracted in *C. A.*, *47*, 11133 (1953)).

rise to the formation of o-bis(diphenylhydroxymethyl)benzene and 2-phenylmercaptotriphenylcarbinol, respectively.[41] No ring opening was observed, however, in the reactions of organolithium compounds with N-phenylphthalimidine or N-methylphthalimide.[42] The former compound gave a 65 percent yield of 1-methyl-2-phenylisoindole with methyllithium; while N-methylphthalimide afforded a 29 percent yield of 2-methyl-3-phenyl-3-hydroxyisoindolinone when allowed to react with phenyllithium in a one to one mole ratio. Similar conversions of phthalimidenes to isoindoles have been reported[43] to occur in excellent yields.

A number of unsaturated aldehydes were prepared by Braude and Evans[44] via the reaction of N,N-dimethylformamide with unsaturated organolithium compounds. For example, 3-methylcrotonaldehyde was synthesized in 27 percent yield by application of isobutenyllithium, while the use of cycloheptenyllithium resulted in the formation of 1-formylcycloheptene in 70 percent yield. Evans[45,46] extended this study to prepare

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[41] A. Mustafa and O. H. Hishmat, J. Am. Chem. Soc., 75, 4647 (1953).

[42] G. Wittig, G. Closs and F. Mindermann, Ann., 594, 89 (1955).

[43] W. Thielacker and W. Schmidt, ibid., 597, 95 (1955).

[44] E. A. Braude and E. A. Evans, J. Chem. Soc. (London), 3334 (1955).

[45] E. A. Evans, ibid., 4691 (1956).

[46] E. A. Evans, Chemistry and Industry, 1596 (1957).

a variety of aldehydes and ketones in yields ranging from 7 to 86 percent.

An interesting example of imine formation from reactions of this type was reported by Gilman and Eisch in 1957.[47] In this study, the authors reported the isolation of 6-n-butylphenanthridine (as the picrate) from the reaction of two equivalents of n-butyllithium with phenanthridinone. When 2-bromophenanthridinone was allowed to react with two equivalents of n-butyllithium at -35°, the amide carbonyl was not attacked; an 82 percent yield of phenanthridinone-2-carboxylic acid was realized.

3. With triaryl group VB elements

Challenger and Ridgway[48] reported no reaction occurred when a mixture of phenylmagnesium bromide and tri-p-chlorophenylbismuthine was heated at 100° for three hours. In 1939, however, it was reported that n-butyllithium was capable of cleaving triarylbismuthines to give n-butyl-substituted bismuthines and aryl carboxylic acids subsequent to carbonation.[49] For example, n-butyllithium reacted with tri-p-

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[47] H. Gilman and J. Eisch, J. Am. Chem. Soc., 79, 5479 (1957).

[48] F. Challenger and L. R. Ridgway, J. Chem. Soc. (London), 121, 104 (1922).

[49] H. Gilman, H. L. Yablunky and A. C. Svigoon, J. Am. Chem. Soc., 61, 1170 (1939).

tolylbismuthine, in a three to one mole ratio, to yield p-toluic acid and tri-n-butylbismuthine. In the same manner, these investigators successfully cleaved tri-p-chlorophenyl-, tri-alpha-naphthyl-, tri-o-ethoxyphenyl- and tri-p-ethoxyphenylbismuthine to obtain the corresponding aryl carboxylic acids in varying yields.

In 1940, the reaction of triphenylamine with the same organolithium compound (in the presence of copper bronze) was reported to yield an unidentified acidic material subsequent to carbonation.[50] Later, this product was identified as m-carboxytriphenylamine.[51]

The metal-metal interconversion reaction, previously reported by Gilman *et al.*,[49] was extended to symmetrical and unsymmetrical triarylstibines in connection with a study concerned with relative reactivities of organoantimony compounds. The reactions were carried out in a one to one mole ratio under comparable conditions, and the yields of acids obtained were used to formulate a series of aryl groups with respect to their cleavability by n-butyllithium.[52]

In contrast to the meta-metalation observed with tri-

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[50] H. Gilman, G. E. Brown, F. J. Webb and S. M. Spatz, *ibid.*, 62, 977 (1940).

[51] H. Gilman and G. E. Brown, *ibid.*, 62, 3208 (1940).

[52] L. A. Woods and H. Gilman, *Proc. Iowa Acad. Sci.*, 48, 251 (1941).

phenylamine,[50,51] N-phenylcarbazole was found to metalate in the ortho-position when treated with n-butyllithium.[53] The product isolated, subsequent to carbonation, was 9-(o-carboxyphenyl)carbazole. Similar reactions with triphenylarsine[54] and triphenylphosphine[55] gave low yields of the corresponding m-carboxylic acids. In the latter study,[55] phenyllithium and phenylmagnesium bromide were also reacted with triphenylphosphine. The solutions were oxidized, and treated with hydrobromic acid to give tetraphenylphosphonium bromide dihydrate in yields of 31 and 82.6 percent, respectively.

A study[56] of the factors effecting the relative ease of cleavage of aryl groups from trisubstituted bismuthines by n-butyllithium was reported by Gilman and Yale in 1950. As in the previous study, the reactions were carried out in a one to one mole ratio under corresponding conditions, and an extended series of aryl groups were arranged in order of their ease of cleavage. The same type of reaction using trisubstituted stibines and bismuthines was used by Talalaeva

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[53] H. Gilman, C. G. Stuckwisch and A. R. Kendall, J. Am. Chem. Soc., 63, 1758 (1941).

[54] H. Gilman and C. G. Stuckwisch, ibid., 63, 3532 (1941).

[55] H. Gilman and G. E. Brown, ibid., 67, 824 (1945).

[56] H. Gilman and H. L. Yale, ibid., 72, 8 (1950).

and Kocheshkov[57,58,59] to prepare a large number of organolithium compounds in good yields. In these studies, ethyllithium was used as the cleaving agent, and the reactions were generally carried out in the inert solvent, benzene. Chernova and Mikhaǐlov[60] also used this reaction to prepare phenyllithium in a study concerned with ether complexes of organolithium compounds. In this case, the product was shown to form a monodioxanate.

In 1958, the effect of solvent and metalating agent on the extent of metalation was investigated with a variety of compounds, among which was triphenylamine.[61,62] Using a mixture of diethyl ether and tetrahydrofuran, triphenylamine was metalated with n-butyllithium to give, subsequent to car-

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[57] T. V. Talalaeva and K. A. Kocheshkov, Doklady Akad. Nauk S.S.S.R., 77, 261 (1951). (Original available but not translated; abstracted in C. A., 45, 10191 (1951)).

[58] T. V. Talalaeva and K. A. Koscheshkov, Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk, 1953, 126. (Original available but not translated; abstracted in C. A., 48, 3285 (1954)).

[59] T. V. Talalaeva and K. A. Kocheshkov, ibid., 1953, 290. (Original available but not translated; abstracted in C. A., 48, 6389 (1954)).

[60] N. G. Chernova and B. M. Mikhaǐlov, Zhur. Obshcheǐ Khim., 25, 2280 (1955). (Original available for examination; translated in J. Gen. Chem. U.S.S.R., 25, 2249 (1956)).

[61] H. Gilman and S. Gray, J. Org. Chem., 23, 1476 (1958).

[62] S. Gray. Some organometallic reactions in tetrahydrofuran. Unpublished M.S. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1958.

bonation, a product which is thought to be 3,3'-dicarboxytriphenylamine; however, the compound was not obtained in pure form.

B. Silicon-Silicon Bond Cleavage by Organometallic Compounds

Friedel and Ladenburg reported[63] the formation of tetraethylsilane and hexaethyldisilane from the reaction of hexaiododisilane with diethylzinc, thus reporting the first cleavage of the silicon-silicon bond by an organometallic compound. Gattermann and Weinlig[64] later reported the isolation of tetraphenylsilane (as the only product) from the reaction of hexachlorodisilane, chlorobenzene and sodium metal in a Wurtz-type reaction. In 1913, Martin[65] obtained low-boiling oils from the reaction of hexachlorodisilane with methylmagnesium iodide, and postulated these to be mixtures of monosilanes with chlorine atoms and methyl groups attached to silicon. When hexachlorodisilane was treated with phenylmagnesium bromide, a mixture of monosilanes was obtained, from which dichlorodiphenylsilane was the only product iso-

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[63] C. Friedel and A. Ladenburg, Compt. rend., 68, 923 (1869); Ann. chim. phys., [5], 19, 401 (1880); Ann., 251 (1880).

[64] L. G. Gattermann and K. Weinlig, Ber., 27, 1946 (1894).

[65] G. Martin, Ber., 46, 2442, 3294 (1913).

lated by distillation.[66]

Twelve years later, Schumb and co-workers[67] reinvestigated the reaction of hexachlorodisilane with alkyl and aryl halides in the presence of sodium, and obtained good yields of tetrasubstituted silanes. The compounds investigated were ethyl bromide, n-amyl chloride, chlorobenzene and p-chlorobiphenyl. Also reported at that time was the attempted cleavage of hexaphenyldisilane with sodium in refluxing xylene and benzene.

In a later study,[68] Schumb and Saffer obtained a mixture of tetraphenylsilane and hexaphenyldisilane from the reaction of phenylmagnesium bromide with octrachlorotrisilane. The same authors[69] reported that the two-stage Wurtz-type reaction of hexachlorodisilane, using chlorobenzene and benzyl chloride to prepare the organosodium compounds, gave satisfactory yields of hexasubstituted disilanes. A small amount of tetraphenylsilane was isolated from the reaction using phenylsodium but no tetrasubstituted silane was obtained in the latter case. Similarly, benzylmagnesium chloride and hexa-

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[66] R. Schwarz and W. Sexauer, ibid., 59B, 333 (1926).

[67] W. C. Schumb, J. Ackerman, Jr. and C. M. Saffer, Jr., J. Am. Chem. Soc., 60, 2486 (1938).

[68] W. C. Schumb and C. M. Saffer, Jr., ibid., 61, 363 (1939).

[69] W. C. Schumb and C. M. Saffer, Jr., ibid., 63, 93 (1941).

chlorodisilane gave hexabenzyldisilane as the only product isolated. These workers concluded that the exothermicity of the reaction between sodium and the organic halide was responsible for the observed bond scission.

In 1951, Gilman and Dunn[70] reported the reaction of p-biphenylyllithium with hexachlorodisilane to give both the tetrasubstituted silane and hexa-p-biphenylyldisilane. In this connection, Dunn reported[71] that hexaphenyldisilane was not cleaved by either n-butyl- or phenyllithium in refluxing diethyl ether or diethyl ether-xylene mixtures. Wu[72] obtained similar results with phenyllithium; however, a small amount of material was isolated which melted over the range 210-240°, but it was not investigated further.

Gilman and Gorsich observed[73] an interesting case of cleavage in the reaction of 2,2'-biphenylenedilithium with hexachlorodisilane. The only product isolated was the mono-

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[70] H. Gilman and G. E. Dunn, ibid., 73, 5077 (1951).

[71] G. E. Dunn. Relationships between some organosilicon compounds and their carbon analogs. Unpublished Ph.D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1951.

[72] T. C. Wu. Comparisons of some organic compounds containing group IVB elements. Unpublished Ph.D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1952.

[73] H. Gilman and R. D. Gorsich, J. Am. Chem. Soc., 80, 3243 (1958).

silane, 5,5'-spirobi-[dibenzosilole].

Lichtenwalter[7] reported that hexaphenyldisilane was unaffected by p-tolyllithium at 0° or by triphenylmethyllithium at room temperature in tetrahydrofuran; a nearly quantitative recovery of the disilane was realized in both cases.

In 1959, Wittenberg et al.[74] reported the isolation of large amounts of hexaphenyldisilane, together with other products, from the reactions of triphenylsilyllithium with a variety of silicon-containing compounds which included pentaphenyldisilane, chloropentaphenyldisilane, diphenyl(diphenylmethoxy)silane, dichlorodiphenylsilane, ethyl silicate, silicon tetrachloride and trichlorosilane. In these reactions, cleavage of compounds containing silicon-silicon bonds by triphenylsilyllithium was postulated to explain the formation of the products isolated.

Shortly thereafter, Gilman et al.[75] observed the facile cleavage of hexasubstitued disilanes by organosilyllithium compounds in tetrahydrofuran. For example, hexaphenyldisilane was cleaved by methyldiphenylsilyllithium and dimethylphenylsilyllithium to give, in addition to recovered starting material, a 26 percent yield of symmetrical dimethyltetraphenyl-

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[74] D. Wittenberg, M. V. George and H. Gilman, ibid., 81, 4812 (1959).

[75] H. Gilman, G. D. Lichtenwalter and D. Wittenberg, ibid., 81, 5320 (1959).

disilane and 56 percent of 1,1,2,2-tetramethyl-1,2-diphenyldisilane, respectively. Also formed in the former case, but not isolated in pure form, was methylpentaphenyldisilane. Similarly, dimethylphenylsilyllithium reacted with 1,1-dimethyl-1,2,2,2-tetraphenyldisilane and 1,2-dimethyl-1,1,2,2-tetraphenyldisilane to give symmetrical tetramethyldiphenyldisilane in yields of 26 and 45 percent, respectively. Methyldiphenylsilane was also isolated in 77.5 percent yield from the latter reaction, after acid hydrolysis.

During the same year, Gilman and Lichtenwalter[76] found diphenylsilane, as the only product, from the reaction of four equivalents of phenylmagnesium bromide with hexachlorodisilane, subsequent to reduction with lithium aluminium hydride. When the reaction was repeated and the products were not reduced, a low yield of dichlorodiphenylsilane was isolated together with an oil, which afforded 1,2-dimethyl-1,1,2,2-tetraphenyldisilane when treated with methyllithium.

C. Reactions of Organosilylmetallic Compounds with the Carbonyl Group

1. Carbon dioxide

In 1951, Benkeser and Severson[3] isolated a product, in low yields, from the reaction of triphenylsilylpotassium with

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[76] H. Gilman and G. D. Lichtenwalter, J. Org. Chem., 24, in press (1959).

carbon dioxide, to which they tentatively assigned the structure of triphenylsilanecarboxylic acid. This compound was reported to be unstable, _via_ decarbonylation, to heat and acids, or simply by dissolution in polar solvents like acetone or ethanol. Brook and Gilman[77] reinvestigated this reaction in 1955 and obtained high yields of triphenylsilanecarboxylic acid, of high purity, by working up the reaction mixtures rapidly and in the cold, out of contact with basic reagents. These workers reported the acid to be moderately stable when pure, undergoing no decarbonylation when exposed to absolute ethanol or ethanol-pyridine mixtures. They were able to demonstrate, however, the instability of this acid and its methyl ester to basic reagents such as aqueous alkali, aqueous pyridine, methoxide ion or ethoxide ion. In these cases, either triphenylsilanol or alkoxytriphenylsilanes were isolated as the decomposition products, together with carbon monoxide.

Incidental to a study concerned with the thermal decomposition of silanecarboxylic esters, Brook and Mauris[78] reported the preparation of tri-_p_-tolylsilanecarboxylic acid _via_ carbonation of tri-_p_-tolylsilylpotassium. They found the yield of acid to be higher when the organosilylpotassium com-

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[77] A. G. Brook and H. Gilman, _J. Am. Chem. Soc._, _77_, 2322 (1955).

[78] A. G. Brook and R. J. Mauris, _ibid._, _79_, 971 (1957).

pound was prepared directly from the corresponding chlorosilane, than when prepared by the cleavage of hexa-p-tolyldisilane.

George and Gilman,[79] while investigating the oxygen-oxidation of triphenylsilyllithium, utilized the carbonation reaction to determine the yield of triphenylsilyllithium obtained from the lithium-cleavage of hexaphenyldisilane in tetrahydrofuran. Triphenylsilanecarboxylic acid was isolated in 83.4 percent yield from this reaction. The carbonation reaction has also been applied to methyldiphenylsilyllithium and dimethylphenylsilyllithium by Trepka.[80] In these cases, fair yields of the silanecarboxylic acids were obtained, even after a normal basic extraction. Based on these results, it is believed[80] that silanecarboxylic acids containing alkyl groups attached to silicon, are more stable to decarbonylation by basic reagents than the previously discussed triaryl derivatives.

2. Aldehydes

The first reaction of an organosilylmetallic compound

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[79] M. V. George and H. Gilman, J. Org. Chem., 24, 1349 (1959).

[80] W. J. Trepka, Ames, Iowa. Information concerning reactions of organosilylmetallic reagents with carbonyl-containing compounds. Private communication. 1959.

with an aldehyde was described by Gilman and Wu in 1954.[81] These investigators reported that triphenylsilylpotassium added normally to formaldehyde to give a low yield of triphenylsilylmethanol. Four years later, Wittenberg and Gilman[82] reacted triphenylsilyllithium with acetaldehyde, and obtained a 39 percent yield of 1-(triphenylsilyl)ethanol together with 38 percent of triphenylsilane. The former compound was also prepared by the reduction of acetyltriphenylsilane with lithium aluminum hydride.[82] Almost simultaneously, Gilman and Peterson[83] succeeded in preparing 1-(triphenylsilyl)-1-propanol from triphenylsilyllithium and propionaldehyde. As is sometimes the case in a rapidly growing field, Brook and co-workers[84] independently reported the synthesis of 1-(triphenylsilyl)ethanol from triphenylsilyllithium and acetaldehyde, in connection with a study of the base-catalized rearrangement of <u>alpha</u>-silylcarbinols. The yield of 1-(triphenylsilyl)ethanol in this investigation was reported to be 53 percent.

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[81] H. Gilman and T. C. Wu, *J. Am. Chem. Soc.*, *76*, 2502 (1954).

[82] D. Wittenberg and H. Gilman, *ibid.*, *80*, 4529 (1958).

[83] H. Gilman and D. J. Peterson, *J. Org. Chem.*, *23*, 1895 (1958).

[84] A. G. Brook, C. M. Wagner and M. E. McGriskin, *J. Am. Chem. Soc.*, *81*, 981 (1959).

In 1959, Wittenberg *et al*.[85] described the reactions of triphenylsilylmetallic compounds with benzaldehyde under a variety of reaction conditions. At -50°, the equimolar reaction gave a 46 percent yield of benzyloxytriphenylsilane; whereas the use of two equivalents of the organosilyllithium compound under similar conditions resulted in the isolation of an oil, which is believed to be composed of stereoisomers of 2-triphenylsiloxy-1,2-diphenylethanol. A one to one reaction at room temperature, however, afforded 66 percent of hexaphenyldisilane and 49 percent of 1,2-dihydroxy-1,2-diphenylethane (as a mixture of isomers). A small amount of the *meso*-form was separated from this mixture of isomers by crystallization techniques. In contrast, triphenylsilylpotassium in diethyl ether gave tetraphenylsilane (77 percent) and 1,2-dihydroxy-1,2-diphenylethane (16 percent), together with triphenylsilanol (11 percent), when reacted with benzaldehyde at room temperature.[85] The reactions of triphenylsilylpotassium with formaldehyde, paraldehyde and paraformaldehyde gave, respectively, triphenylsilylmethanol and an unidentified compound; no identifiable addition products; and a product melting at 128-130° whose structure is not known.[85]

In this connection, the reaction of dimethylphenylsilyllithium with formaldehyde is presently under investigation by

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[85] D. Wittenberg, T. C. Wu and H. Gilman, *J. Org. Chem*., **24**, 1349 (1959).

Trepka;[80] it appears as though addition to the carbonyl group proceeds normally to give the expected alpha-silylcarbinol in good yield.

3. Ketones

In 1953, Gilman and Wu[86] reported the isolation of the "abnormal" addition product, diphenylmethoxytriphenylsilane (instead of triphenylsilyldiphenylmethanol) from the reaction of triphenylsilylpotassium with benzophenone in diethyl ether. This compound was also synthesized (as a proof of structure) from chlorotriphenylsilane and sodium diphenylmethoxide in benzene.[86] The silylether likewise was obtained when di-p-tolyl ketone was reacted with triphenylsilylpotassium in diethyl ether.[86] Later, Brook and Wolfe[87] utilized this type of reaction to demonstrate the occurrence of halogen-metal interconversion in the reactions of triphenylsilylpotassium with aryl halides. In this study, benzophenone was allowed to compete with bromobenzene in a reaction with triphenylsilylpotassium. No diphenylmethoxytriphenylsilane was isolated from this reaction; however, triphenylmethanol was found among the reaction products, thus proving that phenylpotassium was present also. When the reaction was repeated

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[86] H. Gilman and T. C. Wu, J. Am. Chem. Soc., 75, 2935 (1953).

[87] A. G. Brook and S. Wolfe, ibid., 79, 1431 (1957).

without bromobenzene, a 21 percent yield of diphenylmethoxytriphenylsilane was obtained together with benzhydrol and triphenylsilanol.

In order to test the effect of variation of the organosilylmetallic compound and solvent on this reaction, Gilman and Lichtenwalter[88] studied the reactions of triphenylsilyllithium, methyldiphenylsilyllithium and dimethylphenylsilyllithium with benzophenone in tetrahydrofuran. As was the case with triphenylsilylpotassium in diethyl ether, the "abnormal" addition compounds were obtained in yields of 57, 19 and 20 percent, respectively. Small amounts of symmetrical dimethyltetraphenyl- and tetramethyldiphenyldisilane were obtained from the reactions involving methyldiphenylsilyllithium and dimethylphenylsilyllithium. In addition, small amounts of benzhydrol and benzopinacol were isolated from the two last-mentioned reactions.

Later,[89] these investigators extended the reaction to aliphatic ketones, and found that normal addition occurred to give varying yields of <u>alpha</u>-silylcarbinols. Thus, treatment of acetone with triphenylsilyllithium resulted in the formation of 2-triphenylsilyl-2-propanol in 52 percent yield together with some triphenylsilane. Similarly, cyclohexanone,

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[88] H. Gilman and G. D. Lichtenwalter, <u>ibid</u>., <u>80</u>, 607 (1958).

[89] H. Gilman and G. D. Lichtenwalter, <u>ibid</u>., <u>80</u>, 2680 (1958).

8-pentadecanone, 3-octadecanone, 2-nonadecanone 9-nonadecanone and 12-tricosanone afforded the corresponding *alpha*-silylcarbinols in yields ranging up to 34 percent. The results were essentially the same when organosilyllithium compounds containing methyl and phenyl groups attached to silicon were exposed to acetone and cyclohexanone. Hydrogen abstraction from the ketone by the organosilyllithium compound was an important side-reaction in this study, as evidenced by the isolation of large amounts of the trisubstituted silane corresponding to the organosilyllithium compound used. In the extreme case, triphenylsilane was obtained in 78 percent yield from the reaction of triphenylsilyllithium with dibenzyl ketone; no *alpha*-silylcarbinol was isolated from this reaction. In this connection, Lichtenwalter[7] obtained a small amount of product believed to be 2-triphenylsilylethyl phenyl ketone from the reaction of triphenylsilyllithium with benzalacetophenone; either addition across the olefin linkage, or more likely, 1,4-addition followed by rearrangement having occurred.

In a study concerned with organometallic reactions of heterocycles, Diehl[90] reported the isolation of 10-triphenyl-

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

siloxythiaxanthene,[91] in 12 percent yield, together with 34.6 percent of hexaphenyldisilane from the reaction of triphenylsilyllithium with 10-thiaxanthenone. In contrast, no hexaphenyldisilane was isolated from the corresponding reaction with 9-xanthenone (the oxygen analog) and the same organosillithium reagent.[80] The latter reaction gave a product which decomposed over a thirty-degree range when heated, whose analysis and infrared spectrum agree with those expected for the "abnormal" addition compound, 9-triphenylsiloxyxanthene.[91]

Attempts to isolate addition compounds from the reactions of triphenylsilylpotassium with hexamethylacetone, benzalacetophenone and Michler's ketone failed.[85]

4. Carboxylic acids and their derivatives

In 1952, Wu[72] reported that triphenylsilylpotassium failed to react with the potassium salt of *p*-iodobenzoic acid in diethyl ether after 90 hours at room temperature. A 92 percent recovery of starting material (isolated as *p*-iodobenzoic acid) was realized. A few years later, Gilman and Gerow[92] reported the isolation of triphenylsilyltriphenyl-

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[91] Following procedures recommended by *Chemical Abstracts*, these compounds are named as triphenylsiloxy derivatives of the heterocycle, since the triphenylsilyl group is non-functional, although another name had been used previously for 10-triphenylsiloxythiaxanthene. See footnote 90.

[92] H. Gilman and C. W. Gerow, *J. Am. Chem. Soc.*, *77*, 4575 (1955).

germane (84 percent) from the reaction of triphenylsilyllithium with methyl triphenylgermanecarboxylate. Apparently, in this reaction, the germanium atom was attacked in preference to addition across the carbonyl.

In 1957, Brook[93] reported the first reaction of an acid halide with an organosilylmetallic compound. In this study, triphenylsilylpotassium was reported to give a low yield of benzoyltriphenylsilane together with hexaphenyldisilane, when reacted with benzoyl chloride in diethyl ether. Shortly thereafter, Wittenberg and Gilman[82] published an informative and thorough study on the reaction of triphenylsilyllithium with acetyl chloride under a variety of conditions. A large excess of acetyl chloride and low-temperature reactions were employed in attempts to obtain acetyltriphenylsilane in high yields. This result could not be realized, however, because of the facile addition of the organosilyllithium compound across the carbonyl, to give as final products, triphenyl-(1-triphenylsiloxyethyl)silane and 1,1-bis(triphenylsilyl)-ethanol in fair yields, together with varying amounts of triphenylsilane.

The reactions of triphenylsilyllithium with derivatives of carboxylic acids were extended by Gilman and Peterson[83] to a variety of carbonyl-containing compounds. Ethyl acetate,

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[93] A. G. Brook, ibid., 79, 4373 (1957).

for example, gave triphenyl(1-triphenylsiloxyethyl)silane together with 1,1-bis(triphenylsilyl)ethanol when reacted with this reagent. No acetyltriphenylsilane, however, was isolated from this reaction. Similarly, 1,1-bis(triphenylsilyl)ethanol and triphenyl(1-triphenylsiloxypropyl)silane were obtained from acetic anhydride and propionyl chloride, respectively.[83] The former compound, together with triphenyl(1-triphenylsiloxy)silane was prepared <u>via</u> the same synthesis by Brook and co-workers.[84] No addition compounds were obtained from the reaction of triphenylsilyllithium with phenylacetyl chloride.[83] The reaction of triphenylsilyllithium with N,N-dimethylformamide failed to yield triphenylsilylaldehyde, as mentioned early in the Historical section of this Thesis; the only product isolated was triphenylsilanol.[7]

In contrast to the results obtained by Wu,[72] in the attempted reaction of triphenylsilylpotassium with potassium p-iodobenzoate, Diehl[90] obtained a 71 percent yield of hexaphenyldisilane from the reaction of two moles of triphenylsilyllithium with o-bromobenzoic acid. This product was apparently formed <u>via</u> a halogen-metal interconversion reaction. In addition, 24.7 percent of starting material was recovered.

The reaction of triphenylsilyllithium with ethyl benzoate is presently under investigation by Trepka.[80] Thus far, he has been able to isolate hexaphenyldisilane, triphenylsilanol and ethoxytriphenylsilane, together with a small amount of product which may be alpha-triphenylsilyl-alpha-triphenylsiloxytoluene. This reaction appears to be quite complex and is being actively investigated at the time of this writing.

D. Reactions of Organosilylmetallic Reagents with Compounds Containing Group VB Elements

1. Amines

Reynolds *et al.*,[94] while attempting to prepare triphenylsilylsodium *via* the action of sodium on triphenylsilane in liquid ammonia, isolated bis(triphenylsilyl)amine after treatment of the reaction mixture with ammonium bromide. Later, Kraus and Eatough[95] reported the isolation of the solvated free radical, "triphenylsilicyl ethylamine", from the reaction of bromotriphenylsilane with lithium in ethylamine. In both of these cases, as well as in the previously described work of Kraus and Nelson,[8] it appeared as though the organosilylmetallic compounds (if formed under these conditions) underwent transformations with the solvent to yield the products isolated.

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[94] H. R. Reynolds, L. A. Bigelow and C. A. Kraus, *ibid.*, *51*, 3067 (1929).

[95] C. A. Kraus and H. Eatough, *ibid.*, *55*, 5008 (1933).

In 1952, Benkeser et al.[96] reinvestigated the work of Kraus and Eatough, and proved that the solvated free radical described by these early workers was in reality the silylamine, N-ethyl-1,1,1-triphenylsilyamine. Wu[72] arrived at this same conclusion nearly simultaneously after reacting chlorotriphenylsilane with ethylamine, both in the presence and absence of lithium. In either case, the product isolated was N-ethyl-1,1,1-triphenylsilylamine.

Several years later, Lichtenwalter[7] successfully applied this reaction, using pre-formed organosilyllithium compounds, to prepare a variety of silylamines in connection with a study concerned with reactions of organosilyllithium compounds. For example, morpholine, piperidine and piperazine reacted smoothly with triphenylsilyllithium to give 1-triphenylsilylmorpholine, 1-triphneylsilylpiperidine and 1,4-bis(triphenylsilyl)piperazine, in yields of 83, 86 and 93 percent, respectively. Similarly, n-butylamine and di-n-butylamine gave N-n-butyl-1,1,1-triphenylsilylamine and N,N-di-n-butyl-1,1,1-triphenylsilylamine in yields of 56 and 53.5 percent, respectively. Analogous compounds were prepared by Lichtenwalter[7] from the reactions of methyldiphenylsilyllithium and dimethylphenylsilyllithium with di-n-butylamine. An attempt to extend the reaction to diphenylamine[7] with triphenylsilyl-

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[96] R. A. Benkeser, R. E. Robinson and H. Landesman, ibid., 74, 5699 (1952).

lithium failed to give the coupling product even though the organosilyllithium compound was consumed. The amine apparently underwent metalation, but the N-lithio compound failed to displace the hydride ion from triphenylsilane. Wittenberg *et al.*[97] had similar results when, in an attempted proof of structure, they reacted triphenylsilyllithium with N-(diphenylmethyl)aniline in tetrahydrofuran.

Incidental to a study dealing with the cleavage of ethers by organosilyllithium compounds, Wittenberg and co-workers[98] prepared N-(triphenylsilylmethyl)piperidine in 55 percent yield *via* the reaction of triphenylsilyllithium with N-(*n*-butoxymethyl)piperidine in tetrahydrofuran.

It is noteworthy that dicyclohexylamine[90] failed to yield isolable amounts of the silylamine when reacted with triphenylsilyllithium; only triphenylsilane and triphenylsilanol were identified from the reaction products.

Trepka[99] recently has shown that N,N-dimethylaniline failed to undergo metalation when heated with triphenylsilyllithium for 24 hours at 50° in tetrahydrofuran. Subsequent to derivatization with benzophenone, diphenylmethoxytriphenyl-

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[97] D. Wittenberg, M. V. George, T. C. Wu, D. H. Miles and H. Gilman, *ibid.*, *80*, 4532 (1958).

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

[99] W. J. Trepka, Ames, Iowa. Information concerning metalation studies. Private communication. 1959.

silane, hexaphenyldisilane, a trace of an unidentified compound containing no silicon, and starting materials were the only compounds isolated.

2. Nitrogen-heterocycles and their halogenated derivatives

In 1951, Honeycutt[100] failed to isolate addition or coupling products from the reactions of triphenylsilylpotassium with pyridine, quinoline, or their 2-chloro derivatives. A few years later, however, Meen and Gilman[101] succeeded in preparing 3-triphenylsilyl-9-ethylcarbazole, in 57 percent yield, from the reaction of triphenylsilylpotassium with 3-bromo-9-ethylcarbozole in diethyl ether. In contrast, Ranck[102] obtained an unidentified amorphous solid (as the only product) from the reaction of this organosilylmetallic compound with 3-bromo-10-ethylphenothiazine.

Two years later, Diehl[90] used this reaction to prepare a number of silicon-containing derivatives of carbazole and phenothiazine. When triphenylsilyllithium was allowed to

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[100] J. B. Honeycutt, Jr. Preparation of some nitrogen-containing organosilicon compounds. Unpublished M.S. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1951.

[101] R. H. Meen and H. Gilman, J. Org. Chem., 20, 73 (1955).

[102] R. O. Ranck. Some reactions of phenothiazine and its derivatives. Unpublished Ph.D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1957.

react with 3-bromo-9-ethylcarbazole, a 27.5 percent yield of 3-triphenylsilyl-9-ethylcarbazole was obtained together with 57.7 percent of hexaphenyldisilane. Using a mixture of diethyl ether and tetrahydrofuran, the yield of the silylcarbazole was increased to 40.7 percent, while that of hexaphenyldisilane dropped to 44.3 percent.[90] Phenothiazine derivatives were prepared in the same manner from 2-chloro-10-ethyl-, 3-chloro-10-ethyl-, 3-bromo-10-ethyl-, 4-iodo-10-ethyl-, 10-(2-chloroethyl)-, 3,7-dichloro-10-ethyl- and 3,7-dibromo-10-ethylphenothiazine, in yields which were uniformly less than 35 percent. From these reactions, hexaphenyldisilane was isolated in yields ranging between 46.3 and 64.2 percent.

Attempts to metalate 10-ethylphenothiazine-5-oxide and the 5,5-dioxide failed to give any acidic materials subsequent to carbonation.[90] In the former case, 10-ethylphenothiazine was found together with other products, indicating that reduction of the sulfoxide group had occurred, whereas only starting material was isolated from the dioxide reaction. Metalation of 10-ethylphenothiazine, however, was successful as evidenced by the isolation of 10-ethylphenothiazine-4-carboxylic acid subsequent to carbonation.

3. Compounds containing the azo and azomethine linkage

Honeycutt[100] reported the failure of triphenylsilylpotassium to add to the azomethine linkage of pyridine and quinoline, or their 2-chloroderivatives shortly after triphenylsilylpotassium became available as a research tool. Efforts along these lines have given more promising results when triphenylsilyllithium was used. In 1958, Wittenberg and Gilman[103] reported the isolation of 4-triphenylsilyl-1,4-dihydropyridine (63 percent) from the cleavage of hexaphenyldisilane with lithium in pyridine, followed by an _in situ_ 1,4-addition to the solvent. This compound was also formed, but not isolated as such, from the reaction of pre-formed triphenylsilyllithium with pyridine in tetrahydrofuran. Oxidation of the mixture with nitrobenzene gave a 53 percent overall yield of 4-triphenylsilylpyridine.

A similar 1,4-addition of triphenylsilyllithium to acridine was reported almost simultaneously by Gilman and Lichtenwalter.[104] The 10-lithio-9-(triphenylsilyl)acridan so formed was reacted with water, dimethyl sulfate and oxygen to give 9-(triphenylsilyl)acridan, 10-methyl-9-(triphenylsilyl)acridan and 9-(triphenylsilyl)acridine in 27, 60 and 31 percent yields, respectively.

During the same year, the reactions of triphenylsilylpotassium and -lithium with benzophenone anil were reported

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[103] D. Wittenberg and H. Gilman, _Chemistry and Industry_, 390 (1958).

[104] H. Gilman and G. D. Lichtenwalter, _J. Org. Chem._, _23_, 1586 (1958).

to proceed smoothly to give high yields of the addition product, N-diphenylmethyl-N-phenyl-1,1,1-triphenylsilylamine.[97] An attempt to synthesize the last-mentioned compound from triphenylsilyllithium and N-(diphenylmethyl)aniline failed, as did the attempts using chlorotriphenylsilane with N-(diphenylmethyl)aniline or its N-lithio derivative.[97] These investigators also succeeded in adding triphenylsilylpotassium and triphenylsilyllithium to azobenzene; the product isolated being N,N'-diphenyl-N-(triphenylsilyl)hydrazine. It is interesting to note that this compound can be prepared from triphenylsilyllithium and azoxybenzene,[105] as well as from the azobenzene-dilithium adduct and chlorotriphenylsilane.[97]

Attempts by Lichtenwalter[7] to add triphenylsilyllithium to isoquinoline, phenanthridine and phenazine uniformly failed, and either small amounts of unidentified compounds, or no pure products were obtained, except in the last-mentioned case where triphenylsilane was isolated in 38 percent yield. In contrast, Marrs[106] isolated a product from the reaction of triphenylsilyllithium with quinoline, whose analysis agrees quite closely with that of a triphenylsilyl-

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[105] M. V. George, Ames, Iowa. Information concerning reactions of triphenylsilyllithium with nitrogen compounds. Private communication. 1958.

[106] O. L. Marrs, Ames, Iowa. Information concerning reactions of triphenylsilyllithium with aromatic compounds. Private communication. 1959.

substituted quinoline. The position of substitution, however, has not yet been established. An attempt to add triphenylsilylpotassium to benzalaniline gave no addition compound.[85]

4. Nitriles

Reactions of organosilyllithium compounds with nitriles are meagre, and appear to be difficult to reproduce. When triphenylsilyllithium was reacted with acrylonitrile, a resin-like solid was obtained from which no pure compounds could be isolated.[83] The same organosilyllithium compound and acetonitrile gave only triphenylsilanol and a small amount of unidentified solid, whose analysis agrees exactly for a compound containing two moles of acetonitrile to one of triphenylsilane.[83] In contrast, the reaction of triphenylsilyllithium with benzonitrile has been reported to give a 50 percent yield of crude tetraphenylsilane, from which 27 percent of the pure compound was isolated.[83] In addition, triphenylsilanol was obtained in 15 percent yield. Recent attempts to duplicate this high yield of tetraphenylsilane by Peterson,[107] Trepka[108]

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[107] D. J. Peterson, Ames, Iowa. Information concerning reactions of triphenylsilyllithium with nitriles. Private communication. 1959.

[108] W. J. Trepka, Ames, Iowa. Information concerning reactions of triphenylsilyllithium with nitriles. Private communication. 1959.

and Zuech,[109] under comparable conditions or under different conditions, have given only small amounts of tetraphenylsilane together with triphenylsilanol and tars. Investigation of this reaction is still in progress.

5. Miscellaneous compounds

The reaction of triphenylsilyllithium with N,N-dimethylformamide[7] has already been discussed under the section dealing with reactions of organosilylmetallic compounds with derivatives of carboxylic acids.

In 1958, Kögler and Seyferth[110] reported the reaction of triphenylsilyllithium with cyanuric chloride in tetrahydrofuran to give a 44 percent yield of hexaphenyldisilane, together with a polymeric material containing carbon, hydrogen, nitrogen and silicon, whose structure has not been established. They also reported that phosphonitrilic chloride trimer gave only hexaphenyldisilane in 55 percent yield when similarly reacted with triphenylsilyllithium in the same solvent. These two attempts to prepare organosilylmetallic derivatives of inorganic "benzenoid" compounds failed, apparently due to

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[109] E. A. Zuech, Ames, Iowa. Information concerning reactions of triphenylsilyllithium with nitriles. Private communication. 1959.

[110] H. P. Kögler and D. Seyferth. Research on organometallic derivatives of inorganic "benzenoid" compounds. [Wright Air Development Center Quarterly Report, No. 1]. Oct. 31, 1958.

the facile halogen-metal interconversion reaction which takes place between the reactants. Numerous other examples of halogen-metal interconversion reactions involving organosilylmetallic compounds are summarized elsewhere.[6,7,90]

In 1959, the reactions of triphenylsilyllithium with a number of halogenated group VB elements were described by George _et al_.[9] For example, triphenylsilyllithium reacted with phosphorus trichloride in tetrahydrofuran to give 68 percent of hexaphenyldisilane together with triphenylsilanol and hexaphenyldisiloxane. With phosphorus tribromide, hexaphenyldisilane and triphenylsilanol were isolated in 80.5 and 9.7 percent yields, respectively. Similar results were obtained from the reactions using phosphoryl chloride, arsenic trichloride, antimony trichloride and bismuth trichloride. From the reactions employing the arsenic, antimony and bismuth compounds, varying yields of triphenylsilane were also obtained. The authors postulated the formation and cleavage of intermediates containing silicon-group VB element bonds to explain the formation of the products isolated. In this connection, Maier[111] succeeded in isolating compounds containing silicon-phosphorus and silicon-arsenic bonds in low yields from the reactions of triphenylsilyllithium with alkyl-

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[111] L. Maier, Zurich, Switzerland. Information concerning reactions of triphenylsilyllithium with alkyl-substituted phosphorus and arsenic halides. Private communication. 1959.

substituted phosphorus and arsenic halides. He likewise observed the formation of considerable amounts of hexaphenyldisilane from these reactions.

George _et_ _al_.[9] also reported the isolation of _n_-butyltriphenylsilane (83.5 percent) from the reaction of triphenylsilyllithium with tri-_n_-butyl phosphate.

In 1959, Kögler and Seyferth[112] succeeded in preparing B-tris(triphenylsilyl)-N-trimethylborazene from triphenylsilyllithium and B-trichloro-N-trimethylborazene. The reaction was run in a mixture of diethyl ether and tetrahydrofuran.

The action of triphenylsilylpotassium on phenyl isocyanate gave hexaphenyldisilane and symmetrical diphenyl urea; however, the corresponding reaction with phenyl isothiocyanate afforded a product which is thought to be bis(triphenylsilyl) ketone anil.[113]

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[112] H. P. Kögler and D. Seyferth. Research on organometallic derivatives of inorganic "benzenoid" compounds. [Wright Air Development Center Quarterly Report, No. 3]. Sept. 1, 1959.

[113] H. Gilman, Ames, Iowa. Information concerning T. C. Wu's studies with triphenylsilylpotassium. Private communication. 1959.

III. EXPERIMENTAL

A. General Procedure

Melting and boiling points reported herein are in degrees Centigrade and are uncorrected. Generally, melting points were taken in an electrically heated copper block using a 360° thermometer calibrated in one-half degree divisions. For compounds melting below 100°, an electrically heated oil-bath was employed.

Reactions involving organosilylmetallic or organometallic compounds, in general, were carried out in oven-dried glassware under an atmosphere of dried, oxygen-freed, nitrogen. The equipment was assembled while hot and the apparatus was swept with a brisk stream of nitrogen while cooling.

Diethyl ether, when employed as a solvent for organometallic reactions, was sodium-dried. The tetrahydrofuran used in the same capacity was dried and purified by refluxing over sodium wire for at least twenty-four hours, followed by distillation into a refluxing suspension of lithium aluminum hydride under a dry, nitrogen atmosphere. The solvent was distilled from this suspension immediately before use and generally transferred to an addition funnel which was still warm and contained a nitrogen atmosphere.

Silicon analyses were performed by a modified reported procedure[114] using a ten to one mixture of concentrated sulfuric and nitric acids to initiate the decomposition in weighed platinum crucibles. Decomposition was completed with warm fuming nitric acid, and the weight of the residue was used to calculate the percent silicon.

Infrared spectra, reported in microns, were obtained either on a Baird, model B, or Perkin-Elmer, model 21, recording spectrophotometer.

Triphenylsilyllithium was prepared from hexaphenyldisilane by lithium cleavage in tetrahydrofuran according to a published procedure.[1]

B. Reactions of Triphenylsilyllithium with Trialkyl Phosphates

1. Trimethyl phosphate (1:1)

A solution of 0.04 mole of triphenylsilyllithium in 75 ml. of tetrahydrofuran was added dropwise to a stirred solution of 5.6 g. (0.04 mole) of trimethyl phosphate in 50 ml. of the same solvent. Color Test I[115] was negative immediately after the addition was completed. Work-up by hydrolysis, addition of 100 ml. of diethyl ether, separation of the layers, extraction of the aqueous layer with diethyl ether, drying of

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[114] H. Gilman, B. Hofferth, H. W. Melvin and G. E. Dunn, J. Am. Chem. Soc., 72, 5767 (1950).

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

the organic layer and removal of the solvents left an oil, which was poured on a column of dry alumina.

Elution with 400 ml. of petroleum ether (b.p. 60-70°) gave 7.8 g. (71%) of methyltriphenylsilane, m.p. 63-65°, and an oil which contained triphenylsilane as the main constituent, as evidenced by strong absorption bands at 4.75 and 8.97 μ in its infrared spectrum, characteristic of the Si-H and silicon-phenyl bond, respectively. Recrystallization of the solid from methanol raised the melting point to 65-66°. The product was identified by the method of mixed melting points, and by a comparison of its infrared spectrum, as a carbon disulfide solution, with that of an authentic sample.

The reaction was repeated using the same quantities of triphenylsilyllithium and freshly distilled trimethyl phosphate. Hydrolysis and work-up as in the previous reaction gave 9.6 g. (88%) of methyltriphenylsilane, m.p. and mixed m.p. 67-68°, after crystallization from methanol.

2. Tri-*n*-butyl phosphate (1:1)

The addition of one-third of a solution of 0.04 mole of triphenysilyllithium in 90 ml. tetrahydrofuran to a stirred solution of 3.99 g. (0.015 mole) of tri-*n*-butyl phosphate in 30 ml. of the same solvent gave a negative Color Test I, and discharged the color of the silyllithium reagent. The addition of another 0.013 mole of the organometallic compound resulted in a brown solution which gave a positive Color Test I even after stirring for one hour. An additional 6.65 g. (0.025 mole) of tri-n-butyl phosphate in 30 ml. of tetrahydrofuran was added, and the remaining triphenylsilyllithium reagent then was added dropwise. Color Test I became negative and the mixture developed a pale pink coloration.

Hydrolysis with water, and the addition of 100 ml. of diethyl ether produced an emulsion which was cleared by the addition of a small amount of dilute hydrochloric acid. Work-up in the manner described for trimethyl phosphate gave 12.3 g. (97%) of n-butyltriphenylsilane, m.p. 85-87°, identified by mixed melting point and infrared spectra.

3. Tri-n-butyl phosphate (3:1) at reflux, run 1

A solution of 0.08 mole of triphenylsilyllithium in 160 ml. of tetrahydrofuran was added to a stirred solution of 7.1 g. (0.0267 mole) of freshly distilled tri-n-butyl phosphate, in 50 ml. of the same solvent. The dark mixture was stirred for 2.5 hours at room temperature (Color Test I positive) then at reflux for 18 hours. Hydrolysis, filtration and washing of the insoluble material with water and diethyl ether left 2.2 g. of hexaphenyldisilane, m.p. and mixed m.p. 364-366°.

The filtrate, which had a strong phosphine-like odor, was acidified, and the aqueous layer was extracted with diethyl ether, then discarded. Removal of the solvents from the dried organic phase left an oily solid, which was washed with petroleum ether (b.p. 60-70°), and crystallized from benzene to give 0.1 g. of impure hexaphenyldisilane, identified by mixed melting point.

The petroleum ether extract was chromatographed on an alumina column to give 12.5 g. (49.5%) of n-butyltriphenylsilane; 0.1 g. (2.7%) of hexaphenyldisiloxane (eluted with benzene); 0.1 g. of hexaphenyldisilane (total yield, 2.4 g., 11.6%); 1.7 g. (6.4%) of 4-triphenylsilylbutanol (eluted with ethyl acetate); and 1.3 g. (5.9%) of triphenylsilanol. All products were identified by mixed melting points.

4. Run 2

A solution of 0.06 mole of triphenylsilyllithium in 70 ml. of tetrahydrofuran was added to 5.3 g. (0.02 mole) of tri-n-butyl phosphate in a mixture of 40 ml. of tetrahydrofuran and 30 ml. of diethyl ether. The mixture was refluxed gently for 5 days with continuous stirring. At the end of this time, Color Test I was negative. Hydrolysis with 100 ml. of water, followed by filtration and washing, gave 2.15 g. (13.8%) of hexaphenyldisilane, m.p. and mixed m.p. 363-365°. The filtrate had a phosphine-like odor.

Chromatographic separation of the organic layer gave: 9.8 g. (51.5%) of n-butyltriphenylsilane, m.p. 86-88° (mixed m.p. and infrared spectra); and 1.5 g. (9.05%) of triphenylsilanol, m.p. 152-154° (mixed m.p.).

5. Triisobutyl phosphate (1:1), run 1

A mixture of 0.06 mole of triphenylsilyllithium and 16 g. (0.06 mole) of triisobutyl phosphate in 170 ml. of tetrahydrofuran gave, after the initial heat of reaction had dissipated, a negative Color Test I. The pink solution was hydrolyzed with 50 ml. of half-saturated ammonium chloride, and 100 ml. of diethyl ether was added. Drying of the separated organic layer, followed by removal of the solvents and boiling of the residue with 150 ml. of absolute ethanol, gave upon filtration, 0.3 g. (2%) of hexaphenyldisilane, m.p. 357-360° (mixed m.p.).

The ethanolic filtrate yielded upon concentration two crops of isobutyltriphenylsilane (13.75 g., 72.4%), m.p. 75-76° (mixed m.p.). This compound has been previously prepared from triphenylsilyllithium and isobutyl chloride.[116]

6. Run 2

The previous reaction was repeated using 0.04 mole of each reactant in 110 ml. of tetrahydrofuran. Hydrolysis and removal of the solvents from the dried organic layer was accomplished as described in Run 1. The residue was purified

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[116] G. Dappen, Ames, Iowa. Alkylation of triphenylsilyllithium. Private communication. 1959.

by passing it through a column of alumina as a petroleum ether (b.p. 60-70°) solution. Removal of the solvent left 11.1 g. (87.8%) of isobutyltriphenylsilane, m.p. and mixed m.p. 74-76°. Elution with ethyl acetate gave, after crystallization from cyclohexane, 0.5 g. (4.5%) of triphenylsilanol, m.p. 151-153° (mixed m.p.).

C. Alkylation of Sterically Hindered Organolithium and Grignard Reagents with Trialkyl Phosphates

1. Triphenylmethylmagnesium chloride and trimethyl phosphate in diethyl ether

A suspension of *ca*. 0.03 mole of triphenylmethylmagnesium chloride (prepared according to the directions of Gilman and Zoellner[117] from 8.36 g. (0.03 mole) of triphenylmethyl chloride in 100 ml. of diethyl ether) was added to a stirred solution of 4.2 g. (0.03 mole) of trimethyl phosphate in 50 ml. of diethyl ether, and the mixture was stirred for 30 minutes.

Hydrolysis was effected with 5% hydrochloric acid. The aqueous layer was extracted with diethyl ether, then discarded. The bulk of the solvent was distilled and the last traces were removed under an air-jet. The orange, viscous oil which remained, was dissolved in petroleum ether (b.p. 60-70°), and poured onto a column of dry alumina. Elution with the same

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[117] H. Gilman and E. A. Zoellner, *J. Am. Chem. Soc.*, *51*, 3493 (1929).

solvent gave 6.8 g. (88%) of crude 1,1,1-triphenylethane, m.p. 87-90°. Two crystallizations from absolute ethanol afforded 5.97 g. (77%) of pure product, m.p. 93.5-95°, identified by a mixture melting point determination and by infrared spectra.

2. Triphenylmethyllithium and trimethyl phosphate in diethyl ether

The triphenylmethyllithium was prepared according to a modified, reported procedure.[118] A mixture of 8.36 g. (0.03 mole) of triphenylmethyl chloride, excess lithium and 60 ml. of diethyl ether was refluxed gently with stirring for 2 days. The suspension was filtered through a stopcock into a solution of 0.03 mole of trimethyl phosphate (freshly distilled) in 50 ml. of diethyl ether. Reaction was instantaneous as evidenced by the rapid loss of color of the organolithium reagent.

Work-up by hydrolysis, separation of the layers, drying of the organic layer over sodium sulfate, removal of the solvent and two crystallizations of the residue from ethanol gave 6.7 g. (86.5%) of 1,1,1-triphenylethane, m.p. and mixed m.p. 93-95°.

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[118] P. Tomboulian, J. Org. Chem., 24, 229 (1959).

3. 9-Phenyl-9-fluorenyllithium and trimethyl phosphate in tetrahydrofuran, run 1

The 9-phenyl-9-fluorenyllithium was prepared by a modified, reported procedure.[119] A mixture of 4.84 g. (0.02 mole) of 9-phenylfuorene, 0.7 g. (0.1 g. atom) of lithium wire, cut into fine pieces, and 50 ml. of tetrahydrofuran was stirred without cooling for 24 hours. The dark solution was filtered through a stopcock into an addition funnel, and then added to a stirred solution of 2.8 g. (0.02 mole) of trimethyl phosphate in 25 ml. of the same solvent. The mildly exothermic reaction mixture was hydrolyzed with water, and 50 ml. of diethyl ether was added to facilitate separation of the layers.

The solvent was removed from the combined, dried organic layer and diethyl ether extracts of the aqueous layer, and the residue was taken up in petroleum ether (b.p. 60-70°). An unfortunate accident led to the loss of part of the mixture at this point. The remaining solution was chromatographed on an alumina column to give (from the petroleum ether eluates) 2.08 g. (52.5%) of 9-methyl-9-phenylfluorene, m.p. 84-85° after crystallization from ethanol. The reported[120] melting point is 84-85°.

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[119] H. Gilman and R. D. Gorsich, _ibid._, _23_, 550 (1958).

[120] E. Bergman and A. Bond, _Ber._, _64B_, 1455 (1931).

4. Run 2

The preceding reaction was repeated using 0.02 mole of 9-phenyl-9-fluorenyllithium (stirred for 16 hours in the presence of lithium) and 2.8 g. (0.02 mole) of trimethyl phosphate, in 70 ml. of tetrahydrofuran. Work-up by hydrolysis, addition of 50 ml. of diethyl ether, extraction of the aqueous layer with diethyl ether, drying of the combined organic layer, removal of the solvents, passage through an alumina column (as a petroleum ether (b.p. 60-70°) solution), and recrystallization from ethanol afforded 4.5 g. (88%) of 9-methyl-9-phenylfluorene, m.p. 85-86°. A mixed melting point with the product from the preceding reaction was not depressed. The infrared spectrum as a carbon disulfide solution was consistent with the assigned structure.

5. Diphenylmethyllithium and trimethyl phosphate in diethyl ether

A solution of 0.07 mole of diphenylmethyllithium (prepared by the metalation of diphenylmethane with *n*-propyllithium)[121] in 75 ml. of diethyl ether was added to a solution of 9.8 g. (0.07 mole) of trimethyl phosphate in 50 ml. of the same solvent. The reaction mixture refluxed spontaneously and gradually developed a yellow color. Stirring was

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[121] H. Gilman, A. G. Brook and L. S. Miller, *J. Am. Chem. Soc.*, *75*, 3757 (1953).

continued for one hour, then the mixture was hydrolyzed with 50 ml. of 10% hydrochloric acid.

The solvent was removed from the dried organic layer by distillation, and the residue was distilled (after passage through a column of alumina) to give 10.25 g. (80.5%) of 1,1-diphenylethane, b.p. 136-137° (11 mm.), n_D^{20} 1.5730, d_4^{20} 1.0058. The reported[122] constants are: b.p. 136° (12.5 mm.); n_D^{21} 1.573, d^{21} 1.006.

6. Mesitylmagnesium bromide and trimethyl phosphate in diethyl ether

Mesitylmagnesium bromide, prepared in 89% yield (as determined by acid titration) from 19.9 g. (0.1 mole) of 2-bromomesitylene in 100 ml. of diethyl ether, was stirred with 14.08 g. (0.1 mole) of trimethyl phosphate in 30 ml. of diethyl ether. Color Test I[115] was negative after 24 hours; hence, the mixture was hydrolyzed with dilute hydrochloric acid. The usual work-up followed by passage through a column of alumina and distillation of the oil, which was eluted with petroleum ether (b.p. 60-70°), gave 3.65 g. (30%) of mesitylene, b.p. 165°, n_D^{20} 1.4992, and 5.25 g. (39.1%) of isodurene, b.p. 193°, n_D^{20} 1.5125. In addition, 2.7 g. of a mixture of these two compounds was obtained, b.p. 165-193°, n_D^{20} 1.5038.

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[122] P. Sabatier and M. Murat, <u>Compt. rend.</u>, <u>154</u>, 1772 (1912).

The structures of both compounds were confirmed by infrared spectra.

Identity of the isodurene was also confirmed by preparation of the sulfonic acid, m.p. 78°, according to a published procedure.[123] The reported melting point is 79°.

7. Triphenylmethyllithium and tri-*n*-butyl phosphate in diethyl ether

A suspension of 0.03 mole of triphenylmethyllithium[118] in 100 ml. of diethyl ether was allowed to react with a solution of 8 g. (0.03 mole) of tri-*n*-butyl phosphate in 50 ml. of the same solvent. Work-up by hydrolysis, separation of the layers, extraction of the aqueous phase with diethyl ether, drying of the combined organic layer, and removal of the solvents left a yellow-orange, viscous oil which was dissolved in petroleum ether (b.p. 60-70°) and passed through a column of alumina. The petroleum ether eluates gave, after crystallization from ethanol, 6.98 g. (77.5%) of 1,1,1-triphenylpentane, m.p. 60-61°. The reported[124] melting point is 61.5°.

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[123] L. I. Smith and O. W. Cass, *J. Am. Chem. Soc.*, *54*, 1609 (1932).

[124] K. Ziegler and L. Jacob, *Ann.*, *511*, 45 (1934).

8. 9-Phenyl-9-fluorenyllithium and tri-n-butyl phosphate in tetrahydrofuran

A solution of 0.02 mole of 9-phenyl-9-fluorenyllithium[119] (prepared by reacting 4.84 g. (0.02 mole) of 9-phenylfluorene with excess lithium in 50 ml. of tetrahydrofuran) was added to a stirred solution of 5.32 g. (0.02 mole) of tri-*n*-butyl phosphate in 30 ml. of the same solvent. No appreciable heat was evolved, nor was the color of the organolithium reagent discharged; hence, the mixture was refluxed for 2 hours, hydrolyzed, and the layers separated. The residue, after removal of the solvent from the dried organic layer, was chromatographed on an alumina column. The solid, eluted with petroleum ether (b.p. 60-70°), upon recrystallization from absolute ethanol, afforded 5.62 g. (94%) of 9-*n*-butyl-9-phenylfluorene, m.p. 98-99°.

Anal. Calcd. for $C_{23}H_{22}$: C, 92.58; H, 7.42. Found: C, 92.45, 92.54; H, 7.53, 7.41.

9. Diphenylmethyllithium and tri-n-butyl phosphate in diethyl ether

A solution of 0.07 mole of diphenylmethyllithium[121] in 110 ml. of diethyl ether was allowed to react for 2 hours with a solution of 19.62 g. (0.07 mole) of tri-*n*-butyl phosphate in 20 ml. of the same solvent. The mixture was hydrolyzed and worked up in the manner described for 1,1-diphenylethane to give 11.65 g. (74.5%) of 1,1-diphenylpentane, b.p. 80-81° (0.005 mm.), n_D^{20} 1.5510. The reported values[125] are: b.p. 307.8°; n_D^{20} 1.5510.

10. Mesitylmagnesium bromide and tri-*n*-butyl phosphate in diethyl ether (attempted)

A solution of 0.1 mole of mesitylmagnesium bromide in 120 ml. of diethyl ether was refluxed for 24 hours with 26.63 g. (0.1 mole) of tri-*n*-butyl phosphate. Color Test I was positive at the end of this time; hence, the mixture was carbonated and worked up by hydrolysis, extraction of the organic layer with 10% sodium hydroxide, acidification of the aqueous layer and filtration to give (after crystallization from aqueous ethanol) 7.27 g. (44.2%) of *beta*-isodurylic acid, m.p. and mixed m.p. 152-154°.

The dried organic layer was stripped of solvent and distilled to give 9.6% of mesitylene and 87% of recovered tri-*n*-butyl phosphate, identified by infrared spectra.

In a second reaction using the same quantities of reactants, there was isolated 43.3% of *beta*-isodurylic acid after refluxing the mixture for 3 days and carbonating on a Dry Ice-ether slurry.

The organic layer was stripped of solvents and passed

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[125] K. T. Serijan and P. H. Wise, *J. Am. Chem. Soc.*, *73*, 5191 (1951).

through an alumina column, then distilled to give 19.3% of mesitylene and 86% of tri-n-butyl phosphate.

11. Mesitylmagnesium bromide and tri-n-butyl phosphate in tetrahydrofuran (attempted)

A mixture of 0.1 mole of mesitylmagnesium bromide (prepared in 95% yield from 2-bromomesitylene in 100 ml. of tetrahydrofuran) and 26.63 g. (0.1 mole) of freshly distilled tri-n-butyl phosphate in 50 ml. of the same solvent was heated short of reflux for 3 days and then carbonated. Work-up of the basic extract and crystallization of the acid from petroleum ether (b.p. 60-70°) gave, in three crops, 10.75 g. (65.5%) beta-isodurylic acid, m.p. and mixed m.p. 152-154°.

The neutral organic layer furnished 1.05 g. (9.2%) of crude mesitylene, b.p. 65-70° (25 mm.), n_D^{20} 1,4980, identified by infrared spectra; and 22.9 g. (86%) of recovered tri-n-butyl phosphate, b.p. 165-167° (15 mm.).

12. Mesityllithium and tri-n-butyl phosphate in diethyl ether-tetrahydrofuran (attempted)

A solution of 0.1 mole of mesityllithium in tetrahydrofuran (130 ml.) was added rapidly to a solution of 26.63 g. (0.1 mole) of tri-n-butyl phosphate in 100 ml. of diethyl ether, and the solution was stirred overnight (Color Test I positive). Hydrolysis and solvent removal from the dried organic layer left a gel which was suspended in petroleum ether (b.p. 60-70°) and passed through a column of alumina. Distillation of the petroleum ether eluates gave 8.77 g. (73%) of mesitylene, b.p. 57-58° (20 mm.), identified by infrared spectrum, and less than 0.2 g. of material boiling over the range 60-165° (20 mm.) followed by 11.2 g. (42%) of tri-n-butyl phosphate, b.p. 168-172° (20 mm.), identified by infrared spectra. The dark glass-like distillation residue could not be crystallized and appeared to be a polyphosphate by its infrared spectrum.

13. 9-Phenyl-9-fluorenyllithium and triisobutyl phosphate, run 1

A solution of 0.02 mole of 9-phenyl-9-fluorenyllithium[119] in 50 ml. of tetrahydrofuran was added to a stirred solution of 5.32 g. (0.02 mole) of triisobutyl phosphate in 25 ml. of the same solvent. There was no detectable evidence of reaction; hence, the mixture was stirred for 24 hours and then carbonated by pouring it onto a slurry of Dry Ice and diethyl ether. The organic layer was extracted with 10% sodium hydroxide, and the basic extract was boiled to convert the acid salt to 9-phenylfluorene.[126] Filtration afforded, after washing with water, 0.7 g. (14.5%) of 9-phenylfluorene, m.p. and mixed m.p. 145-146°.

The solvents were removed from the dried organic layer

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[126] W. Schlenk and E. Bergman, Ann, 463, 203 (1928).

under an air-jet, and the dark oily residue was passed through an alumina column. The material eluted with petroleum ether (b.p. 60-70°) was boiled with 50 ml. of absolute ethanol and filtered hot to remove 0.25 g. of a hydrocarbon, m.p. 208-209° (after crystallization from a benzene-ethanol pair). The structure of this compound has not yet been established; however, the analysis fits well for a compound containing two 9-phenylfluorenyl groups and one isobutyl group.

Anal. Calcd. for $C_{42}H_{34}$: C, 93.62; H, 6.38. Found: C, 93.53, 93.50; H, 6.43, 6.53.

The ethanol filtrate gave after two additional crystallizations from the same solvent, 1.7 g. (28.5%) of 9-isobutyl-9-phenylfluorene, m.p. 94-95°.

Anal. Calcd. for $C_{23}H_{22}$: C, 92.58; H, 7.42. Found: C, 92.59, 92.65; H, 7.64, 7.49.

No other pure crystalline compounds could be isolated from the benzene, ethyl acetate or methanol eluates, which were uniformly viscous oils.

14. Run 2

The reaction was repeated using the same quantities of reactants. There was obtained 0.6 g. of the unidentified hydrocarbon, m.p. 209-210°, and 1.6 g. of 9-isobutyl-9-phenylfluorene, m.p. 94-95°. No other pure compounds were isolated.

D. Reactions of Triphenylsilyllithium with Triaryl Phosphates

1. Triphenyl phosphate (3:1)

A solution of 4.20 g. (0.0133 mole) of triphenyl phosphate in 10 ml. of tetrahydrofuran was added to a stirred solution of 0.04 mole of triphenylsilyllithium in 90 ml. of the same solvent. The reaction was mildly exothermic, and a suspension developed after the first few ml. of solution had been added. Upon complete addition, Color Test I[115] was negative, hence, the mixture was hydrolyzed with water in a hood (strong phosphine-like odor). Filtration and thorough washing with water and diethyl ether left 2.8 g. (27%) of hexaphenyldisilane, m.p. and mixed m.p. 362-364°. The phenol was extracted from the organic layer with 10% sodium hydroxide solution and discarded.

The solvents were removed from the dried organic layer, which still smelled strongly of phosphine, to leave an oily solid which was crystallized from cyclohexane to give, in several crops, 5.73 g. (52%) of triphenylsilanol, identified by mixed melting point and infrared spectra.

2. Triphenyl phosphate (6:1)

A mixture of 0.12 mole of triphenylsilyllithium and 6.32 g. (0.02 mole) of triphenyl phosphate in 250 ml. of tetrahydrofuran was stirred at room temperatures for 2 days to give a brown suspension. Color Test I was pale green. The mixture was hydrolyzed with 100 ml. of dilute hydrochloric acid, filtered, and the insoluble material was washed thoroughly with water and diethyl ether to leave upon drying, 10.2 g. (33%) of hexaphenyldisilane, m.p. and mixed m.p. 363-365°.

The layers of the filtrate, which had a pronounced phosphine-like odor, were separated and the organic layer was washed with 10% sodium hydroxide to remove phenol, then dried over sodium sulfate. Removal of the solvent pair by distillation and treatment of the residue with cyclohexane afforded 11.25 g. (34%) of triphenylsilanol, m.p. 149-152° (mixed m.p. and infrared spectra). The material in the cyclohexane filtrate oiled upon further concentration; hence, the solvent was removed and the residue passed through a column of alumina. Elution with 600 ml. of petroleum ether (b.p. 60-70°) gave 4.5 g. (14%) of triphenylsilane, m.p. 42-44° (mixed m.p. and infrared spectra). The next 600 ml. of the same solvent gave 0.8 g. (3%) of hexaphenyldisiloxane, m.p. 224-226° after two crystallizations from cyclohexane. Ethyl acetate then eluted 2.5 g. of triphenylsilanol, m.p. 152-154° (total yield, 13.75 g., 41%).

3. Triphenyl phosphate (6:1) at reflux

The preceding reaction was repeated using the same quantities of materials; however, the mixture was refluxed gently for 21 hours, at the end of which time, Color Test I was negative. The mixture was worked up as in the previous reaction to give 12.3 g. (39.6%) of hexaphenyldisilane, m.p. and mixed m.p. 366-368°.

The solvents were removed from the dried organic layer and the residue was chromatographed on alumina to give 3.9 g. (11.8%) of hexaphenyldisiloxane, m.p. and mixed m.p. 226-228°, after crystallization of the material eluted with petroleum ether (b.p. 60-70°) and benzene from cyclohexane. The first 30 ml. of ethyl acetate eluates gave an oil, which when crystallized from petroleum ether (b.p. 60-70°), afforded 1.5 g. (3.75%) of 4-triphenylsilylbutanol, m.p. 107-109° (mixed m.p. and infrared spectra). Further elution with the same solvent gave after recrystallization from cyclohexane, 9.95 g. (30%) of triphenylsilanol and ca. 2 g. of an oil whose infrared spectrum indicated it to be a mixture of triphenylsilanol and 4-triphenylsilylbutanol. This material was not worked up any further.

The basic extract of the organic layer was acidified and extracted with diethyl ether. Drying and removing the ether gave, upon bromination, 16 g. (81%) of tribromophenol, m.p. 92-94° (mixed m.p.).

4. Tri-p-tolyl phosphate (2:1)

A mixture of 0.04 mole of triphenylsilyllithium and 7.37 g. (0.02 mole) of tri-p-tolyl phosphate in 110 ml. of tetrahydrofuran was stirred overnight at room temperature (12 hours), then hydrolyzed with 10% hydrochloric acid. Filtration and washing gave 3.7 g. (35.8%) of hexaphenyldisilane, m.p. and mixed m.p. 365-367°.

The organic layer was separated and washed with 10% sodium hydroxide to remove p-cresol, then dried. The solvent was removed by distillation, and the residue was dissolved in cyclohexane. Concentration afforded 4.78 g. (43.3%) of triphenylsilanol, m.p. 152-154° (mixed m.p.). Further concentration of the filtrate left an oil, which was passed through a short column of alumina to give a trace of hexaphenyldisiloxane, m.p.222-224° (mixed m.p.); 1.1 g. (14.9%) of recovered tri-p-tolyl phosphate, m.p. 74-76° (mixed m.p.); and 0.5 g. (4.5%) of triphenylsilanol, m.p. 152-154° (after crystallization from cyclohexane).

5. Tri-p-tolyl phosphate (3:1)

A mixture of 0.06 mole of triphenylsilyllithium in 100 ml. of tetrahydrofuran was allowed to react for three hours with a solution of 7.37 g. (0.02 mole) of tri-p-tolyl phosphate in 50 ml. of the same solvent. Hydrolysis with 100 ml. of water followed by acidification and filtration gave 5.15 g.

(33%) of hexaphenyldisilane, m.p. and mixed m.p. 360-364°.

The separated organic layer was extracted with 10% sodium hydroxide, then dried. The basic extract was acidified and extracted with diethyl ether and the ether extracts were dried. Solvent removal from the ether extract left an oil which was distilled to give 3.7 g. (57.2%) of p-cresol, b.p. 95-97° (20 mm.), identified by infrared spectra. A considerable amount of distillation residue remained. Attempts to distill it at a lower pressure led to decomposition by charring and fuming.

The neutral organic layer was chromatographed on alumina to give 0.6 g. (3.8%) of triphenylsilane, identified by infrared spectra, and 7.5 g. (45.2%) of triphenylsilanol, identified by mixed melting point.

E. Reactions of Triphenylsilyllithium with Phenylated Group VB Elements

1. Triphenylbismuthine (1:1) at -60°

A solution of 0.02 mole of triphenylsilyllithium in 30 ml. of tetrahydrofuran was added to a stirred solution of 8.8 g. (0.02 mole) of triphenylbismuthine in 50 ml. of the same solvent, while the mixture was cooled in a Dry Ice-acetone bath. The red-brown suspension, which gave a positive Color Test I[115] after stirring for one hour at -60°, was carbonated by pouring it jet-wise onto a slurry of Dry Ice and diethyl ether.

The cream-colored carbonation mixture gradually darkened to black as it warmed to room temperature. Acidification caused the black solid to dissolve leaving a cream-colored suspension. Filtration and washing with water and diethyl ether left 1.30 g. (8.7%) of hexaphenyldisilane, m.p. 362-364° (mixed m.p.). Removal of part of the solvent by aspirator precipitated 0.8 g. (11.9%) of tetraphenylsilane, m.p. 232-234°, after recrystallization from ethyl acetate.

The layers of the filtrate were separated subsequent to making the mixture basic with sodium hydroxide, and allowing it to stand for several hours with occasional stirring to insure conversion of the triphenylsilanecarboxylic acid to triphenylsilanol.[127] The organic layer was extracted with 10% sodium hydroxide and the basic extract boiled to expel organic solvents, then acidified to give 0.5 g. (6.9%) of benzoic acid, m.p. 120-121°, after recrystallization from water.

The dried organic layer was stripped of solvents and the residue was chromatographed on alumina to give 6.05 g. (69%) of triphenylbismuthine, eluted with petroleum ether (b.p. 60-70°), m.p. and mixed m.p. 77-78°. Elution with benzene gave no identifiable compounds, however, ethyl acetate eluted 1.45 g. (26.3%) of triphenylsilanol, m.p. and mixed m.p. 152-154°, after crystallization from cyclohexane.

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[127] A. G. Brook and H. Gilman, _J. Am. Chem. Soc._, _77_, 2322 (1955).

2. Triphenylbismuthine (3:1), run 1

A solution of 0.06 mole of triphenylsilyllithium in 100 ml. of tetrahydrofuran was added to a stirred solution of 8.8 g. (0.02 mole) of triphenylbismuthine in 60 ml. of the same solvent. The addition was carried out at 0 to 5° and the mixture was stirred at this temperature range for one hour, then carbonated by pouring jet-wise onto a Dry Ice-diethyl ether slurry.

The carbonation mixture was hydrolyzed with water and filtered to remove 9.6 g. of wide-melting, insoluble material. Treatment of this solid with dilute hydrochloric acid caused part of the solid to dissolve with gas evolution. The remaining yellow solid was washed with water and a little diethyl ether to leave 5.05 g. of material, m.p. 230-350°. Extraction with hot ethyl acetate left a solid which was recrystallized from dioxane to give 2.8 g. (17.9%) of hexaphenyldisilane, m.p. and mixed m.p. 364-366°. The ethyl acetate extract afforded 2.12 g. (10.2%) of tetraphenylsilane, m.p. and mixed m.p. 233-235°, after crystallization from the same solvent. The ether extract of the hydrolyzed solid left no residue upon solvent removal.

The organic layer was extracted with 10% sodium hydroxide, dried over sodium sulfate and distilled to remove solvents. Treatment of the residue with warm petroleum ether (b.p. 60-70°) followed by filtration gave 0.3 g. (1.92%) of hexaphenyldisilane, m.p. 357-361°. Chromatography of the filtrate and fractional crystallization of the solids, eluted with petroleum ether (b.p. 60-70°) from benzene, ethyl acetate and ethanol eventually led to the isolation of 0.9 g. (5.6%) of hexaphenyldisiloxane and 3.4 g. (16.9%) of tetraphenylsilane. Both compounds were identified by mixed melting points and infrared spectra.

The benzene, ethyl acetate and methanol eluates afforded 4.01 g. (24.2%) of triphenylsilanol, m.p. 152-154° (mixed m.p.), after crystallization from cyclohexane.

Acidification of the basic extract and extraction with diethyl ether followed by crystallization from water gave 3.9 g. (54%, based on the cleavage of three phenyl groups from triphenylbismuthine) of benzoic acid, m.p. and mixed m.p. 120-121°.

3. Run 2

A mixture of 0.06 mole of triphenylsilyllithium and 8.8 g. (0.02 mole) of triphenylbismuthine in 150 ml. of tetrahydrofuran was stirred at 0° for 6 hours and treated with 0.06 mole of chlorotrimethylsilane to obtain a negative Color Test I. The mixture was stirred overnight for convenience, then hydrolyzed with water. Filtration removed 7.0 g. of a white and black solid mixture which melted partially at 300° with preliminary softening.

The solid was extracted with ethyl acetate to give 0.37 g. (1.68%) of tetraphenylsilane, m.p. 232-234° (mixed m.p.), as the soluble portion. Tetralin then extracted 3.46 g. (22.2%) of hexaphenyldisilane, m.p. 363-365° (mixed m.p.) and left 2.75 g. of a black residue which is thought to be largely metallic bismuth, as evidenced by qualitative tests.

The solvents of the organic layer were replaced with petroleum ether (b.p. 60-70°) and distillation was continued until the mixture began to darken. Cooling deposited 4.65 g. of a brown solid which softened at 200° and was not melted completely at 360°. Extraction with hot ethyl acetate removed 3.65 g. (16.6%) of tetraphenylsilane, identified by mixed melting point. The insoluble residue (0.8 g.) was shown to contain bismuth by qualitative tests. Further concentration of the petroleum ether solution gave 1.2 g. (5.45%) of tetraphenylsilane, and 5.23 g. (31.5%) of triphenylsilanol; both compounds were identified by mixed melting point determinations.

The oily filtrate was distilled to give 3.4 g. (37.8%) of trimethylphenylsilane, b.p. 168-171°, n_D^{20} 1.4898. The identity of the latter product was confirmed by its infrared spectrum.

4. Run 3

The reaction was repeated using the same quantities of materials; however, the mixture was stirred at room temperature for 24 hours before carbonation. Work-up in the manner described in Run 1 gave: 0.3 g. (8.25%) of benzoic acid; 0.94 g. (6.03%) of hexaphenyldisilane; 7.63 g. (46%) of triphenylsilanol; and 7.45 g. (37%) of tetraphenylsilane. All products were identified by mixed melting point determinations and infrared spectra. In addition, 4.1 g. of the black insoluble material was isolated.

5. Triphenylstibine (3:1)

A solution of 0.1 mole of triphenylsilyllithium in 200 ml. of tetrahydrofuran was added, at ice-bath temperature, to a solution of 11.65 g. (0.033 mole) of triphenylstibine in 50 ml. of the same solvent. The red-brown mixture developed a suspension early during the addition and gradually turned brown. Stirring was continued after removal of the ice bath for 24 hours. Since Color Test I was still positive at the end of this time, the mixture was treated with a solution of 10.8 g. (0.1 mole) of chlorotrimethylsilane in 50 ml. of diethyl ether.

The solvents were removed by distillation, during which a black solid began to separate. Petroleum ether (b.p. 60-70°) was added and the distillation was continued until the volume was reduced to *ca*. 50 ml. The mixture was cooled to room temperature and 100 ml. of petroleum ether (b.p. 60-70°) was added. Filtration removed a dark solid which melted partially at 220°. Exhaustive extraction of this solid with ethyl acetate gave, as the soluble portion, 14.8 g. (44%) of tetraphenylsilane, m.p. and mixed m.p. 234-236°, together with 0.2 g. of hexaphenyldisilane, m.p. 360-363° (mixed m.p.). There remained a black solid which gave a qualitative test for antimony.

The colorless, clear petroleum ether extract from above was distilled, depositing a finely divided, dark solid which was removed by filtration. Distillation of the clear, colorless filtrate under reduced pressure was accompanied by deposition of more dark, finely divided solid. Two fractions, boiling up to 114° (0.01 mm.), and a small forerun were collected. The two main fractions were redistilled to give 4.4 g. (13.2%) of 1,1,1-trimethyl-2,2,2-triphenyldisilane, b.p. 130-132° (0.05 mm.), m.p. 103-105° (mixed m.p.). The identity of the product was also confirmed by its infrared spectrum.

The forerun from the first distillation together with the material from the Dry Ice-acetone trap was redried in diethyl ether, then distilled to give 2.8 g. (18.7%) of trimethylphenylsilane, b.p. 167-171°, n_D^{20} 1.4876. The infrared spectrum also was used to confirm its identity.

The dark, solid, distillation residue from the first distillation and the black solid which was removed prior to distillation were hydrolyzed with water and extracted with diethyl ether. Drying, followed by removal of the ether left an oily solid, which when chromatographed on alumina, yielded an additional 1.5 g. (4.8%) of 1,1,1-trimethyl-2,2,2-triphenyldisilane and 5.85 g. (20.4%) of triphenylsilanol. Both products were identified by mixture melting points and infrared spectra.

6. Triphenylarsine (3:1), run 1

A solution of 0.06 mole of triphenylsilyllithium in 100 ml. of tetrahydrofuran was added to a stirred solution of 6.12 g. (0.02 mole) of triphenylarsine in 30 ml. of the same solvent at 0°. After warming to room temperature, the reaction mixture was stirred for 36 hours. At the end of this time, Color Test I was weakly positive.

Hydrolysis and work-up as in the reactions with triphenylbismuthine gave: 4.1 g. (26.3%) of hexaphenyldisilane, m.p. and mixed m.p. 362-364°; 4.29 g. (21.2%) of tetraphenylsilane, m.p. and mixed m.p. 233-235°; and 3.75 g. (22.6%) of triphenylsilanol, m.p. 150-152° (mixed m.p.). Considerable amounts of gums and wide-melting solids were also obtained which resisted attempts to separate them into their constituents by chromatography and crystallization techniques.

7. Run 2

A second reaction using the same quantities of reactants was carbonated after 36 hours of stirring at room temperature.

The usual work-up gave no benzoic acid. The neutral layer yielded 23.3% of hexaphenyldisilane, 39.6% of tetraphenylsilane and 28.4% of triphenylsilanol, all identified by the method of mixed melting points. No other pure compounds could be isolated.

8. Triphenylphosphine (attempted)

A mixture of 0.1 mole of triphenylsilyllithium and 8.85 g. (0.033 mole) of triphenylphosphine in 210 ml. of tetrahydrofuran was stirred at room temperature for 24 hours. The reaction mixture gave no evidence of reaction having occurred. The brown solution was carbonated and hydrolyzed with 10% hydrochloric acid. Filtration gave 0.5 g. (1.9%) of hexaphenyldisilane, m.p. 363-365° (mixed m.p.).

The layers of the filtrate were separated after standing in the presence of base for several hours,[127] and the organic layer was extracted with 2-25 ml. portions of saturated sodium bicarbonate. Acidification, extraction with diethyl ether and removal of the ether gave no benzoic acid.

The organic layer afforded, after passage through a column of alumina, 8.3 g. (94%) of triphenylphosphine, m.p. 77-78° (mixed m.p.) and 25.45 g. (92%) of triphenylsilanol, m.p. and mixed m.p. 153-155°.

F. Cleavage of Hexaphenyldisilane with Aryllithium Compounds

1. Phenyllithium in tetrahydrofuran, run 1

Five and nineteen-hundredths grams (0.01 mole) of hexaphenyldisilane, m.p. 366-367°, was added to a stirred, filtered solution of 0.1 mole of phenyllithium[128] in 110 ml. of tetrahydrofuran at -50°. The Dry Ice-acetone bath was replaced with an ice bath and the mixture was allowed to warm to 0° over a 30-minute period. Stirring was continued at this temperature for 1.5 hours, after which the mixture was stirred at room temperature for 24 hours. Work-up by hydrolysis, filtration and thorough washing with water and diethyl ether left 3.88 g. of material, melting over the range 220-350°. Extraction of this solid with ethyl acetate left 2.60 g. (50%) of hexaphenyldisilane, m.p. and mixed m.p. 364-366°. The ethyl acetate extract gave 0.66 g. of tetraphenylsilane, m.p. and mixed m.p. 232-234°.

The organic layer was separated and evaporated to leave a dark, sticky solid. Extraction with methanol, and crystallization of the residue from ethyl acetate-ethanol gave an additional 0.84 g. of tetraphenylsilane. The total yield of tetraphenylsilane was 1.5 g. (89.3%). The methanol extract

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[128] H. Gilman and B. J. Gaj, _J. Org. Chem._, _22_, 1165 (1957).

gave a tar-like residue which yielded only a trace of hexaphenyldisiloxane upon solvent removal and crystallization from ethanol. No triphenylsilane or triphenylsilanol could be isolated by chromatography.

2. Run 2

A mixture of 0.2 mole of phenyllithium and 10.36 g. (0.02 mole) of hexaphenyldisilane in 150 ml. of tetrahydrofuran was stirred at room temperature for 2 days after which it was derivatized with ca. 0.2 mole of chlorotrimethylsilane. Hydrolysis and filtration gave a mixture of tetraphenylsilane (66%) and hexaphenyldisilane (5%), which was separated by ethyl acetate extraction. Chromatography of the organic layer afforded 31% of 1,1,1-trimethyl-2,2,2-triphenyldisilane, m.p. 106-108°. All three products were identified by mixed melting point determinations. In addition, 7.25 g. (24%) of trimethylphenylsilane, b.p. 170-173°, n_D^{20} 1.4905 was isolated and identified by infrared spectrum.

3. Phenyllithium in diethyl ether-tetrahydrofuran, run 1

A mixture of 10.36 g. (0.02 mole) of hexaphenyldisilane and 0.2 mole of phenyllithium in 200 ml. of diethyl ether and 100 ml. of tetrahydrofuran was stirred at room temperature for 5 days and derivatized with dimethyl sulfate. Hydrolysis and the usual work-up afforded 58% of hexaphenyldisilane, 40.5% of tetraphenylsilane and 23.7% of methyltriphenylsilane. All three products were identified by the method of mixed melting points and infrared spectra.

4. Run 2, at reflux

A mixture of 0.1 mole of phenyllithium and 10.36 g. (0.02 mole) of hexaphenyldisilane in 100 ml. of diethyl ether and 50 ml. of tetrahydrofuran was refluxed for 2 days and derivatized with 0.1 mole of chlorotrimethylsilane. Hydrolysis and the usual work-up gave 10% of hexaphenyldisilane, 86% of tetraphenylsilane and 67.5% of 1,1,1-trimethyl-2,2,2-triphenyldisilane together with 14.3% of 4-triphenylsilylbutanol. All products were identified by mixed melting point determinations.

5. Phenyllithium in diethyl ether, run 1

A solution of 0.1 mole of phenyllithium (filtered through a tight glass-wool plug) in 100 ml. of diethyl ether was added rapidly to 5.18 g. (0.01 mole) of hexaphenyldisilane and the resulting suspension was stirred at room temperature for 24 hours. Hydrolysis and filtration afforded 4.94 g. (95.5%) of recovered hexaphenyldisilane, m.p. 362-365° (mixed m.p.). The organic layer gave after crystallization from an ethanol-ethyl acetate mixture, 0.15g. (4.4%) of tetraphenylsilane, m.p. 230-233° (mixed m.p.).

6. Run 2

The preceding reaction was repeated using 0.2 mole of phenyllithium and 10.36 g. (0.02 mole) of hexaphenyldisilane in 200 ml. of diethyl ether and the mixture was stirred for 5 days. Hydrolysis, followed by the usual work-up gave 9.61 g. (92.8%) of hexaphenyldisilane, 0.35 g. (5.2%) of tetraphenylsilane and 0.15 g. (2.72%) of triphenylsilanol; all products were identified by mixed melting point determinations.

7. Phenylmagnesium bromide in tetrahydrofuran (attempted)

Stirring a mixture of 0.15 mole of phenylmagnesium bromide and 5.18 g. (0.01 mole) of hexaphenyldisilane in 100 ml. of tetrahydrofuran for 24 hours at reflux, followed by hydrolysis and filtration gave a 96% recovery of hexaphenyldisilane, m.p. 364-366°. No tetraphenylsilane could be isolated from the organic layer.

8. p-Tolyllithium in diethyl ether-tetrahydrofuran, run 1

A solution of 0.1 mole of p-tolyllithium in 200 ml. of diethyl ether was added to a suspension of 10.36 g. (0.02 mole) of hexaphenyldisilane in 100 ml. of tetrahydrofuran. The mixture became orange-red immediately. After stirring for 2 days at gentle reflux, no hexaphenyldisilane was visible in the red-brown mixture. Cooling to room temperature followed by carbonation and the usual work-up gave a yellow gummy solid from the acidified basic extract, melting over the range 100-166° (odor of phenylacetic acid). The acid was reprecipitated twice by extraction of a diethyl ether solution with sodium bicarbonate, followed by acidification to give, with much loss of material, 1.05 g. (7.7%) of p-toluic acid, m.p. and mixed m.p. 176-178°.

The filtrates from the three precipitations of the yellow acid were combined and extracted with diethyl ether, and the ether was removed by distillation. The residual oily solid was crystallized twice from petroleum ether (b.p. 60-70°) with no marked improvement in melting range (55-60°). The gummy solid then was sublimed in vacuo and recrystallized three times from petroleum ether (b.p. 60-70°) to give 0.47 g. (3.45%) of phenylacetic acid, m.p. 75-77° (mixed m.p.).

The dried organic layer was distilled to remove the bulk of the solvents, then evaporated to dryness. The residue was washed with petroleum ether (b.p. 60-70°), and the insoluble material was recrystallized from cyclohexane to give 2.74 g. (50%) of triphenylsilanol, m.p. and mixed m.p. 152-154°.

The petroleum ether extract was poured onto a column of dry alumina. Elution with the same solvent, and fractional crystallization of the eluted material gave a trace of unidentified solid, melting over the range 190-205°, together with

0.8 g. of material, m.p. 128-130°. The infrared spectrum of the latter product was identical with that of an authentic sample of p-tolyltriphenylsilane, m.p. 140°, prepared later by the reaction of p-tolyllithium with chlorotriphenylsilane. In addition, there remained an oil (0.9 g.), whose infrared spectrum indicated it to be a mixture of triphenylsilane and benzyltriphenylsilane which was not worked up any further.

Elution with benzene gave an oil; and ethyl acetate eluted 0.5 g. of 4-triphenylsilylbutanol, m.p. 105-107°, together with 0.7 g. of triphenylsilanol, m.p. 150-152°. The latter two products were identified by mixture melting points.

9. Run 2

The p-tolyllithium was prepared from 34.2 g. (0.2 mole) of p-bromotoluene and excess lithium in 150 ml. of diethyl ether. One-half of this mixture was carbonated by pouring it jet-wise onto a slurry of Dry Ice and diethyl ether. Hydrolysis and extraction with sodium bicarbonate solution, followed by acidification of the aqueous extract gave 11.6 g. (85%) of p-toluic acid, m.p. and mixed m.p. 178-180°, after recrystallization from ethanol-water.

The organic layer afforded 0.8 g. (7.6%) of di-p-tolyl ketone, m.p. 92-94° (from ethanol). The latter product was identified by mixed melting point and infrared spectra. No odor of phenylacetic acid was detected during work-up.

The remaining p-tolyllithium solution was refluxed for 2 days with 10.36 g. (0.02 mole) of hexaphenyldisilane in 50 ml. of tetrahydrofuran. Work-up by water hydrolysis, extraction with diethyl ether, drying of the combined organic phase over sodium sulfate and removal of the solvents left an oil. The oil was chromatographed; the eluted material was fractionally crystallized, and the residual oils were rechromatographed to eventually yield: 0.9 g. (8.7%) of triphenylsilane, m.p. 43-45°; 1.8 g. (25.7%) of p-tolyltriphenylsilane; m.p. 128-130°; and 3.02 g. (43.1%) of benzyltriphenylsilane, m.p. 94-97°. All three products were eluted with petroleum ether (b.p. 60-70°) and identified by mixture melting points and infrared spectra.

In addition, 1.4 g. (21.1%) of 4-triphenylsilylbutanol was eluted with 30 ml. of ethyl acetate and recrystallized from petroleum ether (b.p. 60-70°). Further elution with the same solvent afforded 1.5 g. (27%) of triphenylsilanol, m.p. and mixed m.p. 152-154°.

10. p-Tolyllithium and chlorotriphenylsilane

p-Tolyllithium was prepared from 0.2 mole of p-bromotoluene. One-tenth of this material was carbonated and worked up as in the previously described reaction to give 58% of p-toluic acid and 34% of di-p-tolyl ketone.

The remaining solution (ca. 0.18 mole) was added to 50 ml. of tetrahydrofuran, and the mixture was refluxed for 2 days. The reaction mixture was then derivatized with 0.2 mole of chlorotriphenylsilane. Hydrolysis was effected with water, and the aqueous layer extracted with diethyl ether before discarding. The residue, after removal of solvents from the dried organic phase was alternately crystallized from ethyl acetate and petroleum ether (b.p. 60-70°) to give several crops of triphenylsilanol (from petroleum ether) and p-tolyltriphenylsilane (from ethyl acetate). Recrystallization of the p-tolyltriphenylsilane from ethyl acetate afforded 40.68 g. (64.5%) of p-tolyltriphenylsilane, m.p. 139-140°. The crude triphenylsilanol was recrystallized from cyclohexane to give 11.96 g. (21.6%) of triphenylsilanol, m.p. 152-154°. Both products were identified by infrared spectra as well as by mixture melting points.

The oily residues from the alternate crystallizations and from the recrystallizations were combined and chromatographed on an alumina column. The infrared spectra of the petroleum ether (b.p. 60-70°) eluates indicated the absence of benzyltriphenylsilane. The only products isolated were 4.06 g. (6.4%) of p-tolyltriphenylsilane (in the form of long needles), m.p. 130-132°, after recrystallization from petroleum ether (b.p. 60-70°). Attempts to raise this melting point to 140° by crystallization from dilute ethyl acetate, ethanol or petroleum ether (b.p. 60-70°) failed; however, recrystallization from 10 ml. of ethyl acetate gave the higher melting product, m.p. 140-141°. Ethyl acetate eluted 1.2 g. (2.2%) of triphenylsilanol, m.p. 150-152° (mixed m.p.).

11. Polymorphism in p-tolyltriphenylsilane

The difficulty encountered in raising the melting point of the 4.06-g. fraction of p-tolyltriphenylsilane from 130-132° to 140-141° in the preceding reaction suggested that polymorphism may be involved. To test this possibility, three separate 5-g. fractions of p-tolyltriphenylsilane were crystallized separately from ethyl acetate (10 ml.), ethanol and petroleum ether (b.p. 60-70°). The material which was deposited from ethyl acetate did not alter in melting point or crystal structure (clumps of radiating prisms).

The crystals which separated from ethanol and from petroleum ether (b.p. 60-70°) were in the form of long needles and melted at 130-132°. The melted material was held above its melting point for 5 minutes, then cooled to solidify it. When the melting point capillary was reheated, the material melted at 140°. A portion of the needle-shaped crystals was recrystallized from a concentrated ethyl acetate solution (2 g. in 5 ml.). The p-tolyltriphenylsilane which deposited, melted at 140-141° and had the same appearance as the original compound.

G. Reactions of Triphenylsilyllithium with N,N-Disubstituted Amides

1. N,N-Dimethylbenzamide (1:1), run 1

The addition of 0.05 mole of triphenylsilyllithium in 100 ml. of tetrahydrofuran to a stirred solution of 7.45 g. (0.05 mole) of N,N-dimethylbenzamide in 60 ml. of the same solvent gave a negative Color Test I[115] after the initial heat of reaction had dissipated. Hydrolysis was accomplished by pouring the red reaction mixture into an ice-cold, saturated solution of ammonium chloride. The yellow organic layer was washed with water, after adding 100 ml. of diethyl ether, then dried over anhydrous sodium sulfate.

The aqueous layer was extracted with diethyl ether and discarded. Removal of the solvent from the dried ether extract left 3.5 g. (42.6%) of an oil whose infrared spectrum was superimposable with that of authentic N,N-dimethylbenzamide.

The dried organic layer was concentrated to 50 ml. and cooled to deposit 4.5 g. of a pale orange solid, m.p. 113-120°. Recrystallization from a (1:1) mixture of methanol and ethanol, after removal of a trace of orange, insoluble material, afforded 3.23 g. (16.4%, based on the amide) of a product which contained carbon, hydrogen, nitrogen and silicon, but no oxygen, m.p. 124-125°. This compound was later identified (with the aid of its infrared spectrum, analysis, molecular weight and mixed melting point) as N,N-dimethyl-alpha-triphenylsilyl)benzylamine, which was prepared unambiguously from alpha-bromobenzyltriphenylsilane and dimethylamine.

Anal. Calcd. for $C_{27}H_{27}NSi$: C, 82.5; H, 6.9; N, 3.56; Si, 7.15; Mol. Wt., 393.6. Found: C, 82.6, 82.44; H, 6.68, 6.81; N, 3.54, 3.55; Si, 7.16, 7.12; Mol. Wt. (Rast), 360.

The filtrate from the organic layer afforded, after methanol extraction, 2.2 g. (16.4%) of hexaphenyldisiloxane, m.p. 224-226° (mixed m.p.), upon recrystallization from benzene-petroleum ether (b.p. 60-70°). The methanol extract was crystallized twice from cyclohexane to give 4.96 g. (35.9%) of triphenylsilanol, m.p. 150-152° (mixed m.p.), leaving a dark, viscous oil from which no pure compounds could be crystallized.

The amine forms a picrate when refluxed with a saturated solution of picric acid in absolute ethanol, m.p. 163-165° dec.

Anal. Calcd. for $C_{33}H_{30}N_4O_7Si$: C, 63.7; H, 4.86; N, 8.99. Found: C, 63.45, 63.40; H, 5.05, 5.04; N, 8.99, 8.81.

The amine also forms an unstable hydrochloride when a benzene solution is saturated with dry, hydrogen chloride gas. The benzene solution remains clear, but the product is obtained as a powder by rubbing the viscous residue (from solvent removal under an air-jet) with a spatula, while in contact with petroleum ether (b.p. 60-70°). The air-dried powder appeared to evolve a gas over the range 75-150°, during a melting point determination. An attempted crystallization from a mixture of benzene and petroleum ether (b.p. 60-70°) gave a viscous oil, which could be converted to the same powder by scratching with a spatula, after the solvent had been removed and petroleum ether (b.p. 60-70°) was added. An attempted crystallization from methanol-water reverted the hydrochloride to the amine. The crude, air-dried product was analyzed.

Anal. Calcd. for $C_{27}H_{28}ClNSi$: C, 75.45; H, 6.57; Si, 6.53. Found: C, 75.43, 75.46; H, 6.98, 6.93; Si, 6.48, 6.59.

2. Run 2

A solution of 0.1 mole of triphenylsilyllithium in 150 ml. of tetrahydrofuran was added to 14.9 g. (0.1 mole) of N,N-dimethylbenzamide in 100 ml. of the same solvent. After complete addition, the mixture was cooled in an ice bath and treated with 100 ml. of half-saturated ammonium chloride solution. The separated organic layer was extracted with 10% hydrochloric acid, and the acid extract was made distinctly basic with solid sodium hydroxide, while cooling it in an ice bath. The liberated amine (14.1 g.) was crystallized from an ethanol-petroleum ether (b.p. 60-70°) pair to give 13.1 g. (33.4%) of N,N-dimethyl-alpha-(triphenylsilyl)benzylamine, m.p. and mixed m.p. 122-124°.

Distillation of the solvent from the dark brown, dried organic layer left a dark viscous oil, which was allowed to stand overnight to deposit 5.26 g. (38.1% of the theoretical amount) of triphenylsilanol, in the form of large, colorless prisms, which melted at 149-151° (mixed m.p.), after washing with a little ethanol.

The dark oily residue was distilled to give 2.1 g. (14.1%) of recovered N,N-dimethylbenzamide, b.p. 150-155° (25-30 mm.), identified by its infrared spectrum. Further distillation at 115-145° (0.02 mm.) gave an oily solid. By crystallizing first from petroleum ether (b.p. 60-70°), there was obtained 3.3 g. (11.9%) of triphenylsilanol, m.p. 149-151° (mixed m.p.). Treatment of the filtrate, after solvent removal, with ethanol, and concentration gave 1.25 g. (8.5%) of ethoxytriphenylsilane, m.p. 63-65°. The identity of this product was established by a mixture melting point and by a comparison of its infrared spectrum with that of an authentic sample.

The distillation residue afforded 1.07 g. (4%) of hexaphenyldisiloxane, m.p. 224-226° (mixed m.p.) after crystallization from cyclohexane. In addition, a viscous, glass-like solid remained upon solvent removal. No pure compounds could be isolated from this residue by attempted crystallizations from a variety of solvents.

3. N,N-Dimethylbenzamide (2:1)

A solution of 7.45 g. (0.05 mole) of N,N-dimethylbenzamide in 50 ml. of tetrahydrofuran was added dropwise to a stirred solution of *ca*. 0.1 mole of triphenylsilyllithium in 150 ml. of the same solvent. The resulting red solution gave a positive Color Test I after stirring for two hours at room temperature. The mixture was hydrolyzed with ice-cold saturated ammonium chloride, and the layers were separated. The aqueous layer was made basic with sodium hydroxide solution and extracted with diethyl ether, then discarded.

The combined organic layer was extracted with several small portions of 10% hydrochloric acid, then with water, before being dried over sodium sulfate. The product, N,N-dimethyl-*alpha*-(triphenylsilyl)benzylamine, was isolated by making the aqueous layer basic with solid sodium hydroxide (while cooling in an ice bath), and extracting with diethyl ether. Removal of the solvent and crystallization from ethanol gave 13.4 g. (68.2%) of product, m.p. 123-124°.

The solvents were removed from the neutral layer leaving a red, gummy residue, which was extracted with 200 ml. of hot petroleum ether (b.p. 60-70°) to give as the soluble portion, 3.7 g. of triphenylsilanol, m.p. and mixed m.p. 152-154°. Concentration of the filtrate left an oil which was combined with the original petroleum ether-insoluble portion and dissolved in ethanol. Eventually this ethanol solution yielded

9.45 g. (31%) of ethoxytriphenylsilane, m.p. and mixed m.p. 63-65°. The identity of this material was further confirmed by its infrared spectrum. In addition, another 0.9 g. of triphenylsilanol was isolated by crystallization of the residue from cyclohexane. The total yield of triphenylsilanol was 4.6 g. (16.6%).

4. N,N-Dimethylbenzamide (3:1)

A solution of 0.1 mole of triphenylsilyllithium was allowed to react for one hour with 4.92 g. (0.033 mole) of N,N-dimethylbenzamide in 160 ml. of tetrahydrofuran. Color Test I was still positive. Hydrolysis was effected with cold ammonium chloride solution, and the layers were separated, after adding 100 ml. of diethyl ether. The solvents were removed from the dried organic layer, and benzene was added to the residue. Four crops of wide-melting solids (21.8 g.) were obtained upon concentration. The infrared spectra of these solids indicated the presence of triphenylsilanol, hexaphenyldisiloxane and N,N-dimethyl-alpha-(triphenylsilyl)benzylamine.

The amine (8.95 g., 69%) was separated by acid extraction of a diethyl ether solution of the solid, as previously described. The acidified organic layer was washed with sodium bicarbonate and distilled water to neutralize the acid. Drying, followed by removal of the ether, and extraction of the residue with ethanol left 2.5 g. (9.06%) of hexaphenyldisiloxane, m.p. 225-227° (after crystallization from cyclohexane). The ethanol extract gave 9.35 g. (33.8%) of triphenylsilanol, m.p. 152-154°, after crystallization from cyclohexane.

The oil which remained after removal of the benzene from the original organic layer was distilled to give 2.7 g. (10.2%) of triphenylsilane, b.p. 115-117° (0.05 mm.), which solidified when seeded, m.p. 42-44° (mixed m.p., infrared spectra). No ethoxytriphenylsilane could be detected in the reaction mixture.

5. Preparation of ethoxytriphenylsilane

A mixture of 5.0 g. (0.0181 mole) of triphiphenylsilanol, 10 ml. of absolute ethanol and one drop of 10% hydrochloric acid was boiled and concentrated to give, in two crops, 5.2 g. (94.5%) of ethoxytriphenylsilane, m.p. 63-65°. The identity of the product was established by a mixture melting point determination, and by a comparison of its infrared spectrum, as a carbon disulfide solution, with that of an authentic sample.

6. Preparation of methoxytriphenylsilane

Using the same procedure, 5.0 g. (0.0181 mole) of triphenylsilanol, 10 ml. of absolute methanol and one drop of 10% hydrochloric acid yielded 4.9 g. (98.7%) of methoxytriphenylsilane, m.p. 51-53°. Recrystallization from methanol raised the melting point to 55-57° (90.7%). The product was identified by mixed melting point and infrared spectra.

7. Preparation of benzyloxytriphenylsilane

A mixture of 5.0 g. (0.0181 mole) of triphenylsilanol, 10 ml. of benzyl alcohol and one drop of 10% hydrochloric acid was heated to 150°, then concentrated on a hot plate under an air-jet to deposit, upon cooling, 5.2 g. (82.2%) of benzyloxytriphenylsilane, m.p. 84-86° (mixed m.p.). The reported[129] melting point is 84-85.5°. The structure was also confirmed by its infrared spectrum.

8. Preparation of diphenylmethoxytriphenylsilane (attempted)

A solution of 3.68 g. (0.02 mole) of benzhydrol, 5.52 g. (0.02 mole) of triphenylsilanol and two drops of 10% hydrochloric acid, in 10 ml. of acetone, was refluxed for 15 minutes and the solvent was distilled to *ca*. 5 ml. The remaining solvent was removed under an air-jet leaving a solid residue, melting over the range 80-150°. Extraction with 50 ml. of warm petroleum ether (b.p. 60-70°) left 3.4 g. of triphenylsilanol, m.p. and mixed m.p. 151-153°. Concentration

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[129] H. Gilman, G. E. Dunn, H. Hartzfeld and A. G. Smith, *J. Am. Chem. Soc.*, *77*, 1287 (1955).

and cooling of the petroleum ether extract deposited an additional 1.45 g. of triphenylsilanol, m.p. 151-153° (total recovery, 4.85 g., 87%). The residue was crystallized twice from ethanol to give 2.88 g. (82.3%) of benzhydryl ether, m.p. and mixed m.p. 107-109°. The filtrate was allowed to stand in an open flask for one week, and the semi-solid residue was washed with petroleum ether (b.p. 60-70°) to give 0.25 g. (6.7%) of benzhydrol, m.p. 67-68° (mixed m.p.).

9. Alternate synthesis of N,N-dimethyl-alpha-(triphenylsilyl)benzylamine

alpha-Bromobenzyltriphenylsilane was prepared from 24.8 g. (0.07 mole) of benzyltriphenylsilane and 13.35 g. (0.075 mole) of N-bromosuccinimide in 400 ml. of carbon tetrachloride according to a published procedure.[130] The yield of product, m.p. 147-148°, crystallized from benzene, was 16.66 g. (55.5%). The reported melting point and yield are 145° and 52%, respectively.[130] The amine was prepared by a modification of the directions of Noll *et al.*,[131] for similar compounds.

A mixture of 8.59 g. (0.02 mole) of bromobenzyltriphenylsilane and *ca*. 4.5 g. (0.1 mole) of dimethylamine was sealed

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[130] C. R. Hauser and C. R. Hance, *ibid*., *74*, 5091 (1952).

[131] J. E. Noll, J. L. Speier and B. F. Daubert, *ibid*., *73*, 3867 (1951).

in a Carius tube while the mixture was cooled in a Dry Ice-acetone bath. The reaction vessel was then heated to 150-160° for 8 hours, cooled to room temperature overnight, and reheated to 160° for an additional 8 hours. The mixture was cooled in a Dry Ice-acetone bath, opened, and the excess dimethylamine was allowed to evaporate in a hood.

The solid residue was hydrolyzed and extracted with 10% hydrochloric acid, after adding 100 ml. of diethyl ether. Work-up in the usual manner from this point on, and crystallization from an ethanol-petroleum ether (b.p. 60-70°) mixture, afforded 4.7 g. (60%) of the amine, m.p. 123-124°. This product did not depress the melting point of the amine isolated from the reaction of triphenylsilyllithium and N,N-dimethylbenzamide. The infrared spectra, as carbon tetrachloride solutions, were identical.

10. Methiodide of N,N-dimethyl-alpha-(triphenylsilyl)benzylamine

A mixture of 2.0 g. (0.0051 mole) of the amine and 7.1 g. (0.05 mole) of methyl iodide in 25 ml. of methanol was refluxed for 10 hours, then distilled to one-half of its original volume. Two crops of needle-like crystals separated, weighing 2.6 g. (90%) after air-drying, m.p. 141° (with effervescence). The material gradually resolidified with continued heating, then decomposed at 228°. Recrystallization from methanol failed to alter the melting-point behavior. The infrared spectrum as a Nujol mull had a sharp band at 2.98 μ, indicative of the hydroxyl group. The melting-point behavior, infrared spectrum, and analysis indicated the possibility that it had methanol of crystallization.

Anal. Calcd. for $C_{28}H_{30}INSi \cdot CH_3OH$: C, 61.5; H, 6.04; I, 22.18; Si, 4.95. Found: C, 61.76, 61.65; H, 6.14, 6.03; I, 21.8, 21.9; Si, 4.92, 4.98.

A portion of the product was dried at 130° in an oven for 18 hours. This dried product did not have a band in the 2.98 μ region of its infrared spectrum, nor did it effervesce at 141°. It melted at 225° with decomposition.

Anal. Calcd. for $C_{28}H_{30}INSi$: C, 62.8; H, 5.65; N, 2.62; Si, 5.25. Found: C, 63.4, 63.27; H, 5.77, 5.66; N, 2.70, 2.69; Si, 5.34, 5.27.

11. Triphenylsilyllithium and N,N-dimethyl-alpha-(triphenylsilyl)benzylamine (attempted)

A solution of 0.02 mole of triphenylsilyllithium in 70 ml. of tetrahydrofuran was added to a solution of 7.9 g. (0.02 mole) of N,N-dimethyl-alpha-(triphenylsilyl)benzylamine in 50 ml. of the same solvent. The mixture was stirred at room temperature for 16 hours, at the end of which time there appeared to be no evidence of reaction. A solution of 0.02 mole of methyl iodide in 50 ml. of diethyl ether was added, and the mixture, which contained some suspended material, was hydrolyzed with half-saturated ammonium chloride. Filtration afforded 1.25 g. (24.1%) of hexaphenyldisilane, m.p. 360-362° (mixed m.p.).

The layers of the filtrate were separated, and the amine was extracted from the organic layer with 10% hydrochloric acid. The usual work-up, followed by crystallization from ethanol afforded 6.85 g. (86% recovery) of the original amine, m.p. 123-125° (mixed m.p.).

The dried organic layer was chromatographed to give 3.6 g. (65.7%) of methyltriphenylsilane, m.p. 66-67° and a trace of triphenylsilanol.

12. N,N-Dimethylbenzamide (2:1), followed by methyl iodide

A solution of 0.1 mole of triphenylsilyllithium in 150 ml. of tetrahydrofuran was added to a solution of 7.45 g. (0.05 mole) of N,N-dimethylbenzamide in 50 ml. of the same solvent. The mixture was refluxed gently for one hour, and then stirred at room temperature for 18 hours. Color Test I appeared to be negative. The blood-red mixture was nevertheless treated with a solution of *ca*. 0.11 mole of methyl iodide to discharge the red color, and give a pale yellow suspension. After stirring overnight at room temperature, hydrolysis was effected with 100 ml. of saturated ammonium chloride solution. Some ether was added, and work-up by acid extraction gave 14.7 g. (72.2%) of N,N,*alpha*-trimethyl-*alpha*-(triphenylsilyl)benzylamine, m.p. 143-144° (from petroleum ether (b.p. 60-70°)).

Anal. Calcd. for $C_{28}H_{29}NSi$: C, 82.5; H, 7.19; N, 3.44; Si, 6.89. Found: C, 82.80, 82.70; H, 6.83, 6.92; N, 3.63, 3.58; Si, 6.92, 6.96.

Work-up of the neutral organic layer gave 12.69 g. (93.6%) of triphenylsilanol, identified by mixed melting point and infrared spectra.

13. N,N-Dimethylacetamide (1:1)

A solution of 0.06 mole of triphenylsilyllithium in 75 ml. of tetrahydrofuran was added to a solution of 5.23 g. (0.06 mole) of N,N-dimethylacetamide in 50 ml. of the same solvent. The reaction mixture gave a negative Color Test I at the end of the addition. Hydrolysis was accomplished by pouring into 50 ml. of 10% hydrochloric acid. Work-up as in the previously described reactions afforded 8.0 g. (40.2%, based on triphenylsilyllithium) of N,N-dimethyl-alpha-(triphenylsilyl)ethylamine, m.p. 116-117.5°, from petroleum ether (b.p. 60-70°).

Anal. Calcd. for $C_{22}H_{26}NSi$: C, 79.8; H, 7.61; N, 4.24; Si, 8.49. Found: C, 79.96, 80.05; H, 7.50, 7.42; N, 4.32, 4.24; Si, 8.39, 8.28.

The neutral organic layer was evaporated. The residue was crystallized from cyclohexane to give 7.5 g. (45.3%) of triphenylsilanol, m.p. 152-153° (mixed m.p.).

The amine forms a picrate when refluxed with an excess of saturated picric acid in 95% ethanol, m.p. 177° dec.

Anal. Calcd. for $C_{28}H_{28}N_4O_7Si$: C, 60.8; H, 4.92; N, 9.79. Found: C, 60.21, 60.09; H, 4.87, 4.69; N, 9.35, 9.52.

14. N,N-Dimethylacetamide (2:1), reverse addition

To a solution of 0.08 mole of triphenylsilyllithium in 120 ml. of tetrahydrofuran was added a solution of 3.48 g. (0.04 mole) of N,N-dimethylacetamide in 50 ml. of the same solvent. The mixture was stirred at room temperature for one day, then at gentle reflux for two days, after which it was hydrolyzed with 10% hydrochloric acid and 100 ml. of diethyl ether was added. The organic layer was extracted with 10% hydrochloric acid then washed with water and dried. The acid extract was made basic with solid sodium hydroxide and extracted with diethyl ether. Drying of the ether extract, removal of the solvent, and crystallization of the residue from petroleum ether (b.p. 60-70°) gave 8.15 g. (61.5%) of N,N-dimethyl-alpha-(triphenylsilyl)ethylamine, m.p. 115.5-117°, identified by mixed melting point and infrared spectrum. An additional 1.0 g. (7.55%) of less pure product, m.p. 112-116°, was obtained also.

The neutral organic layer furnished 9.24 g. (41.8%) of triphenylsilanol, identified by mixed melting point.

15. N,N-dimethyl-p-toluamide (2:1)

A solution of 0.04 mole of triphenylsilyllithium and 3.26 g. (0.02 mole) of N,N-dimethyl-p-toluamide in 105 ml. of tetrahydrofuran was stirred until the initial heat of reaction had dissipated. Hydrolysis with 50 ml. of 10% hydrochloric acid, followed by extraction of the organic phase with 2-25 ml. portions of the same acid, led to the isolation of 4.95 g. (60.7%) of N,N-dimethyl-alpha-(triphenylsilyl)-p-xylylamine, m.p. 144-145°, from petroleum ether (b.p. 60-70°).

Anal. Calcd. for $C_{28}H_{29}NSi$: C, 82.5; H, 7.19; N, 3.44; Si, 6.89. Found: C, 82.41, 82.45; H, 6.96, 7.06; N, 3.51, 3.43; Si, 6.79, 6.75.

The neutral organic layer yielded 5.2 g. (94.5%) of triphenylsilanol, m.p. 149-151° (mixed m.p.).

16. N,N-Diphenylacetamide (1:1)

A solution of 0.06 mole of triphenylsilyllithium in 200 ml. of tetrahydrofuran was added to a suspension of 12.7 g. (0.06 mole) of N,N-diphenylacetamide in 100 ml. of the same solvent. The blue-green mixture turned brown when the addition was complete, and Color Test I was negative. Hydrolysis was accomplished by adding 100 ml. of saturated ammonium chloride solution. Diethyl ether (100 ml.) was added, and the organic layer was washed with 10% hydrochloric acid, then with distilled water. The acid extract gave no amine when made basic, and extracted with diethyl ether after drying and removal of the solvent.

The dried organic layer was distilled to remove solvents leaving a dark brown oil which was distilled under reduced pressure to give 9.2 g. of material, b.p. 95-100° (0.06 mm.). Further distillation gave 10.37 g. of material boiling over the range 100-143° (0.04 mm.). An infrared spectrum of the low-boiling material indicated it to be a mixture of diphenylamine and triphenylsilane. The higher boiling fraction appeared to contain triphenylsilane, triphenylsilanol and a carbonyl-containing compound.

The 9.2-g. fraction was washed with petroleum ether (b.p. 60-70°) to give (in two crops) 5.6 g. (55.2%) of diphenylamine, m.p. and mixed m.p. 53-54°. No other crystalline compounds could be isolated upon concentration.

The second fraction from the distillation was treated similarly to obtain 1.8 g. (10.9%) of triphenylsilanol, m.p. 154-156° (mixed m.p.). The two petroleum ether extracts were combined with the distillation residue and chromatographed on alumina. The first 50 ml. of petroleum ether (b.p. 60-70°) eluted 6.7 g. (43%) of triphenylsilane, m.p. and mixed m.p. 45-46°. The next 50 ml. of the same solvent eluted 5.93 g. (23%) of an oil, whose infrared spectrum as a carbon disulfide solution, indicated it to be a mixture of triphenylsilane and diphenylamine. Further elution with 100 ml. of the same solvent yielded 1.3 g. (8.33%) of diphenylamine, m.p. 52-54° (mixed m.p.). Cyclohexane eluted an oil from which no pure compounds could be isolated, and further elution with benzene afforded 1.0 g. (6.04%) of triphenylsilanol, m.p. 149-152° (mixed m.p.). No pure compounds could be isolated from the ethyl acetate or methanol eluates.

17. N,N-Diphenylacetamide (2:1)

A mixture of 0.08 mole of triphenylsilyllithium and 8.45 g. (0.04 mole) of N,N-diphenylacetamide in 320 ml. of tetrahydrofuran was stirred at room temperature for two days, at the end of which time Color Test I was still positive. The mixture was hydrolyzed with saturated ammonium chloride and filtered to remove 1.1 g. of hexaphenyldisilane, m.p. and mixed m.p. 364-366°.

The layers of the filtrate were separated and the organic layer, together with the diethyl ether extracts of the aqueous layer, was dried over sodium sulfate. The solvents were removed and the residual brown oil was distilled to give five wide-boiling fractions. Fraction one, 5.15 g., b.p. 96-103° (0.05 mm.), was swirled with petroleum ether (b.p. 60-70°) and filtered to remove 2.4 g. (35.4%) of diphenylamine, m.p. 51-52° (mixed m.p.). The infrared spectrum of the other fractions, and of the oily residue from fraction one, indicated the presence of Si-H (4.75μ), the carbonyl group (6μ), silicon-phenyl (8.98μ) and aliphatic, as well as aromatic C-H.

These fractions were chromatographed on alumina to give 12.8 g. (61.5%) of triphenylsilane; 1.55 g. (7%) of triphenylsilanol; and 2.55 g. (31.8%) of recovered N,N-diphenylacetamide. All compounds were identified by mixed melting point determinations and infrared spectra.

The distillation residue from the original distillation afforded 0.15 g. of hexaphenyldisilane, m.p. 360-363°, and 0.9 g. (4.06%) of hexaphenyldisiloxane, m.p. 224-226° (mixed m.p.). The total yield of hexaphenyldisilane was 1.25 g. (6.05%).

18. N,N-Diphenylbenzamide (2:1)

A solution of 0.04 mole of triphenylsilyllithium in 50 ml. of tetrahydrofuran was added to a suspension of 5.46 g. (0.02 mole) of N,N-diphenylbenzamide in 50 ml. of diethyl ether. The mixture turned green, then red-brown during the addition. After stirring at room temperature for 6 hours, the suspension was hydrolyzed with 50 ml. of water to give an emulsion, which was dispersed by adding 20 ml. of 10% hydrochloric acid and 100 ml. of diethyl ether. The mixture was stirred for 1 hour, then filtered to remove 5.25 g. of a pale pink solid, m.p. 236-238°. Several recrystallizations from benzene failed to alter the melting point of the N,N-diphenyl-*alpha*-(triphenylsilyl)benzylamine.

Anal. Calcd. for $C_{37}H_{31}NSi$: C, 85.8; H, 6.04; N, 2.70; Si, 5.43. Found: C, 86.2, 86.25; H, 5.95, 6.08; N, 2.68, 2.79; Si, 5.42, 5.40.

The layers of the filtrate were separated, and the ether extracts of the aqueous layer were combined with the organic layer, and then dried. Concentration to 15 ml., followed by the addition of 50 ml. of diethyl ether, deposited an additional 2.9 g. of the amine, which melted at 235-237° after crystallization from benzene. The total yield was 8.15 g. (78.7%).

The red residue gave upon treatment with cyclohexane 3.1 g. (27%) of triphenylsilanol, m.p. 150-153°, identified by mixed melting point and infrared spectra. Chromatography of the oily filtrate gave 0.5 g. (9.15%) of recovered N,N-diphenylbenzamide (benzene eluate), m.p. 178-179°, together with viscous oils which could not be identified.

H. Reactions of Triphenylsilyllithium with Imides

1. Phthalimide (1:1)

Color Test I[115] became negative immediately after 0.02 mole of triphenylsilyllithium in 30 ml. of tetrahydrofuran was added to a solution of 2.94 g. (0.02 mole) of phthalimide in 80 ml. of the same solvent. Hydrolysis with dilute, cold sulfuric acid and filtration gave 0.2 g. (3.85%) of crude hexaphenyldisilane, m.p. 358-362° (mixed m.p.).

The aqueous layer of the filtrate was extracted with 2-25 ml. portions of diethyl ether then discarded. Removal of the solvents from the dried organic layer left an oily solid which was treated with 200 ml. of warm petroleum ether (b.p. 60-70°), and filtered to remove 2.62 g. (89%) of recovered phthalimide, m.p. 233-235° (mixed m.p.), after crystallization from ethanol.

The petroleum ether extract gave, after passage through a column of alumina, 2.88 g. (55.5%) of triphenylsilane and 1.32 g. (23.9%) of triphenylsilanol. Both compounds were identified by mixture melting points and infrared spectra. In addition, oils, from which no pure compounds could be isolated, were eluted with benzene.

2. Phthalimide (2:1)

The addition of 0.1 mole of triphenylsilyllithium in 150 ml. of tetrahydrofuran to 7.36 g. (0.05 mole) of phthalimide in 100 ml. of the same solvent gave a yellow-brown suspension, which did not respond to Color Test I at the end of the addition. The mixture was hydrolyzed with water and filtered to remove 0.6 g. (2.3%) of hexaphenyldisilane, m.p. 360-363° (mixed m.p.).

Work-up of the dried organic layer by chromatography gave 19.73 g. (71.3%) of triphenylsilanol, identified by mixed melting point, together with 1.2 g. (4.5%) of hexaphenyldisiloxane. In addition, chloroform eluted 3.15 g. of a yellow oil which was not identified, and could not be crystallized from a variety of solvents.

3. <u>N-Methylphthalimide (4:1), run 1</u>

A solution of 4.04 g. (0.025 mole) of N-methylphthalimide in 100 ml. of tetrahydrofuran was added to a tetrahydrofuran solution of 0.1 mole of triphenylsilyllithium. The red reaction mixture was stirred for 1 hour, at the end of which time it had cooled to room temperature. To this solution (Color Test I positive) was added an excess of chlorotrimethylsilane (*ca*. 0.11 mole). The mixture was then stirred overnight for convenience, and the solvent, together with unreacted chlorotrimethylsilane was removed by distillation. Benzene was added to the residue and 13.5 g. of insoluble material was removed by filtration. The solid melted partially at 360°, and was shown to contain lithium chloride by qualitative tests.

Hydrolysis of the solid with water, followed by filtration left 8.95 g. (34.5%) of hexaphenyldisilane, m.p. and mixed m.p. 364-366°. Extraction of the aqueous filtrate with diethyl ether, and removal of the solvent from the dried extract, gave only a trace of material from which no pure compounds could be isolated.

The benzene extract furnished an additional 2.15 g.

(8.3%) of hexaphenyldisilane upon concentration. The dark brown residue from solvent removal gave, upon crystallization from ethanol and methanol, 12.24 g. (36.8%) of 1,1,1-trimethyl-2,2,2-triphenyldisilane, m.p. and mixed m.p. 107-108°. Chromotography of the oily filtrates failed to yield any other pure compounds.

4. Run 2

A solution of 0.1 mole of triphenylsilyllithium in 200 ml. of tetrahydrofuran was added to a stirred solution of 4.04 g. (0.025 mole) of N-methylphthalimide in 20 ml. of diethyl ether and 50 ml. of tetrahydrofuran. The mixture was stirred at room temperature for 24 hours. Color Test I was positive at this time. The mixture was hydrolyzed with saturated ammonium chloride solution and filtered to remove 8.3 g. of hexaphenyldisilane, m.p. 365-367° (mixed m.p.). The identity of the compound was further confirmed by its infrared spectrum.

The layers of the filtrate were separated, and the dark brown organic layer together with the ether extracts of the aqueous layer, was dried over sodium sulfate and the solvents removed. Treatment of the residue with hot benzene left 0.5 g. of insoluble hexaphenyldisilane, m.p. and mixed m.p. 360-363° (total yield, 34%). The benzene filtrate failed to crystallize upon concentration, hence it was poured on a column of alumina.

Elution with petroleum ether gave 7.1 g. (27.2%) of triphenylsilane, m.p. 43-45° (mixed m.p.). Further elution with the same solvent gave 0.4 g. of a compound, m.p. 130-132°, which is thought to be o-formyl-N-methyl-benzamide. Further elution with cyclohexane, benzene and ethyl acetate gave (after recrystallization from cyclohexane) 6.35 g. (23%) of triphenylsilanol, m.p. 151-153° (mixed m.p.).

5. Run 3, at reflux

The preceding reaction was repeated using the same quantities of reactants; however, the mixture was gently refluxed for 24 hours. Work-up as in the previous reaction gave 7.88 g. (30.4%) of hexaphenyldisilane, m.p. and mixed m.p. 364-366°; 4.1 g. (15.8%) of triphenylsilane, m.p. 42-44° (mixed m.p.); 7.83 g. (23.6%) of 4-triphenylsilylbutanol (eluted with ethyl acetate and crystallized from petroleum ether (b.p. 60-70°)); and 2.35 g. (8.52%) of triphenylsilanol. No product derived from the phthalimide reactant was isolated; however, oils and tar-like substances remained after crystallizing out the triphenylsilanol from the ethyl acetate and methanol eluates, and only unidentified, viscous oils were eluted with benzene.

6. N-Methylphthalimide (2:1)

A solution of 0.08 mole of triphenylsilyllithium in 170 ml. of tetrahydrofuran was added to a stirred suspension of 6.43 g. (0.04 mole) of N-methylphthalimide in 50 ml. of diethyl ether and 20 ml. of tetrahydrofuran. The mixture became green during the addition of the first equivalent, then turned red and a precipitate developed. Hydrolysis was effected with a half-saturated ammonium chloride solution, after stirring overnight. Filtration gave 14.13 g. (68.3%) of hexaphenyldisilane, m.p. 360-363° (mixed m.p.).

The separated and dried organic layer was concentrated and filtered to remove 0.2 g. of hexaphenyldisilane, m.p. 359-362° (mixed m.p.). Complete removal of the solvent followed by treatment with a benzene-petroleum ether (b.p. 60-70°) mixture, gave only an orange, vixcous material. The oil was then redissolved in benzene and distilled to give one fraction, boiling over a wide range up to 150° (0.07 mm.), and a solid which crystallized in the side-arm of the distilling flask. The fraction which distilled and dropped into the receiver was extracted with cold petroleum ether (b.p. 60-70°) to give 2.55 g. of material, m.p. 122-129°. Recrystallization from benzene raised the melting point to 133-135°. The product is thought to be o-formyl-N-methylbenzamide.

Anal. Calcd. for $C_9H_9NO_2$: C, 66.25; H, 5.55; N, 8.59. Found: C, 66.55, 66.41; H, 5.70, 5.75; N, 8.43, 8.45.

The aldehyde forms a phenylhydrazone, m.p. 231-233°.

Anal. Calcd. for $C_{15}H_{15}N_{3}O$: C, 70.9; H, 5.96; N, 16.52. Found: C, 71.59, 71.4; H, 6.13, 6.08; N, 16.50, 16.54.

The infrared spectrum of the aldehyde, as a KBr pellet, has strong absorption bands at 3.04, 3.44, 3.51, 5.98 (broad) and 13.35μ, indicative of N-H, aromatic C-H, aliphatic C-H, the amide carbonyl and o-disubstitution, respectively. In addition, a weak but distinct band at 3.7 , indicative of the aldehyde C-H bond was present.

The solid which condensed in the side-arm of the distillation flask yielded, after fractionation from benzene and benzene-petroleum ether (b.p. 60-70°) mixtures, 0.2 g. of the same aldehyde, m.p. 131-133° (mixed m.p.), and 0.2 g. of triphenylsilanol, m.p. 150-152° (mixed m.p.). The total yield of the aldehyde was 2.75 g. (42.2%).

No crystalline compounds could be isolated from the petroleum ether extract of the distilled material, hence it was combined with the distillation residue and chromotographed on alumina to give 0.5 g. (2.4%) of triphenylsilane; 0.8 g. (3.61%) of triphenylsilanol; and 0.85 g. (3.74%) of hexaphenyldisiloxane. All three products were identified by mixture melting points. In addition, ca. 3.5 g. of viscous oils remained, from which no pure compounds could be isolated by crystallization techniques.

7. N-Phenylphthalimide (4:1)

A solution of 0.1 mole of triphenylsilyllithium and 5.58 g. (0.025 mole) of N-phenylphthalimide in 200 ml. of tetrahydrofuran was stirred for 24 hours at room temperature, then at gentle reflux for the same length of time. Hydrolysis was accomplished by adding 50 ml. of saturated ammonium chloride, after which 100 ml. of diethyl ether was added. Filtration afforded 13.4 g. (51.7%) of hexaphenyldisilane, m.p. 359-362° (mixed m.p.).

The dark organic layer was washed with 10% hydrochloric acid, but no pure compounds could be isolated from the small amount of dark oil which remained after treatment with solid sodium hydroxide, extraction with diethyl ether, drying of the ether extract, and solvent removal.

The still darkly colored organic layer was dried. The solvents were removed to leave a dark viscous oil, which was separated partially into its constituents with much difficulty, by chromatography and fractional crystallization. The products isolated were: 6.95 g. (26.7%) of triphenylsilane, m.p. 42-44° (mixed m.p.), eluted with petroleum ether (b.p. 60-70°); 2.15 g. (38.2%) of a product thought to be o-formyl-N-phenylbenzamide, m.p. 169-170°, eluted with benzene together with a viscous oil, and crystallized from benzene-ethyl acetate mixtures; 2.4 g. (7.21%) of 4-triphenylsilylbutanol, m.p. 107-109° (mixed m.p.), eluted with ethyl acetate, together with an unidentified, dark oil, and crystallized from petroleum ether (b.p. 60-70°); and 1.08 g. (3.9%) of triphenylsilanol, m.p. 148-151° (mixed m.p., infrared spectra).

The infrared spectrum of the aldehyde, which was eluted with benzene, had sharp absorption bands at 2.96, 3.26, 3.7, 5.92, 7.13 and 13.4 μ, indicative of N-H, aromatic C-H, aldehyde C-H, the amide carbonyl, the amide linkage and *o*-disubstitution, respectively.

Anal. Calcd. for $C_{14}H_{11}NO_2$: C, 74.7; H, 4.91; N, 6.21. Found: C, 74.66, 74.49; H, 4.80, 4.61; N, 6.14, 6.14.

8. N-Phenylphthalimide (2:1)

A solution of 0.04 mole of triphenylsilyllithium in 70 ml. of tetrahydrofuran was reacted with a suspension of 4.46 g. (0.02 mole) of N-phenylphthalimide in 30 ml. of the same solvent. The imide dissolved after the addition of the first 10 ml. of the triphenylsilyllithium. The mixture developed a suspension after one-half of the organosilyllithium compound had been added. Subsequent to stirring for one hour, the suspension was hydrolyzed with saturated ammonium chloride, filtered, and the solid was washed with water and diethyl ether to leave 5.9 g. (57%) of hexaphenyldisilane, m.p. 365-367° (mixed m.p.).

The dried organic layer was stripped of solvents leaving a dark, viscous oil. Attempts to crystallize products from this oil failed to give more than trace amounts of wide-melting yellow solids, even though a wide variety of solvents were tried. The oil was not worked up any further.

IV. DISCUSSION

A. Alkylation *vs*. Displacement with Trialkyl Phosphates

The difference in behavior toward Grignard reagents of alkyl sulfates and phosphates has been known for many years. Grignard reagents are alkylated when exposed to dialkyl sulfates, the process involving scission of a carbon-oxygen bond and formation of a carbon-carbon bond (I).[132] Phosphate esters (both alkyl and aryl), on the other hand, are attacked at the central phosphorus atom, the process entailing rupture of the phosphorus-oxygen bond, with the concomitant creation of a carbon-phosphorus linkage (II) (refer to the Historical section of this Thesis). Alkyl esters of aryl sulfonic acids similarly react according to path I, and extensive use has

$$\text{I} \quad R'MgX + ROSO_2OR \longrightarrow RR' + ROSO_2OMgX$$

$$\text{II} \quad R'MgX + ROP(O)(OR)_2 \longrightarrow R'P(O)(OR)_2 + ROMgX$$

been made of this reaction to prepare alkyl derivatives of Grignard reagents.[132] In general, however, esters of other inorganic oxygen acids undergo displacements of the type shown in equation II. To illustrate: alkyl borates give boronic acids; carbonates yield ketones and tertiary alcohols;

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[132] M. S. Kharasch and O. Reinmuth. Grignard reactions of nonmetallic substances. New York, N.Y., Prentice-Hall, Inc. 1954.

orthocarbonates give substituted orthoformates; nitrates and nitrites generally yield disubstituted hydroxylamine derivatives; sulfites and sulfinates give sulfoxides; sulfenates yield thioethers; silicates give silane derivatives; and esters of other inorganic oxygen acids, as a general rule, have been observed to undergo similar transformations when treated with Grignard reagents.[11,12,132]

On this basis, one might expect products containing silicon attached to phosphorus to result from reactions of triphenylsilyllithium with phosphate esters. Compounds of this type had previously been prepared by other methods,[133] but this reaction was of interest in the present study from the standpoint of the organosilylmetallic chemistry involved. As mentioned in the Historical section, the reaction of triphenylsilyllithium with tri-n-butyl phosphate gave a high yield of n-butyltriphenylsilane, the alkylation product.[9] This observation prompted further study of the reaction to test its general applicability and to determine, if possible, the reason for this unexpected course of reaction with triphenylsilyllithium.

One equivalent of triphenylsilyllithium was found to

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[133] See, for example: G. Fritz, Z. Naturforsch, 8b, 776 (1953); B. J. Aylett, H. J. Emeléus and A. G. Maddock, J. Inorg. Nuclear Chem., 1, 187 (1955); W. H. Keeber and H. W. Post, J. Org. Chem., 21, 509 (1956); F. Fehér, G. Kuhlbörsch, A. Blüneke, H. Keller and K. Lippert, Chem. Ber., 90, 134 (1957); W. Kuchen and H. Buchwald, Angew. Chem., 69, 307 (1957); and references cited in these papers.

react smoothly and promptly with trimethyl, tri-n-butyl and triisobutyl phosphate to give the corresponding alkyltriphenylsilanes in yields of 88, 97 and 87.8 percent, respectively. The use of three equivalents of triphenylsilyllithium with tri-n-butyl phosphate, however, required forced conditions in order to consume all of the organosilyllithium reagent. Apparently the removal of a second or third alkyl group from the ester is much more difficult than is the removal of the first. This has also been found to be the case in the hydrolysis of phosphate esters.[134] Moreover, it was evident from this reaction that all three alkyl groups were not functioning as alkylating agents since n-butyltriphenylsilane was formed in only 49.5 and 51.5 percent yields from two reactions where forced conditions were employed. Considerable amounts of hexaphenyldisilane (11.6 and 13.8 per cent) together with varying yields of triphenylsilanol, 4-triphenylsilylbutanol and hexaphenyldisiloxane were also obtained. Since previously,[9] hexaphenyldisilane was reported to have been formed via cleavage of intermediates having silicon attached to phosphorus, it appeared likely that this type of reaction might likewise be involved here. The phosphine-like odors noticed after hydrolysis supported this

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[134] G. M. Kosolapoff. Organophosphorus compounds. New York, N.Y., John Wiley and Sons, Inc. 1950. pp. 211-277.

mechanism; hydrolysis of the phosphorus-lithium intermediate, so produced, would lead to the formation of a product having a phosphorus-hydrogen bond. The proposed transformations are illustrated in the following equations:

$$2\ \mathrm{Ph_3SiLi} + (\underline{\mathrm{n}}\text{-}\mathrm{BuO})_3\mathrm{P(O)} \longrightarrow 2\ \mathrm{Ph_3SiBu}\text{-}\underline{\mathrm{n}} + \mathrm{(LiO)_2P(P)OBu}\text{-}\underline{\mathrm{n}}$$

$$\mathrm{Ph_3SiLi} + \mathrm{(LiO)_2P(O)OBu}\text{-}\underline{\mathrm{n}} \longrightarrow \underline{\mathrm{n}}\text{-}\mathrm{BuOLi} + \mathrm{(LiO)_2P(O)SiPh_3}$$

$$\mathrm{Ph_3SiLi} + \mathrm{(LiO)_2P(O)SiPh_3} \longrightarrow \mathrm{Ph_6Si_2} + \mathrm{(LiO)_2P(O)Li}$$

$$\mathrm{(LiO)_2P(O)SiPh_3} + 3\ \mathrm{H_2O} \longrightarrow \mathrm{Ph_3SiOH} + \mathrm{(HO)_2P(O)H} + 2\ \mathrm{LiOH}$$

$$\mathrm{(LiO)_2P(O)Li} + 3\ \mathrm{H_2O} \longrightarrow \mathrm{(HO)_2P(O)H} + 3\ \mathrm{LiOH}$$

The 4-triphenylsilylbutanol can be accounted for by cleavage of the solvent, since this reaction is known to occur when triphenylsilyllithium solutions are refluxed in tetrahydrofuran.[7,90,98]

The explanation for the formation of hexaphenyldisilane becomes even more probable when one considers that silicon-oxygen[7,74,135] and silicon-sulfur[136,137,138] bonds are readily cleaved by triphenylsilylmetallic compounds to give hexaphenyldisilane as a major product. Analogous cleavages

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[135] H. Gilman and T. C. Wu, _J_. _Org_. _Chem_., in press (1960).

[136] H. Gilman and D. Wittenberg, _J_. _Am_. _Chem_. _Soc_., _79_, 6339 (1957).

[137] D. Wittenberg, T. C. Wu and H. Gilman, _J_. _Org_. _Chem_., _23_, 1898 (1958).

[138] D. Wittenberg, H. A. McNinch and H. Gilman, _J_. _Am_. _Chem_. _Soc_., _80_, 5418 (1958).

involving organosilylmercury intermediates have also been reported.[139]

The results of these experiments strongly suggest (as had been felt previously) that the steric requirements of the triphenylsilyl group might be responsible for the observed alkylation of triphenylsilyllithium with trialkyl phosphates. To test this, a variety of relatively large organometallic compounds (including both organolithium compounds and Grignard reagents) were reacted with these same esters and found to behave similarly to triphenylsilyllithium. The size of the organometallic compound was gradually reduced from that of the triphenylmethyl to that of the mesityl group, hoping that somewhere in between, an organometallic compound of proper size would be encountered which would react by both mechanisms simultaneously, affording both alkylation and displacement products. Since Willans[26] had observed displacement with _o_-anisyllithium, the mechanistic change ought to occur somewhere between it and triphenylmethyllithium.

High yields of alkylated compounds were obtained when trimethyl and/or tri-_n_-butyl phosphate were allowed to react with triphenylmethylmagnesium chloride, triphenylmethyllithium, 9-phenyl-9-fluorenyllithium and diphenylmethyl-

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[139] M. V. George, G. D. Lichtenwalter and H. Gilman, _ibid._, _81_, 978 (1959).

lithium. Triisobutyl phosphate also alkylated 9-phenyl-9-fluorenyllithium, however, in a much lower yield. Large amounts of viscous oils were obtained from the latter reaction together with small amounts of a hydrocarbon, which appears to be composed of two 9-phenylfluorenyl groups and one isobutyl group. The structure of this product is not known.

When the reaction of mesitylmagnesium bromide with the trimethyl ester was investigated, mesitylene (30 percent) and isodurene (39.1 percent) were found to be the products of reaction. However, none of the alkylated compound was obtained from the corresponding reaction using tri-n-butyl phosphate, although several attempts were made. In every case employing mesitylmagnesium bromide, varying yields of mesitylene were obtained even when the reactions were terminated by carbonation. Its mode of formation is not understood since the Grignard reagent appeared to be formed in high yield, and freshly distilled esters were employed. The fact that high recoveries of tri-n-butyl phosphate were realized, indicates that no reaction occurred between the ester and organometallic compound. Apparently, the steric hindrance of both the ester and Grignard reagent could not be overcome by the low reactivity of the Grignard reagent. In this connection, mesityllithium also failed to undergo alkylation with tri-n-butyl phosphate in refluxing tetrahydrofuran-diethyl ether. This reaction gave a viscous gel from which no pure compounds could be isolated other than recovered ester (42 percent) and mesitylene (73 percent).

The failure of tri-n-butyl phosphate to alkylate mesityllithium and the corresponding Grignard reagent, together with the large number of possible organometallic compounds having sizes between o-anisyllithium and mesityllithium, discouraged any further attempts to find the turning point in this reaction mechanism.

The results of these experiments indicate that organometallic compounds, having both steric requirements and reactivities comparable to or greater than those of mesitylmagnesium bromide, may be successfully alkylated by trialkyl phosphates. The limitations on size and reactivity will undoubtedly hinder the extensive application of these esters for this purpose. However, the high yields obtainable through their use could make their future application in this capacity advantageous.

Others at these Laboratories have also made use of this reaction. Peterson,[140] for example, derivatized the 1,3-dilithium salt of hexaphenyltrisilane with both dimethyl sulfate and trimethyl phosphate. He obtained a somewhat higher yield of the dimethyl derivative from the phosphate reaction;

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[140] D. J. Peterson, Ames, Iowa. Information concerning reactions of organosilylmetallic compounds. Private communication. 1959.

however, the work-up procedures differed, and the comparison may not be strictly valid. Trepka[141] likewise used the reaction incidental to some relative reactivity studies. He found that trimethyl phosphate was one of the most reactive derivatizing agents tested for triphenylsilyllithium.

The side-reaction converting Grignard reagents to disubstituted magnesium compounds (observed with dialkyl sulfates)[132] has not yet been found to occur with phosphate esters. Because of this, an excess of the sulfate should be employed to obtain good yields; whereas high yields of alkylation products resulted when one mole of the phosphate ester was employed in this study.

Alkyl halides have been used extensively to prepare compounds of this type from Grignard reagents[132] and organosilylmetallic compounds.[6] In many cases, high yields were realized. Relative to the reactions involving organosilylmetallic compounds,[142] the alkyl chlorides and fluorides are best-suited because the other halides exhibit a tendency to undergo halogen-metal interconversion reactions.[6,142,143] In this

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[141] W. J. Trepka, Ames, Iowa. Information on relative reactivity studies. Private communication. 1959.

[142] Reactions of organosilylmetallic compounds with alkyl and aryl halides have been recently reviewed by Lichtenwalter and Diehl. See Theses cited in Footnotes 7 and 90.

[143] G. Dappen, Ames, Iowa. Information concerning reactions of triphenylsilyllithium with alkyl and aryl halides. Private communication. 1959.

connection, varying yields (in some cases excellent) were obtained from the reactions of alpha,omega-dihalides with triphenylmethyl- and diphenylmethylsodium in liquid ammonia.[144] Ethylene chloride, for example, gave a 93 percent yield of the bis(diphenylmethyl) compound via this reaction. Comparable yields have been obtained from reactions employing phosphate esters; moreover, these reactions do not require the special techniques necessary for reactions in liquid ammonia.

In the light of these facts, it is suggested that trialkyl phosphates supplement the previously used alkylating agents in this reaction. Where applicable, this may be the method of choice, particularly for the derivatization of organosilylmetallic compounds.

B. Reactions of Triphenylsilyllithium with Triaryl Phosphates

The reactions of triphenylsilyllithium with triaryl phosphates, although not extensively studied, appear to proceed via displacements of aryloxy groups from phosphorus. As mentioned in the preceding section, this type of reaction was postulated to account for the formation of hexaphenyldisilane in the forced reactions of triphenylsilyllithium with tri-n-butyl phosphate.

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[144] C. R. Hauser, C. F. Hauser and P. J. Hamrick, Jr., J. Org. Chem., 24, 397 (1959).

The reactions using triaryl phosphates also have been observed to give considerable amounts of hexaphenyldisilane.

This course of reaction is not surprising since the aryl-oxygen bond is expected to be more resistant to cleavage by triphenylsilyllithium than is the alkyl-oxygen bond due to resonance interaction between oxygen and the aryl group. In this connection, some sulfonic esters have been found to yield sulfones when treated with Grignard reagents.[132] This is particularly true for esters of alkane sulfonic acids and aryl esters of aryl sulfonic acids. Similar displacements are involved in these reactions; however, the carbon-sulfur bonds are not subsequently cleaved.

At room temperature, the yields of hexaphenyldisilane did not exceed 33 percent when triphenylsilyllithium was allowed to react with triphenyl phosphate, even though long reaction times were employed. From the first reaction using three equivalents of triphenylsilyllithium, a 27 percent yield of hexaphenyldisilane was realized together with 52 percent of triphenylsilanol. All of the organosilylmetallic reagent was consumed as evidenced by a negative Color Test I prior to hydrolysis. When six equivalents of triphenylsilyllithium were used, these products were isolated in 33 and 41 percent yields, respectively, together with 3 percent of hexaphenyldisiloxane and 14 percent of triphenylsilane. Color Test I was positive when the reaction was terminated, which accounts for the formation of triphenylsilane in the latter reaction. These results can be rationalized via the following reaction scheme:

$$Ph_3SiLi + (PhO)_3PO \longrightarrow PhOLi + Ph_3Si\underset{I}{P}(O)(OPh)_2$$

$$PH_3SiLi + Ph_3SiP(O)(OPh)_2 \begin{array}{l} \nearrow Ph_6Si_2 + LiP\underset{II}{(O)}(OPh)_2 \\ \searrow PhOLi + (Ph_3Si)_2\underset{III}{P(O)}OPh \end{array}$$

$$Ph_3SiLi + (Ph_3Si)_2\underset{III}{P(O)}OPh \longrightarrow Ph_6Si_2 + Ph_3SiP(O)(Li)OPh$$

$$\underset{IV}{Ph_3SiP(O)(Li)OPh} \xrightarrow{H_2O} Ph_3SiOH + H_2\underset{V}{P(O)}OPh + LiOH$$

The first step in the reaction involves the displacement of either one or two phenoxide anions from the phosphate ester by triphenylsilyllithium to give I or III, as the case may be. Subsequent cleavage of the silylphosphorus compounds with triphenylsilyllithium yields hexaphenyldisilane. Based on considerations already discussed in the preceding section, these cleavages are expected to occur with relative ease. However, the removal of a triphenylsilyl group from IV would be difficult via this cleavage reaction, because the process would entail an anionic displacement from a position of high electron density. This accounts for the failure to realize more than 33 percent of the disilane from the reaction employing six equivalents of triphenylsilyllithium.

The low yield of hexaphenyldisilane from the three to one reaction, together with the fact that Color Test I was negative before hydrolysis, indicates that the displacement of a second phenoxide ion from I is indeed occurring. If this were not so, the yield of hexaphenyldisilane should have been closer to 67 percent, the maximum obtainable from this ratio of reactants. Apparently, III and probably IV are formed in this reaction.

Similarly, the hydrolysis of these intermediates containing silicon-phosphorus bonds would account for the formation of triphenylsilanol, as well as the phosphine-like odors noticed after hydrolysis. Some of this odor is also derived from the hydrolysis of phosphorus-lithium intermediates. The fact that these odors are carried into the organic layer after hydrolysis indicates that hydrolysis of the ester is not complete. No products containing phenoxide groups attached to phosphorus, however, were isolated from these reactions. The mechanism for the formation of silanols _via_ the hydrolysis of silylphosphorus compounds is well-known.[145]

In order to determine whether or not forced conditions

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[145] See, for example: G. Fritz, _Z. Naturforsch_, _8b_, 776 (1953); G. Fritz, _Z. anorg. u. allgem. chem._, _280_, 332 (1955); W. Keeber and H. W. Post, _J. Org. Chem._, _21_, 509 (1956); G. Fritz and H. O. Berkenhoff, _Z. anorg. u. allgem. chem._, _289_, 250 (1957); F. Fehér, G. Kuhlbörsch, A. Blüneke, H. Keller and K. Lippert, _Chem. Ber._, _90_, 134 (1957).

might cause cleavage of a second triphenylsilyl group from intermediates of type IV, the reaction using six equivalents of triphenylsilyllithium was repeated under reflux conditions for 21 hours. Color Test I was negative after this time. The products isolated were: hexaphenyldisilane, hexaphenyldisiloxane, 4-triphenylsilylbutanol, triphenylsilanol and phenol (isolated as the tribromo-derivative), in yields of 39.6, 11.8, 3.75, 30 and 81 percent, respectively. The slight increase in yield of hexaphenyldisilane together with the high yield of phenol suggests that placing a second negative charge on phosphorus via this reaction is possible but not readily accomplished, and that all three phenoxide groups are capable of displacement in this reaction.

Similar results were obtained from reactions employing either two or three equivalents of triphenylsilyllithium with tri-*p*-tolyl phosphate. The former reaction gave 35.8 percent of hexaphenyldisilane together with triphenylsilanol (47.8 percent) and recovered ester (14.9 percent). These results indicate that the second displacement occurred to at least some extent here also. The three to one reaction afforded the disilane, triphenylsilanol, triphenylsilane and *p*-cresol in yields of 33, 45.2, 3.8 and 57.2 percent, respectively. These yields are also consistent with the proposed mechanism.

Although compounds containing silicon-phosphorus bonds were not isolated from these reactions, there is strong evidence that they exist as reaction intermediates. Compounds of this type may be isolated from reactions of a similar nature, providing the reaction mixtures are derivatized with suitable reagents, and anhydrous work-ups are employed; however, the problem of separation might discourage future use of this reaction for that purpose.

C. Reactions of Triphenylsilyllithium with Phenylated Group VB Elements

Although triaryl derivatives of all group VB elements have been reported to undergo cleavage reactions with alkali metals,[146,147,148,149,150] the corresponding reactions with alkyllithium compounds are known only for the triaryl derivatives of bismuth and antimony. Triphenylarsine, -phosphine and -amine, on the other hand, undergo slow metalation in the _meta_-position when treated with _n_-butyllithium (refer to the Historical section of this Thesis). In contrast, triphenyl-

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[146] R. V. Talalaeva and K. A. Kocheshkov, _J. Gen. Chem., U.S.S.R._ _8_, 1831 (1938).

[147] H. Gilman and J. J. Dietrich, _J. Am. Chem. Soc._, _80_, 380 (1958).

[148] D. Wittenberg and H. Gilman, _J. Org. Chem._, _23_, 1063 (1958).

[149] K. Issleib and H. O. Fröhlich, _Z. Naturforsch_, _14b_, 349 (1959).

[150] K. Issleib and A. Tzschach, _Chem. Ber._, _92_, 1118 (1959).

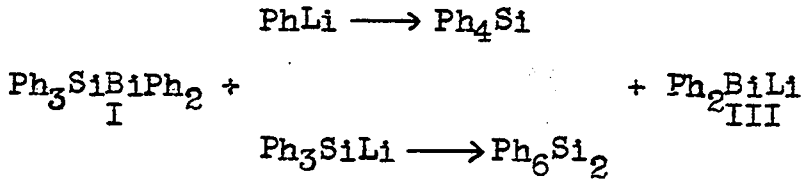
silyllithium has been found to cleave not only triphenylbismuthine and triphenylstibine, but triphenylarsine as well.

In this study, triphenylbismuthine was chosen as the first compound to be investigated, since the earlier work employing alkali metals and alkyllithium compounds indicated that cleavage would occur more readily and quantitatively with this compound than with the other members of the series. Low reaction temperatures were desirable due to the instability of organolithium compounds in tetrahydrofuran.[128] The results of these experiments are tabulated for convenience in Table 1.

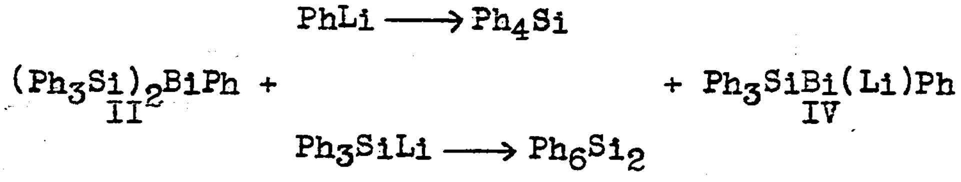
Using triphenylbismuthine as an example, the results of these experiments can best be explained by the following sequence of reactions:

$$\mathrm{Ph_3SiLi + Ph_3Bi \longrightarrow \underset{I}{Ph_3SiBiPh_2} + PhLi}$$

$$\mathrm{2\ Ph_3SiLi + Ph_3Bi \longrightarrow \underset{II}{(Ph_3Si)_2BiPh} + 2\ PhLi}$$



$$\mathrm{\underset{I}{Ph_3SiBiPh_2}} + \begin{matrix} \mathrm{PhLi \longrightarrow Ph_4Si} \\ \\ \mathrm{Ph_3SiLi \longrightarrow Ph_6Si_2} \end{matrix} + \mathrm{\underset{III}{Ph_2BiLi}}$$



$$\mathrm{\underset{II}{(Ph_3Si)_2BiPh}} + \begin{matrix} \mathrm{PhLi \longrightarrow Ph_4Si} \\ \\ \mathrm{Ph_3SiLi \longrightarrow Ph_6Si_2} \end{matrix} + \mathrm{\underset{IV}{Ph_3SiBi(Li)Ph}}$$

$$\mathrm{3\ Ph_2BiLi \longrightarrow Ph_3Bi + 3\ PhLi + 2\ Bi}$$

Table 1. Reactions of triphenylsilyllithium with phenylated group VB elements

Compound[a] reacted; (moles R_3SiLi: moles R_3E)	Reaction conditions hr.; °C	Products (%)			
		R_6Si_2	R_4Si	R_3SiOH	Other products
R_3Bi; (1:1)[b]	1; -60	8.7	11.90	26.3	R_3Bi(69); RCO_2H(6.9)
R_3Bi; (3:1)[b]	1; 0-5	19.82	27.10	24.2	R_6Si_2O(5.6); RCO_2H(54)
R_3Bi; (3:1)[c]	6; 0-5	22.20	23.73	31.5	$RSiMe_3$(37.8); bismuth
R_3Bi; (3:1)[b]	24; 25	6.03	37.00	46.0	RCO_2H(8.25); bismuth
R_3Sb; (3:1)[c]	24; 25	trace	44.00	20.4	$R_3SiSiMe_3$(18); $RSiMe_3$(18.7); antimony
R_3As; (3:1)[d]	36; 25	26.30	21.20	22.6	Unidentified mixtures
R_3As; (3:1)[b]	36; 25	23.30	39.60	28.4	Unidentified mixtures
R_3P; (3:1)[b]	24; 25	1.90	--	92.0	R_3P(94)

[a] R in these reactions is a phenyl group.

[b] Derivatized by carbonation.

[c] Derivatized with chlorotrimethylsilane.

[d] Derivatized with water.

A similar disproportionation reaction involving IV probably occurs, but a formulation of it is more difficult because of the various possible products which may be formed. An analogous mechanism, with the exception of the disproportionation reaction is proposed for the cleavage of triphenylarsine and triphenylstibine.

The initial reaction involves the displacement of a phenyl anion from triphenylbismuthine. By analogy to the reactions of triphenylsilyllithium with triaryl phosphates, triphenylsilyllithium apparently is capable of displacing two, or perhaps all three of the phenyl groups in this reaction. Evidence for this is found in the high yield of benzoic acid (54 percent) isolated from the second reaction. One might argue that some of the phenyllithium forming this may have come from the disproportionation reaction; however, no bismuth was found in this case, therefore this seems unlikely.

Cleavage of the organosilylbismuthine intermediates (I and II) by phenyllithium or triphenylsilyllithium would give rise to the formation of tetraphenylsilane or hexaphenyldisilane, as the case may be. All of these cleavages apparently occur simultaneously. The bismuth and antimony isolated from the third, fourth and fifth reactions can be accounted for by the disproportionation of III and IV or their derivatized antimony analogs. Disproportionation reactions of compounds of type III have been reported to occur slowly in liquid ammonia, giving rise to the formation of bismuth and the triarylbismuthine.[151]

Hydrolysis of triphenylsilyllithium, or intermediates having silicon-bismuth, -antimony or -arsenic bonds, would give rise to the formation of the triphenylsilanol isolated. That the latter mechanism is contributing to the formation of this compound is evident from the high yields obtained when chlorotrimethylsilane was used to terminate the reaction. Since care was taken to exclude moisture, the triphenylsilanol could only have arisen _via_ this path.

An attempt to isolate products having silicon-antimony bonds failed, apparently due to a disproportionation reaction having occurred while attempting to separate them by distillation (refer to the Experimental section). A colorless petroleum ether extract of the reaction mixture, prior to hydrolysis, deposited a dark, finely divided solid when the solvent-free extract was subjected to reduced pressure distillation. The distilled material was identified as 1,1,1-trimethyl-2,2,2-triphenyldisilane. This product was probably formed earlier by the reaction of triphenylsilyllithium with chlorotrimethylsilane. The possibility of this compound having been formed by the coupling of free radicals is not held very likely since none of the symmetrical coupling products were found.

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[151] H. Gilman and H. L. Yablunky, _J. Am. Chem. Soc._, _63_, 212 (1941).

As noted in Table 1, triphenylphosphine failed to react with triphenylsilyllithium when the mixture was stirred at room temperature for 24 hours. Carbonation failed to give any acidic material and a high recovery of the phosphine was realized. Although n-butyllithium metalated this compound in low yield,[55] it is not surprising that triphenylsilyllithium failed to do so, since Diehl[90] reported that only those compounds with relatively active hydrogens are capable of metalation by this reagent. Perhaps cleavage or metalation might be effected if forced conditions were employed, but the separation problem, if cleavage were to occur, discouraged attempting this reaction.

The yields of hexaphenyldisilane obtained from this series of reactions deserve some comment. As expected, the yield of this compound increases with increasing reaction time in the low-temperature reactions with triphenylbismuthine. However, these yields fall off abruptly when long reaction times at room temperature are employed with triphenylbismuthine and triphenylstibine, implying that some type of cleavage reaction is removing it from the reaction mixture. The concomitant increase in yield of tetraphenylsilane in reactions where this occurs, indicates that phenyllithium may be effecting this cleavage. That phenyllithium is capable of doing so under these conditions has been proven by using pre-formed hexaphenyldisilane and phenyllithium (refer to the

Experimental section). These reactions will be discussed later.

One might logically wonder then, why the yields of hexaphenyldisilane were so high in the two reactions of triphenylsilyllithium with triphenylarsine, particularly since even longer reaction times were employed. However, the failure to isolate benzoic acid from the second reaction involving this compound, indicates that phenyllithium is not available to effect this cleavage. The reason for this probably centers around the disproportionation reaction previously discussed. Since arsenic is less metallic than antimony or bismuth, diphenylarseniclithium, or the other organoarseniclithium compounds which may be present in the reaction mixture, would be less apt to undergo disproportionation. Organoarsenicmetallic compounds are known[148,152,153,154,155] and have been employed in synthetic work, but there has been no report of their ability to undergo disproportionation reactions of the type observed with the bismuth compounds.

In this connection, the reaction of triphenylsilyllithium

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[152] M. H. Beeby and F. G. Mann, _J. Chem. Soc._ (London), 886 (1951).

[153] F. G. Mann and B. B. Smith, _ibid._, 4544 (1952).

[154] G. Wittig, M. A. Jesaitis and M. Glos, _Ann._, _577_, 1 (1952).

[155] L. Anshütz and H. Wirth, _Naturwissenschaften_, _43_, 59 (1956).

with triphenylarsine is not completely understood, since the fate of the arsenic in these two reactions is not known. Considerable difficulty was encountered during work-up of these reaction mixtures, and no compounds containing arsenic could be separated. It is not unlikely, on the basis of the lithium cleavage of triphenylarsine, previously reported by Wittenberg and Gilman,[148] that phenyl- or triphenylsilyl-substituted arsenic oxides or arsines were present in the reaction mixtures, but such compounds could not be isolated.

As is the case with triaryl phosphate esters, there is strong evidence that compounds containing silicon attached to group VB elements exist as reaction intermediates, but the complexity of the cleavage reactions involved, coupled with the separation difficulties, makes the application of these reactions for their synthesis rather doubtful.

D. Cleavage of Hexaphenyldisilane with Aryllithium Compounds

Cleavage studies involving the use or formation of organosilylmetallic compounds have become relatively important during the past ten years.[6,7] Although the silicon-silicon bond in halogenated polysilanes has been cleaved by a variety of organometallic compounds (refer to section IIB), hexaphenyldisilane has been found to be resistant to such cleavages by these reagents. Both Dunn[71] and Wu[72] failed to accomplish this in diethyl ether or diethyl ether-xylene mixtures with phenyllithium. Likewise, Dunn[71] obtained an 82 percent recovery of the disilane from an attempted cleavage with n-butyllithium in these solvents. The loss of material from the last-mentioned reaction was thought to be mechanical. More recently, Lichtenwalter[7] obtained nearly quantitative recoveries of hexaphenyldisilane from attempts to cleave this compound in tetrahydrofuran with p-tolyllithium at ice-bath temperature, or with triphenylmethyllithium at room temperature.

On the other hand, the cleavability of hexaphenyldisilane by alkali metals and sodium-potassium alloy is well-known.[1,4,5,7,98,103,156] In fact, this method for preparing organo-

$$Ph_3SiSiPh_3 + 2M \longrightarrow 2Ph_3SiM$$

silylmetallic compounds has been largely responsible for the rapid growth in this field during the last decade.

Based on the results obtained from the experiments discussed in the preceding section, there was reason to believe that hexaphenyldisilane was being cleaved by phenyllithium in some of these reactions. In order to test this hypothesis, as

$$Ph_3SiSiPh_3 + PhLi \longrightarrow Ph_3SiPh + Ph_3SiLi$$

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[156] See also: H. Gilman, T. C. Wu, H. A. Hartzfeld, G. A. Guter, A. G. Smith, J. J. Goodman and S. H. Eidt, J. Am. Chem. Soc., 74, 561 (1952); H. Gilman and T. C. Wu, J. Org. Chem., 18, 753 (1953); T. C. Wu and H. Gilman, ibid., 23, 913 (1958).

well as to confirm or disprove the long-held belief that hexaphenyldisilane could not be cleaved by organolithium compounds, pre-formed hexaphenyldisilane, of the highest purity available, was reacted with phenyllithium in tetrahydrofuran for 24 hours at room temperature. Hydrolysis and filtration of the reaction mixture gave a 50 percent recovery of the disilane. Work-up of the organic layer afforded a high yield of tetraphenylsilane, but no triphenylsilanol. The viscous oil which remained, after removal of the tetraphenylsilane, yielded only a trace of hexaphenyldisiloxane.

A second reaction (stirred for two days and derivatized with chlorotrimethylsilane) gave hexaphenyldisilane (5 percent), 1,1,1-trimethyl-2,2,2-triphenyldisilane (31 percent), tetraphenylsilane (66 percent) and trimethylphenylsilane (24 percent). A large excess of phenyllithium was used in these reactions because of the instability of phenyllithium in this solvent.[128]

Although tetraphenylsilane was isolated in satisfactory yields, indicating that cleavage by phenyllithium was taking place, the derivatized triphenylsilyllithium could only be separated with difficulty from the viscous decomposition products of the organometallic compounds.

In order to circumvent this difficulty, the reaction was repeated in a mixture of diethyl ether and tetrahydrofuran, since earlier studies had indicated that this solvent was superior to tetrahydrofuran alone in metalation[61,62,157] and coupling[90] reactions. Although cleavage took place much slower in the mixed solvent, considerably less difficulty was encountered in separating the products of reaction. To illustrate, refluxing a mixture of the disilane and phenyllithium for two days in a (2:1) mixture of diethyl ether and tetrahydrofuran gave, subsequent to treatment with chlorotrimethylsilane, hexaphenyldisilane (10 percent); 1,1,1-trimethyl-2,2,2-triphenyldisilane (67.5 percent); tetraphenylsilane (86 percent); and 4-triphenylsilylbutanol (14.3 percent). The isolation of products was nearly quantitative. A similar reaction, stirred for 5 days at room temperature, gave a 58 percent recovery of the disilane in addition to the cleavage products.

High recoveries of hexaphenyldisilane were realized when the reaction was carried out in diethyl ether. However, small amounts of tetraphenylsilane and triphenylsilanol were also isolated, indicating that cleavage was even possible in this solvent. The reaction was extremely slow. Phenylmagnesium bromide failed to accomplish this cleavage in refluxing tetrahydrofuran.

The encouraging results obtained with phenyllithium prompted the extension of this reaction to another organo-

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[157] H. Gilman and R. D. Gorsich, J. Org. Chem., 22, 687 (1957).

lithium compound. *p*-Tolyllithium was chosen for this purpose since the compound was readily preparable, and the corresponding tetrasubstituted silane was well-characterized. Although cleavage of the disilane occurred, as in the reactions employing phenyllithium, several unanticipated complications made separation of the products difficult. The reaction is still not completely understood.

The first reaction of the disilane with *p*-tolyllithium, subsequent to carbonation after two days at reflux, gave a yellow, acidic gum having the odor of phenylacetic acid. Eventually this gum afforded phenylacetic acid (3.4 percent) and *p*-toluic acid (7.7 percent). The neutral organic layer furnished triphenylsilanol (50 percent), but no *p*-tolytriphenylsilane having the reported[158] melting point of 140°. Instead, a small amount of material melting at 128-130° was obtained. The infrared spectrum of this product was identical with that of authentic *p*-tolytriphenylsilane. An oil was also obtained whose infrared spectrum indicated it to be a mixture of triphenylsilane and benzyltriphenylsilane.

This reaction was repeated, after insuring that the *p*-tolyllithium had no benzyllithium in it by carbonating part of the reaction mixture. The remaining solution of the

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[158] R. A. Benkeser, C. E. DeBoer, R. E. Robinson and D. M. Sauve, *J. Am. Chem. Soc.*, *78*, 682 (1956).

organolithium compound was allowed to react with hexaphenyldisilane as in the preceding reaction. After a very meticulous work-up, involving two chromatographic separations and fractional crystallization of the eluted material, there was obtained: triphenylsilane (8.7 percent); benzyltriphenylsilane (43.1 percent); p-tolyltriphenylsilane (25.7 percent); 4-triphenylsilylbutanol (21.1 percent); and triphenylsilanol (27 percent). The p-tolyltriphenylsilane melted at 128-130°.

An attempt was made to explain the formation of benzyltriphenylsilane in this reaction by refluxing a p-tolyllithium solution under similar conditions without having hexaphenyldisilane present. After two days, the solution was derivatized with chlorotriphenylsilane. Only p-tolyltriphenylsilane and triphenylsilanol could be isolated from this mixture. Most of the tetrasubstituted silane melted at 140°; however, a small amount of material isolated from the mother liquors melted at the lower temperature. This suggested that an interesting case of polymorphism may be involved, especially since the lower melting product was eventually converted to the higher melting form by crystallization from a concentrated solution in ethyl acetate. The reverse transformation was also accomplished by changing solvents. Crystallization of the material from ethanol, methanol or petroleum ether (b.p. 60-70°) gave fine needles, which melted at 130-132°. Heating this above its melting point, and remelting caused it to melt at 140°, as did recrystallization from ethyl acetate. The higher melting compound crystallized in the form of hard agglomerates of radiating prisms or thick needles.

Although rare, polymorphism in organosilicon compounds is known. Lichtenwalter,[159] in conjunction with Brook, found two crystalline forms of methoxytriphenylsilane. Similarly, two forms have been reported for tetramethylsilane,[160] vinylsilane,[160] diethylsilanediol[161] and 1,2-dibromo-1,2-bis(trimethylsilyl)ethane.[162] The last-mentioned case apparently involves stereoisomers.

Another case which may involve polymorphism of the type found in p-tolyltriphenylsilane is that observed with beta-phenylethoxytriphenylsilane. Gerrard and Kilburn[163] report

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[159] See G. D. Lichtenwalter. Organosilylmetallic compounds and derivatives. Unpublished Ph.D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1958. p. 48.

[160] S. Tannenbaum, S. Kaye and G. F. Lewenz, J. Am. Chem. Soc., 75, 3753 (1953).

[161] J. J. Duane. Silanol and siloxane preparation. British Patent 683,182. Nov. 26, 1952. (Original not available for examination; abstracted in C.A., 47, 5720 (1953)); P. D. George, L. H. Sommers and F. C. Whitmore, J. Am. Chem. Soc., 75, 1585 (1953).

[162] V. F. Mironov, V. G. Glukhovtsev and A. D. Petrov, Doklady Akad. Nauk S.S.S.R., 104, 865 (1955). (Original available but not translated; abstracted in C.A., 50, 11234 (1956)). See also H. Gilman and G. N. R. Smart, J. Org. Chem., 15, 720 (1950); and G. N. R. Smart, H. Gilman and H. W. Otto, J. Am. Chem. Soc., 77, 5193 (1955) for other examples.

[163] W. Gerrard and K. D. Kilburn, J. Chem. Soc. (London), 1536 (1956).

metalated was most likely toluene which conceivably could have arisen *via* a reaction of *p*-tolyllithium with the solvent. In

$$Ph_3SiLi + PhCH_3 \longrightarrow Ph_3SiH + PhCH_2Li$$
$$PhCH_2Li + Ph_3SiSiPh_3 \longrightarrow Ph_3SiCH_2Ph + Ph_3SiLi$$

this connection, Marrs[166] attempted to metalate toluene with triphenylsilyllithium in tetrahydrofuran, but was unable to isolate any derivatized benzyllithium, although red solutions were obtained when the mixtures were stirred at room temperature. This might indicate that the metalation involved in this reaction, as well as in the reaction with *p*-tolyllithium is an equilibrium process, strongly favoring the triphenylsilyllithium or *p*-tolyllithium side, as the case may be. Attempts to derivatize the metalated product would give too small a quantity of derivative to detect. Providing this is true, the reaction of *p*-tolyllithium with hexaphenyldisilane could go to completion forming considerable amounts of benzyltriphenylsilane, because the benzyllithium is continuously being removed from the equilibrium by cleavage of the disilane. The low yield of triphenylsilane from this reaction is explainable when it is recalled that silicon hydrides undergo

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[166] O. L. Marrs, Ames, Iowa. Information concerning metalation reactions with triphenylsilyllithium. Private communication. 1959.

hydrolysis to silanols in basic media.[167]

The possibility that p-tolyllithium is effecting the metalation, however, cannot be discounted since analogous benzilic rearrangements of other tolylmetallic compounds are known.[168]

Although it must be admitted that the preceding discussion is largely speculative and based on inadequate evidence, it does account for the observed results. Exactly what is undergoing metalation, and what the metalating agent is, can only be surmised. Apropos the answers to these questions, it might be interesting to repeat the reaction of triphenylsilyllithium with toluene in the presence of hexaphenyldisilane. The isolation of benzyltriphenylsilane from this reaction would substantiate this mechanism.

These experiments have shown that hexaphenyldisilane may be cleaved by aryllithium, and probably alkyllithium compounds as well. Should further research along these lines be done, it is recommended that an excess of the organolithium compound be used and that the reaction be done in a mixture of diethyl

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[167] See, for example, H. Gilman and G. E. Dunn, J. Am. Chem. Soc., 73, 3404 (1951).

[168] See, for example: M. Tiffeneau and R. Delange, Compt. rend., 137, 573 (1903); W. E. Bachmann and H. T. Clarke, J. Am. Chem. Soc., 49, 2089 (1927); H. Gilman and F. Breuer, ibid., 56, 1127 (1934); H. Gilman and R. L. Bebb, ibid., 61, 109 (1939); H. Gilman and H. A. Pacevitz, ibid., 62, 673 (1940); H. Gilman, H. A. Pacevitz and O. Baine, ibid., 62, 1514 (1940); M. Pacevitz, Iowa State Coll. J. Sci., 16, 117 (1941).

ether and tetrahydrofuran.

Although this cleavage reaction has no forseeable value as a synthetic tool, its use in the same capacity for which it was employed in this study may find some degree of future application, namely, to explain what appear to be unusual experimental results from reactions involving organosilicon compounds.

E. The Rearrangement Theory

Since 1953, when Gilman and Wu[86] reported the isolation of diphenylmethoxytriphenylsilane (the "abnormal" addition product) from the reaction of triphenylsilylpotassium with benzophenone, there has been considerable speculation as to the mode of formation of compounds of this type from similar reactions. Reverse addition to the carbonyl did not seem likely because of the known polarity of the carbonyl group; therefore, these investigators postulated a normal addition, followed by a rearrangement to the silyl ether, as the probable course of reaction.

$$Ph_3SiK + Ph_2CO \longrightarrow Ph_3SiC(OK)Ph_2$$
$$Ph_3SiC(OK)Ph_2 \longrightarrow Ph_3SiOC(K)Ph_2$$

Although support for this rearrangement mechanism has been amassed through the years, no real proof has yet been presented. This support centers around the fact that normal addition products have been isolated from reactions of organosilylmetallic compounds with aliphatic aldehydes,[81,83,84] ketones,[89] acid chlorides,[82,83] ethyl acetate[83,84] and acetic anhydride.[83] From some of these reactions, the rearranged silyl ethers were isolated together with the normal addition compounds.[82,83,84] Reactions of triphenylgermyllithium with formaldehyde and benzophenone, likewise, gave the normal addition products.[169] In this connection, the isolation of N-diphenylmethyl-N-phenyl-1,1,1-triphenylsilylamine from the reactions of triphenylsilylmetallic compounds with benzophenone anil has been explained by a similar rearrangement.[97]

Support for the rearrangement theory from another aspect was furnished by Brook,[170] Brook and co-workers,[84] as well as by Wittenberg and Gilman.[82] These investigators demonstrated that alpha-silylcarbinols undergo rearrangements to the isomeric silyl ethers when exposed to basic reagents. Brook,[170] for example, succeeded in preparing triphenylsilyldiphenylmethanol, and then isomerized it to diphenylmethoxytriphenylsilane in the presence of mildly basic reagents. Later, Brook and co-workers[84] showed that this reaction was general for a

$$Ph_3SiC(OH)Ph_2 \xrightarrow{base} Ph_3SiOC(H)Ph_2$$

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[169] H. Gilman and C. W. Gerow, J. Am. Chem. Soc., 77, 5740 (1955).

[170] A. G. Brook, ibid., 80, 1886 (1958).

variety of alpha-silylcarbinols containing both aliphatic and aromatic groups. The only compound tested by these workers, which failed to undergo rearrangement was triphenylsilylmethanol. Wittenberg and Gilman[82] similarly isomerized 1,1,-bis(triphenylsilyl)ethanol to 1-triphenyl(1-triphenylsiloxyethyl)silane by treating it with ethanolic potassium hydroxide. Triphenylsilyldimethylcarbinol,[89] at first appeared to be an exception to the rule; however, its isomerization to isopropoxytriphenylsilane has also been accomplished using sodium-potassium alloy as the catalyst.[84]

In an attempt to prove the rearrangement theory, Brook and Schwartz[171] reinvestigated the reaction of triphenylsilylmetallic compounds with benzophenone. By isolating and characterizing the potassium salt of diphenylmethoxytriphenylsilane, these workers demonstrated that the rearrangement, if it actually occurs, takes place before hydrolysis of the reaction mixtures. By varying the reaction conditions, they also obtained a hitherto unreported compound from this reaction, namely, 2-triphenylsiloxy-1,1,2,2-tetraphenylethanol. This product was formed in high yields when two equivalents of benzophenone were employed. The analogous compound, derived from triphenylsilyllithium and benzaldehyde, has been

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[171] A. G. Brook and N. V. Schwartz, ibid., in press (ca. 1960).

described by Wittenberg et al.[85]

The last-mentioned investigation[85] also reported the isolation of large amounts of hexaphenyldisilane from triphenylsilyllithium and benzaldehyde, when the reaction was carried out at room temperature. It has been postulated[85] that this product arises via cleavage (by triphenylsilyllithium) of the lithium salt of benzyloxytriphenylsilane or 2-triphenylsiloxy-1,2-diphenylethanol. The isolation of hexaphenyldisilane from a number of reactions involving triphenylsilyllithium and compounds having silicon attached to a hetero atom has been explained by similar cleavage reactions (refer to the Discussion section dealing with reactions of triphenylsilyllithium with phenylated group VB elements). Cleavages of this type, therefore, appear to be quite general for compounds having silicon attached to elements other than carben, and use might be made of this reaction to explain certain observed phenomena.

For example, Gilman and Lichtenwalter[88] reported the isolation of symmetrical dimethyltetraphenyl- and tetramethyldiphenyldisilane from reactions of methyldiphenylsilyllithium and dimethylphenylsilyllithium, respectively, with benzophenone. Although these disilanes may be uncleaved starting materials from the preparations of the organosilyllithium reagents, they may also be reaction products formed via cleavage of the silyl ethers by the organosilyllithium compounds.

A similar type of cleavage reaction may be involved in the reactions of phenyllithium and/or phenylmagnesium bromide with benzyltriphenylsilane,[93] ethyl triphenylsilanecarboxylate[170] and triphenylsilyldiphenylmethanol,[170] all of which have been reported to give tetraphenylsilane. In these reactions, a mechanism involving displacement of carbon from silicon has been proposed to explain the isolation of this product. However, in the light of the rearrangement theory, it would appear equally probable, if not more probable, that either rearrangement (for the case involving triphenylsilyldiphenylmethanol), or addition followed by rearrangement (for the carbonyl compounds) occurred, and the rearranged products then were attacked by the organometallic compounds to give the tetraphenylsilane isolated. This displacement of oxygen from silicon by anion attack is well-known.[132] Unfortunately, the other fragments of reaction were not isolated except from the reaction involving the alpha-silylcarbinol, in which case, benzhydrol was also found.

This rearrangement mechanism appears to be even more probable since methylmagnesium iodide has been reported to add to benzoyltriphenylsilane to give 1-phenyl-1-triphenylsilylethanol.[84] These investigators reported[84] that they observed some conflicting results; however, they did not elaborate on these. They also reported that they are presently reinvestigating the mechanism for the rearrangement of alpha-silylcarbinols, upon which the mechanism for the formation of tetraphenylsilane was based.

In this connection, it should be relatively easy to test which of these displacements is actually occurring. The reaction of a catalytic amount of phenyllithium with triphenylsilyldiphenylmethanol should convert the alcohol to the silyl ether, since this rearrangement has been effected in a matter of minutes with sodium-potassium alloy.[170] The isolation of diphenylmethoxytriphenylsilane from this reaction would imply that the rearrangement occurs before displacement. The isolation of the oxygen-containing fragments from the equimolar reaction using benzoyltriphenylsilane, similarly should tell whether or not addition and rearrangement occurred prior to displacement. Perhaps, if moderate reaction conditions were employed, the rearranged addition compound could be isolated from this reaction.

Apropos the inclusion and discussion of the "rearrangement theory" at this time, use will be made of it to explain the formation of products isolated from the reactions of triphenylsilyllithium with amides and imides. These reactions will be discussed in the following section.

F. Reactions of Triphenylsilyllithium with Amides and Imides

The failure to isolate triphenylsilylaldehyde or its derivatives from reactions of N,N-dimethylformamide or ethyl orthoformate with triphenylsilyllithium[7] might well be due to an inherent instability of this compound, since related compounds containing carbonyl groups adjacent to silicon are only moderately stable. Triarylsilanecarboxylic acids and their esters, for example, have been shown to undergo thermal and base catalyzed decompositions quite readily.[3,77,78,172] Similarly, alpha-silylketones are reported to be unstable to basic reagents.[82,93] In fact, many compounds containing elements other than carbon adjacent to a silicon atom exhibit a certain degree of instability. Examples include silyl ethers[86,170,173] silylamines,[173] alpha-halosilanes,[174] alpha-silyl carbinols,[82,84,89,170] and as mentioned in section IVC in connection with cleavage reactions by organometallic reagents, numerous other compounds of this type. It is not unreasonable then to assume that triphenylsilylaldehyde might be too unstable to isolate from reactions employing basic reagents.

Although somewhat unstable, benzoyltriphenylsilane[93] has sufficient stability to enable its isolation from the reaction of triphenylsilylpotassium with benzoyl chloride; hence, it was felt that the reaction of triphenylsilyllithium with an

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[172] A. G. Brook, ibid., 77, 4827 (1955).

[173] E. G. Rochow. Chemistry of the silicones. 2nd ed. New York, N.Y., John Wiley and Sons, Inc. 1951.

[174] F. C. Whitmore and L. H. Sommer, J. Am. Chem. Soc., 68, 481 (1946).

N,N-disubstituted benzamide might be a useful exploratory reaction for this class of compounds.

Several reactions employing either one, two or three equivalents of triphenylsilyllithium with N,N-dimethylbenzamide were performed; however, none of the expected benzoyltriphenylsilane could be isolated. The first reactions, using one equivalent of triphenylsilyllithium gave recovered N,N-dimethylbenzamide together with hexaphenyldisiloxane, triphenylsilanol, ethoxytriphenylsilane and a compound, whose structure was not known at the time, which appeared to be a silicon-containing amine. This compound formed a picrate and hydrochloride salt, but the hydrochloride was of doubtful use as a derivative since it could not be crystallized and was thermally unstable.

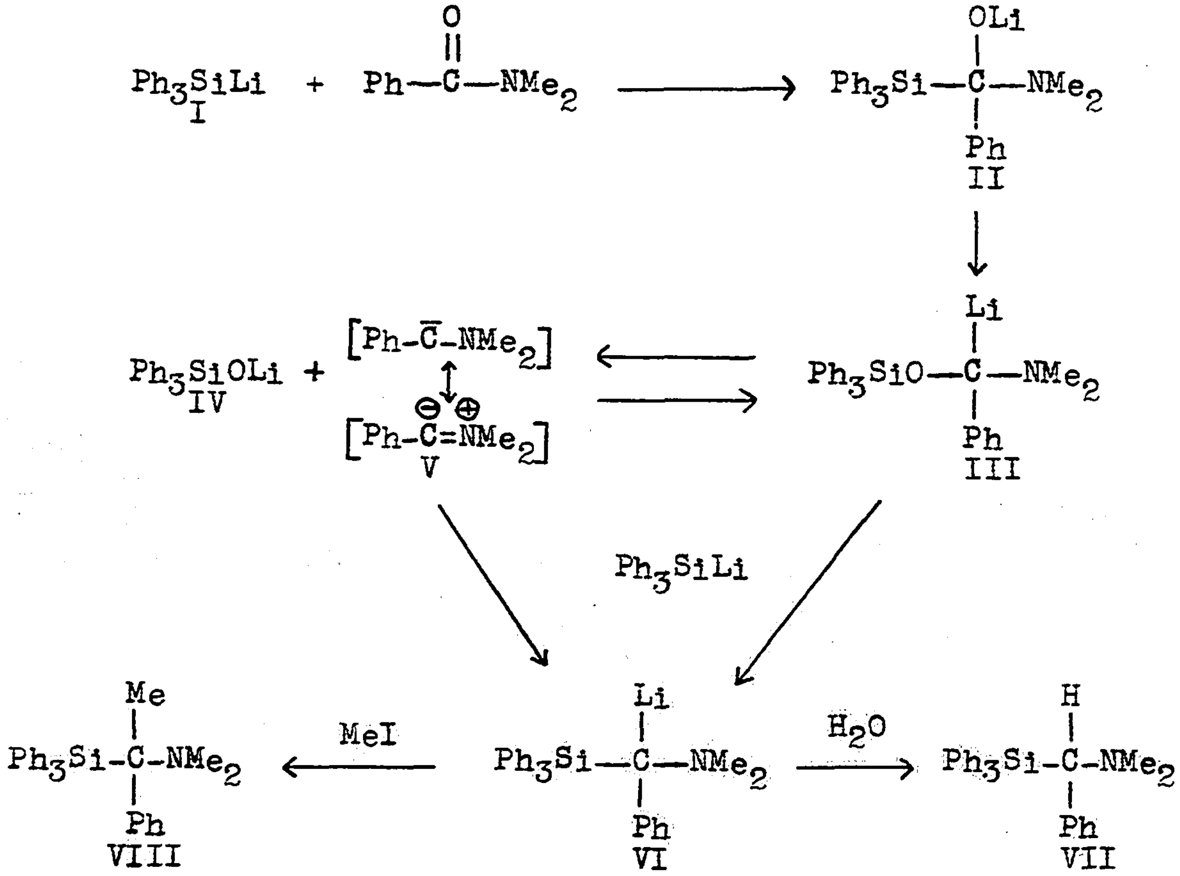
The use of two and three equivalents of the organosilyllithium reagent indicated that the reaction forming the amine required two moles of triphenylsilyllithium to one of the amide, since triphenylsilane was found among the reaction products from the three to one reaction, and the yield of the amine was improved considerably when either two or three moles of the former reagent were employed.

Eventually, with the aid of its elemental analysis, infrared spectrum and molecular weight, the amine was identified as N,N-dimethyl-*alpha*-(triphenylsilyl)benzylamine. The structure was proven unambiguously *via* an alternate synthesis from alpha-bromobenzyltriphenylsilane and dimethylamine.

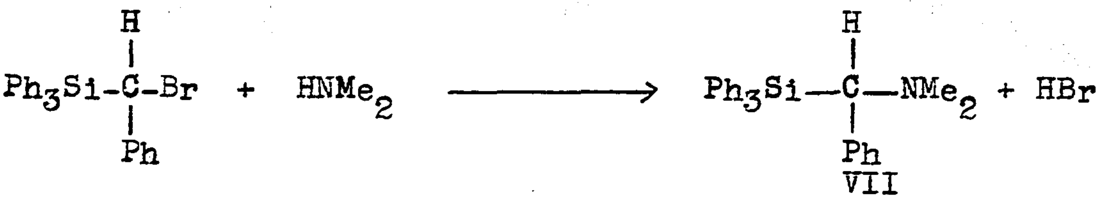
The deep red colors of the reaction mixtures from triphenylsilyllithium and the amide suggested that an organometallic compound was the final reaction product prior to hydrolysis, in spite of the fact that these solutions failed to respond to Color Test I. That this was so, was demonstrated by treating one of these mixtures with methyl iodide. From this reaction, an amine was obtained whose analysis indicated it to have one more methyl group than the product obtained by hydrolysis of the reaction mixture. This compound is thought to be N,N,alpha-trimethyl-alpha-(triphenylsilyl)benzylamine, although its structure has not been proven.

On the basis of the fore-mentioned experimental results, it appeared as though a reaction resembling reductive alkylation of N,N-disubstituted amides, sometimes observed with Grignard reagents and these compounds (refer to section IIA) had occurred between triphenylsilyllithium and N,N-dimethylbenzamide. The reactions involving Grignard reagents incorporate two moles of the organometallic compound in the tertiary amine isolated, whereas, in the reactions studied here, only one mole of the organosilyllithium reagent appears in the product. The second mole of triphenylsilyllithium apparently serves to remove the oxygen and appears as triphenylsilanol, ethoxytriphenylsilane or hexaphenyldisiloxane.

Although conjectural, the following reaction scheme accounts for the products isolated:



$$Ph_3SiOLi + HCl \longrightarrow Ph_3SiOH + LiCl$$



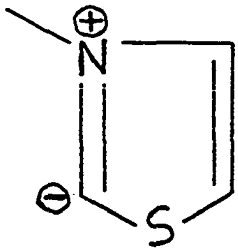
$$Ph_3Si{-}\overset{\displaystyle H}{\underset{\displaystyle Ph}{C}}{-}Br + HNMe_2 \longrightarrow Ph_3Si{-}\overset{\displaystyle H}{\underset{\displaystyle Ph}{C}}{-}NMe_2 + HBr$$

VII

The first step of the reaction probably involves a normal addition to the carbonyl to give II. By analogy to the rearrangements observed with other carbonyl-containing compounds (refer to the preceding section), this intermediate then undergoes isomerization to the organometallic compound, III. The reversible loss of the triphenylsiloxide anion would give rise to the formation of the very reactive species, V (shown in two possible resonance forms). The reaction of triphenylsilyllithium with V then yields the organometallic compound VI, which upon hydrolysis would give the observed product, N,N-dimethyl-alpha-(triphenylsilyl)benzylamine (VII). Similarly, the action of methyl iodide on VI gives rise to the formation of N,N,alpha-trimethyl-alpha-(triphenylsilyl)benzylamine (VIII).

As indicated in the reaction scheme, III or some intermediate between it and V could be undergoing attack by triphenylsilyllithium to give VI. Attack by triphenylsilyllithium on III itself, is highly unlikely since this would involve an anionic displacement from a position of high electron density. The nature of the intermediate actually reacting with triphenylsilyllithium in this step is unknown; however, the structures shown in V appear to be most likely. The charged form is reminiscent of the zwitterion (IX) proposed by Breslow in his paper on the "Mechanism of Thiamine

Action".[175] Such an intermediate would be expected to be extremely reactive toward triphenylsilyllithium, much more so than its precursor, III.



IX

The non-charged species depicted in V (a non-free radical carbene) also appears to be an equally possible intermediate in this reaction; considerable evidence for the existence of analogous non-radical carbenes has been presented recently.[176]

It appears quite likely that the non-bonded electrons on nitrogen participate in the removal of the triphenylsiloxide moiety during the formation of V since this type of reaction is not observed with other carbonyl-containing compounds not having nitrogen adjacent to the carbonyl group (refer to the preceding section). For example, the reaction of triphenylsilyllithium with benzaldehyde afforded a considerable amount of hexaphenyldisilane when carried out at

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[175] R. Breslow, ibid., 80, 3719 (1958).

[176] See, for example, R. C. Woodworth and P. S. Skell, ibid., 81, 3383 (1959), and pertinent references cited therein.

room temperature; this was apparently formed *via* cleavage of the silicon-oxygen bond of an intermediate silyl ether.[85] This type of cleavage does not occur in the reactions with N,N-disubstituted amides. On this basis therefore, it appears quite likely that the unshared pair of electrons on nitrogen are contributing toward the removal of oxygen (as lithium triphenylsiloxide) from III, otherwise, one might expect hexaphenyldisilane to be a major product from these reactions. Actually, none of this disilane was isolated from reactions involving N,N-disubstituted amides.

The proposed sequence of reactions, thus accounts for the formation of all products isolated except triphenylsilane, ethoxytriphenylsilane and hexaphenyldisiloxane. The triphenylsilane is probably formed *via* hydrolysis of unreacted triphenylsilyllithium, and hexaphenyldisiloxane by dehydration of triphenylsilanol during work-up. Ethoxytriphenylsilane appears to have been formed *via* an acid catalyzed reaction between ethanol (employed during work-up) and triphenylsilanol. This product was not found when the acid-

$$Ph_3SiOH + HOEt \xrightarrow{acid} Ph_3SiOEt + H_2O$$

extracted organic layer was washed with sodium bicarbonate. Evidence that this is the mode of formation of this product is given in the preparation of methoxy-, ethoxy- and benzyloxytriphenylsilane from triphenylsilanol and the respective alcohols, using a drop or two of 10 percent aqueous hydrochloric acid as the catalyst. Undoubtedly, other acids would work equally as well, perhaps even those Lewis acids which are not destroyed by reaction with water. The yields in these three preparations were excellent except for benzyloxytriphenylsilane, where removal of the excess alcohol may have led to a slight loss of material. An attempt to prepare diphenylmethoxytriphenylsilane from triphenylsilanol and benzhydrol in acetone solution by this method failed, due to the ease of dehydration of the alcohol to benzhydryl ether. The triphenylsilanol was recovered in 87 percent yield.

Based on these few experiments, it would appear that the method is satisfactory only for liquid, primary alcohols; however, secondary alcohols and possibly tertiary alcohols, if liquids, may also undergo this reaction. It might be better to run these reactions with dry hydrogen chloride in water-free alcohols, since conversion of triethylsilanol to hexaethyldisiloxane has been reported to occur in ethanolic or methanolic solutions containing relatively high concentrations of aqueous hydrochloric acid.[177]

The methiodide of N,N-dimethyl-alpha-(triphenylsilyl)-benzylamine apparently crystallized with a molecule of methanol of crystallization. Drying the product in an oven

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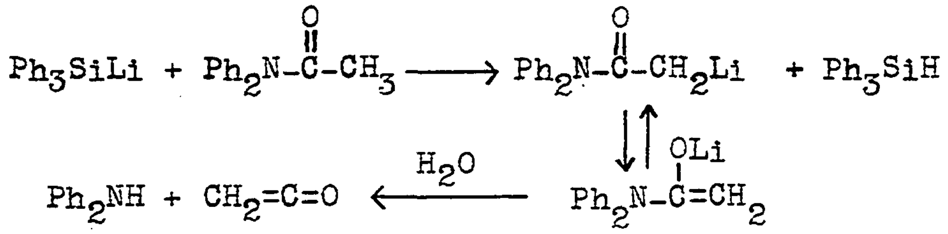
[177] U. Takahashi, J. Chem. Soc. Japan, Pure Chem. Sect., 75, 245 (1954).

at 130° caused it to lose this solvent of crystallization; however, the analysis of the dried compound was marginal. This aspect was not investigated further.

After having established the nature of the products from the reaction of triphenylsilyllithium with N,N-dimethylbenzamide, an investigation designed to test the general applicability of this reaction was conducted. The amides tested had various combinations of alkyl and aryl groups attached to carbon and nitrogen. N,N-Dimethylacetamide, N,N-dimethyl-p-toluamide and N,N-diphenylbenzamide were found to undergo similar transformations, giving the expected asymmetric alpha-silylamines in yields of 61.5, 60.7 and 78.8 percent, respectively.

However, when N,N-diphenylacetamide was reacted with triphenylsilyllithium, the only compounds isolated were diphenylamine, triphenylsilane, triphenylsilanol and recovered amide. It is not known for certain how the products were formed, but the fact that Color Test I was negative at the end of the reaction using one equivalent of triphenylsilyllithium indicates that enolization of the amide may have occurred. The electron-withdrawing power of the phenyl groups attached to nitrogen, coupled with the inductive effect of the methyl group may make a methyl-hydrogen acidic enough to be removed by triphenylsilyllithium, thus forming triphenylsilane. Hydrolysis of the enol could then give rise to the formation of the diphenylamine isolated. The amide was isolated only when two moles of triphenylsilyllithium were used, indicating that this was unreacted starting material. No products indicating that addition to the carbonyl group occurred were isolated. The proposed reaction scheme is illustrated below:



$$\begin{tikzcd}[column sep=small] Ph_3SiLi + Ph_2N-\overset{O}{\overset{\parallel}{C}}-CH_3 \arrow[r] & Ph_2N-\overset{O}{\overset{\parallel}{C}}-CH_2Li \arrow[d, shift right] + Ph_3SiH \\ Ph_2NH + CH_2{=}C{=}O & Ph_2N-\overset{OLi}{\overset{|}{C}}{=}CH_2 \arrow[u, shift right] \arrow[l, "H_2O"'] \end{tikzcd}$$

In this connection, hydrogen abstraction by triphenylsilyllithium from aliphatic carbonyl-containing compounds has been observed in several investigations.[82,83,89]

The rather interesting results obtained with N,N-disubstituted amides prompted the extension of this reaction to phthalimide and its N-substituted derivatives. From the early reactions involving phthalimide, varying yields of hexaphenyldisilane, triphenylsilanol and triphenylsilane were isolated, but no product derived from the imide could be identified except recovered phthalimide, and this only from the equimolar reaction. In this case, metalation of the imide probably occurred giving rise to the formation of triphenylsilane and N-lithiophthalimide. The latter compound reverted back to phthalimide on hydrolysis.

Similar results were obtained with the N-substituted phthalimides except when distillation was attempted to separate the products. In these cases, small amounts of products, thought to be o-formyl-N-substituted benzamides were isolated from the distilled fractions. Although the structures of these compounds have not been confirmed, their analyses and infrared spectra agree with those expected for o-formyl-N-substituted benzamides. The compound derived from N-methylphthalimide (isolated in 42 percent yield from a reaction employing two equivalents of triphenylsilyllithium) forms a phenylhydrazone whose analysis agrees quite closely with that for the phenylhydrazone of o-formyl-N-methylbenzamide.

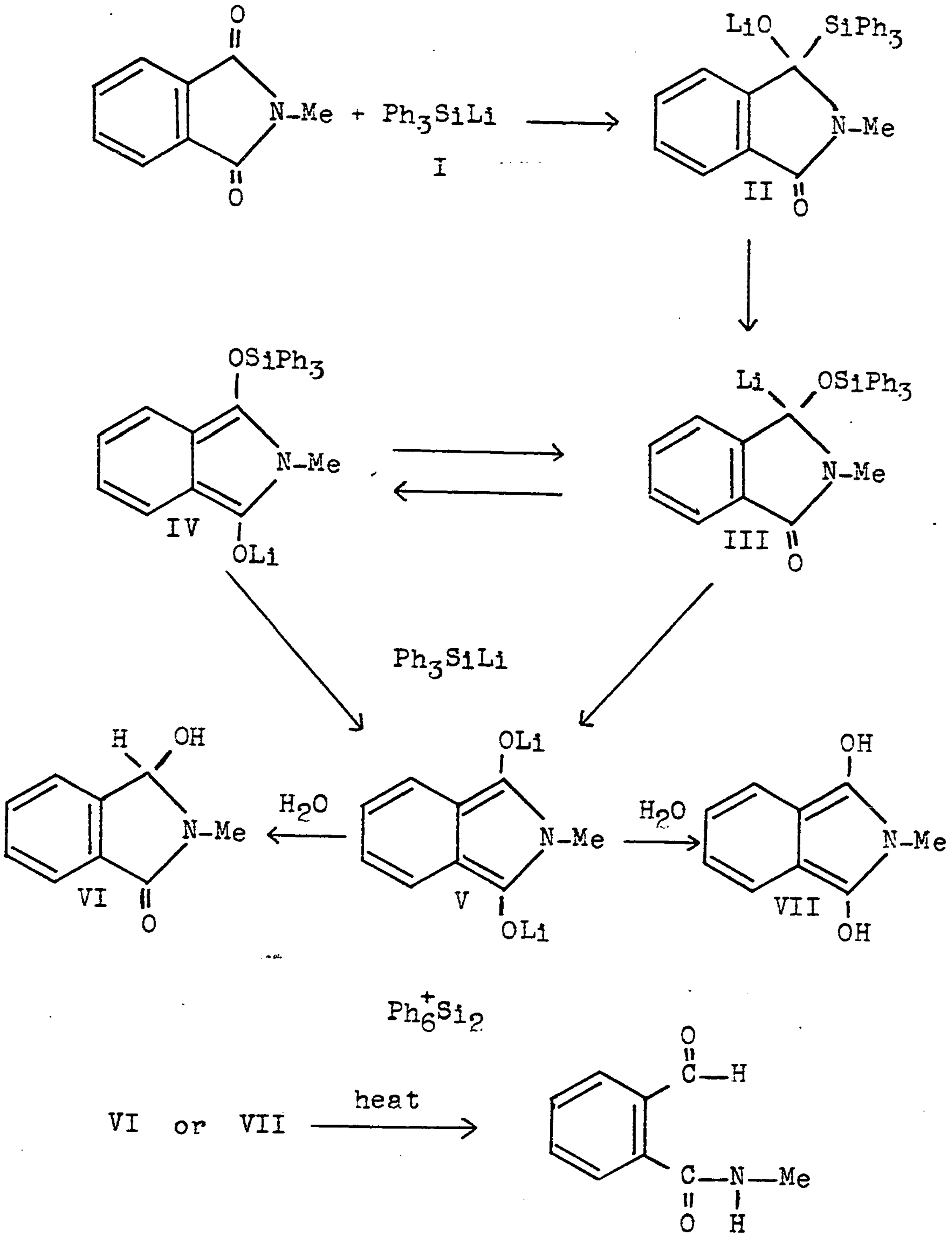
In spite of the fact that these compounds are readily crystallized from benzene or benzene-ethyl acetate mixtures, they could not be separated by crystallization techniques from the darkly colored, crude oils which remained after solvent removal. Also, the infrared spectra of the crude oils had only one or two absorption bands in common with the spectra of the pure compounds. These compounds could only be separated after distillation of the dark, viscous oils.

These facts tend to indicate that the compounds isolated (which are thought to be o-formylbenzamides) are not present as such in the crude oils obtained after hydrolysis, but rather, are formed during distillation by thermal decompositions or rearrangements of compounds present in the oil.

Working on this assumption, attempts were made to isolate the precursor from a reaction of two moles of triphenylsilyllithium with N-phenylphthalimide by crystallization techniques employing a variety of solvents. Only trace amounts of wide-melting solids could be isolated from the dark organic residue, although hexaphenyldisilane was formed in 57 percent yield from this reaction. The mode of formation of the compounds isolated is unknown; however, it is interesting to speculate upon possible reaction paths leading to the formation of these products.

By analogy with the reactions of triphenylsilyllithium and amides as well as with other carbonyl-containing compounds, it is quite likely that normal addition to the carbonyl group occurs first, and is followed by a rearrangement to the isomeric siloxy-compound (III or IV). Cleavage of this intermediate by the second equivalent of triphenylsilyllithium could explain the formation of hexaphenyldisilane in these reactions. As mentioned previously (see section IVE), there has been some evidence in earlier work that this type of cleavage occurs, particularly in the work of Wittenberg _et al_.[85] The triphenylsilanol could then arise by hydrolysis of the same intermediate (III or IV), since apparently all of it is not being cleaved, as evidenced by the low yields of hexaphenyldisilane obtained. The nature of the imide residue after the cleavage has occurred can only be surmised, but structure VI appears to be most likely after hydrolysis. Compounds with analogous structures, having an alkyl or aryl group in place of hydrogen on the hydroxylic carbon atom have been isolated from reactions of Grignard reagents with N-ethyl-phthalimide[32] or from the reaction of phenyllithium with N-methylphthalimide.[42] Similar products have been obtained from reactions of Grignard reagents with N-methyl-glutarimide[38,40] and N-methylsuccinimide.[34] Thielacker and Schmidt,[43] however, isolated 1,2,3-triphenylisoindole from the reaction of phenyllithium with 1,2-diphenylphthalimidine followed by heating. This compound has a structure similar to VII with phenyl groups replacing the methyl and hydroxyl groups. Thermal rearrangement of either VI or VII could lead to the formation of o-formyl-N-methylbenzamide.

This series of transformations illustrated on page 163 accounts for the products isolated; however, it must be admitted that this mechanism is largely speculative and based on the minimum of experimental evidence, hence, it may be quite incorrect. On the other hand, analogous transformations for other reactions of a similar nature are known. The present interpretation is merely a combination of mechanisms which have already been presented in the literature, with the exception of the final thermal rearrangement, which apparently has not yet been reported. This rearrangement, however,


N-Me
Ph3SiLi
I
LiO
SiPh3
II
OSiPh3
IV
OLi
Li
III
Ph3SiLi
H
OH
VI
H2O
OLi
V
VII
+ Ph6Si2
VI or VII
heat
C—H
C—N—Me

appears sound on the basis of the work done in the present study.

In conclusion, several general comments about these reactions might be made. The reaction of triphenylsilyllithium with N,N-disubstituted amides may prove to be a useful method for preparing compounds of the type isolated in these reactions, namely, asymmetric alpha-silylamines. The reaction appears to be quite general except for aryl amides of aliphatic carboxylic acids, in which case enolization of the amide apparently occurs. Other methods have been described for the preparation of compounds of this type.[178] It is suggested that this method be used to supplement those used previously. The yields are relatively high, and when acid extraction can be employed to separate the amine, the work-up procedure is uncomplicated. The wide variety of N,N-disubstituted amides available both commercially and by utilization of well-known synthetic procedures, makes the synthesis developed in this study an attractive method for preparing these alpha-silylamines. Compounds of this type may find use in the future as anti-oxidant additives for high-temperature lubricants.

The reactions of triphenylsilyllithium with N-substituted

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

imides, when developed further, may prove to be a useful method for preparing aldehydes of the type formed here. The reaction may also be applicable to imides derived from aliphatic dicarboxylic acids, however, enolization may occur here also. By varying reaction conditions and work-up procedures, compounds of the type shown in III may even by isolable from these reactions, and this aspect should be investigated in the future.

G. Suggestions for Future Research

The alkylation reaction observed with trialkyl phosphate esters might be worthy of further extension, particularly to esters having branched-chain alkyl groups. This procedure proved to be a suitable method for preparing isobutyltriphenylsilane, and may be equally suited for the synthesis of compounds having tertiary alkyl groups attached to silicon, or for that matter, to carbon as well.

The present methods for preparing such compounds are far from satisfactory, especially those procedures using alkyl halides, due to side reactions which occur. It may be possible to synthesize such compounds readily from organosilylmetallic compounds <u>via</u> this reaction.

The effect of variation of groups in the organosilyllithium compound should be tested also. Apparently these compounds need not have a great deal of steric hindrance to effect this reaction. Dimethylphenylsilyllithium should behave similarly.

Although only three organosilyllithium reagents have been used to any great extent in the past, the possibilities for variation of the groups attached to silicon are very great. It might be interesting to test the effect of this variation with electron-withdrawing and -donating groups incorporated in the aryl groups of the organosilyllithium reagents, not only in this reaction but in others as well.

Another extension which might be made in connection with the alkylation reaction involves the use of esters of other inorganic acids. Borates, sulfites, phosphites, phosphonates and arsenates, for example, might undergo similar reactions with sufficiently large and reactive organometallic compounds. This aspect should be investigated. Even if these esters should fail to alkylate organosilylmetallic compounds, the reaction may prove to be a useful means for preparing compounds having silicon attached to an element other than carbon.

Numerous attempts have been made in the past to prepare trialkylsilyllithium compounds by methods which were suitable for the aryl types; however, no useful method has yet been found. The ready cleavage of the silicon-group VB element bond, (except for nitrogen) by triphenylsilyllithium, suggests that these compounds might also be readily cleaved by alkali metals. Should this cleavage occur, it may be possible to effect it under such conditions where the trialkylsilylmetallic compounds produced would be relatively stable, such as in inert solvents, or at low temperatures.

The problem involved in this line of reasoning is the preparation of compounds having silicon-hetero atom bonds. Some of these are already known, as for example, the silylphosphines and thiosilanes. The phosphorus compounds are readily synthesized from phosphorus-lithium derivatives and halotrialkylsilanes. To illustrate, the reaction of an organolithium compound with phosphine would give lithium phosphide, which could be reacted with chlorotrimethylsilane to give tris(trimethylsilyl)phosphine. Subsequent cleavage of this by an alkali metal should lead to the formation of trimethylsilyllithium, providing it is possible to prevent side-reactions involving the organosilylmetallic compound. For this reason, it might be best to employ an inert solvent such as petroleum ether or benzene.

There is no reason why similar reactions cannot be effected with the corresponding compounds of other elements as well, although the possibility still remains that such starting materials may be preparable from organosilylmetallic compounds of lesser reactivity than the lithium derivatives. These starting materials might also be obtainable from reactions of organosilylmetallic compounds with the free elements, as already proposed by Lichtenwalter.[7]

The disilane cleavage which has been shown to occur with organolithium compounds should be investigated further both with respect to the groups attached to silicon in the disilane and the organometallic compounds used to effect the cleavage. With a sufficiently reactive organometallic compound, one may conceivably be able to prepare a trialkylsilylmetallic compound by this method also.

From the theoretical point of view, it should be interesting to study the metalation reaction with triphenylsilyllithium in the presence of hexaphenyldisilane to trap the metalated product as formed. This reaction, especially with toluene, should prove whether or not the reaction is an equilibrium process. Perhaps the other tolyllithium compounds would behave similarly. The difficulties encountered in separation of the products might discourage further research along these lines; however, the reactions involving metalations with triphenylsilyllithium should cause little difficulty, since the triphenylsilane formed could be hydrolyzed to the silanol, giving only the tetrasubstituted silane and hexaphenyldisilane as the non-polar products in the reaction mixture. The difference in solubility could be used advantageously to separate these, and the tetrasubstituted silane could be easily purified by chromatography. If this reaction be attempted, it is recommended that a diethyl ether-tetrahydrofuran mixture be used as the solvent, since this mixture has proven to be better than tetrahydrofuran alone, due to less tar formation.

Another aspect of this reaction which should be investigated is the mode of decomposition of organolithium compounds in tetrahydrofuran. This reaction apparently is not a simple cleavage of the ether, as is the case with organosilyllithium compounds. It is the opinion of the author that a metalation of the solvent by the organometallic reagent is the first step in the reaction. This could be tested by using a fairly high-molecular weight organolithium compound, which would enable the separation (from the solvent) of the hydrocarbon, derived from it. The ability of tetrahydrofuran to co-distill with so many compounds makes this separation difficult for low-molecular weight compounds.

The cleavage by triphenylsilyllithium of compounds having hetero atoms attached to silicon might be investigated further. Although some work has been done on siloxane and silicon-sulfur compounds, the general applicability of these reactions has not been studied. To date, no silicon-nitrogen bonds have been cleaved by organosilyllithium compounds and only a few instances involving oxygen and sulfur compounds have been reported, hence the surface has only been scratched in relation to this type of reaction.

The interesting reactions observed with the carbonyl group and organosilylmetallic compounds deserve further investigation. Considerable attention has been given to aldehydes and ketones, but other types of carbonyl-containing compounds have been studied only slightly. Further research along these lines may lead to an explanation for the rearrangements which have been shown to occur. This rearrangement certainly deserves further study since it appears to be a useful tool for explaining the formation of certain products isolated from these reactions. It would be enlightening, from a theoretical point of view, to determine why it occurs in some cases and not in others. In this connection, some aliphatic compounds have been observed to rearrange while some of the alpha-silylcarbinols derived from aliphatic ketones appear to be resistant to this isomerization.

The reactions with the amide group, in particular, should be investigated further since all cases where addition to the carbonyl group occurred have been shown to give products explainable by the rearrangement reaction. The large number of variations possible for compounds having the amide group, both cyclic and acyclic, should make this reaction a fruitful field for future endeavors. The work-up procedure is relatively simple when N,N-dialkyl compounds are used, since the asymmetric alpha-silylamines can be readily separated by acid extraction.

The availability of phosphorus-lithium compounds, as well as their arsenic analogs, suggests the extension of this reaction to amide analogs of phosphorus and arsenic. Some of the former compounds have already been prepared by the reaction of phosphorus-lithium compounds with acid halides. It might be interesting to study their reactions with triphenylsilyllithium and other organosilyllithium compounds to see if an analogous reaction would occur with these compounds. These studies may lead to the preparation of asymmetric *alpha*-silylphosphines and -arsines, as was the case with their nitrogen analogs. This investigation should prove both enlightening and challenging.

Finally, the acid-catalyzed reaction of silanols with alcohols should be tested for its general applicability. No primary, solid alcohols or secondary and tertiary, liquid alcohols have yet been investigated, nor have any phenols been subjected to the reaction. The simplicity of the reaction, as it presently appears, indicates that a study along these lines would require relatively little time, but much could be learned from it. The possibility of its extension to mercaptans and similar compounds should be considered. It would be interesting to determine in which direction the reaction would proceed with such compounds, providing a reaction were to occur.

This sequence of reactions could be varied further by using polyhydroxy compounds such as glycols and glycerols, as well as sugars. Further variations could be made by using other silanols, since only one has been tested in this study. Perhaps cyclic compounds might result from those reactions employing silane- or disilanediols and polyhydroxy alcohols. Similar reactions might also occur with the corresponding sulfur and selenium compounds; however, precautions against the harmful physiological effects of the latter should be exercised.

V. SUMMARY

This study has been concerned with reactions of triphenylsilyllithium with compounds containing group VB elements.

Trialkyl esters of phosphoric acid, for example, have been shown to alkylate this reagent in good yields. Similar reactions have been observed to occur with certain sufficiently hindered and reactive organolithium compounds and Grignard reagents. The steric requirements of the organometallic compounds apparently are largely responsible for this unexpected course of reaction.

A study has been made of the analogous reactions involving triphenylsilyllithium and triaryl phosphates. These esters were found to behave as anticipated, undergoing displacements of aryloxide anions. Evidence has been presented for the existence of compounds having silicon attached to phosphorus as reaction intermediates. Subsequent cleavage of these intermediates by triphenylsilyllithium was used to explain the formation of hexaphenyldisilane from these reactions.

Similar displacements and cleavages were postulated to explain the formation of products isolated from the reactions of triphenylsilyllithium with triphenyl-derivatives of the more-metallic group VB elements. In this study, the apparent disproportionation of silylstibines has been observed. Colorless, clear solutions of compounds thought to contain silicon-antimony bonds have been observed to deposit a dark, finely divided solid when attempts were made to distill them. This solid is thought to be elemental antimony.

In connection with the last-mentioned series of reactions, the ability of aryllithium compounds to cleave hexaphenyldisilane has been demonstrated, contrary to earlier beliefs. Use may be made of this reaction in future work to interpret the formation of certain products from reactions where this type of cleavage may occur.

When p-tolyllithium was used to effect this cleavage, an interesting case of polymorphism involving p-tolyltriphenylsilane was found. The two crystalline forms are interconvertable through the use of different solvents.

This reaction also uncovered a rearrangement of p-tolyllithium to benzyllithium, although the path by which this rearrangement occurs has not been established. In the light of experimental results obtained from this reaction, it appears that triphenylsilyllithium may play a part in this transformation. A possible reaction to test this hypothesis has been suggested.

An interesting series of reactions involving N,N-disubstituted amides and triphenylsilyllithium has been studied. Several types of amides containing alkyl and aryl groups have been found to give satisfactory yields of alpha-silylamines having an asymmetric carbon atom when reacted with triphenylsilyllithium. N,N-Diphenylacetamide was the only compound tested which failed to react in this way. This compound apparently underwent enolization by the organosilyllithium compound. The study of the amide series also revealed what appears to be a new type of synthesis for alkoxysilanes from silanols and alcohols employing a trace of acid as a catalyst.

For all of the reactions studied, possible mechanisms have been proposed to explain the formation of products isolated. Although several of these are based on inadequate evidence, most of the postulated transformations have their counterpart in mechanisms proposed in other reactions. Based on the small amount of evidence accumulated in this study from the mechanistic point of view, these proposed reaction paths presently appear to be possible, if not probable.

Finally, a number of suggestions for future research have been made. Endeavors along these lines may possibly lead to a better understanding of organosilylmetallic chemistry.

VI. ACKNOWLEDGEMENTS

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