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SOME CORRELATIONS BETWEEN ORGANOSILICON COMPOUNDS AND ORGANOGERMANIUM COMPOUNDS

by

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Dean of Graduate College

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TABLE OF CONTENTS

INTRODUCTION

The excellent thermal stabilities of some organogermanium and organosilicon compounds have made these classes of compounds important ones in the field of high temperature lubricants. However, the methods available for the introduction of a germanium or silicon atom into custom-made molecules are very limited.

Triarylgermyllithium compounds attack reactive sites of various organic compounds,[1-4] but the resultant products usually exhibit melting points too high for the compounds to be utilized as lubricants over the temperature range desired. Polychlorogermanes react with organometallic reagents to give partially substituted chlorogermanes, but the difficulties of separating the mixtures obtained militate against use of these compounds as intermediates for the preparation of tetrasubstituted organogermanes.

The present situation is somewhat better for the preparation of organosilicon compounds. The recent preparation of

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

[2] H. Gilman and C. W. Gerow, ibid., 77, 4675 (1955).

[3] H. Gilman and C. W. Gerow, ibid., 77, 5509 (1955).

[4] H. Gilman and C. W. Gerow, ibid., 79, 342 (1957).

methyldiphenyl- and dimethylphenylsilyllithium[5] should permit the preparation of more unsymmetrically substituted silanes. At the time this work was initiated, however, essentially the same methods of preparation were available in this area as for the analogous germanium compounds.

The original purpose of this investigation was to prepare trialkylgermyl- and trialkylsilylmetallic compounds and to study their reactions. Previous attempts to prepare intermediates of this type have failed or have been only partially successful. There is little doubt that the derivatives of these organometallic compounds would have lower melting points than the corresponding triaryl compounds and evaluation of their thermal stabilities would be of great interest.

A second phase of this research involved a study of the reaction of alkyl Grignard reagents with organosilicon hydrides in tetrahydrofuran, which would enable one to prepare highly unsymmetrical silanes for evaluation as lubricants. Furthermore, an attempt was made to elucidate some of the chemical and physical properties of the silicon-hydrogen bond.

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

HISTORICAL

For the purpose of this review, the following reference sources have been checked to the dates indicated: C. A. through no. 5, vol. 52, 1958; J. Am. Chem. Soc. through no. 7, vol. 80, 1958; J. Org. Chem. through no. 3, vol. 23, 1958; J. Chem. Soc. through no. 3, 1958; and Current Chemical Papers through no. 3, 1958. Furthermore, all cross references contained in individual papers were checked.

All of the pertinent references are not given in some sections, and this fact is so indicated, due to the large number of references to reactions which involve only minor variations in experimental conditions. In such cases, the references cited contain good bibliographies to related studies.

The major sections of this thesis have all been divided into three subdivisions: trialkylgermylmetallic compounds, trialkylsilylmetallic compounds, and organosilicon hydrides, for ease in locating data pertinent to each topic.

Trialkylgermylmetallic Compounds

The preparation and characterization of only one trialkylgermylmetallic compound has been reported in the literature. Kraus and Flood[6] were successful in cleaving hexaethyldigermane with metallic potassium in ethylamine over a period of 6 weeks. Derivatization with ethyl bromide gave tetraethylgermane in near quantitative yield. Hexaethyldigermane and sodium in liquid ammonia did not react to any extent, most likely due to the low solubility of the digermane in the solvent.[6] Cleavage of hexaethyldigermane with lithium in ethylamine was successful, but the germyllithium compound immediately underwent ammonolysis to give triethylgermane.[6]

These same authors investigated the reaction of triethylhalogermanes with metals in ammonia and in ethylamine. When triethylchlorogermane was treated with lithium in ethylamine, the only product isolated was hexaethyldigermane in low yields. The reaction was accompanied by the evolution of large quantities of hydrogen gas.[6] Triethylbromo-, -chloro-, and -iodogermane underwent no reaction with sodium in refluxing xylene; in the absence of any solvent, triethylgermane gave some hexaethyldigermane upon refluxing with sodium at 270° for 5 days.[6]

In another approach, Kraus and Flood found that lithium in ethylamine did react with hexaethyldigermoxane as evidenced by the appearance of a red color in the solution, but upon evaporation of the solvent, solvolysis occurred and triethyl-

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[6] C. A. Kraus and E. A. Flood, ibid., 54, 1635 (1932).

germane was formed.[6] No reaction occurred when triethylgermane itself and sodium were stirred in liquid ammonia, whereas potassium in the same solvent did react with triethylgermane but the product subsequently underwent ammonolysis.

In a more recent investigation, Gerow[7] studied the cleavage of some tetrasubstituted germanes in ethylene glycol dimethyl ether. After stirring a mixture of tetra-*n*-butylgermane and lithium wire in ethylene glycol dimethyl ether for 96 hours, the solution was black in color but Color Test I[8] was negative. Hydrolysis and distillation resulted in the recovery of 92 percent of starting material. Sodium-potassium alloy under essentially the same experimental conditions did not effect cleavage either, there being a quantitative recovery of tetra-*n*-butylgermane. Tetra-*n*-octylgermane was recovered in 67 percent yield after stirring for 67 hours with lithium wire in ethylene glycol dimethyl ether.[7] When tetrabenzylgermane was stirred with lithium wire in the same solvent, a deep red color developed and Color Test I[8] was positive after 5 hours. Derivatization by addition to ethyl bromide caused evolution of heat and dissipation of the

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[7] C. W. Gerow. The preparation and cleavage of some organogermanium compounds. Unpublished Ph.D. Thesis. Ames, Iowa, Iowa State College Library. 1956.

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

red color. Distillation of the reaction mixture gave four unidentified liquids but no tribenzylethylgermane, m.p. 56-57°,[9] was isolated. Attempted cleavage of tetrakis(2-phenylethyl)germane with lithium wire resulted in the quantitative recovery of starting material.[7]

Whereas in alkylarylgermanes aryl groups are easily replaced by halogen,[10-12] Gerow was unsuccessful in cleaving either aryl or alkyl groups from tri-n-hexylphenylgermane. After stirring for 24 hours with lithium wire in ethylene glycol dimethyl ether, there was a 65 percent recovery of starting material and no evidence of formation of an organometallic intermediate.

Teal and Kraus[13] have reported the preparation of methyl-, ethyl-, and n-propylgermane via reaction of the corresponding alkyl bromide or iodide with monogermylsodium, H_3GeNa. The monogermylsodium was prepared in liquid ammonia from monogermane and sodium metal. Monogermylpotassium was prepared under analogous conditions.

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[9] H. Bauer and K. Burschkies, Ber., 67, 1041 (1934).

[10] E. A. Flood, J. Am. Chem. Soc., 54, 1663 (1932).

[11] R. Schwarz and M. Lewinsohn, Ber., 64B, 2352 (1931).

[12] C. E. Trautman and H. A. Ambrose, U. S. Patent 2,416,360. Feb. 25, 1947. [Original not available for examination; abstracted in C. A., 42, 2760 (1948)].

[13] G. K. Teal and C. A. Kraus, J. Am. Chem. Soc., 72, 4706 (1950).

Glarum and Kraus[14] extended the above investigation and report the preparation of methylgermyllithium, ethylgermyllithium, isoamylgermyllithium and ethylisoamylgermyllithium from the corresponding mono- or disubstituted germane and lithium metal in ethylamine. They report no success, however, in preparing a trialkylgermylmetallic compound.

Until a few years ago, the greatest deterrent to a more complete investigation of trialkylgermylmetallic reagents in particular, and all germanium compounds in general, was the unavailability of the necessary starting materials. This situation has been remedied somewhat, but the present high cost of the compounds available still remains an obstacle.

Trialkylsilylmetallic Compounds

Efforts to prepare trialkylsilylmetallic compounds have been more successful. Triethylsilyllithium was prepared in low yields by the lithium cleavage of triphenylgermyltriethylsilane in ethylamine.[15] Low yields of trimethylphenylsilane and triethylphenylsilane were realized after 1,1,1-trimethyl-2,2,2-triphenyldisilane and 1,1,1-triethyl-2,2,2-triphenyldisilane, respectively, had been stirred with sodium-potassium

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[14] S. N. Glarum and C. A. Kraus, ibid., 72, 5398 (1950).

[15] C. A. Kraus and W. K. Nelson, ibid., 56, 195 (1934).

alloy in diethyl ether for 6 hours and derivatized with bromobenzene.[16] Wu[17] repeated the cleavage of 1,1,1-trimethyl-2,2,2-triphenyldisilane with sodium-potassium alloy in ether. Addition of bromobenzene as the derivatizing agent resulted in the isolation of a 50 percent yield of tetraphenylsilane but no trimethylphenylsilane was encountered.

In tetrahydrofuran, Wittenberg[18] cleaved 1,1,1-triethyl-2,2,2-triphenyldisilane with lithium and isolated upon hydrolysis 11 percent triethylsilane and 14 percent hexaethyldisilane, in addition to triphenylsilane and other, unidentified products. These results indicate cleavage of the Si-Si bond and formation of triethylsilyllithium, which then partially cleaves starting material to give triphenylsilyllithium and hexaethyldisilane.

The cleavage of hexaethyldisilane, the compound of choice because it would give rise to only triethylsilyllithium, has been studied. Kraus and Nelson[15] found this disilane to be unaffected by sodium in liquid ammonia or lithium in ethylamine. More recently, the reaction of hexaethyldisilane with

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[16] H. Gilman, R. K. Ingham, and A. G. Smith, J. Org. Chem., 18, 1743 (1953).

[17] T. C. Wu. Comparisons of some organic compounds containing group IV-B elements. Unpublished Ph.D. Thesis. Ames, Iowa, Iowa State College Library. 1952.

[18] D. Wittenberg, Chemistry Dept., Iowa State College, Ames, Iowa. Information on cleavage of 1,1,1-triethyl-2,2,2-triphenyldisilane. Private communication. 1958.

alkali metals has been reinvestigated.[16] With sodium in liquid ammonia there was a 99 percent recovery of the disilane. When sodium-potassium alloy was used in four reactions, with variations in time, temperature and solvent, the recovery of starting material ranged from 69 to 79 percent. When rubidium was employed, a light blue color was observed in the solution but hexaethyldisilane was recovered to the extent of 49 percent. No indication of reaction was noticed when cesium was stirred with hexaethyldisilane in a 1:1 mixture of diethyl ether and di-n-butyl ether.[19] Phenyllithium in diethyl ether was also ineffectual.[16]

Attempts to cleave trialkylarylsilanes have also been unsuccessful. Kraus and Nelson observed no reaction when triethylphenylsilane was stirred with sodium in liquid ammonia.[15] If lithium in ethylamine was employed, an orange color developed but, upon hydrolysis, no benzene was isolated, which indicated the silicon-aromatic carbon bond had not been cleaved. There was isolated some material, b. p. 236-238°, which was described as a partially reduced (hydrogenated) derivative of triethylphenylsilane.[15] A 38 percent recovery of trimethylphenylsilane plus unidentified higher boiling material was reported after a mixture of trimethylphenylsilane

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[19] A. G. Smith. Some cleavage reactions of alkyl and aryl silanes. Unpublished M.S. Thesis. Ames, Iowa, Iowa State College Library. 1953.

and sodium-potassium alloy in diethyl ether had been stirred for 8 days.[19] In ethylamine, Benkeser, *et al.* observed take-up of six equivalents of lithium by trimethylphenylsilane to give a reduced compound.[20]

In the same paper in which they report the preparation of triphenylsilylpotassium via the cleavage of phenylisopropyltriphenylsilane with sodium-potassium alloy, Benkeser and Severson[21] report no reaction between the alloy and phenylisopropyltrimethylsilane although the mixture was stirred at room temperature for 30 hours and at ether reflux for 20 hours. Investigations of other trialkylaralkylsilanes have also proved fruitless. There was no reaction between benzyltriethylsilane and sodium in liquid ammonia, and with lithium in ethylamine a partially reduced product was isolated but no toluene.[15] Smith recovered 83 percent of starting material after benzyltriethylsilane and sodium-potassium alloy had been stirred for 8 days.[19] Hauser and Hance[22] found trimethyl-(triphenylmethyl)silane was unaffected by ethylmagnesium bromide, *n*-butyllithium or phenylsodium in ether, and

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[20] R. A. Benkeser, R. E. Robinson, and H. Landesman, *J. Am. Chem. Soc.*, *74*, 5699 (1952).

[21] R. A. Benkeser and R. G. Severson, *ibid.*, *73*, 1424 (1951).

[22] C. R. Hauser and C. R. Hance, *ibid.*, *73*, 5846 (1951).

9-fluorenyltrimethylsilane metalated in the 9-position when treated with *n*-butyllithium.[23]

In somewhat related experiments, Steele and Kipping[24] found that dichlorodibenzylsilane with sodium in refluxing toluene gave fair yields of tetrabenzylsilane, but that the bulk of the silicon was converted to an infusible white solid quite similar to silicon dioxide but which contained a low percentage of organic material, arising undoubtedly from further reaction of the dichlorobenzylsilylsodium moiety. Evison and Kipping[25] repeated the reaction later and realized essentially the same results except that they also isolated a small amount of tribenzylsilane. Thompson and Kipping[26] were able to isolate tetraphenoxysilane from the reaction of dichlorodiphenoxysilane and sodium but they were unable to derivatize the dichlorophenoxysilylsodium which they postulated as an intermediate.

In a similar reaction, Benkeser and Foster[27] report a 50 percent yield of tetrabenzylsilane after treating tribenzyl-

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[23] H. Gilman and H. Hartzfeld, *ibid.*, *73*, 5878 (1951).

[24] A. R. Steele and F. S. Kipping, *J. Chem. Soc.*, 1431 (1928).

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

[26] R. A. Thompson and F. S. Kipping, *ibid.*, 1176 (1929).

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

silane with sodium in decalin, the rest of the silicon being incorporated in an infusible solid containing low percentages of carbon and hydrogen. Tetraphenylsilane and an infusible inorganic-appearing material were isolated when phenyl- or diphenylsilane was heated with sodium-potassium alloy.[28]

Quite a bit of work has also been done on the reaction of trialkylsilanes with metals and organometallic compounds. Kraus and Nelson[15] isolated hexaethyldisilazane upon treatment of triethylsilane with potassium in liquid ammonia. They also report the preparation of ethyl(triethylsilyl)amine when triethylsilane was stirred with lithium in ethylamine. When triethylsilane and sodium-potassium alloy in ether were stirred at reflux for 26 hours, there was a 46 percent recovery of starting material.[19] Benkeser, *et al.*[29] realized an 88 percent recovery of triethylsilane after stirring the compound with sodium-potassium alloy in ether for 30 hours at room temperature.

Meals[30] observed that treatment of triethylsilane with *n*-propyllithium, *n*-butyllithium, and phenyllithium in ether gave triethylpropylsilane, butyltriethylsilane and

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[28] R. A. Benkeser and D. J. Foster, *ibid.*, *74*, 4200 (1952).

[29] R. A. Benkeser, H. Landesmann and D. J. Foster, *ibid.*, *74*, 648 (1952).

[30] R. N. Meals, *ibid.*, *68*, 1880 (1946).

triethylphenylsilane in yields of 74.5, 58 and 81 percent, respectively. Methyllithium and triethylsilane in ether gave triethylmethylsilane in yields of 54, 35 and 38 percent in three runs.[31] Triphenylsilane reacts similarly.[32]

Trialkylhalosilanes and trialkylalkoxysilanes have also been studied as starting materials for the preparation of trialkylsilylmetallic compounds. Kraus and Nelson[15] found that triethylbromosilane with lithium in ethylamine gave ethyl(triethylsilyl)amine. Wu[17] found no evidence of reaction between triethylchlorosilane and sodium-potassium alloy after stirring for 70 hours at room temperature. The reaction between trialkyliodosilanes and molten sodium gives the coupling products, hexaalkyldisilanes, in yields of 60 percent or better.[33] Triethyliodosilane and magnesium, with or without added iodine as a catalyst, gave no reaction in ether over extended periods of reflux.[34] Emeléus, _et al._[35] have reported that iodosilane reacts with mercury, zinc, magnesium

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[31] H. Gilman and S. P. Massie, _ibid._, _68_, 1128 (1946).

[32] H. Gilman and H. W. Melvin, _ibid._, _71_, 4050 (1949).

[33] M. G. Voronkov and Yu. I. Khudobin, _Zhur. Obshchei Khim._, _26_, 584 (1956). [Original available but not translated; translated in _J. Gen. Chem. U.S.S.R._, _26_, 629 (1956); also abstracted in _C. A._, _50_, 13729 (1956)].

[34] C. Eaborn, _J. Chem. Soc._, 2755 (1949).

[35] H. J. Emeléus, A. G. Maddock, and C. Reid, _ibid._, 353 (1941).

or sodium in ether. The final products of the reactions are silane and iodides of the metals, and they postulate the reaction proceeding through an unstable silylmetallic intermediate.

Sodium-potassium alloy and trimethylethoxysilane in ether gave no evidence of reaction, and the same silane and cesium in ether-benzene gave, after addition of chlorotriphenylsilane, no 1,1,1-trimethyl-2,2,2-triphenyldisilane.[19]

One explanation for the high reactivity, non-selectivity of a trialkylsilylmetallic compound, if formed, or the non-formation of such an intermediate under most experimental conditions, may be that there exists no chance for resonance stabilization of the trialkylsilyl anion. The stability of dimethylphenylsilyllithium and methyldiphenylsilyllithium,[5] where resonance stabilization is possible, lends some credence to this theory.

Organosilicon Hydrides

A priori, one might expect that organosilicon compounds of the type $RSiH_3$, R_2SiH_2, and R_3SiH would resemble closely their carbon analogs. Experimentally, however, the least reactive (tertiary) type of silicon-hydrogen is more reactive in most cases than the most reactive (tertiary) type of carbon-hydrogen bond. The two bonds have about the same amount of ionic character, 4 percent in carbon compounds versus 3 percent in silicon compounds,[36] but the great difference lies in the direction of polarization. The relative electronegativities of carbon, hydrogen and silicon are 2.5, 2.1 and 1.8, respectively,[37] which means that the hydrogen atom is at the negative end of the polar silicon-hydrogen bond, resulting in enormously greater reactivity toward polar reagents as compared to the oppositely polarized carbon-hydrogen bond.

Preparation

By direct synthesis The first organic compound containing a silicon-hydrogen bond was prepared by Pape[38] who treated silicochloroform with di-*n*-propylzinc and isolated tri-*n*-propylsilane. Taurke[39] prepared several trialkyl- and triarylsilanes by coupling silicochloroform and organic halides with sodium in a Wurtz-type reaction. Stock and Somieski[40] were able to prepare chloro- and dichlorosilane from silane and hydrogen chloride and obtained mono- and

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[36] L. Pauling. The nature of the chemical bond. 2nd ed. Ithaca, New York, Cornell Univ. Press. 1948. p. 70.

[37] L. Pauling, *ibid.*, p. 64.

[38] C. Pape, *Ann.*, *222*, 354 (1884).

[39] F. Taurke, *Ber.*, *38*, 1661 (1905).

[40] A. Stock and C. Somieski, *ibid.*, *52*, 695 (1919).

disubstituted silanes upon treatment of these intermediates with dialkylzinc compounds.

In the past decade, there has been an increased interest in the chemistry of compounds containing one or more hydrogens bonded to silicon. Peake, et al.[41] have reported the reaction of organolithium compounds with silane (SiH_4) in diethyl ether to give some di- and trisubstituted silanes, although the main products were the tetrasubstituted compounds. Under the same conditions, phenylsodium gave tetraphenylsilane while Grignard reagents did not react at all. Using low boiling petroleum ether rather than diethyl ether, it is possible to prepare the trisubstituted silanes in good yields.[41] This failure of the last hydrogen to react in the nonpolar petroleum ether had been observed earlier.[30,42] Meals[43] studied the stepwise reaction of organolithium reagents with $RSiH_3$ types and realized a mixture of products in all cases.

Other investigators have employed silicochloroform and organometallic reagents to prepare trisubstituted silanes. However, if a ratio of organometallic compound to silico-

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[41] J. S. Peake, W. H. Nebergall and Yun Ti Chen, J. Am. Chem. Soc., 74, 1526 (1952).

[42] W. H. Nebergall, ibid., 72, 4702 (1950).

[43] R. N. Meals, U. S. Patent 2,444,784. July 6, 1948. [Original not available for examination; abstracted in C. A., 42, 7317 (1948)].

chloroform of less than 3 to 1 was used, a mixture of $RSiHCl_2$, R_2SiHCl and R_3SiH was obtained.[44,45]

Another approach which gives triarylsilanes in good yields utilizes a Wurtz-Fittig reaction between silicochloroform and aryl halides, preferably the chlorides. Wannagat and Brandmair[46] prepared tri-(p-dimethylaminophenyl)-silane and Bassett, et al.[47] were successful in synthesizing triphenylsilane and tri-o-, m-, and p-tolylsilanes by this method. Diallylethylsilane was prepared via a slightly modified procedure employing ethyldichlorosilane, allyl iodide and magnesium.[48] Wurtz reactions cannot be applied to the preparation of trialkylsilanes in general due to the extensive coupling of alkyl halides to give hydrocarbons.

The fact that Grignard reagents do react with the silicon-halogen bond, but do not react with the silicon-hydrogen bond under ordinary circumstances has been exploited

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[44] J. W. Jenkins, N. L. Lavery, P. R. Guenther, and H. W. Post, J. Org. Chem., 13, 862 (1948).

[45] J. W. Jenkins and H. W. Post, ibid., 15, 552 (1950).

[46] U. Wannagat and F. Brandmair, Z. anorg. u. allgem. Chem., 280, 223 (1955).

[47] E. A. Bassett, H. G. Emblem, M. Frankel, and D. Ridge, J. Soc. Chem. Ind., 67, 177 (1948).

[48] A. D. Petrov, V. F. Mironov, and V. G. Glukhovtsev, Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk, 1954, 1123. [Original available but not translated; translated in Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., 1954, 983; also abstracted in C. A., 49, 7510 (1955)].

by several investigators. Opitz, et al.[49] bubbled bromosilane and dibromosilane into solutions of Grignard reagents in diethyl ether to prepare mono- and disubstituted silanes, respectively, in high yields. West and Rochow[50] used dichlorosilane to prepare diethyl-, di-*n*-propyl-, diisopropyl-, di-*n*-butyl-, dicyclohexyl-, diphenyl-, di-*p*-anisyl-, and di-1-naphthylsilane from the corresponding Grignard compound. West[51] also prepared silacyclohexane from 1,5-pentamethylenedilithium and dichlorosilane. Phenylbromosilane has been found to react smoothly with alkyl Grignard reagents to give phenylalkylsilanes[52] and Shostakovskiĭ, et al.[53] realized similar results with diethylchlorosilane. This latter reaction has been extended to R_aSiHX_{3-a} compounds in general to give $R_aR'_{3-a}SiH$ compounds, where R and R' may or may not be the same.[54]

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[49] H. E. Opitz, J. S. Peake, and W. H. Nebergall, J. Am. Chem. Soc., 78, 292 (1956).

[50] R. West and E. G. Rochow, J. Org. Chem., 18, 303 (1953).

[51] R. West, J. Am. Chem. Soc., 76, 6012 (1954).

[52] M. C. Harvey, W. H. Nebergall, and J. S. Peake, ibid., 76, 4555 (1954).

[53] M. F. Shostakovskiĭ, D. A. Kochkin, and V. M. Rogov, Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk, 1956, 1062. [Original available but not translated; translated in Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., 1956, 1079; also abstracted in C. A., 51, 4983 (1957)].

[54] A. D. Petrov, V. A. Ponomarenko, B. A. Sokolov, and Yu. P. Egorov, ibid., 1957, 310. [Original not available for examination; abstracted in C. A., 51, 14588 (1957)].

Another method of preparing R_aSiH_{4-a} compounds has been developed only recently. Fritz[55] found that silane added across the double bond of ethylene at ca. 450° to give a mixture of ethyl-, diethyl-, and triethylsilane. Also isolated from the reaction were some methylsilanes and higher boiling polymeric materials. Approximately the same results were obtained by White and Rochow[56] at 500°, although they also isolated some disilane and trisilane. From silane and acetylene at 500°, there was obtained ethylsilane plus a mixture of ethylvinylsilanes.[56] Wolfe and Cook[57] were able to achieve some control over the distribution of products by regulation of the temperature. Below 250°, the main product was ethylsilane; at higher temperatures a mixture of diethyl-, triethyl-, and tetraethylsilane was obtained.

Irradiation of a mixture of silane and ethylene with a mercury vapor lamp at lower temperatures gave ethylsilane, _n_-butylsilane and 1,2-disilylbutane.[56] When acetylene was substituted for ethylene and the mixture irradiated, 1,2-disilylethane and polymeric materials were obtained.[56]

This addition of organosilicon hydrides to double bonds will be dealt with in greater detail in the section concerning reactions of silicon-hydrogen compounds.

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[55] G. Fritz, _Z. Naturforsch._, _7b_, 207 (1952).

[56] D. G. White and E. G. Rochow, _J. Am. Chem. Soc._, _76_, 3897 (1954).

[57] J. K. Wolfe and N. C. Cook, U. S. Patent 2,786,862. Mar. 26, 1957. [Original not available for examination; abstracted in _C. A._, _51_, 13904 (1957)].

By reduction With the development of the metal hydrides, and lithium aluminum hydride[58] in particular, as reducing agents, an entirely new avenue of approach was opened in organosilicon hydride chemistry. Finholt, et al.[59] reported the preparation of ethyl-, n-propyl-, n-butyl-, phenyl, di-n-propyl-, and diethylsilane by reduction of the corresponding chlorosilanes with lithium aluminum hydride. In the same paper, lithium hydride was reported to be slower than lithium aluminum hydride but that replacement of diethyl ether by p-dioxane increased the efficiency considerably. This has been verified by Petrov, et al.[54] in a more recent publication. Sodium hydride was ineffectual in either solvent. That the solvent plays an important role in the reaction by complexing the reducing species was demonstrated by Paddock,[60] who found that no silane was formed when a mixture of silicon tetrachloride and lithium aluminum hydride was refluxed for extended periods of time in the absence of any solvent. When ether was present, the yield of silane was 96 percent at a temperature of -115°.

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[58] A. E. Finholt, A. C. Bond, and H. I. Schlesinger, J. Am. Chem. Soc., 69, 1199 (1947).

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

[60] N. L. Paddock. Nature, 167, 1070 (1951).

Nebergall and Johnson[61] were able to reduce tricyclohexylchlorosilane to tricyclohexylsilane with lithium aluminum hydride in diethyl ether, although the chloride was resistant to attack by either acid or base. Kaye and Tannenbaum[62] prepared mono-, di-, and trimethylsilane, mono-, di-, and triethylsilane, n-butyl-, isobutyl-, and vinylsilane via reduction of the chloro compounds with lithium aluminum hydride. The following is an incomplete list of references[51,63-70] to the reduction of variously substituted chlorosilanes to

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[61] W. H. Nebergall and O. H. Johnson, J. Am. Chem. Soc., 71, 4022 (1949).

[62] S. Kaye and S. Tannenbaum, J. Org. Chem., 18, 1750 (1953).

[63] W. D. English, A. Taurins, and R. V. V. Nicholls, Can. J. Chem., 30, 646 (1952).

[64] P. A. McCusker and E. L. Rielly, J. Am. Chem. Soc., 75, 1583 (1953).

[65] S. Tannenbaum, S. Kaye, and G. F. Lewenz, ibid., 75, 3753 (1953).

[66] A. D. Petrov and V. A. Ponomarenko, Doklady Akad. Nauk S.S.S.R., 90, 387 (1953). [Original not available for examination; abstracted in C. A., 48, 5080 (1954)].

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

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

[69] S. N. Borisov, M. G. Voronkov, and B. N. Dolgov, Doklady Akad. Nauk S.S.S.R., 114, 93 (1957). [Original not available for examination; abstracted in C. A., 52, 1057 (1958)].

[70] H. D. Kaesz and F. G. A. Stone, J. Chem. Soc., 1957, 1433.

silanes, which occur throughout the recent literature with very little variation in procedure. The reduction is very rapid, being complete, usually, after two hours at ether-reflux temperature.

Lithium aluminum hydride also reduces Si-O-C and Si-O-Si linkages to Si-H bonds. Gilman and Brannen[71] prepared tri-1-naphthylsilane from tri-1-naphthylethoxysilane and Westermark[72] isolated di- and tri-*n*-propylsilane, di- and tri-*n*-butylsilane, mono-, di-, and tri-*n*-amylsilane, *n*-hexylsilane and diphenylsilane upon reduction of the corresponding ethoxy compounds. He reported low yields in diethyl ether, but in the absence of any solvent or in di-*n*-butyl ether, yields of 80 percent or better were realized.

Tetraalkoxysilanes, hexaalkoxydisiloxanes, and hexachlorodisiloxanes gave only silane when stirred with lithium aluminum hydride.[73] Schumb and Robinson[74] realized the same result when hexachlorodisiloxane was reduced with lithium aluminum hydride, lithium hydride, sodium borohydride or sodium hydride, none of the desired disiloxane being

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[71] H. Gilman and C. G. Brannen, *J. Am. Chem. Soc.*, *73*, 4640 (1951).

[72] H. Westermark, *Acta Chem. Scand.*, *8*, 1830 (1954).

[73] G. Fritz, *Z. Naturforsch.*, *10b*, 423 (1955).

[74] W. C. Schumb and D. Robinson, *J. Am. Chem. Soc.*, *77*, 5294 (1955).

encountered. Reduction of 1,3-diphenyldisiloxane with lithium aluminum hydride gave phenylsilane in good yields.[75]

Two quite recent publications report redistribution during reduction of halosilanes with aluminum-containing hydrides. Goodspeed and Sanderson[76] obtained a mixture of di-, tri-, and tetramethylsilane from the reaction of dimethyldichlorosilane and aluminum borohydride. When a mixture of diethylaluminum hydride, triethylaluminum and silicon tetrafluoride was heated for one hour at 260°, the products were mono-, di-, and triethylsilane.[77] Tetrachloro- and tetraalkoxysilanes gave similar products.

Grignard reagents themselves can function as the reducing agents in certain cases. Cusa and Kipping reported that treatment of phenyltrichlorosilane with an excess of cyclohexylmagnesium bromide gave dicyclohexylphenylsilane as the sole product.[78] That steric hindrance toward introduction of a third cyclohexyl group was the determining factor has been demonstrated more recently. It was found that isopropyl-

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[75] M. C. Harvey, W. H. Nebergall, and J. S. Peake, ibid., 79, 1437 (1957).

[76] N. C. Goodspeed and R. T. Sanderson, J. Inorg. Nuclear Chem., 2, 266 (1956).

[77] Kali-Chemie A.-G., British Patent 781,533. Aug. 21, 1957. [Original not available for examination; abstracted in C. A., 52, 2049 (1958)].

[78] N. W. Cusa and F. S. Kipping, J. Chem. Soc., 1040 (1933).

magnesium chloride, cyclopentylmagnesium bromide or _tert_-butylmagnesium bromide gave dialkylphenylsilanes and the corresponding alkene with phenyltrichlorosilane.[79]

Harvey, _et al._,[75] in a study of the reaction of 1,3-diphenyldisiloxane with alkyl, aryl or aralkyl Grignard reagents, found that the Si-O-Si linkage was reductively cleaved. With methylmagnesium iodide, the products were phenylsilane and methylphenylsilane; with ethylmagnesium bromide, phenylsilane and ethyl phenylsilane were isolated. Using phenylmagnesium bromide or benzylmagnesium chloride, analogous products were obtained. They postulate initial reaction between the silane and Grignard reagent to form a trisubstituted disiloxane and a magnesium halohydride. The halohydride then cleaves the Si-O-Si linkage in either of two ways to give the products isolated.

By disproportionation or redistribution In 1867, Friedel and Ladenburg[80] reported that upon passage of hydrogen chloride over elemental silicon at elevated temperatures a mixture of silicon tetrachloride and silicochloroform was formed. Stock and Somieski[40] obtained chlorosilane, dichlorosilane and trichlorosilane when silane and hydrogen chloride were admixed and heated to 200°. Investigating the use of

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[79] M. C. Harvey, W. H. Nebergall, and J. S. Peake, _J. Am. Chem. Soc._, _79_, 2762 (1957).

[80] C. Friedel and A. Ladenburg, _Ann._, _143_, 118 (1867).

catalysts, they found that aluminum chloride converted a mixture of dichlorosilane and silane to chlorosilane in good yields below 100°. The explosive nature of these mixtures, however, militated against extensive use of these reactions.

In 1945, it was found that metallic aluminum or zinc catalyzed redistribution reactions between chlorosilanes and hydrogen gas at 350-450°.[81] Silicon tetrachloride and hydrogen gave good yields of di- and trichlorosilane while from silicochloroform under the same conditions, silane, chlorosilane and dichlorosilane could be prepared. Methyltrichlorosilane, hydrogen and aluminum at 450° gave methyldichlorosilane.[81]

Dimethyl cyanamide, at temperature above 150°, was effective in converting trichlorosilane to dichlorosilane,[82] or ethyldichlorosilane to ethylchlorosilane.[83] Pretreatment of the cyanamide with a Lewis acid, such as BF_3, $AlCl_3$, or $TiCl_4$, had the two-fold effect of reducing the temperature necessary for the redistribution and increasing the yields.[84]

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[81] D. T. Hurd, J. Am. Chem. Soc., 67, 1545 (1945).

[82] D. L. Bailey and G. H. Wagner, U. S. Patent 2,732,280. Jan. 24., 1956. [Original not available for examination; abstracted in C. A., 50, 12097 (1956)].

[83] D. L. Bailey and G. H. Wagner, U. S. Patent 2,732,281. Jan. 24, 1956. [Original not available for examination; abstracted in C. A., 50, 12097 (1956)].

[84] D. L. Bailey and G. H. Wagner, U. S. Patent 2,732,282. Jan. 24, 1956. [Original not available for examination; abstracted in C. A., 50, 12097 (1956)].

Nitriles have a catalytic effect on the same redistributions but temperatures above 150° are necessary. Aluminum chloride effected a 15 percent conversion of trichlorosilane to dichlorosilane at 400°;[85] while basic catalysts, such as tertiary amines, accomplished essentially the same results at temperatures below 50°.[86] With the availability of these chlorosilanes on a commercial basis, the preparation of various organosilicon hydrides via Grignard reactions discussed earlier should become possible on a larger scale.

Aluminum chloride also catalyzes the rearrangement of alkylchlorosilanes. A mixture of trialkylchlorosilane, dialkyldichlorosilane and dialkylsilane was obtained when a trialkylsilane and a dialkyldichlorosilane were heated together in the presence of aluminum chloride.[69,87] A recent patent[88] describes the conversion of dialkylchlorosilanes to dialkyl- and dialkyldichlorosilanes and it has been reported that simple distillation of the lower boiling compounds of the

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[85] C. E. Erickson and G. H. Wagner, U. S. Patent 2,735,861. Feb. 21, 1956. [Original not available for examination; abstracted in C. A., 50, 13986 (1956)].

[86] General Electric Co., British Patent 761,205. Nov. 15, 1957. [Original not available for examination; abstracted in C. A., 51, 10559 (1957)].

[87] F. C. Whitmore, E. W. Pietrusza, and L. H. Sommer, J. Am. Chem. Soc., 69, 2108 (1947).

[88] S. N. Borisov, B. N. Dolgov, and M. G. Voronkov, U.S.S.R. Patent 106,223. July 25, 1957. [Original not available for examination; abstracted in C. A., 51, 16516 (1957)].

type R_aSiHX_{3-a} results in fair yields of R_aSiH_{4-a} compounds.[69] Alkoxysilanes redistribute in the presence of alkali metal alkoxides below 50°.[89,90]

Compounds of the type R_aSiHX_{3-a} are formed in low yields when vapors of alkyl or aryl halides are passed over silicon or a silicon alloy at elevated temperatures. This mode of preparation was first reported by Rochow[91] and has been extended and expanded by others.[92-94] That this type of reaction is complex has been demonstrated during several independent studies in which it was found that tetraalkylsilanes give complex mixtures of silane, olefins and hydrocarbons, in addition to small amounts of trialkylsilanes, at 600° in the

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[89] D. L. Bailey, U. S. Patent 2,723,983. Nov. 15, 1955. Original not available for examination; abstracted in C. A., 50, 10125 (1956) .

[90] D. L. Bailey, U. S. Patent 2,745,860. May 15, 1956. Original not available for examination; abstracted in C. A., 51, 2021 (1957) .

[91] E. G. Rochow, J. Am. Chem. Soc., 67, 963 (1945).

[92] R. N. Lewis, ibid., 69, 717 (1947).

[93] R. Okawara and M. Sakiyama, Bull. Chem. Soc. Japan, 29, 236 (1956).

[94] A. D. Petrov, N. P. Smetankina, and G. I. Nikishin, Zhur. Obschei Khim., 25, 2332 (1955). Original available but not translated; translated in J. Gen. Chem. U.S.S.R., 25, 2305 (1955); abstracted also in C. A., 50, 9280 (1956) .

absence of any catalyst.[95,96] Furthermore, it has been reported that diphenylsilane disproportionates into silane, phenylsilane, triphenylsilane and tetraphenylsilane at 100° in the presence of a platinum catalyst while temperatures above 230° will cause the same disproportionation in the absence of any added catalyst.[97] It would be interesting to consider whether many other organosilicon hydrides may redistribute in the absence of added catalysts, provided their decomposition temperatures are not too low.

Reactions

With metals and organometallic compounds Some of the reactions of organosilicon hydrides with metals have already been discussed in preceding sections. Benkeser, *et al.*[29] and Smith[19] reported that trialkylsilanes and sodium-potassium alloy in diethyl ether did not react. In ethylamine, ethyl(triethylsilyl)amine was isolated from the reaction between lithium and triethylsilane.[15]

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[95] G. Fritz and B. Raabe, *Z. anorg. u. allgem. Chem.*, *286*, 149 (1956).

[96] B. N. Dolgov, G. V. Golodnikov, and N. E. Glushkova, *Zhur. Obshchei Khim.*, *26*, 1688 (1956). [Original available but not translated; translated in *J. Gen. Chem. U.S.S.R.*, *26*, 1893 (1956); also abstracted in *C. A.*, *51*, 1828 (1957)].

[97] H. Gilman and D. H. Miles, *J. Org. Chem.*, *23*, 326 (1958).

The solvent plays an important role in the reaction between triphenylsilane and alkali metals. Triphenylsilylpotassium is formed from triphenylsilane and sodium-potassium alloy in diethyl ether and can be derivatized with various reagents;[29] but with lithium, a 21 percent yield of hexaphenyldisilane is realized.[98] Sodium and triphenylsilane in liquid ammonia gave hexaphenyldisilazane in high yields,[99] while in ethylamine, Milligan and Kraus[100] were able to prepare tris(triphenylgermyl)silyllithium from tris(triphenylgermyl)silane and lithium. Already mentioned have been the reactions of phenyl- and diphenylsilane and tribenzylsilane with sodium-potassium alloy in diethyl ether to give tetrasubstituted silanes and inorganic material.[27,28]

Reaction of the silicon-hydrogen bond with organometallic compounds is dependent on the solvent and the particular organosilicon hydride used. Generally, an organosilicon hydride and an organolithium reagent will give the tetrasubstituted product in diethyl ether[30-32,41,42,75] but in low boiling petroleum ether, the last hydrogen is not replaced upon treatment with an organolithium compound.[30,41,42]

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[98] H. Gilman and G. E. Dunn, J. Am. Chem. Soc., 73, 5077 (1951).

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

[100] J. G. Milligan and C. A. Kraus, ibid., 72, 5297 (1950).

Grignard reagents do not react at all with the silicon-hydrogen bond of silanes in petroleum ether, xylene or p-dioxane.[32] Until last year, there has not been reported any reaction in diethyl ether,[31,32,41] but Harvey, et al.[75] have since isolated products from the reaction of 1,3-diphenyldisiloxane which indicate initial replacement of one hydrogen by the anion of a Grignard reagent. Gilman and Zueck[101] realized fair yields of diphenyl- and triphenylsilane from phenyl- and diphenylsilane, respectively, after extended reflux with phenylmagnesium bromide in ether. In refluxing tetrahydrofuran, introduction of an alkyl, aryl, or aralkyl group into phenyl-, diphenyl- or triphenylsilane is extremely facile using Grignard reagents.[101]

Peake, et al.,[41] attempted to prepare tetraisopropylsilane from silane and isopropyllithium, but only the trisubstituted compound was isolated. That steric hindrance was dictating the course of reaction was borne out when tri-1-naphthylsilane was the only product obtained from the reaction of silane and excess 1-naphthyllithium.[41] Gilman and Clark[102] report that phenyllithium reacts with triisopropylsilane but they were unsuccessful in attempts to synthesize tetraisopropylsilane from triisopropylsilane and

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[101] H. Gilman and E. A. Zueck, ibid., 79, 4560 (1957).

[102] H. Gilman and R. N. Clark, ibid., 69, 1499 (1947).

isopropyllithium. When these same authors investigated the reaction of isopropyllithium with silicochloroform, diisopropylchlorosilane was formed exclusively.[102]

With carbon-carbon multiple bonds Eleven years ago, Sommer, et al.[103] first reported the addition of organosilicon hydrides to an olefinic hydrocarbon under the influence of either ultraviolet light or diacetyl peroxide. Numerous references to variations of the original reaction conditions have appeared in the literature, especially in the patent literature, since that time. Rather than attempt to list all of them, key references are given which contain good bibliographies of similar studies.

That the reaction is free radical in nature, with non-Markownikoff addition of the silyl fragment to the unsaturated linkage has been quite well established. The addition is catalyzed by peroxides,[103-105] azodinitriles,[106,107]

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[103] L. H. Sommer, E. W. Pietrusza, and F. C. Whitmore, ibid., 69, 188 (1947).

[104] J. L. Speier, R. E. Zimmerman and J. Webster, ibid., 78, 2278 (1956).

[105] E. T. McBee, C. W. Roberts and G. W. R. Puerckhauer, ibid., 79, 2326 (1957).

[106] J. Curtice, H. Gilman and G. S. Hammond, ibid., 79, 4754 (1957).

[107] R. D. Lipscomb, U. S. Patent 2,570,462. Oct. 9, 1951. [Original not available for examination; abstracted in C. A., 46, 6141 (1952)].

ultraviolet light,[108,109] Lewis acids,[110,111] and Group VIII metals[112-114] or may be carried out thermally.[115-118] The efficiency of formation and subsequent addition of the silyl free radical is dependent on the original silicon hydride. The more electron withdrawing groups attached to the silicon atom, the more facile is the generation of the radical. As

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[108] A. M. Geyer, R. N. Haszeldine, K. Leedham, and R. J. Marklow, J. Chem. Soc., 1957, 4472.

[109] A. M. Geyer and R. N. Haszeldine, Nature, 178, 808 (1956).

[110] J. L. Speier and R. E. Zimmerman, J. Am. Chem. Soc., 77, 6395 (1955).

[111] G. H. Wagner and P. W. Shafer, U. S. Patent 2,775,606. Dec. 25, 1956. [Original not available for examination; abstracted in C. A., 51, 7413 (1957)].

[112] L. H. Sommer, F. P. MacKay, O. W. Steward and P. G. Campbell, J. Am. Chem. Soc., 79, 2764 (1957).

[113] V. A. Ponomarenko, B. A. Sokolov, Kh. M. Minachev, and A. D. Petrov, Doklady Akad. Nauk S.S.S.R., 106, 76 (1956). [Original available but not translated; translated in Proc. Acad. Sci. U.S.S.R., Sec. Chem., 106, 17 (1956); also abstracted in C. A., 50, 13726 (1956)].

[114] J. L. Speier, J. A. Webster and G. H. Barnes, J. Am. Chem. Soc., 79, 974 (1957).

[115] A. J. Barry, L. DePree, J. W. Gilkey and D. E. Hook, ibid., 69, 2916 (1947).

[116] E. T. McBee, C. W. Roberts and G. W. R. Pureckhauer, ibid., 79, 2329 (1957).

[117] A. M. Geyer and R. N. Haszeldine, J. Chem. Soc., 1957, 1038.

[118] A. N. Nesmeyanov, R. Kh. Freidlina, and E. C. Chukovskaya, Tetrahedron, 1, 248 (1957).

might be expected, the bulkier the substituents, the more difficult is the addition.[119]

In a unique study of a silyl free radical itself, Curtice *et al.*[106] found oxygen to be a very good scavenger for triphenylsilyl free radical, obtaining triphenylsilanol. In the absence of oxygen, triphenylsilyl free radicals were able to abstract the halogen of chlorobenzene, forming triphenylchlorosilane, a reaction without precedent in the study of hydrocarbon free radicals.

With alcohols The preparation of alkoxysilanes from alcohols and organosilicon hydrides is catalyzed by either acid or base. Ruff and Albert[120] obtained tetraalkoxysilanes from trifluorosilane and aliphatic alcohols, the H_2SiF_6 formed during the reaction catalyzing the reaction of the silicon-hydrogen bond. Havill, *et al.*,[121] were able to isolate trialkoxysilanes when the reaction between silicochloroform and alcohols was cooled to 0°, but upon warming of the mixture to room temperature, the tetraalkoxy compounds were isolated.[122]

In a more comprehensive study, it has been reported that in the presence of alkali metal alkoxides the rate of reaction

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[119] C. A. Burkhard and R. H. Krieble, *J. Am. Chem. Soc.*, *69*, 2687 (1947).

[120] O. Ruff and K. Albert, *Ber.*, *38*, 53 (1905).

[121] M. E. Havill, I. Joffe, and H. W. Post, *J. Org. Chem.*, *13*, 280 (1948).

[122] I. Joffe and H. W. Post, *ibid.*, *14*, 421 (1949).

between trialkylsilanes and alcohols was dependent on several factors.[123] The velocity of the reaction decreased as the length of the alkyl groups attached to silicon increased or as branching of the alkoxy group became greater. The alkali metal involved also affected the course of reaction. With lithium alkoxides, only primary alcohols reacted with trisubstituted silanes while secondary alcohols reacted slowly if sodium alkoxides were used. Potassium alkoxides increased the rate of reaction of both primary and secondary carbinols while rubidium alkoxides would even catalyze the reaction of tertiary alcohols with trisubstituted silicon hydrides.[123] Pyridine has been reported to catalyze the reaction between triphenylsilane and some primary alcohols, but failed with allyl alcohol, _tert_-butyl alcohol, or di- and triphenylmethanol.[124]

In a recent publication, metallic copper was reported to catalyze the stepwise reaction of alkoxy groups with phenylsilane in yields of 20 to 30 percent;[125] although, in light

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[123] B. N. Dolgov, N. P. Kharitonov, and M. G. Voronkov, _Zhur. Obshchei Khim_, _24_, 1178 (1954). [Original available but not translated; translated in _J. Gen. Chem. U.S.S.R._, _24_, 1169 (1954); also abstracted in _C. A._, _49_, 12275 (1955)].

[124] H. Gilman, G. E. Dunn, H. Hartzfeld, and A. G. Smith, _J. Am. Chem. Soc._, _77_, 1287 (1955).

[125] W. S. Miller, J. S. Peake, and W. H. Nebergall, _ibid._, _79_, 5604 (1957).

of the low yields, it may well be that a small amount of cupric oxide was the actual catalyst.

With compounds that are easily reduced Reducing properties of the Si-H bond have been known for a long time but very little use has been made of this information. Buchner[126] first reported that silane reduced silver nitrate to metallic silver in aqueous solutions. Later, Stock and Somieski[127] found that silane reduced Fe(III), Cu(II) and Hg(II) to Fe(II), Cu(I) and Cu(0) and Hg(I) and Hg(0), respectively. Silicochloroform is able to reduce various reagents such as CrO_3, SO_3, SO_2, As(III), and Sb(III).[128,129] Eaborn has reported the reduction of silver perchlorate[130] and silver isothiocyanate[131] by trialkylsilanes, metallic silver being deposited during the reactions.

Organic carbonyl compounds are reduced to alcohols by silanes. Jenkins and Post[132] found trisubstituted silanes were able to reduce benzoyl chloride and substituted benzoyl

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[126] G. Buchner, Ber., 18, 317 (1885).

[127] A. Stock and C. Somieski, ibid., 49, 111 (1916).

[128] O. Ruff and K. Albert, ibid., 38, 2222 (1905).

[129] A. Besson and L. Fournier, Compt. rend., 148, 1192 (1909).

[130] C. Eaborn, J. Chem. Soc., 1955, 2517.

[131] C. Eaborn, ibid., 1950, 3077.

[132] J. W. Jenkins and H. W. Post, J. Org. Chem., 15, 556 (1950).

chlorides to benzaldehyde and substituted benzaldehyde derivatives. Irradiation of a mixture of acetone and silicochloroform or triphenylsilane gave isopropyl alcohol upon hydrolysis,[133] while phenyl-, diphenyl- and triphenylsilane are all able to reduce benzophenone to diphenylcarbinol.[134] Nitzsche and Wick[135] report that 1,3-dimethyldisiloxane, in the presence of catalytic amounts of dibutyltin dilaurate, is an active reducing agent at room temperature, being capable of reducing carbonyl groups to alcohols and nitro compounds to amines. Under the same conditions, however, olefinic double bonds were not affected.[135] 10-Ethylphenothiazine-5-oxide is reduced to 10-ethylphenothiazine upon being heated to 250° with diphenylsilane.[136]

Organosilicon hydrides are rapidly converted to halosilanes upon treatment with iodine, bromine or

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[133] R. Calas and N. Duffaut, Compt. rend., 245, 906 (1957).

[134] H. Gilman and D. Wittenberg, J. Org. Chem., 23, 501 (1958).

[135] S. Nitzsche and M. Wick, Angew. Chem., 69, 96 (1957).

[136] D. Wittenberg, H. A. McNinch and H. Gilman, J. Am. Chem. Soc., 80, in press (1958).

chlorine.[64,137-139]

With acids and bases The reaction of organosilicon hydrides with hydrohalic acids has been well documented, replacement of one or more hydrogens being possible.[35,40,140,141] A study of the reaction mechanism indicates initial formation of a pentacovalent intermediate, and removal of the hydrogen by an oxonium ion in the rate determining step.[142,143]

Basic hydrolysis of organosilicon hydrides also proceeds through a pentacovalent intermediate, as proposed by Swain, *et al.*,[144] to give silanols or disiloxanes. Price[145] studied the kinetics of hydrolysis of trialkylsilanes in aqueous alcoholic potassium hydroxide and found the rate of hydrogen

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[137] D. R. Deans and C. Eaborn, *J. Chem. Soc.*, *1954* (3169).

[138] M. G. Voronkov and Yu. I. Khudobin, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, *1956*, 805. [Original available but not translated; translated in *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.*, *1956*, 823; also abstracted in *C. A.*, *51*, 3440 (1957)].

[139] H. Rosenberg and C. Tamborski, Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio. Information on the preparation of trialkylhalosilanes. Private communication. 1956.

[140] H. J. Emeléus and L. E. Smythe, *J. Chem. Soc.*, *1958*, 609.

[141] A. Stock and C. Somieski, *Ber.*, *52*, 695 (1919).

[142] A. Taketa, M. Kumada, and K. Tarama, *Bull. Inst. Chem. Res., Kyoto Univ.*, *31*, 260 (1953).

[143] J. E. Baines and C. Eaborn, *J. Chem. Soc.*, *1956*, 1436.

[144] C. G. Swain, R. M. Esteve, Jr., and R. H. Jones, *J. Am. Chem. Soc.*, *71*, 965 (1949).

[145] F. P. Price, *ibid.*, *69*, 2600 (1947).

evolution decreased as the alkyl groups became longer or more branched. The same conclusions were reached by Baines and Eaborn.[146] Gilman and Dunn[147] investigated the hydrolysis of substituted triphenylsilanes and found that electron withdrawing groups in the *para* position accelerated the liberation of hydrogen in wet piperidine whereas electron donating substituents reduced the rate.

The reaction of triphenylsilane and base has also been studied via the isotope effect. Kaplan and Wilzbach[148,149] report a k_H/k_D ratio of 1.15, while Brynko, *et al.*[150] favor a value of 1.41. The disagreement is one of magnitude, both investigations confirming that breaking of the Si-H bond occurs during the rate determining step.

Metal amides also react with trisubstituted silanes, disilazanes being formed when unsubstituted amides are used,[15] whereas N,N-dialkylsilazanes are isolated if dialkylamides are

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[146] J. E. Baines and C. Eaborn, *J. Chem. Soc.*, *1955*, 4023.

[147] H. Gilman and G. E. Dunn, *J. Am. Chem. Soc.*, *73*, 3404 (1951).

[148] L. Kaplan and K. E. Wilzbach, *ibid.*, *74*, 6152 (1952).

[149] L. Kaplan and K. E. Wilzbach, *ibid.*, *77*, 1297 (1955).

[150] C. Brynko, G. E. Dunn, H. Gilman and G. S. Hammond, *ibid.*, *78*, 4909 (1956).

employed.[151] Kipping and Sands[152] found that organic bases, such as piperidine or pyridine, reacted also with organosilicon hydrides upon gentle heating, hydrogen being evolved, and used the reaction as a qualitative test for the organosilicon hydrides they prepared.

The rate of hydrogen evolution in all of these reactions with acids and bases is dependent on the particular organosilicon hydride involved. Silane itself explodes in the presence of moisture, and monosubstituted silanes, while not explosive, react too rapidly with bases for the rate to be studied kinetically. As the degree of substitution increases, rates decrease and a comparison of Price's data[145] with Gilman and Dunn's[147] indicates that trialkylsilanes react more slowly than do triarylsilanes. This implies electronic variations in the Si-H bond from compound to compound. If such is the case, the infrared spectra of these compounds should reveal a shift in the Si-H absorption frequency dependent on the degree and type of substitution.

That such an investigation has not been reported is attributable to the fact that no one has had a large number of the compounds to compare. West and Rochow[50] published the

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

[152] F. S. Kipping and J. E. Sands, *J. Chem. Soc.*, *119*, 848 (1921).

spectra of eight disubstituted silanes, wherein the Si-H bond absorbs between 4.77 and 4.80 μ if both substituents are alkyl, and between 4.72 and 4.77 μ if they are both aromatic. Nine mono-, di- and trisubstituted silanes, prepared by Kaye and Tannenbaum,[62] had absorption frequencies between 4.7 and 4.8 μ. In a more recent article, Kaplan[153] reported that triphenylsilane absorbs at 2135 cm^{-1} (4.68 μ) while tri-n-propylsilane absorbs at 2108 cm^{-1} (4.74 μ).

The only attempt to date to correlate absorption frequency with chemical constitution was made by Batuev, et al.,[154] who studied the isomeric silanes, n-hexyl- (2152 cm^{-1}, 4.65 μ) di-n-propyl- (2127 cm^{-1}, 4.70 μ), and triethylsilane (2098 cm^{-1}, 4.77 μ). They proposed that as the number of hydrogen atoms attached to a silicon atom decreases, there is a decrease in bond energy and a concomitant increase in bond length between the silicon and the remaining hydrogen or hydrogens. The effect of branched alkyl groups or aromatic substituents was not reported.

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[153] L. Kaplan, J. Am. Chem. Soc., 76, 5880 (1954).

[154] M. I. Batuev, A. D. Petrov, V. A. Ponomarenko and A. D. Matveeva, Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk, 1243 (1956). [Original available but not translated; translated in Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., 1269 (1956); abstracted also in C. A., 51, 5555 (1957)].

EXPERIMENTAL

All reactions involving organometallic reagents or lithium aluminum hydride were carried out under an atmosphere of dry, oxygen-free nitrogen. The glassware used for the reactions was dried in an oven at 110° and assembled while hot as nitrogen was passed through the system.

Common solvents used with organometallic reagents or lithium aluminum hydride were of commercially available "reagent" grade and had been dried over sodium wire at least 72 hr. before use. Ethylene glycol dimethyl ether was refluxed over sodium metal under nitrogen until, upon addition of a small amount of benzophenone, the blue color of benzophenone ketyl persisted. Tetrahydrofuran was refluxed over sodium metal for at least 24 hr. and distilled from lithium aluminum hydride immediately prior to use, a nitrogen atmosphere being maintained throughout the drying operation.

The infrared data cited were obtained on a Baird, model B, recording spectrophotometer if reported in microns (μ). If recorded in reciprocal centimeters (cm.$^{-1}$), the values were obtained on a Perkin-Elmer, model 112, photometer.

All melting points and boiling points are uncorrected and molar refractions were calculated using the bond refraction values of Vogel, et al.[155,156]

Trialkylgermylmetallic Compounds

The *n*-butyl-, benzyl-, and 2-biphenylyltriethylgermane, prepared as reference compounds, were analyzed for germanium by the following procedure: 0.2 g. of the sample in a Vycor glass crucible was treated with 20 drops of concentrated sulfuric acid and 5 drops of fuming nitric acid. The crucible was then heated cautiously with a Rogers ring burner in the manner used in silicon analyses.[151] When all acid was gone, the oxide was ignited to constant weight with a Bunsen burner.

Tetraethylgermane

The technique of Kraus and Flood[6] was used to prepare this starting material, employing ethylmagnesium bromide and germanium tetrabromide in ether. In nine preparations, the yields varied from 35 to 80% of the theoretical. In later preparations of the tetrasubstituted compound, hexaethyldigermane, b.p. 61-62° (0.007 mm.), n_D^{20} 1.4960, was isolated in 8% yield also.

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[155] A. I. Vogel, W. T. Cresswell, and J. Leicester, *J. Phys. Chem.*, *58*, 174 (1954).

[156] A. I. Vogel, W. T. Cresswell, G. H. Jeffrey, and J. Leicester, *J. Chem. Soc.*, *1952*, 514.

Utilizing germanium tetrachloride rather than the tetrabromide did not change the yield of products appreciably. However, ethyllithium and germanium tetrabromide, used in hopes of increasing the yield of the digermane, gave low yields of both tetraethylgermane (12%) and hexaethyldigermane (8.6%), in addition to a large amount of polymeric material.

Triethylgermane

This compound was prepared by the reduction of triethylchlorogermane with lithium aluminum hydride, a procedure recently published by Anderson.[157] The method of work-up was slightly different than that reported and yields were somewhat lower.

n-Butyltriethylgermane

To a stirred solution of 5.6 g. (0.029 mole) of triethylchlorogermane in ether was added 0.032 mole of *n*-butyllithium.[158] A white solid appeared suspended in the liquid shortly

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[157] H. H. Anderson, *J. Am. Chem. Soc.*, *79*, 326 (1957).

[158] H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, *ibid.*, *71*, 1499 (1949).

after addition was begun and heat was evolved. After addition was complete, the mixture was stirred overnight.

Hydrolysis was effected with ice-water and the aqueous layer was separated and extracted three times with ether before being discarded. Distillation of the organic material, after drying over sodium sulfate, afforded 3.93 g. of crude product, b.p. 175-182°. Redistillation gave 3.21 g. (51.1%) of pure n-butyltriethylgermane, b.p. 181-181.5°, n_D^{20} 1.4475.

Anal. Calcd. for $C_{10}H_{24}Ge$: Ge, 33.51. Found: Ge, 33.28.

Benzyltriethylgermane

To a stirred solution of 5.8 g. (0.03 mole) of triethylchlorogermane in ether was added 0.033 mole of benzylmagnesium chloride. A solid formed and a small amount of heat was generated during the addition. Work-up as described above, followed by two distillations of the crude product, resulted in the isolation of 5.94 g. (79%) of benzyltriethylgermane, b.p. 78-81° (1.0 mm.), n_D^{20} 1.5178.

Anal. Calcd. for $C_{13}H_{22}Ge$: Ge, 28.97. Found: Ge, 29.15.

2-Biphenylyltriethylgermane

As 11.5 g. (0.059 mole) of triethylchlorogermane in ether was stirred, an ethereal solution of 0.067 mole of 2-biphenylyllithium was added at such a rate as to maintain gentle reflux. The mixture was stirred for 12 hr. after addition was complete.

After hydrolysis with water, the aqueous layer was separated, extracted four times with ether and discarded. Distillation of the dried organic material gave 12.54 g. of crude product, b.p. 145-149° (2.5 mm.). Redistillation afforded 11.5 g. (62.4%) of 2-biphenylyltriethylgermane, b.p. 150-152° (3.3 mm.), n_D^{20} 1.5697.

Anal. Calcd. for $C_{18}H_{24}Ge$: Ge, 23.20. Found: Ge, 23.06, 23.00.

Metalation of triethylgermane

With *n*-butyllithium To a stirred solution of 8 g. (0.05 mole) of triethylgermane in ether was added 0.05 mole of *n*-butyllithium.[158] After 7 hr. at reflux, the solution exhibited a positive Color Test I[8] and a negative Color Test II.[159] Addition of an ethereal solution of 9.5 g. (0.075 mole) of

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

benzyl chloride caused gentle refluxing. Hydrolysis was effected with 50 ml. of a saturated ammonium chloride solution. Three distillations of the organic material remaining after the usual work-up gave 0.76 g. (6.1%) of benzyltriethylgermane, b.p. 138-140° (15 mm.), n_D^{20} 1.5181.

In a second run using 0.034 mole of triethylgermane and essentially the same conditions, the yield of benzyltriethylgermane was 5.7%.

With phenyllithium After 0.022 mole of triethylgermane in ether and 0.03 mole of phenyllithium had been stirred at gentle reflux for 7 hr., the mixture was cooled and 2.87 g. (0.023 mole) of benzyl chloride in ether added. After stirring for 12 hr., Color Test I[8] was negative. Hydrolysis, work-up, and distillation of the organic material afforded 0.1 g. of impure benzyltriethylgermane, b.p. 82-86° (2.6 mm.), n_D^{20} 1.5202.

Cleavage of tetraethylgermane with lithium wire

In ethylene glycol dimethyl ether Seven attempts to cleave tetraethylgermane were made using lithium wire in ethylene glycol dimethyl ether. Variations in time and temperature, as well as the use of compounds as initiators which have been useful in similar reactions, were studied. In all but the last run, the reaction mixture was hydrolyzed with a saturated ammonium chloride solution, the expected product being triethylgermane. In the seventh reaction, triphenylchlorosilane was added as derivatizing agent. None of the reactions gave the expected product and all but the last resulted in moderate to high recovery of starting material.

In a typical reaction, 5 ml. (4.9 g., 0.026 mole) of tetraethylgermane, 5 ml. of ethylene glycol dimethyl ether and 20 cm. (0.66 g., 0.094 g. atom) of finely cut lithium wire were stirred. If bromobenzene, ethyl bromide or tetrahydrofuran was employed as an initiator, 0.5 ml. was added during the first 30 min., as well as an additional 20 ml. of solvent. Color Test I[8] was taken at regular intervals and was usually negative. Toward the end of the extended cleavage reactions, the Color Test was sometimes weakly positive, possibly indicative of the formation of triethylgermyllithium and ethyllithium; but in the light of the high recovery of starting material, the positive test could also have been due to the presence of finely subdivided lithium metal which is known to give a weak Color Test I.

The results are summarized in Table 1.

In tetrahydrofuran A mixture of 5 ml. (4.9 g., 0.026 mole) of tetraethylgermane, 25 cm. (0.75 g., 0.11 g. atom) of finely cut lithium wire and 5 ml. of tetrahydrofuran was stirred for one hour, at which time Color Test I[8] was negative and the liquid grey in color. The mixture was refluxed

Table 1. Cleavage of tetraethylgermane with lithium wire in ethylene glycol dimethyl ether

Run	Initiator	Reaction time, hr.	Temp., °C.	Derivatizing agent	Recovery of Et_4Ge, %
1	---	8	25	H_2O	72
2	---	12	80	H_2O	72
3	---	48	80	H_2O	35
4	tetrahydrofuran	8	80	H_2O	70
5	bromobenzene	30	80	H_2O	72
6	ethyl bromide	30	80	H_2O	50
7	---	60	80	$(C_6H_5)_3SiCl$	0

for 96 hr. after an additional 45 ml. of solvent had been added.

Although the Color Test was still negative, the mixture was filtered through a glass-wool plug into another flask and 5 g. (0.04 mole) of benzyl chloride added. After hydrolysis and work-up as above, distillation afforded a near quantitative recovery of starting material.

Cleavage of tetraethylgermane with lithium dispersion

A mixture of 5 ml. (4.9 g., 0.026 mole) of tetraethylgermane, 40 ml. of xylene and 0.38 g. (0.055 g. atom) of lithium contained in 1.27 g. of a lithium dispersion in xylene (courtesy of Lithium Corporation of America) was stirred for 4 days at room temperature. A brown color developed in the solution during this time.

Addition of excess n-butyl bromide caused gentle refluxing. Following hydrolysis with water and the usual work-up, distillation failed to yield any identifiable material.

Cleavage of tetraethylgermane with sodium-potassium alloy

In the absence of any solvent A mixture of 5 ml. (4.9 g., 0.026 mole) of tetraethylgermane and 4 ml. (0.08 g. atom of potassium) of sodium-potassium alloy was stirred for 48 hr. A blue-grey color developed during the first hour and persisted throughout. An ethereal solution of 8.25 g. (0.06 mole) of n-butyl bromide was added to derivatize. Refluxing was vigorous during the addition. Mercury was added to amalgamate the unreacted alloy and the organic material was decanted into water to effect hydrolysis. Following the usual work-up, distillation of the dried organic material resulted in the recovery of 0.41 g. (8.4%) of tetraethylgermane. No n-butyltriethylgermane was isolated.

In ether Five attempts to cleave tetraethylgermane with sodium-potassium alloy were made using ether as the solvent. The time and temperature were varied and bromobenzene was employed in one run as an initiator. None of the various fractions of liquids or solids obtained upon work-up of the reaction mixtures could be identified, nor was starting material recovered. Various colors were noticed during the cleavages and it is possible that triethylgermylpotassium was formed but immediately reacted in some unknown manner with the solvent.

In a typical experiment, 5 ml. (4.9 g., 0.026 mole) of tetraethylgermane, 4 ml. (0.08 g. atom of potassium) of sodium-potassium alloy and 5 ml. of solvent were stirred. An additional 30 ml. of solvent and 0.5 ml. of initiator, when employed, were added within the first 0.5 hr. after stirring was begun. The reaction was terminated by amalgamation of the unreacted alloy, decantation of the organic material and addition of an ethereal solution of the derivatizing agent. Work-up was as described above.

The experimental conditions are summarized in Table 2.

In ethylene glycol dimethyl ether The experimental quantities used were the same as those used when ether was the solvent. In runs 7 and 8, excess n-butyl bromide was added as the derivatizing agent before amalgamation of the unreacted alloy. Once again, none of the various fractions obtained upon distillation of the organic material could be identified.

The experimental details are summarized in Table 2.

Table 2. Cleavage of tetraethylgermane with sodium-potassium alloy

Run	Solvent	Initiator	Reaction time, hr.	Temp. °C.	Derivatizing agent
1	Et_2O	---	1	25	$(C_6H_5)_3SiCl$
2	Et_2O	---	24	25	$(C_6H_5)_3SiCl$
3	Et_2O	---	36	35	H_2O
4	Et_2O	---	72	25	$(C_6H_5)_3SiCl$
5	Et_2O	bromobenzene	12	25	$(C_6H_5)_3SiCl$
6	GDME[a]	---	144	85	H_2O
7	GDME	bromobenzene	108	25	n-C_4H_9Br
8	GDME	bromobenzene	48	85	n-C_4H_9Br
9	GDME	bromobenzene	96	85	H_2O
10	Et_3N	---	2.5	25	n-C_4H_9Br
11	Et_3N	---	2	25	$(C_6H_5)_3SiCl$
12	Et_3N	---	2	25	$(C_6H_5)_3GeCl$
13	Et_3N	---	72	25	n-C_4H_9Br
14	THF[b]	---	2	25	n-C_4H_9Br
15	THF	---	96	65	$C_6H_5CH_2Cl$
16	THF	---	1	-10	n-C_4H_9Br

[a] Ethylene glycol dimethyl ether.

[b] Tetrahydrofuran.

In triethylamine In four attempts to cleave tetraethylgermane with sodium-potassium alloy, 5 ml. (4.9 g., 0.026 mole) of the germane, 4 ml. (0.08 g. atom of potassium) of alloy and 5 ml. of triethylamine were stirred at room temperature. The reactions were terminated by amalgamation of the unreacted alloy, decantation of the organic material, and the addition of an ethereal solution of the derivatizing agent to it. No product containing a triethylgermyl group could be isolated from any of the reactions.

The experimental conditions are summarized in Table 2.

In tetrahydrofuran This solvent was used in three attempts to prepare triethylgermylpotassium from tetraethylgermane. The same quantities of reactants and solvent were used as with the other solvents. In run 16, the reaction mixture was maintained at -10°, the melting point of the alloy, for 1 hour before being worked up. In all three runs, no identifiable materials were isolated, indicating that the triethylgermylpotassium, if formed, isn't any less reactive at -10° than it is at higher temperatures.

The experimental details are summarized in Table 2.

In di-n-butyl ether A mixture of 5 ml. (4.9 g., 0.026 mole) of tetraethylgermane, 25 ml. of di-n-butyl ether, and 4 ml. (0.08 g. atom of potassium) of sodium-potassium alloy was stirred for 18 hr., a light yellow-green color developing. Heat was applied and the mixture stirred at reflux for 80 hr.

with no further color changes occurring. To the cooled mixture was added 13.7 g. (0.10 mole) of n-butyl bromide and after stirring for 15 min., enough mercury to amalgamate the unreacted alloy. The mixture was hydrolyzed with water and the organic layer worked up as usual.

Distillation of the dried liquid afforded no identifiable materials other than di-n-butyl ether.

In p-dioxane After stirring a mixture of 5 ml. (4.9 g., 0.026 mole) of tetraethylgermane and 4 ml. (0.08 g. atom of potassium) of sodium-potassium alloy in 5 ml. of p-dioxane for 12 hr., there was no evidence of reaction. No change in the solution was apparent after 20 ml. of p-dioxane was added and the mixture stirred for another 36 hr., but a light yellow color did develop after the solution had been refluxed for 24 hr. Addition of excess n-butyl bromide, hydrolysis with water, and work-up as usual resulted in the isolation of p-dioxane and six unidentified fractions weighing less than 0.5 g. apiece.

In benzene The same quantities of the germane and alloy as used above were stirred for 72 hr. in 25 ml. of benzene, a light blue color developing; and after 4 days at reflux, the solution was dark green in color. The excess alloy was amalgamated with mercury before an ethereal solution of 8.25 g. (0.06 mole) of n-butyl bromide was added. After stirring for 20 min., water was added to hydrolyze the mixture. Distillation of the dried organic material, after the usual work-up, afforded 2.55 g. (52.0% recovery) of tetraethylgermane.

In xylene Five milliliters (4.9 g., 0.026 mole) of tetraethylgermane, 4 ml. (0.08 g. atom of potassium) of sodium-potassium alloy and 25 ml. of xylene were stirred for 48 hr.; a blue color which developed after the first hour persisted throughout the cleavage period. The unreacted alloy was amalgamated with mercury and an ethereal solution of 7.6 g. (0.06 mole) of benzyl chloride added. The mixture was stirred for 15 min. before being hydrolyzed with water. Following the usual work-up, distillation afforded 3.88 g. of liquid, boiling over the range 145-150°, which appeared to be an azetrope of xylene and tetraethylgermane.

Cleavage of hexaethyldigermane with sodium-potassium alloy

A light yellow color developed after a mixture of 1.95 g. (0.006 mole) of hexaethyldigermane, 1 ml. (0.02 g. atom of potassium) of sodium-potassium alloy and 2 ml. of ethylene glycol dimethyl ether had been stirred for 1 hr. An additional 13 ml. of solvent was added and the mixture stirred for another 25 hr. with no further change being observed. The unreacted alloy was amalgamated and a solution of 2.5 g. (0.02 mole) of benzyl chloride in ethylene glycol dimethyl ether added. After hydrolysis and the usual work-up, distillation of the organic material resulted in the recovery of 0.12 g. (6.2%) of slightly impure hexaethyldigermane.

Reaction of triethylchlorogermane with lithium

In ether A mixture of 50 cm. (1.67 g., 0.236 g. atom) of lithium wire, 25 ml. of ether and 9.39 g. (0.048 mole) of triethylchlorogermane was stirred at room temperature for 72 hr. and at gentle reflux for 36 hr. Hydrolysis with a saturated ammonium chloride solution and the usual work-up, followed by reduced pressure distillation, afforded 4.61 g. (60.2%) of slightly impure hexaethyldigermane.

In tetrahydrofuran A solution of 24.68 g. (0.164 mole) of triethylchlorogermane in tetrahydrofuran was added slowly to a stirred suspension of 1 m. (3.0 g., 0.43 g. atom) of finely cut lithium wire in tetrahydrofuran. As soon as the lithium became shiny, the temperature was lowered to -50° by means of a Dry Ice-acetone bath and the addition completed.

The reaction mixture was allowed to warm slowly over a period of 6 hr. The liquid became turbid at 5° but Color Test I[8] was negative. Hydrolysis and work-up as usual, followed by distillation of the organic material, afforded 8.78 g. (16.8%) of hexaethyldigermane.

Trialkylsilylmetallic Compounds

Cleavage of hexaethyldisilane

The cleavage of this compound has been investigated previously[15,16,19] and was repeated primarily to become oriented in the field and to study the effect of tetrahydrofuran as the solvent for the cleavage.

With lithium in ether A mixture of 1 ml. of ether, 30 cm. (0.9 g., 0.13 g. atom) of finely cut lithium wire and 5 g. (0.021 mole) of hexaethyldisilane was stirred for 20 min. with no sign of reaction. Upon the addition of 20 drops of tetrahydrofuran a light blue color appeared. After stirring for another 30 min., a solution of 30 ml. of ether and 2 ml. of tetrahydrofuran was added and the mixture stirred for 23 hr. The color did not become more intense during this period.

The liquid was poured into ice-water to hydrolyze and was worked up as usual. Two distillations of the dried organic material resulted in the recovery of 3.8 g. (76%) of starting material.

With lithium in tetrahydrofuran After stirring a mixture of 5 g. (0.021 mole) of hexaethyldisilane, 30 cm. (0.9 g., 0.13 g. atom) of finely cut lithium wire and 15 ml. of tetrahydrofuran for 1 hr., there was no evidence of reaction.

The addition of 5 drops of ethyl bromide had no effect. After being stirred for an additional 48 hr., the liquid was pipetted into ice-water to hydrolyze. Work-up as usual and fractionation of the organic material resulted in the recovery of 3.62 g. (72.4%) of hexaethyldisilane.

Another run, exactly as above, except that only 10 drops of tetrahydrofuran was added initially, resulted in the isolation of 2.84 g. (56.8%) of recovered starting material.

With sodium-potassium alloy in tetrahydrofuran A blue color developed after a mixture of 5.1 g. (0.022 mole) of hexaethyldisilane and 3 ml. (0.06 g. atom of potassium) of sodium-potassium alloy had been stirred for 0.5 hr. Addition of 2 ml. of tetrahydrofuran decreased the intensity of the color and the alloy, which had appeared coated, became shiny. Another 23 ml. of tetrahydrofuran was added over the next 6 hr. and the mixture then stirred for 36 hr.

The unreacted alloy was amalgamated and the supernatant liquid pipetted into ice-water to hydrolyze. After the usual work-up, distillation of the organic material afforded 3.0 g. (60% recovery) of hexaethyldisilane.

Cleavage of trimethylphenylsilane

With lithium In the presence of ether, there was no evidence of reaction between 30 g. (0.2 mole) of trimethylphenylsilane and 80 cm. (2.8 g., 0.4 g. atom) of finely cut lithium wire. Addition of 10 drops of ethyl bromide failed to initiate reaction. Upon addition of a solution of 25 ml. of tetrahydrofuran and 50 ml. of ether, a red color developed but the bulk of the lithium remained unreacted and Color Test I[8] was negative. After refluxing for 6 hr. the liquid was filtered through glass wool and added rapidly to an ethereal solution of 25 ml. (21.4 g., 0.2 mole) of trimethylchlorosilane. Hydrolysis was effected with a saturated solution of ammonium chloride and work-up was as usual. Distillation of the dried organic material resulted in the recovery of 19.14 g. (63.8%) of starting material.

In the presence of tetrahydrofuran alone, a red color developed shortly after 7.50 g. (0.05 mole) of trimethylphenylsilane and 33 cm. (1.05 g., 0.15 g. atom) of lithium were admixed. After 48 hr., Color Test I[8] was positive but the bulk of the lithium remained unreacted. The liquid was filtered through glass wool and added rapidly to a stirred solution of 26 g. (0.1 mole) of triphenylsilane in tetrahydrofuran. The Color Test was negative after the mixture had been stirred for 6 hr., and 50 ml. of 5% hydrochloric acid was added to effect hydrolysis. The usual work-up, followed by distillation of the organic material, gave 4.80 g. (64% recovery) of starting material.

With sodium-potassium alloy When sodium-potassium alloy in tetrahydrofuran was used to cleave trimethylphenylsilane at room temperature, a brown color developed immediately. After 15 min., the alloy was amalgamated and a solution of triphenylsilane in tetrahydrofuran added. Hydrolysis, work-up as usual, and fractional crystallization of the solid obtained gave only triphenylsilanol and hexaphenyldisiloxane.

When the cleavage was carried out at -30° and the mixture derivatized by the addition of triphenylsilane in tetrahydrofuran, the results were the same.

If the cleavage mixture was cooled to -50°, at which temperature the alloy is a solid, it was possible to derivatize the phenylpotassium formed with triphenylsilane to give a 53.3% yield of tetraphenylsilane, or with trimethylchlorosilane to give a 67% yield of trimethylphenylsilane, but a derivative of the trimethylsilylpotassium formed could not be isolated.

Cleavage of triethylphenylsilane

With lithium in tetrahydrofuran Three attempts were made to cleave this compound with lithium in tetrahydrofuran, the only variation being in the derivatizing agent.

When a mixture of 9.62 g. (0.05 mole) of triethylphenylsilane, 33 cm. (1.05 g., 0.15 g. atom) of finely cut lithium wire and 5 ml. of tetrahydrofuran was stirred at room temperature, a yellow color developed, to be rapidly replaced by a dark green coloration. The liquid exhibited a positive Color Test I[8] and most of the lithium was used up.

In the first reaction, triphenylchlorosilane was added in tetrahydrofuran. Investigation of only the solid material remaining after the usual work-up resulted in the isolation of triphenylsilanol and hexaphenyldisiloxane, but no 1,1,1-triethyl-2,2,2-triphenyldisilane or tetraphenylsilane.

In the second run, ethyl bromide was added to derivatize. Work-up as usual and distillation of the organic material gave a 67.7% recovery of triethylphenylsilane. When another cleavage mixture was carbonated, no acids were obtained and distillation of the organic material resulted in the recovery of 73.1% of starting material.

<u>With sodium-potassium alloy in ether</u> A mixture of 9.62 g. (0.05 mole) of triethylphenylsilane, 3 ml. of ether and 5 ml. (0.10 g. atom of potassium) of sodium-potassium alloy was stirred, a blue-grey color developing. After 30 min., the solution was green and 25 ml. of ether was added. The mixture was stirred for an additional 2 hr. before the unreacted alloy was amalgamated. The supernatant liquid was pipetted into an addition funnel and added dropwise to 26 g. (0.1 mole) of triphenylsilane in ether. Hydrolysis was effected with a saturated ammonium chloride solution and worked up as usual.

Distillation of the organic liquid resulted in the recovery of 7.0 g. (72.8%) of starting material. No 1,1,1-triethyl-2,2,2-triphenyldisilane was isolated from the solid fraction.

In a second reaction, in which water was added as derivatizing agent, there was a 55.3% recovery of triethylphenylsilane.

<u>With sodium-potassium alloy in tetrahydrofuran</u> A solution of 9.62 g. (0.05 mole) of triethylphenylsilane in tetrahydrofuran was added to a stirred suspension of 5 ml. (0.10 g. atom of potassium) of sodium-potassium alloy in tetrahydrofuran at -50°. A green color developed, and was replaced, as addition progressed, by a black coloration. After 2 hr., the liquid was filtered through glass wool into a pre-cooled flask at -40°. A tetrahydrofuran solution of 26 g. (0.10 mole) of triphenylsilane was added slowly. After the solution had warmed to room temperature, dilute hydrochloric acid was added to effect hydrolysis.

The solid which collected at the interface was separated and recrystallized from benzene to give 14.53 g. (88.3%) of tetraphenylsilane, m.p. 231-234°. No 1,1,1-triethyl-2,2,2-triphenyldisilane could be isolated from the liquid portion after the usual work-up.

Cleavage of 2-biphenylyltrimethylsilane

With lithium in ether After a mixture of 5.66 g. (0.025 mole) of 2-biphenylyltrimethylsilane, 22 cm. (0.69 g., 0.10 g. atom) of finely cut lithium wire and 25 ml. of ether had been stirred for 2 hr., a brown color had developed. No further change was evident after an additional 14 hr. of stirring. The liquid was filtered through glass wool and hydrolyzed with water. Work-up as usual and distillation of the organic material, using an electrically-heated air oven, afforded 3.55 g. (62.7%) of starting material but no hexamethyldisiloxane.

With lithium in ethylene glycol dimethyl ether All of the lithium had reacted and the solution was green after a mixture of 5.66 g. (0.025 mole) of 2-biphenylyltrimethyl silane, 10 ml. of ethylene glycol dimethyl ether and 16.5 cm. (0.50 g., 0.75 g. atom) of finely cut lithium wire had been stirred for 1 hr. at room temperature. The mixture was hydrolyzed with water and worked up as usual. Distillation of the dried organic material using an electrically-heated air-oven afforded no hexamethyldisiloxane. Three and four-tenths grams (60%) of starting material was recovered.

With sodium-potassium alloy in ether A mixture of 11.31 g. (0.05 mole) of 2-biphenylyltrimethylsilane, 5 ml. of ether and 5 ml. (0.10 g. atom of potassium) of sodium-potassium alloy was stirred at room temperature. Over the first hour, 20 ml. of ether was added and a light green color developed. After an additional 3 hr., the solution became quite viscous so 75 ml. more of solvent was added. The unreacted alloy was amalgamated and the black solution decanted into another flask and hydrolyzed with water.

Following the usual work-up, distillation of the organic material using an electrically-heated air-oven afforded a 47.7% recovery of starting material but no hexamethyldisiloxane.

Cleavage of 2-biphenylyltriethylsilane with lithium in tetrahydrofuran

Within 5 min. after stirring was begun, a green color had developed in a mixture of 25 ml. of tetrahydrofuran, 33 cm. (1 gm., 0.15 g. atom) of finely cut lithium wire and 13.42 g. (0.05 mole) of 2-biphenylyltriethylsilane. An additional 25 ml. of tetrahydrofuran was added and the mixture stirred for 45 min. The small amount of lithium remaining was removed and water added to effect hydrolysis. Work-up as usual and distillation of the organic material using an electrically-heated air-oven gave 9.02 g. (67%) of recovered starting material.

In another run, similar to the one above except the mixture was stirred for 5 hr., at which time all of the lithium had been used up, resulted in a 70% recovery of starting material.

Cleavage of trimethyl-*o*-tolylsilane with lithium

In ether A mixture of 8.2 g. (0.05 mole) of trimethyl-*o*-tolylsilane and 33 cm. (1.05 g., 0.15 g. atom) of lithium wire was stirred for 6 hr., a grey color developing, but Color Test I[8] was negative. Twenty-five milliliters of ether was added and the mixture was stirred overnight. After 18 hr., the Color Test was negative. The metal was removed by filtration and the filtrate hydrolyzed with water. Following the usual work-up, distillation using an electrically-heated air-oven yielded 5.45 g. (66.4% recovery) of starting material.

In tetrahydrofuran No apparent reaction had occurred after a mixture of 8.2 g. (0.05 mole) of trimethyl-*o*-tolylsilane, 33 cm. (1.05 g., 0.15 g. atom) of lithium wire and 50 ml. of tetrahydrofuran had been stirred for 24 hr. The liquid was filtered through glass wool and hydrolyzed with water. Fractionation of the dried organic material, following the usual work-up, resulted in the recovery of 7.26 g. (88.5%) of starting material.

Cleavage of trimethyl-*o*-tolylsilane with sodium-potassium alloy in ether

At room temperature When a mixture of 8.2 g. (0.05 mole) of trimethyl-*o*-tolylsilane, 5 ml. (0.10 g. atom of potassium) of sodium-potassium alloy and 25 ml. of ether was stirred for 3 hr., a light green color was evident in the solution but Color Test I[8] was negative. The unreacted alloy was amalgamated and the supernatant liquid pipetted into water. Fractionation of the organic material was accomplished using an electrically-heated air-oven and afforded 5.37 g. (65.5%) of starting material.

At 0° Using the same quantities of reactants as above, cleavage was not effected upon stirring the mixture for 30 hr. at 0°. The unreacted alloy was amalgamated and the liquid portion worked up as usual. Fractionation of the dried organic material resulted in the recovery of 5.57 g. (67.9%) of starting material.

Cleavage of trimethyl-1-naphthylsilane with lithium in ether

A mixture of 10 g. (0.05 mole) of trimethyl-1-naphthylsilane, 20 cm. (0.7 g., 0.10 g. atom) of finely cut lithium wire and 1 ml. of ether was stirred until a green color appeared. One hundred and fifty milliliters of ether was added slowly and the black solution stirred for 1.5 hr. before being filtered through glass wool. The filtrate was added rapidly to a stirred solution of 11.96 g. (0.11 mole) of trimethylchlorosilane in ether. Reaction was quite vigorous and Color Test I[8] was negative immediately after addition was complete. Hydrolysis was effected with a saturated ammonium chloride solution and work-up was as usual. Distillation afforded 5.15 g. (29.8%) of 1,4,5-tris(trimethylsilyl)-1,4-dihydronaphthalene, b.p. 91-94° (0.21 mm.), n_D^{20} 1.5290 (lit.[160] values, b.p. 150-153° (11 mm.), n_D^{20}, 1.5270).

In a repeat reaction, the yield of product was 37%. In a third reaction, triphenylsilane was employed as the derivatizing agent. Color Test I[8] did not become negative in the presence of a large excess of triphenylsilane, but was negative upon the addition of one equivalent of trimethylchlorosilane. No pure product could be isolated from the reaction mixture, however.

Cleavage of 9-fluorenyltrimethylsilane with lithium

In ether 9-Fluorenyltrimethylsilane (5 g., 0.021 mole), 10 cm. (0.35 g., 0.05 g. atom) of lithium and enough ether to

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[160] E. A. Chernyshev and L. G. Kozhevnikova, Doklady Akad. Nauk S.S.S.R., 98, 419 (1954). [Original not available for examination; abstracted in C. A., 49, 12405 (1955)].

form a thick paste were stirred for 4 hr. with no evidence of reaction. An additional 45 ml. of ether was introduced and the mixture stirred for 24 hr., at which time Color Test I[8] was negative and the lithium remained unreacted. The metal was removed by filtration and the filtrate hydrolyzed with cold, dilute hydrochloric acid. After the usual work-up, the solvent was stripped off and the residue recrystallized from ethanol to give 4.52 g. (90.4% recovery) of starting material.

In tetrahydrofuran When tetrahydrofuran was employed as the solvent, a dark green color developed rapidly in a mixture of 5 g. (0.021 mole) of 9-fluorenyltrimethylsilane and lithium wire. Color Test I[8] was positive after 30 min. The mixture was filtered through glass wool and 5.4 g. (0.05 mole) of trimethylchlorosilane added to derivatize. The Color Test was negative immediately after addition was complete. Hydrolysis was effected with a saturated ammonium chloride solution and, following the usual work-up and removal of solvent, 4.0 g. (80% recovery) of starting material was obtained.

Cleavage of 9-methyl-9-trimethylsilylfluorene with lithium

In ether There was no evidence of reaction after a mixture of 5 g. (0.02 mole) of 9-methyl-9-trimethylsilylfluorene, 10 cm. (0.35 g., 0.05 g. atom) of lithium wire and enough ether to form a thick paste had been stirred for 4 hr. at room temperature. Forty-five milliliters of ether was added and the mixture stirred for 24 hr., at which time Color Test I[8] was negative and the bulk of the metal remained. Hydrolysis was effected with cold, dilute hydrochloric acid and work-up was as usual. After removal of the solvent and recrystallization of the residue from ethanol, there was obtained 4.6 g. (92.8% recovery) of starting material.

<u>In tetrahydrofuran</u> A dark green color appeared soon after 5 g. (0.02 mole) of 9-methyl-9-trimethylsilylfluorene, 10 cm. (0.35 g., 0.05 g. atom) of lithium and enough tetrahydrofuran to form a paste had been admixed. Over the next 30 min., 25 ml. of tetrahydrofuran was added with a red-brown coloration developing. Color Test I[8] was positive. The excess metal was removed by filtration and the filtrate was added to a stirred solution of 5.4 g. (0.05 mole) of trimethylchlorosilane in tetrahydrofuran. The reaction was exothermic and the Color Test was negative shortly after addition was complete. Cold, dilute hydrochloric acid was added to hydrolyze the mixture followed by the usual work-up. Distillation of the organic material afforded no hexamethyldisilane and recrystallization of the distillation residue from ethanol resulted in the recovery of 3.72 g. (74%) of starting material.

<u>Cleavage of 9,9-bis(trimethylsilyl)fluorene with lithium</u>

<u>In ether</u> A mixture of 5 g. (0.016 mole) of 9,9-bis(trimethylsilyl)fluorene, 10 cm. (0.35 g., 0.05 g. atom) of

lithium wire and enough ether to form a thick paste was stirred for 4 hr. at room temperature with no sign of reaction. An additional 45 ml. of solvent was introduced and the mixture stirred for 24 hr. Color Test I[8] was negative and the bulk of the lithium remained at the end of the cleavage period. After filtration through glass wool, the filtrate was added to cold, dilute hydrochloric acid. Work-up as usual, followed by removal of solvent, afforded 5 g. (100%) of slightly impure starting material.

In tetrahydrofuran Color Test I[8] was positive and a green color had developed after a mixture of 5 g. (0.016 mole) of 9,9-bis(trimethylsilyl)fluorene, 10 cm. (0.35 g., 0.05 g. atom) of lithium wire and enough tetrahydrofuran to form a paste had been stirred for 30 min. Upon addition of 25 ml. of tetrahydrofuran over the next 30 min., a deep green color was evident in the solution. The excess metal was removed by filtration and the filtrate was added to a stirred solution of 5.40 g. (0.05 mole) of trimethylchlorosilane in tetrahydrofuran. Reaction was exothermic and Color Test I[8] became negative. The mixture was hydrolyzed with a saturated ammonium chloride solution and worked up as usual. Distillation of the dried organic material afforded no hexamethyldisilane and recrystallization of the distillation residue from ethanol resulted in the isolation of 3 g. (60% recovery) of starting material.

Cleavage of allyltrimethylsilane with lithium in ether

A mixture of 5.7 g. (0.05 mole) of allyltrimethylsilane (Penisular Chemresearch, Inc.) and 25 cm. (0.88 g., 0.125 g. atom) of finely cut lithium wire was stirred for one hour with no evidence of reaction. Ten milliliters of ether was added and the mixture was refluxed gently. After 2 hr., the liquid was opaque but Color Test I[8] was negative. An additional 40 ml. of ether was introduced and the mixture was stirred at reflux overnight. The Color Test was still negative. Hydrolysis was effected with an ammonium chloride solution and the usual method of work-up was used. Distillation of the organic material afforded 2 g. (34.7% recovery) of starting material in addition to some undistillable, polymeric material.

Cleavage of trimethylethoxysilane with lithium

In ether A mixture of 6.06 g. (0.05 mole) of trimethylethoxysilane (Penisular Chemresearch, Inc.) and 33 cm. (1.05 g., 0.15 g. atom) of lithium wire was stirred for 2 hr. with no apparent reaction. Addition of 25 ml. of ether and refluxing for 48 hr. had no effect. After hydrolysis with a saturated ammonium chloride solution and work-up at ice-bath temperature distillation afforded no trimethylsilane.

In tetrahydrofuran Under the same conditions as above except that tetrahydrofuran was employed as the solvent, no trimethylsilane was isolated after 6.06 g. (0.05 mole) trimethylethoxysilane and lithium had been stirred together for 6 hr.

Cleavage of trimethylethoxysilane with sodium-potassium alloy

In ether When 6.06 g. (0.05 mole) of trimethylethoxysilane (Penisular Chemresearch, Inc.) and 5 ml. (0.10 g. atom of potassium) of sodium-potassium alloy were admixed, a small amount of heat was generated. Twenty-five milliliters of ether was added and the mixture was stirred for 24 hr. The unreacted alloy was amalgamated and the supernatant liquid pipetted into a stirred solution of triphenylchlorosilane in tetrahydrofuran. Hydrolysis was with a saturated ammonium chloride solution and work-up was as above. Investigation of only the solid portion of the organic material afforded no 1,1,1-trimethyl-2,2,2-triphenyldisilane.

A repeat reaction, similar to the one above except the alloy and silane were stirred for 48 hr. before amalgamation and derivatization with triphenylchlorosilane, did not yield any 1,1,1-trimethyl-2,2,2-triphenylsilane, either.

In tetrahydrofuran There was no sign of reaction after a mixture of 6.06 g. (0.05 mole) of trimethylethoxysilane, 5 ml. (0.10 g. atom of potassium) of sodium potassium alloy and 5 ml. of tetrahydrofuran had been stirred for 24 hr. The unreacted alloy was amalgamated and the supernatant liquid added to a tetrahydrofuran solution of triphenylchlorosilane. Hydrolysis was effected with a saturated ammonium chloride solution and work-up was as usual. The residue remaining after removal of all liquids by distillation was dissolved in benzene and chromatographed on alumina. No 1,1,1-trimethyl-2,2,2-triphenyldisilane was isolated, only triphenylsilanol and hexaphenyldisiloxane being encountered.

Cleavage of hexamethyldisiloxane

With lithium in tetrahydrofuran One meter (3.0 g., 0.45 g. atom) of finely cut lithium wire and 16.2 g. (0.1 mole) of hexamethyldisiloxane were stirred together for 12 hr. The liquid was grey in color but Color Test I[8] was negative. Fifty milliliters of tetrahydrofuran was introduced and the mixture was stirred for an additional 38 hr. at reflux. The liquid was filtered through glass wool and 0.1 mole of methyl iodide added to it. The mixture was stirred for 45 min. before being hydrolyzed with water. After the usual work-up, no tetramethylsilane could be isolated.

With sodium-potassium alloy in ether A light blue color developed after 8.1 g. (0.05 mole) of hexamethyldisiloxane and 6 ml. (0.12 g. atom of potassium) of sodium-potassium alloy had been stirred for 30 min. Thirty milliliters of ether was added slowly and the mixture was stirred for 48 hr. The excess alloy was amalgamated and the supernatant liquid pipetted into a solution of 3 g. (0.01 mole) of triphenylchlorosilane. Hydrolysis was effected with water, and after the usual work-up, the organic material was distilled. No 1,1,1-trimethyl-2,2,2-triphenyldisilane could be isolated from the distillation residue.

Organosilicon Hydrides

Unexpected difficulties were encountered during analyses of the compounds reported in this section. The poor results have been attributed to two causes: (a) the volatility of some of the compounds resulting in loss of undecomposed material before oxidation, and (b) the disproportionation of the compounds into silane and olefins at the temperature of decomposition.

Molar refraction values were determined immediately after purification of the compounds was achieved and agreed quite well with calculated values. All the compounds were analyzed for silicon using the technique of Gilman, et al.,[151] and where successful will be indicated in the text by Method I. If the method failed, a second procedure, indicated by Method II, involved addition of 1 ml. of distilled water and 4-6 drops of piperidine to the weighed sample and allowing the mixture to stand for 1 hr. The liquids were then evaporated and the residue treated with sulfuric and nitric acid as in Method I. In several instances, neither method gave good results, nor did carbon and hydrogen analyses, and the molar refractions are the only analytical data reported.

A qualitative test for the degree of substitution of an organosilicon hydride was also employed. The test, the details of which will be published in the near future,[161] depends on the development of different colors when an organosilicon hydride and a copper (II) chloride-pyridine-water reagent are mixed. Monosubstituted silicon hydrides changed the original blue color of the reagent to yellow, disubstituted organosilicon hydrides developed a green coloration while trisubstituted organosilicon hydrides do not change the original blue color.

n-Dodecylsilane

To a slurry of 15.2 g. (0.4 mole) of lithium aluminum hydride in tetrahydrofuran was added a solution of 92.34 g. (0.305 mole) of *n*-dodecyltrichlorosilane (Dow Corning Corporation) in tetrahydrofuran. After addition was complete, the mixture was refluxed for 18 hr. One hundred milliliters of ethyl acetate was added slowly to the cooled mixture to destroy

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[161] H. Gilman, H. G. Brooks, Jr., and M. B. Hughes, *J. Org. Chem.*, **23**, in press (1958).

the excess lithium aluminum hydride, followed by acidification with hydrochloric acid. The aqueous layer was separated and extracted three times with ether before being discarded. The organic layer, upon drying with sodium sulfate, was observed to be giving off a gas. The solvents were stripped off rapidly and an attempt was made to distill the remaining liquid at 250° and 0.04 mm. pressure, but no distillate was collected. An infrared spectrum of this undistilled material, determined as a carbon disulfide solution, had a broad absorption band at $9.5\,\mu$, indicative of the Si-O-Si linkage.

A second experiment, run under exactly the same conditions, resulted in the isolation of similar material.

The disiloxane from these two runs was added again, as a tetrahydrofuran solution, to a slurry of lithium aluminum hydride and stirred for 72 hr. at reflux. The cooled mixture was then poured onto ice-sulfuric acid. The organic layer was immediately separated and washed with distilled water until the extract was neutral to litmus. The aqueous layer was extracted three times with ether and these extracts washed with water until neutral. After drying, the organic layer was distilled to give 27.19 g. of n-dodecylsilane, b.p. 83° (1.0 mm.), n_D^{20} 1.4396, d_{20}^{20} 0.7753.

Anal. Calcd. for $C_{12}H_{28}Si$: MR_D, 68.19. Found: MR_D, 68.11.

The infrared spectrum of the compound as a carbon tetrachloride solution had a sharp absorption band at 2151 cm.$^{-1}$ The $CuCl_2$-Py-H_2O reagent turned yellow.

n-Hexadecylsilane

To a slurry of lithium aluminum hydride in tetrahydrofuran was added 226.8 g. (0.63 mole) of n-hexadecyltrichlorosilane (Dow Corning Corporation) and the mixture refluxed for 48 hr. After cooling, it was poured onto a mixture of ice and sulfuric acid and worked up using the modified method outlined above. Distillation of the material remaining after the bulk of the solvents had been removed afforded 120.57 g. (74.6%) of n-hexadecylsilane, b.p. 119-120° (1.1 mm.), n_D^{20} 1.4480, d_{20}^{20} 0.7932.

Anal. Calcd. for $C_{16}H_{36}Si$: MR_D, 86.78; Found: MR_D, 86.57.

The infrared spectrum of a carbon tetrachloride solution of the compound had a sharp absorption band at 2150 cm.$^{-1}$ The $CuCl_2$-Py-H_2O reagent developed a yellow coloration.

Allyl-n-hexadecylsilane

To a stirred solution of 10.26 g. (0.04 mole) of n-hexadecylsilane in tetrahydrofuran was added 0.04 mole of allylmagnesium chloride in tetrahydrofuran. After the mixture had been stirred at reflux for 18 hr., Color Test I[8] was negative. Hydrolysis was effected by pouring the mixture onto ice-sulfuric acid. The modified method of work-up was used and two distillations of the liquid remaining after the bulk of the solvents had been stripped off resulted in the isolation of 1.81 g. (17.6% recovery) of n-hexadecylsilane and 3.67 g. (37.5%, based on unrecovered starting material) of allyl-n-hexadecylsilane, b.p. 138.5-139.5° (1.0 mm.), n_D^{20} 1.4578, d_{20}^{20} 0.8099.

Anal. Calcd. for $C_{19}H_{40}Si$: Si, 9.46; MR_D, 99.97. Found: Si, 9.42, 9.35 (Method II); MR_D, 99.88.

The infrared spectrum of the compound as a carbon tetrachloride solution had a sharp band at 2131 cm.$^{-1}$ and a green color developed in the $CuCl_2$-Py-H_2O reagent.

Diallyl-n-hexadecylsilane

Six hundredths of a mole of allylmagnesium chloride was added to a tetrahydrofuran solution of 7.7 g. (0.03 mole) of n-hexadecylsilane. Color Test I[8] was negative after the mixture had been stirred at reflux for 66 hr. Hydrolysis was effected by pouring onto ice-sulfuric acid and the modified method of work-up followed. Three fractionations of the material remaining after removal of solvents afforded 1.88 g.

(21.1%) of allyl-n-hexadecylsilane and 2.71 g. (26.8%) of diallyl-n-hexadecylsilane, b.p. 147-149° (0.28 mm.), n_D^{20} 1.4654, d_{20}^{20} 0.8247.

Anal. Calcd. for $C_{22}H_{44}Si$: MR_D, 113.17. Found: MR_D, 112.93.

The infrared spectrum of the compound as a carbon tetrachloride solution exhibited a sharp band at 2114 $cm.^{-1}$; no color change was observed with the $CuCl_2$-Py-H_2O reagent.

n-Hexadecylphenylsilane

To 7.7 g. (0.03 mole) of n-hexadecylsilane was added 0.03 mole of phenylmagnesium bromide in tetrahydrofuran. The mixture was stirred for 66 hr. at reflux before Color Test I[8] was negative. The liquid was poured onto ice-sulfuric acid and worked up using the modified procedure. Four fractionations of the liquid remaining after removal of solvents resulted in the isolation of 3.38 g. (33.8%) of n-hexadecylphenylsilane, b.p. 153-154° (0.2 mm.), n_D^{20} 1.4880, d_{20}^{20} 0.8660.

Anal. Calcd. for $C_{22}H_{40}Si$: Si, 8.44; MR_D 111.05. Found: Si, 8.56, 8.31 (Method II); MR_D, 110.65.

The infrared spectrum of the compound as a carbon tetrachloride solution had a sharp absorption band at 2132 $cm.^{-1}$ A green color developed in the $CuCl_2$-Py-H_2O reagent.

n-Hexadecyldiphenylsilane

After 80 hr. at reflux, a mixture of 7.7 g. (0.03 mole) of n-hexadecylsilane and 0.06 mole of phenylmagnesium bromide in tetrahydrofuran exhibited a negative Color Test I.[8] Ice-sulfuric acid was used to effect hydrolysis and the modified method of work-up was employed. Three distillations of the liquid remaining after the solvents had been stripped from the organic layer resulted in the isolation of a small amount of n-hexadecylphenylsilane and 2.53 g. (20.8%) of n-hexadecyldiphenylsilane, b.p. 166-169° (0.08 mm.), n_D^{20} 1.5163, d_{20}^{20} 0.9154.

Anal. Calcd. for $C_{28}H_{44}Si$: Si, 6.87; MR_D, 135.31. Found: Si, 7.02, 6.40 (Method I); MR_D, 134.92.

The infrared spectrum of the compound as a carbon tetrachloride solution exhibited a sharp band at 2118 $cm.^{-1}$ No color change was observed with the $CuCl_2$-Py-H_2O reagent.

Benzyl-n-hexadecylsilane

Color Test I[8] was negative after a mixture of 10.26 g. (0.04 mole) of n-hexadecylsilane and 0.04 mole of benzylmagnesium chloride in tetrahydrofuran had been stirred at reflux for 24 hr. Three fractionations of the organic material, obtained after hydrolysis with ice-sulfuric acid and the modified method of work-up, resulted in the isolation of 7.7 g. (55.6%) of benzyl-n-hexadecylsilane, b.p. 170-171° (0.25 mm.), n_D^{20} 1.4890, d_{20}^{20} 0.8648.

Anal. Calcd. for $C_{23}H_{42}Si$: Si, 8.09; MR_D, 115.28. Found: Si, 8.25, 8.17 (Method II); MR_D, 115.67.

A green coloration was developed with the $CuCl_2$-Py-H_2O reagent. The infrared spectrum of the compound as a carbon tetrachloride solution had a sharp band at 2134 cm.$^{-1}$

n-Butyl-n-hexadecylsilane

After a mixture of 0.03 mole of butylmagnesium bromide and 7.7 g. (0.03 mole) of n-hexadecylsilane in tetrahydrofuran had been stirred for 40 hr., Color Test I[8] was negative. Hydrolysis and work-up as above, followed by four distillations of the organic material, afforded 3.93 g. (39.8%) of n-butyl-n-hexadecylsilane, b.p. 153-155° (0.3 mm.), n_D^{20} 1.4521, d_{20}^{20} 0.8057.

Anal. Calcd. for $C_{20}H_{44}Si$: Si, 8.98; MR_D, 105.10. Found: Si, 8.20 (Method I); MR_D, 104.70.

The infrared spectrum of the compound as a carbon tetrachloride solution had a sharp band at 2120 cm.$^{-1}$ A green coloration was developed with the $CuCl_2$-Py-H_2O reagent.

Cyclohexylsilane

Cyclohexyltrichlorosilane (54.25 g., 0.25 mole) (Dow Corning Corporation) was added to a slurry of 11.4 g. (0.3 mole) of lithium aluminum hydride in tetrahydrofuran. The mixture was stirred at reflux for 24 hr. before being hydrolyzed with ice-sulfuric acid. Following the modified method of work-up, two distillations of the organic material resulted in the isolation of 15.42 g. (54.2%) of cyclohexylsilane, b.p. 102-104°, n_D^{20} 1.4461, d_{20}^{20} 0.7976 (lit.[49] values, b.p. 119.5°, n_D^{25} 1.4464, d^{25} 0.7958).

Anal. Calcd. for $C_6H_{14}Si$: C, 63.08; H, 12.35; MR_D, 38.24. Found: C, 63.16, 63.30; H, 12.47, 12.35; MR_D, 38.20.

The infrared spectrum of the compound as a carbon tetrachloride solution had a sharp band at 2143 $cm.^{-1}$ A yellow color developed with the $CuCl_2$-Py-H_2O reagent.

Dicyclohexylsilane

Three tenths of a mole of cyclohexylmagnesium chloride was added to a solution of 25.5 g. (0.15 mole) of silicon tetrachloride in tetrahydrofuran and the mixture stirred for 72 hr. at reflux, at which time Color Test I[8] was negative. Four grams (0.105 mole) of lithium aluminum hydride was added in small portions to the cooled solution and when addition was complete, the mixture was stirred at reflux for 24 hr. After hydrolysis with ice-sulfuric acid and work-up, three fractionations of the organic material afforded 4.6 g. (15.7%) of dicyclohexylsilane, b.p. 125-130° (15 mm.), n_D^{20} 1.4880 (lit.[50] values, b.p. 140-141° (23 mm.), n_D^{25} 1.4854), plus a large amount of polymeric material.

The infrared spectrum of the compound as a carbon tetrachloride solution had a sharp band at 2111.5 cm.$^{-1}$ A green color was developed with the $CuCl_2$-Py-H_2O reagent.

tert-Butylphenylsilane

To a stirred solution of 10.82 g. (0.10 mole) of phenylsilane in tetrahydrofuran was added 0.10 mole of tert-butylmagnesium chloride. After 30 hr. at reflux, Color Test I[8] was negative. Distillation of the organic material, after hydrolysis with ice-sulfuric acid and work-up, gave 6.06 g. (36.9%) of tert-butylphenylsilane, b.p. 186-188°, n_D^{20} 1.4954, d_{20}^{20} 0.8599.

Anal. Calcd. for $C_{10}H_{16}Si$: MR_D, 55.27. Found: MR_D, 55.70.

The infrared spectrum of the compound as a carbon tetrachloride solution exhibited a sharp band at 2129.5 cm.$^{-1}$ A green color was developed with the $CuCl_2$-Py-H_2O reagent.

Di-*n*-butylsilane

One mole of *n*-butylmagnesium bromide was added to 85 g. (0.50 mole) of silicon tetrachloride in ether and the mixture stirred at reflux for 24 hr. Lithium aluminum hydride (12 g., 0.32 mole) was added to the cooled solution and the mixture refluxed for 72 hr. Hydrolysis and work-up were followed by two distillations of the organic material to give 26.38 g. (36.6%) of di-*n*-butyl silane, b.p. 156°, n_D^{20} 1.4233 (lit.[50] values, b.p. 160° (773 mm.), n_D^{25} 1.4221).

The infrared spectrum of the compound determined as a carbon tetrachloride solution had a sharp band at 2123 $cm.^{-1}$ A green color developed with the $CuCl_2$-Py-H_2O reagent.

Allyldi-*n*-butylsilane

After a mixture of 0.05 mole of allylmagnesium chloride and 0.05 mole of di-*n*-butylsilane in tetrahydrofuran had been stirred for 42 hr. at reflux, Color Test I[8] was negative. Hydrolysis with ice-sulfuric acid and work-up as above, followed by three fractionations of the organic material, afforded 0.86 g. (12% recovery) of di-*n*-butylsilane and 4.29 g. (46.5%) of allyldi-*n*-butylsilane, b.p. 32-33° (0.15 mm.), n_D^{20} 1.4448, d_{20}^{20} 0.7858.

Anal. Calcd. for $C_{11}H_{24}Si$: MR_D, 62.52. Found: MR_D, 62.42.

The infrared spectrum of a carbon tetrachloride solution of the compound had a sharp band at 2106 $cm.^{-1}$ No color change was observed with the $CuCl_2$-Py-H_2O reagent.

Tri-n-butylsilane

When di-n-butylsilane was reacted with n-butyl magnesium bromide under conditions similar to the preceding experiment, 38.5% of starting material was recovered and 0.78 g. (7.8%) of tri-n-butylsilane, b.p. 110-111° (15 mm.), n_D^{20} 1.4375 (lit.[72] values, b.p. 104° (12 mm.), n_D^{20} 1.4380), was isolated.

The infrared spectrum of the material as a carbon tetrachloride solution exhibited a sharp band at 2094 $cm.^{-1}$ No color change occurred with the $CuCl_2$-Py-H_2O reagent.

Di-n-decylsilane

Eighty-five grams (0.224 mole) of di-n-decyldichlorosilane (Peninsular Chemresearch, Inc.) was reduced with excess lithium aluminum hydride in refluxing tetrahydrofuran. Distillation of the organic material, after the usual work-up, afforded 31.05 g. (44.4%) of di-n-decylsilane, b.p. 168-169° (1.5 mm.), n_D^{20} 1.4510, d_{20}^{20} 0.8031.

Anal. Calcd. for $C_{20}H_{44}Si$: Si, 8.98; MR_D, 105.10. Found: Si, 8.53 (Method I); MR_D, 104.82.

The infrared spectrum of a carbon tetrachloride solution of the compound had a sharp band at 2125 $cm.^{-1}$ A green color developed with the $CuCl_2$-Py-H_2O reagent.

Allyldi-*n*-decylsilane

After a mixture of 0.025 mole of allylmagnesium chloride and 0.025 mole of di-*n*-decylsilane had been stirred for 60 hr. in refluxing tetrahydrofuran, there was obtained, after the usual hydrolysis and work-up, 3.23 g. (41.3% recovery) of starting material and 2.68 g. (56.3%, based on unrecovered starting material) of allyldi-*n*-decylsilane, b.p. 169-171° (0.8 mm.), n_D^{20} 1.4570, d_{20}^{20} 0.8125.

Anal. Calcd. for $C_{23}H_{48}Si$: Si, 7.96; MR_D, 118.30. Found: Si, 8.10 (Method II); MR_D, 118.22.

The infrared spectrum of the compound as a carbon tetrachloride solution had a sharp band at 2114 $cm.^{-1}$ No color change was observed with the $CuCl_2$-Py-H_2O reagent.

Benzyldi-*n*-decylsilane (attempted)

Distillation of the organic material, obtained after 0.025 mole of benzylmagnesium chloride and 0.025 mole of di-*n*-decylsilane in tetrahydrofuran had been stirred for 72 hr. at reflux, resulted in the recovery of 22% of di-*n*-decylsilane. No benzyldi-*n*-decylsilane could be isolated.

Di-*n*-decylphenylsilane (attempted)

In two reactions, phenylmagnesium bromide and di-*n*-decylsilane in tetrahydrofuran were stirred at reflux for 44 hr. Distillation of the organic material, after hydrolysis and work-up, afforded recoveries of 65.6% and 54.6% of starting material. No di-*n*-decylphenylsilane was isolated in either reaction.

Di-*n*-octadecylsilane

One hundred grams (0.165 mole) of di-*n*-octadecyldichlorosilane (Dow Corning Corporation) was reduced with lithium aluminum hydride in refluxing tetrahydrofuran over a 24-hr. period. Hydrolysis was effected with ethyl acetate; the solution was acidified with hydrochloric acid, and the organic solvents were evaporated. The solid residue remaining was recrystallized twice from petroleum ether (b.p. 60-70°) to give 55 g. (62.1%) of di-*n*-octadecylsilane, m.p. 58-59°.

Anal. Calcd. for $C_{36}H_{76}Si$: C, 80.51; H, 14.15. Found: C, 80.47; H, 13.90.

The infrared spectrum of the compound as a carbon tetrachloride solution had a sharp band at 2121 cm.$^{-1}$ A green color was developed in the $CuCl_2$-Py-H_2O reagent.

Allyldi-n-octadecylsilane (attempted)

A 70% recovery of starting material was obtained when 0.02 mole of allylmagnesium chloride was stirred for 72 hr. with 0.02 mole of di-n-octadecylsilane at tetrahydrofuran reflux and worked up as above. No allyldi-n-octadecylsilane was isolated.

Di-n-octadecylphenylsilane (attempted)

Only starting material could be isolated in yields of 85% and higher after di-n-octadecylsilane had been refluxed in tetrahydrofuran for periods of 35, 60 and 72 hr. with excess phenylmagnesium bromide in three reactions.

Tri-n-dodecylsilane

Reduction of 75 g. (0.131 mole) of tri-n-dodecylchlorosilane (Peninsular Chemresearch, Inc.) with excess lithium aluminum hydride in refluxing tetrahydrofuran afforded, after the usual work-up, 50.77 g. (72.2%) of tri-n-dodecylsilane, b.p. 218-220° (0.01 mm.), n_D^{20} 1.4605, d_{20}^{20} 0.8238.

Anal. Calcd. for $C_{36}H_{76}Si$: MR_D, 179.18. Found: MR_D, 178.71.

The infrared spectrum of the compound as a carbon tetrachloride solution had a sharp band at 2097 $cm.^{-1}$ No color change was observed with the $CuCl_2$-Py-H_2O reagent.

Mono-, di-, and tri-n-hexylsilane

Five tenths of a mole of n-hexylmagnesium bromide was added to a solution of 42.5 g. (0.25 mole) of silicon tetrachloride in ether and the mixture refluxed for 36 hr., at which time Color Test I[8] was negative. The salts were filtered off under a nitrogen atmosphere and the filtrate added to a slurry of 6 g. (0.158 mole) of lithium aluminum hydride in ether. After being stirred at reflux for 48 hr., ice-sulfuric acid was used to hydrolyze the mixture and the work-up was as usual. Four fractionations of the organic material afforded 2.61 g. (9%) of n-hexylsilane, b.p. 113-115°, n_D^{20} 1.4134 (lit.[162] values, b.p. 114.5° (751 mm.), n_D^{20} 1.4129); 3.68 g. (7.3%) of di-n-hexylsilane, b.p. 55-56° (0.15 mm.),

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[162] M. I. Batuev, V. A. Ponomarenko, A. D. Matveeva, and A. D. Petrov, Doklady Akad. Nauk S.S.S.R., 95, 805 (1954). [Original not available for examination; abstracted in C. A., 49, 6089 (1955)].

n_D^{20} 1.4378, d_{20}^{20} 0.7758; and 0.88 g. (1.2%) of impure tri-n-hexylsilane, b.p. 110-112° (0.8 mm.), n_D^{20} 1.4469, d_{20}^{20} 0.8070.

n-Hexylsilane gave a yellow color with the $CuCl_2$-Py-H_2O reagent and a carbon tetrachloride solution of the material had a band at 2152 cm.$^{-1}$ in its infrared spectrum.

Anal. Calcd. for $C_{12}H_{28}Si$: MR_D, 67.92. Found: MR_D, 67.78.

A green color developed with the $CuCl_2$-Py-H_2O reagent and a sharp band at 2125 cm.$^{-1}$ was evident in the infrared spectrum of a carbon tetrachloride solution of the compound.

Anal. Calcd. for $C_{18}H_{40}Si$: MR_D, 95.53. Found: MR_D, 94.20.

There was no color change with the $CuCl_2$-Py-H_2O reagent. The infrared spectrum of the material as a carbon tetrachloride solution had a sharp band at 2095 cm.$^{-1}$

Mono-, di-, and tri-n-octylsilane

To a solution of 85 g. (0.50 mole) of silicon tetrachloride in ether was added 1.05 moles of n-octylmagnesium bromide. Color Test I[8] was negative after the mixture had been stirred at reflux for 24 hr. Twenty grams (0.526 mole) of lithium aluminum hydride was added in small portions and the resultant mixture stirred for 48 hr. at ether reflux. Hydrolysis was effected by pouring onto a mixture of ice and sulfuric acid and work-up was as previously described. Distillation of the organic material afforded 6.14 g. (8.5%) of n-octylsilane, b.p. 162-163°, n_D^{20} 1.4263, d_{20}^{20} 0.7526; 65.3 g. (50.9%) of di-n-octylsilane, b.p. 102-104° (0.1 mm.), n_D^{20} 1.4462, d_{20}^{20} 0.7925; and 3.42 g. of material which appeared to be impure tri-n-octylsilane, b.p. 163-165 (0.15 mm.), n_D^{20} 1.4545, d_{20}^{20} 0.8207. Attempts to purify this last fraction by redistillation failed to improve the material.

Anal. Calcd. for $C_8H_{20}Si$: MR_D, 49.59. Found: MR_D, 49.10.

The infrared spectrum of the compound as a carbon tetrachloride solution had a sharp band at 2151 $cm.^{-1}$ A yellow color developed with the $CuCl_2$-Py-H_2O reagent.

Anal. Calcd. for $C_{16}H_{36}Si$: MR_D, 86.51. Found: MR_D, 86.34.

The infrared spectrum of the compound as a carbon tetrachloride solution had a sharp band at 2121 $cm.^{-1}$ A green color was produced with the $CuCl_2$-Py-H_2O reagent.

Anal. Calcd. for $C_{24}H_{52}Si$: MR_D, 123.42. Found: MR_D, 121.77.

The infrared spectrum of the compound as a carbon tetrachloride solution had a sharp band at 2098 $cm.^{-1}$ No color change was observed with the $CuCl_2$-Py-H_2O reagent.

Benzyldi-n-octylsilane

Fractionation of the organic material obtained upon work-up of the reaction mixture of 0.03 mole of benzylmagnesium chloride and 0.03 mole of di-n-octylsilane, which had been stirred in refluxing tetrahydrofuran for 90 hr., resulted in the recovery of 61.2% of the di-n-octylsilane and the isolation of 0.49 g. (4.7%) of benzyldi-n-octylsilane, b.p. 135-137° (0.25 mm.), n_D^{20} 1.4878, d_{20}^{20} 0.8718.

Anal. Calcd. for $C_{23}H_{42}Si$: MR_D, 115.03. Found: MR_D, 114.60.

The infrared spectrum of the compound as a carbon tetrachloride solution had a sharp band at 2106.5 $cm.^{-1}$ No color change was observed with the $CuCl_2$-Py-H_2O reagent.

Di-n-octylphenylsilane

Three hundredths of a mole of phenylmagnesium bromide was added to a solution of 7.7 g. (0.03 mole) of di-n-octylsilane in tetrahydrofuran. The Color Test[8] was still positive after 90 hr. at reflux. Hydrolysis and work-up as usual, followed by fractionation of the organic material, resulted in the isolation of 3.80 g. (50% recovery) of starting material and 0.32 g. of material having the properties of di-n-octylphenylsilane, b.p. 142-144° (0.2 mm.),

n_D^{20} 1.4821, but the small amount of product isolated prevented more complete characterization.

No color change was observed with the $CuCl_2$-Py-H_2O reagent.

Mono- and di-p-anisylsilane

A solution of 0.545 mole of p-anisylmagnesium bromide was added to 91.0 g. (0.535 mole) of silicon tetrachloride in ether. Color Test I[8] was negative after 16 hr at reflux and 8.5 g. (0.22 mole) of lithium aluminum hydride was added to the cooled solution. After refluxing for 24 hr., the mixture was poured onto ice-sulfuric acid and worked up as usual. Fractionation of the organic material afforded 28.13 g. (38.0%) of p-anisylsilane, b.p. 183-183.5°, n_D^{20} 1.5300, d_{20}^{20} 0.9763 (lit.[49] values, b.p. 180°, n_D^{25} 1.5251, d^{25} 0.9797).

Anal. Calcd. for $C_7H_{10}OSi$: C, 60.83; H, 7.29; MR_D, 43.32. Found: C, 60.68, 60.56; H, 7.22, 7.26; MR_D, 43.73.

The infrared spectrum of the compound determined as a carbon tetrachloride solution exhibited a sharp band at 2153.5 cm.$^{-1}$ A yellow color developed with the $CuCl_2$-Py-H_2O reagent.

When 0.15 mole of silicon tetrachloride was stirred at reflux for 18 hr. in tetrahydrofuran with 0.324 mole of p-anisylmagnesium bromide, there was obtained 12.25 g. (33.4%)

of di-p-anisylsilane, m.p. 58.5-60°, after two recrystallizations from petroleum ether (b.p. 77-117°).

Anal. Calcd. for $C_{14}H_{16}O_2Si$: Si, 11.48. Found: Si, 11.43, 11.32 (Method II).

The infrared spectrum of the compound as a carbon tetrachloride solution had a band at 2134 $cm.^{-1}$ A green color developed with the $CuCl_2$-Py-H_2O reagent.

Tri-p-anisylsilane

Six and one-tenths grams (0.025 mole) of di-p-anisylsilane was refluxed for 48 hr. with 0.025 mole of p-anisylmagnesium bromide in tetrahydrofuran. Following the usual work-up, the solvents were distilled. Recrystallization of the solid residue from methanol afforded 4.0 g. (45.7%) of tri-p-anisylsilane, m.p. 75-77°.

Anal. Calcd. for $C_{21}H_{22}O_3Si$: Si, 8.01. Found : Si, 8.13, 8.15 (Method II).

The infrared spectrum of the compound as a carbon tetrachloride solution had a band at 2117.5 $cm.^{-1}$ No color change was observed with the $CuCl_2$-Py-H_2O reagent.

Mono-, di-, and tri-o-anisylsilane (attempted)

Two attempts to prepare o-anisylsilanes from the Grignard reagent and silicon tetrachloride, followed by reduction with lithium aluminum hydride, failed. The low-boiling fractions of distillate evolved a gas and turned purple and large amounts of polymeric material remained undistilled.

Mono- and di-*p*-tolylsilane

From the reaction of 0.348 mole of *p*-tolylmagnesium bromide and 0.30 mole of silicon tetrachloride in refluxing ether, followed by reduction with lithium aluminum hydride, was obtained 10.13 g. (30.8%) of *p*-tolylsilane, b.p. 147-148°, n_D^{20} 1.5112, d_{20}^{20} 0.8775.

Anal. Calcd. for $C_7H_{10}Si$: MR_D, 41.60. Found: MR_D, 41.74.

The $CuCl_2$-Py-H_2O reagent gave a yellow color with the compound; and its infrared spectrum, determined as a carbon tetrachloride solution, had a sharp band at 2154.5 $cm.^{-1}$

When 0.23 mole of silicon tetrachloride was reacted with 0.5 mole of *p*-tolylmagnesium bromide in refluxing ether for 18 hr., reduced and worked up as above, 5.40 g. (10.2%) of di-*p*-tolylsilane, b.p. 85° (0.06 mm.), n_D^{20} 1.5699, d_{20}^{20} 0.9847, was obtained. The sample turned brown upon standing for 4 hr. in a stoppered vial.

Anal. Calcd. for $C_{14}H_{16}Si$: MR_D, 70.51. Found: MR_D, 70.74.

A green color developed with the $CuCl_2$-Py-H_2O reagent.

DISCUSSION

Trialkylgermylmetallic Compounds

The preparation and stability of triethylgermylpotassium in ethylamine[6] and of triethylgermyllithium in diethyl ether[163] demonstrate that it is not impossible to prepare stable trialkylgermylmetallic compounds. However, much work must still be done before this class of compounds can be elevated from the level of laboratory curiosities to the plane of useful synthetic intermediates.

Hexaalkyldigermanes remain the compounds of choice for the preparation of trialkylgermylmetallic intermediates. Successful cleavage, as realized by Kraus and Flood,[6] would give rise to only the desired organometallic reagent, without the added complication of other organometallic compounds which would be formed during the cleavage of tetraalkyl- or trialkylarylgermanes. Furthermore, the germanium-germanium bond energy is less than the germanium-carbon bond energy and cleavage of digermanes should be more facile than cleavage of tetrasubstituted germanes. However, until a method of preparing hexaalkyldigermanes at a reasonable price is developed,

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[163] This thesis, p. 45.

interest in the cleavage of this class of compounds must remain on a theoretical basis.

The metalation of trialkylgermanes with organolithium compounds is a method of preparation which should be investigated more completely. A means of synthesizing the trialkylgermanes in good yield would be an important first step.

The low yields of metalation product obtained upon treatment of triethylgermane with n-butyl- or phenyllithium[163] are surprising when compared with the high yields of triphenylgermyllithium obtained from the reaction of triphenylgermane and methyl-, n-butyl- or phenyllithium.[4] It is possible that in the reactions of triethylgermane, optimum conditions for the metalation were not realized, and a study of variations of time and temperature may be necessary. Conversely, the germanium-hydrogen bond of a trialkylgermane may be quite different electronically from the germanium-hydrogen bond of a triarylgermane and the same type of reaction should not, therefore, be expected. Trisubstituted silanes under the same conditions give the tetrasubstituted compounds[30,32] but there was no n-butyltriethylgermane or triethylphenylgermane isolated in these reactions.

In all the solvents used, the non-recovery of starting material when tetraethylgermane was stirred with sodium-potassium alloy would seem to indicate that a germanium-carbon bond was being cleaved. The fate of the triethylgermylpotassium, if formed, remains unknown. Cleavage of metalation of the solvent are possibilities while disproportionation into ethylpotassium and diethylgermanium, in a manner analogous to the one postulated for tin and lead lithium compounds, is not impossible.

$$(C_2H_5)_3GeK \longrightarrow C_2H_5K + (C_2H_5)_2Ge:$$

The germanium-aromatic carbon bond is weaker than a germanium-aliphatic carbon bond and an investigation of the cleavage of trialkylarylgermanes is worthy of consideration. If compounds of this class become available at reasonable prices, it may be that cleavage with a less active metal, to give a trialkylgermylmetallic compound of lower reactivity and higher stability, would be possible.

An aspect common to all of the preceding problems is the discovery of a solvent basic and/or polar enough to facilitate cleavage or metalation but which does not itself undergo appreciable reaction with either the organometallic compound formed or the derivatizing agents. In ethylamine, the disadvantages of slowness of the cleavage of hexaethyldigermane and, under the experimental conditions, reaction of the solvent with derivatizing agents containing carbonyl groups outweigh the fact that triethylgermylpotassium is stable in the medium. The metalation of triethylgermane with organolithium compounds in diethyl ether suffers from slowness of reaction and, apparently, instability of the germyllithium compound formed. The reaction of triethylchlorogermane with lithium, which may proceed through a germyllithium intermediate, also indicates that the solvent plays an important role in the reaction. In diethyl ether, a 60 percent yield of the

$$(C_2H_5)_3GeCl + 2\ Li \longrightarrow LiCl + (C_2H_5)_3GeLi$$

$$(C_2H_5)_3GeLi + (C_2H_5)_3GeCl \longrightarrow (C_2H_5)_3GeGe(C_2H_5)_3 + LiCl$$

digermane was obtained, whereas in tetrahydrofuran, the digermane was isolated in a 16.8 percent yield.

Trialkylsilylmetallic Compounds

The cleavage of hexalkyldisilanes has been quite thoroughly investigated and the results uniformly indicate that the silicon-silicon bond is not cleaved by lithium, sodium or sodium-potassium alloy.[16,164] The solvents employed for the cleavage were diethyl ether, ethylene glycol dimethyl ether, liquid ammonia and tetrahydrofuran. Recently, tetrahydropyran had been found to be excellent solvent for the cleavage of

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[164] This thesis, p. 56.

hexaaryldisilanes and other compounds,[165] and cleavage of hexaalkyldisilanes may be possible using this solvent. On the other hand, in light of the ease of cleavage of 1,1,2,2-tetramethyl-1,2-diphenyldisilane with lithium in tetrahydrofuran and the stability of the dimethylphenylsilyllithium so formed, it is not unreasonable to postulate a basic difference, dependent on steric strain and electronic interactions, between the silicon-silicon bond in this compound and the silicon-silicon in hexaalkyldisilanes. And, as pointed out earlier, no chance for resonance stabilization of a trialkylsilyl anion may explain its low order of stability, if formed.

Initially, trialkylarylsilanes looked very promising as starting materials for the preparation of trialkylsilylmetallic compounds. Although neither lithium nor sodium-potassium alloy affected trimethylphenylsilane or triethylphenylsilane in diethyl ether, sodium-potassium alloy did cleave the compounds in tetrahydrofuran at -50° to give phenylpotassium in high yields. However, the fate of the trialkylsilylpotassium compounds also formed remains unknown. Reaction with the solvent, either by cleavage or metalation, is not unreasonable, but products one would expect from such reactions could not be isolated. Recently, it has been found that silyl-

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[165] M. V. George, Chemistry Dept., Iowa State College, Ames, Iowa. Information concerning metallic cleavages in tetrahydropyran. Private communication. (1958).

metallic compounds will react with a disilane in tetrahydrofuran to produce a less reactive silylmetallic intermediate

$$(C_6H_5)_3SiSi(C_2H_5)_3 + 2\ Li \longrightarrow (C_6H_5)_3SiLi + (C_2H_5)_3SiLi$$

$$(C_2H_5)_3SiLi + (C_6H_5)_3SiSi(C_2H_5)_3 \rightarrow (C_2H_5)_3SiSi(C_2H_5)_3 + (C_6H_5)_3SiLi$$

and another disilane.[18] If these findings can be extended to tetrasubstituted silanes, it may be that the trialkylsilyl-

$$(CH_3)_3Si(C_6H_5) + (CH_3)_3SiK \longrightarrow (CH_3)_3SiSi(CH_3)_3 + C_6H_5K$$

potassium compound reacted with starting material to give hexaalkyldisilane and phenylpotassium. A reinvestigation of the higher boiling fractions from these reactions would seem to be called for.

The cleavage of trialkylarylsilanes with bulky substituents in the ortho position was investigated, in hopes that steric strain on the silicon-aromatic carbon bond might facilitate cleavage with lithium to give a less reactive, more stable trialkylsilyllithium intermediate. But reduction similar to that reported in low boiling amines[20,160] rather

$$(CH_3)_3Si(C_6H_5) + Li \longrightarrow (CH_3)_3Si(C_6H_5 \cdot 6\ Li)$$

than cleavage seemed to be the rule and high recoveries of starting materials resulted.

Organosilicon Hydrides

If recent industrial interest in chloro- and dichlorosilane continues to the point where the compounds become commercially available, rapid advances in the field of organosilicon hydrides will be possible. The potential of compounds containing one or more hydrogens bonded to a silicon atom as starting materials for the preparation of high temperature lubricants, as reducing agents and as tools for the elucidation of reaction mechanisms is tremendous, and other uses may develop as time passes.

Of these possibilities, efforts are closest to fruition in the area of high temperature lubricants. Almost any group may be added to an organosilicon hydride by proper choice of organometallic reagent and solvent. In particular, the technique of Gilman and Zueck[101] enables one to prepare tetrasubstituted silanes of any desired degree of symmetry. With a minimum of effort it would be possible to evaluate the intrinsic thermal stability of organic groups when bonded to silicon and arrive at the most thermally stable silane possible. Evaluation of the effect of groupings on the melting point, boiling point, viscosity and pour point of the finished product would also be possible.

From the data accumulated in this study several conclusions about the preparation of high temperature lubricants from organosilicon hydrides are possible. Alkylsilanes of the type $RSiH_3$ are difficult to prepare in high yields and purity from the Grignard reagents and silicon tetrachloride, and reduction of the intermediate chlorosilanes. Further reaction of the compounds with Grignard reagents in tetrahydrofuran is slow and yields are low. The reaction of dialkylsilanes proceeds only with reactive organomagnesium compounds such as allylmagnesium chloride and even then yields are low. Alkyl groups do impart good lubricity to tetrasubstituted silanes, nonetheless, and at present it would appear best to introduce the alkyl group into R_3SiH types.

While the infrared data are not complete, enough information is available to make the following generalizations. The position of the absorption band for the Si-H stretching vibration is affected by the degree of substitution of an organosilicon hydride and by the nature of the substituent. The following order (decreasing wave numbers) is an indication of this: p-anisylsilane > n-hexylsilane > di-p-anisylsilane > n-hexadecylphenylsilane > di-n-hexylsilane > tri-p-anisylsilane > tri-n-hexylsilane. Although the p-anisyl group is higher than n-hexyl on Kharasch and Flenner's scale of electronegativities,[166] mesomeric return of electrons from the aromatic system to the d-orbitals of the silicon makes the silicon-hydrogen bonds in p-anisylsilane (2153.5 cm.$^{-1}$) nearly equivalent to the silicon-hydrogen bonds in n-hexylsilane (2152 cm.$^{-1}$), which implies double bond character to a silicon-aromatic carbon bond. That this double bond character is an important consideration is borne out by a comparison of di-p-anisylsilane (2134 cm.$^{-1}$) with di-n-hexylsilane (2125 cm.$^{-1}$).

Branching at the alpha carbon atom of an aliphatic substituent shifts the position of the absorption band to lower frequencies. This is best illustrated by comparison of cyclohexylsilane (2143 cm.$^{-1}$) with n-hexylsilane (2152 cm.$^{-1}$) or of dicyclohexylsilane (2111.5 cm.$^{-1}$) with di-n-hexylsilane (2125 cm.$^{-1}$). The data would seem to indicate that there is some double bond character in a silicon-aliphatic carbon bond, hyperconjugative effects being the controlling factor.

An arrangement of organosilicon hydrides according to decreasing wave number corresponds very closely to an arrangement dependent on the rate of hydrogen evolution with base. Correlating the two, it would appear that as more organic groups are attached to an organosilicon hydride, the remaining silicon-hydrogen bonds become more covalent, and that variations in the structure of the organic group further

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[166] M. S. Kharasch and A. L. Flenner, J. Am. Chem. Soc., 54, 674 (1932).

affect the degree of covalency. If this indeed is the case, it is entirely possible that a series of reducing agents of varying potential could be developed from organosilicon hydrides. Little work has been done along this line but from the information at hand this field appears to be an interesting one of great practical significance.

Organosilicon hydrides may also be useful in the elucidation of reaction mechanisms. One is often pressed to prepare a particular hydrocarbon for study; whereas using an organosilicon hydride and organometallic reagents the analogous silane may be comparatively easy to prepare. Eaborn and co-workers[167,168] have used silicon compounds quite successfully to determine directive effects and Hammett sigma and rho values for aromatic substituents. Kreevoy and Erying[169] have recently suggested what they call α-hydrogen bonding as an explanation of the Baker-Nathan effect, i.e., stabilization of a carbonium ion through interactions between 1,3-atoms in complex molecules. Silicon, which is $\delta+$ in its compounds due to electronegativity differences, is somewhat analogous to a carbonium ion and a study of silanes using nuclear magnetic resonance could shed some light on the original proposal.

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[167] C. Eaborn, J. Chem. Soc., 1956, 4858.

[168] C. Eaborn and D. E. Webster, ibid., 1957, 4449.

[169] M. M. Kreevoy and H. Erying, ibid., 79, 5121 (1957).

The copper(II) chloride-pyridine-water reagent proved to be a valuable tool during the synthesis part of this study. Whenever silicon tetrachloride was reacted with a Grignard reagent and reduced with lithium aluminum hydride, a mixture of products was obtained. Distillation gave several fractions, and this test proved to be a simple, rapid means of pin-pointing the identity of each fraction. The general applicability of the test was proved when over seventy organosilicon hydrides were found to conform to the specifications without exception.

Suggestions for Further Research

Suggestions for further research are embodied in the preceding material under the subdivisions to which they apply.

SUMMARY

Organic compounds containing silicon or germanium as hetero atoms have been a subject of interest as high temperature lubricants and hydraulic fluids in recent years. The possibility that trialkylsilylmetallic and trialkylgermylmetallic compounds could be interacted with a wide variety of organic molecules to give compounds of low melting point and high thermal stability, as well as a fundamental interest in the intermediates themselves, prompted an investigation of the preparation and stability of compounds of this type.

Metalation of triethylgermane with n-butyllithium or phenyllithium in diethyl ether was slow and gave triethylgermyllithium in yields of less than 10 percent. Attempts to prepare triethylgermylmetallic compounds by cleavage of tetraethylgermane or hexaethyldigermane with lithium or sodium-potassium alloy failed. With tetraethylgermane and the alloy, colors were observed during the cleavage period and it was impossible to recover starting material or product. This was taken as an indication that triethylgermylpotassium was formed but immediately underwent reaction with the solvent in some unknown manner. Reaction between triethylchlorogermane and lithium in ether and in tetrahydrofuran gave hexaethyldigermane in 60 and 18 percent yields, respectively.

Endeavors to prepare trialkylsilylmetallic compounds were unsuccessful. Hexaethyldisilane and various trialkylarylsilanes were unaffected by lithium or sodium-potassium alloy in diethyl ether. In tetrahydrofuran or ethylene glycol dimethyl ether, lithium reduced the aryl substituent of trialkylarylsilanes without cleavage. With sodium-potassium alloy in tetrahydrofuran at -50°, cleavage of trimethylphenylsilane and triethylphenylsilane did occur. It was possible to derivatize the phenylpotassium so formed in yields of about 80 percent but derivatives of the trialkylsilylpotassium could not be isolated, indicating that this class of compounds is extremely reactive.

Various organosilicon hydrides were prepared and the chemical and physical properties of the silicon-hydrogen bond investigated. Although there is little evidence of reaction in diethyl ether, organosilicon hydrides do react with Grignard reagents in tetrahydrofuran under specific reaction conditions. Alkylsilanes of the type $RSiH_3$ react with alkyl, aryl, or aralkyl Grignard compounds in a 1:1 ratio to give $RR'SiH_2$ compounds in fair yields. Dialkylsilanes, R_2SiH_2, react only with active Grignard compounds, such as allylmagnesium chloride, to give a trisubstituted silane and then only in low yields.

The infrared spectra of the organosilicon hydrides prepared were investigated. The band attributed to stretching of the silicon-hydrogen bond was found to shift to lower frequencies as the number of hydrogens attached to a silicon atom decreased. Further variations due to mesomeric and hyperconjugative contributions of the organic groups were also observed, implying double bond character to silicon-carbon bonds.

A copper(II) chloride-pyridine-water reagent was found to be a rapid and simple indicator of the degree of substitution of an organosilicon hydride.

For the purpose of this review, a literature search for data pertinent to each of the three sections prior to April, 1958, has been made.

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