1951

Relationships between some organosilicon compounds and their carbon analogs

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RELATIONSHIPS BETWEEN SOME ORGANOSILICON COMPOUNDS AND THEIR CARBON ANALOGS

by

Gerald Emery Dunn

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

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Signature was redacted for privacy.

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Iowa State College

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ACKNOWLEDGMENTS

The author wishes to express his appreciation to Dr. Henry Gilman for the advice and encouragement proffered during the course of this investigation.

Thanks are also due to E.I. Du Pont de Nemours and Co. for a Fellowship which made part of the work possible, and to Dr. George S. Hammond for many helpful and stimulating discussions.

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INTRODUCTION

In 1863 Friedel and Crafts synthesized the first organosilicon compound, tetraethylsilane,[1] and in the same year Wöhler suggested that this synthesis might initiate a whole new branch of chemistry similar to that of carbon.[2] Friedel and Ladenburg approved of this idea,[3] and for many years the motivating force behind research in organosilicon chemistry was the desire to demonstrate and develop the similarity in the two branches of the science.

Kipping entered the field with this point of view. His original purpose was to demonstrate the tetrahedral arrangement of atoms bonded to silicon by showing optical activity in compounds having four different groups attached to silicon. In this he succeeded, but the extended series of investigations in which he became engaged led him to the conclusion that the field of organosilicon chemistry did not match that of carbon chemistry and that, indeed, the differences between the two fields were greater than the similarities.[4] Later workers have tended to confirm this viewpoint.

---

[1] C. Friedel and J.M. Crafts, Ann., **127**, 28 (1863).

[2] F. Wöhler, Ann., **127**, 257 (1863).

[3] C. Friedel and A. Ladenburg, Ann., **145**, 179 (1868).

[4] F.S. Kipping, Proc. Roy. Soc. (London), **159A**, 139 (1937).

It has been the purpose of this investigation to compare the chemistries of silicon and carbon from the point of view of reaction mechanisms. Special emphasis has been given to two aspects of the problem: (1) the study of the displacement of groups from silicon by basic reagents, and (2) the mechanism by which the polar effects of substituents are transmitted through the silicon atom to adjacent groups.

The first problem was approached through examination of the cleavage of organic groups from silicon by organolithium reagents, and the cleavage of hydrogen from organosilicon hydrides by aqueous piperidine. The second problem was approached through an examination of the sigma constants of various polar groups when found in organosilicon hydrides. Some attention was also devoted to the study of compounds which might be expected to dissociate into organosilicon radicals.

HISTORICAL

Up to the present time there has been no comprehensive comparison of the properties of the organic compounds of silicon and carbon. Kipping touched on some points of similarity and difference in his Bakerian lecture,[4] and specific points of comparison were occasionally mentioned in the long series of papers which preceded it. The group of workers led by Whitmore made a fairly extensive comparison of the physical properties of organosilicon compounds and their carbon analogs,[5] and many of their papers drew attention to the contrast between the reactions of the organosilicon compounds being discussed and reactions of analogous carbon compounds. Other such comparisons have been of a very limited nature, and are reported as the specific points in question are taken up below.

The historical survey of comparisons between compounds of silicon and carbon which follows includes both relationships which were specifically stated by the authors of the papers concerned, and others which were not so specifically stated. Where the conclusions are those of the original worker, an attempt has been made to indicate this by some suitable statement in the report. Obviously, all the literature references to analogous compounds of silicon and carbon could be recorded only in a

---

[5] F.C. Whitmore, L.H. Sommer, P.A. DiGiorgio, W.A. Strong, R.E. Van Strien, D.L. Bailey, H.K. Hall, E.W. Pietrusza, and G.T. Kerr, J. Am. Chem. Soc., 68, 475 (1946).

monograph of considerable extent. The citations given here are intended to be illustrative rather than exhaustive. Only those compounds of silicon which contain a silicon-carbon bond have been considered, except in a few special cases.

A bibliography of general references to the chemistry of organosilicon compounds has been compiled at the end of this dissertation.

Physical Properties

From the relative positions of silicon and carbon in the periodic table, the following facts can be derived: (1) both have a normal covalency of four; (2) both have their normal bonding orbitals directed tetrahedrally; (3) silicon is larger and heavier than carbon; (4) silicon is less electronegative than carbon; and (5) under favorable circumstances silicon may have a coordination number greater than four. All of the similarities and differences between the compounds of carbon and silicon may be traced to one or more of these five fundamental relationships.

In the first two of the relationships silicon and carbon are similar and, among the properties of the compounds of these two elements, those which depend in large part upon relationships (1) and (2) show striking similarities. Some of these may be illustrated here.

As is stated by relationship (1), the normal covalence of both elements is four. In a sense, silicon adheres to this generalization even better than carbon, since no organic compound has ever been isolated in which silicon has a formal covalence either greater or less than four, while in the free radicals, such as triphenylmethyl, carbon has a formal covalence of three.

In consequence of relationship (2), compounds in which four different groups are attached to either element show optical activity. Kipping's successful attempt to establish this point, and consequently to confirm the tetrahedral arrangement around silicon, started him on the forty-year series of investigations which laid the groundwork of organosilicon chemistry.[4]

Relationships (1), (2), and (3) are all involved in the agreement which exists between the boiling points of analogous compounds of carbon and silicon. Lewis and Newkirk[6] have shown that an additive system of atomic and group boiling point numbers developed by Kinney[7] for carbon compounds can be extended to organosilicon compounds. This suggests that a simple relationship should exist between the boiling points of silicon and carbon analogs, and such is shown to be the case in Figure 1. A similar relationship is illustrated for densities in Figure 2. In each case, a property of about twenty organosilicon compounds picked at random from the literature is plotted against the corresponding property of their

---

[6] R.N. Lewis and A.E. Newkirk, J. Am. Chem. Soc., 69, 701 (1947).

[7] C.R. Kinney, J. Am. Chem. Soc., 60, 3032 (1938); Ind. Eng. Chem., 32, 559 (1940); ibid., 33, 791 (1941); J. Org. Chem., 6, 220, 224 (1941); ibid., 7, 111 (1942).

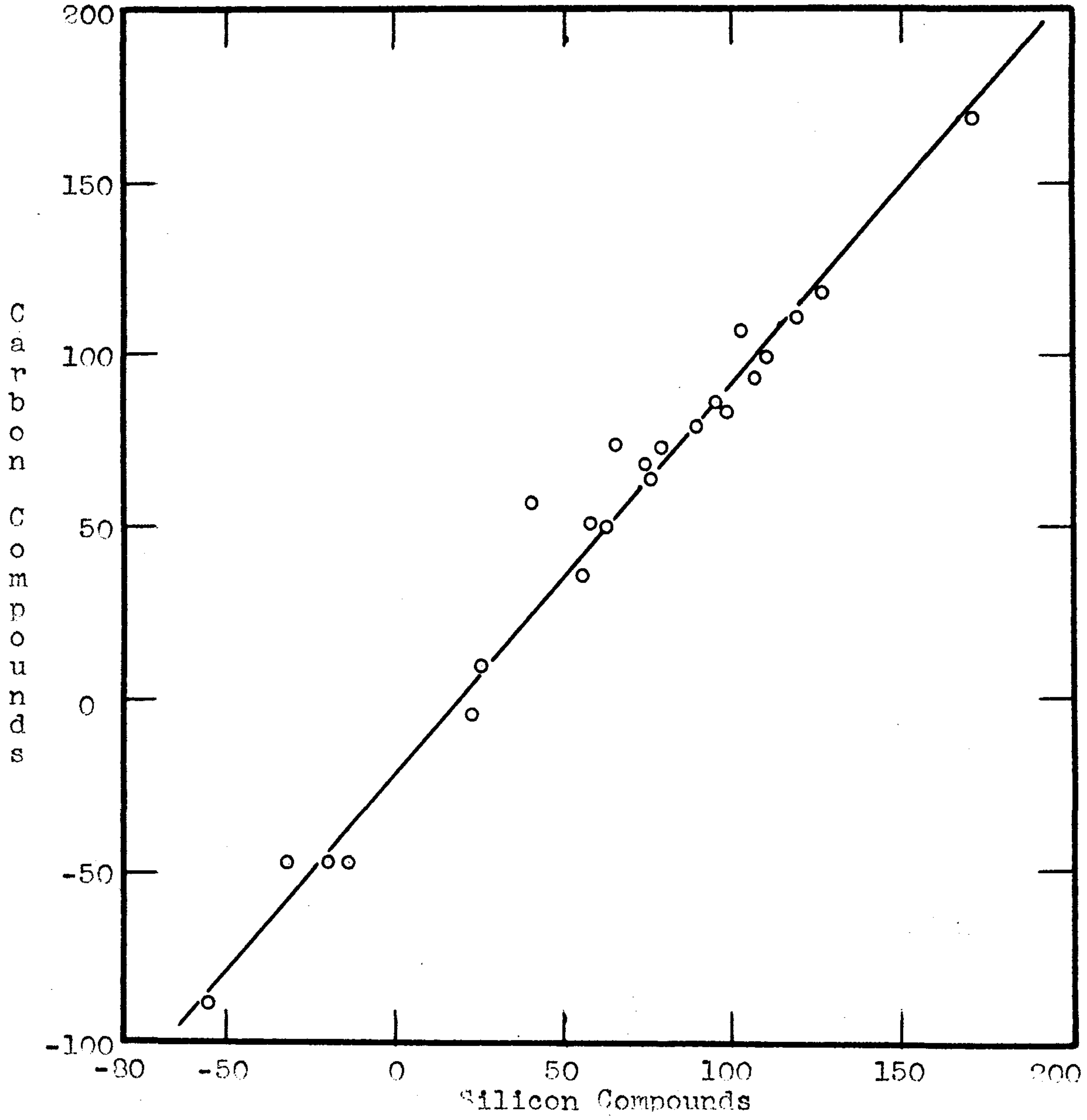

Fig. 1. Relationship between the boiling points (760 mm) of silicon[56] and carbon analogs. The values for the carbon compounds are from N. A. Lange, "Handbook of Chemistry", Handbook Publishers Inc., Sandusky, Ohio, 6th. Ed., 1946, and from B. Prager and P. Jacobson, "Beilsteins Handbuch der organischen Chemie", Julius Springer, Berlin, 4th. Ed., 1918.

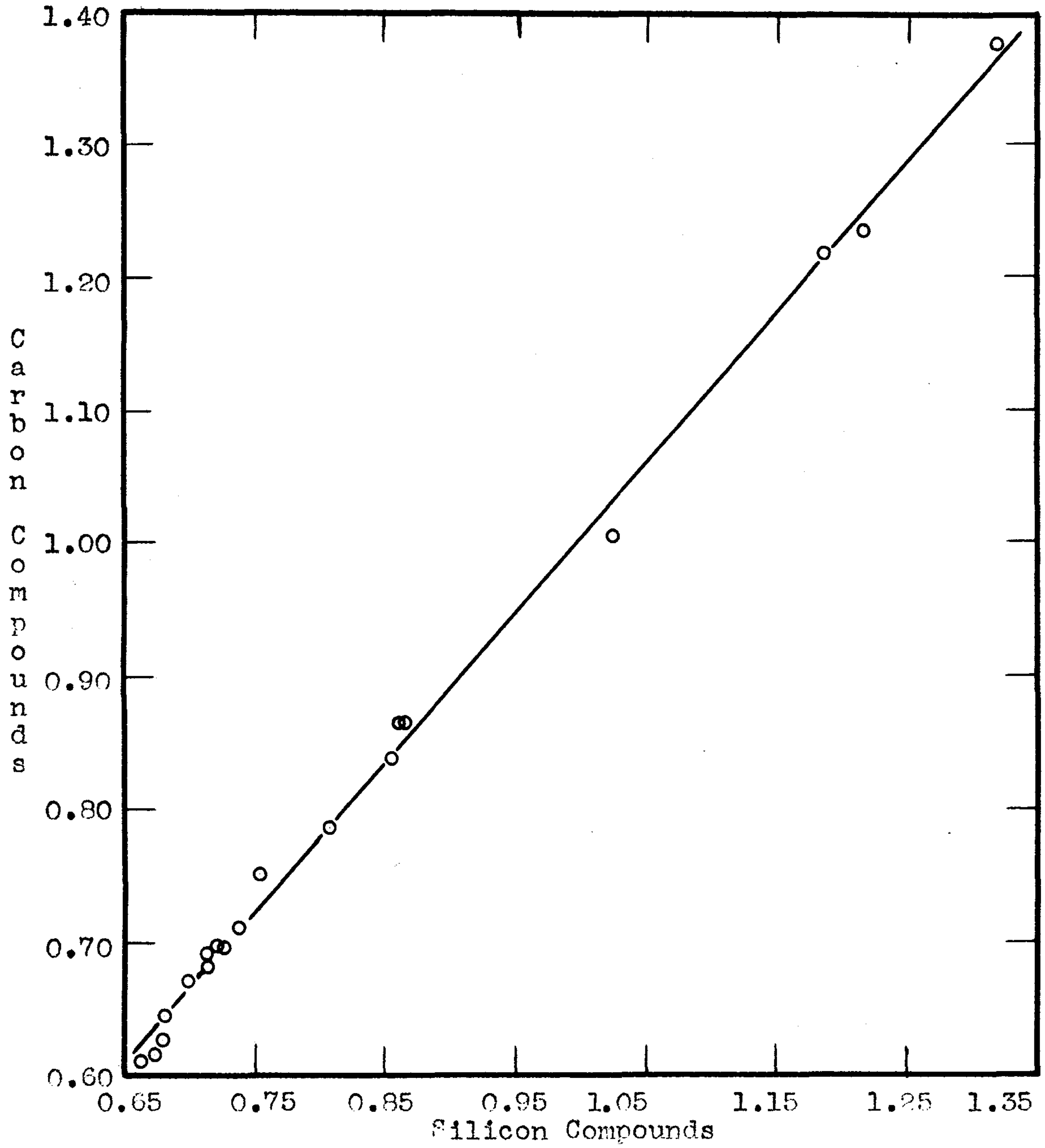

Fig. 2. Relationship between the densities of silicon and carbon analogs.

carbon analogs. The linear relationship is reasonably good in each case. The constants of silicon and carbon analogs are related by the equations $S = 19.8 + 0.878C$ for boiling points and $S = 0.118 + 0.878C$ for densities, where S is the constant for a silicon compound and C is the corresponding constant for its carbon analog. Since Trouton's law has been shown to hold with about the same accuracy for silicon compounds as for carbon compounds,[8,9,10] it is apparent that a similar relationship must hold for molar heats of vaporization.

In the case of molar refractions the situation is not so simple. Warrick[11] and Sauer[12] have shown that an additive system containing bond refractivities gives better results than one of atomic or group refractivities alone, and Warrick has shown that the bond refractivity values derived by Denbigh for carbon compounds[13] can also be applied to similar bonds in organosilicon compounds. This suggests the possibility of a linear relationship between the molar refractivities of silicon and carbon analogs.

---

[8] H.J. Emeleus and S.R. Robinson, *J. Chem. Soc.*, *1947*, 1592; G.S. Forbes and H.H. Anderson, *J. Am. Chem. Soc.*, *70*, 1222 (1948); H.S. Booth and R.L. Jarry, *ibid.*, *71*, 971 (1949).

[9] A.E. Finholt, A.C. Bond, K.E. Wilzbach, and H.I. Schlesinger, *J. Am. Chem. Soc.*, *69*, 2692 (1947).

[10] G.S. Forbes and H.H. Anderson, *J. Am. Chem. Soc.*, *70*, 1043 (1948); H.H. Anderson, *ibid.*, *70*, 1220 (1948).

[11] E.L. Warrick, *J. Am. Chem. Soc.*, *68*, 2455 (1946).

[12] R.O. Sauer, *J. Am. Chem. Soc.*, *68*, 954 (1946).

[13] K.G. Denbigh, *Trans. Faraday Soc.*, *36*, 936 (1946).

Unfortunately, there are not enough comparable data in the literature to test this possibility. However, since there is a linear relationship between the densities of silicon and carbon analogs, and since the relationship between n and $(n^2-1)/(n^2+2)$ is almost exactly linear for the short range 1.4-1.5, a satisfactory test can be made by comparing analogous refractive indices. The meager data available are plotted in Figure 3.

It is seen that when compounds having all four valences of silicon attached to carbon are compared with their carbon analogs, a linear relationship holds in which $S = 0.193 + 0.870C$. When compounds containing silicon-oxygen and silicon-halogen bonds are compared with their carbon analogs there is also a linear relationship, but the slope and intercept of the line are quite different. Not enough data are available to make possible any conclusions for compounds having silicon-hydrogen or silicon-nitrogen bonds. These plots provide striking evidence for the validity of the postulate by Denbigh[13] and Warrick[11] that bond refractivities are more generally applicable than atomic refractivities. Refraction of visible light depends upon the electronic polarizabilities of molecules, and for any atom this will vary as other atoms of different electronegativities are attached. Evidently relationship (4) is of importance in comparing refraction by silicon and carbon analogs.

It is hardly to be expected that any simple relationship should exist between the melting points of silicon and carbon compounds. Relatively small changes in molecular size and shape may cause large changes in

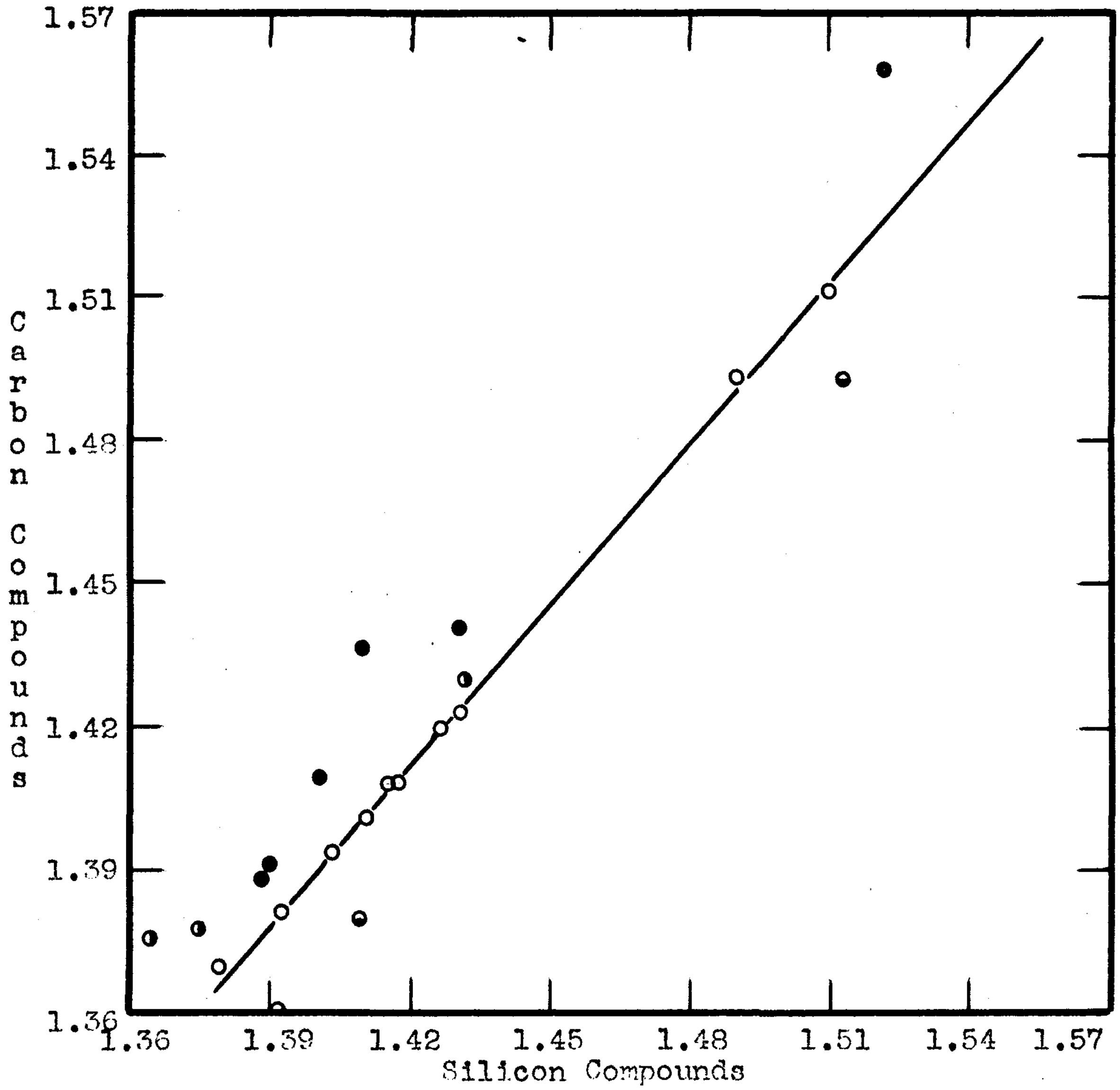

Fig. 3. Relationship between the refractive indices of silicon and carbon analogs: ○ ○ represent compounds with silicon-carbon bonds only; ● ● represent compounds having silicon-halogen bonds; ◑ ◑ represent compounds having silicon-oxygen bonds; and ● ◒ represent compounds having silicon-hydrogen bonds.

crystal structure, with consequent erratic effect on melting-point relationships. From Figure 4, where the available data are plotted, it is seen that, while there is a general linear trend, the average deviation from linearity is large. The equation for the melting-point relationship is $S = -13 + 0.878C$, and from this the melting point of an organosilicon compound can be calculated with a probable error of 17°, as compared to a probable error of 5° in the boiling point calculation. The three solid circles, which do not fit the plot, represent hexasubstituted disilane-ethane pairs. The large deviations here are probably due to the highly strained nature of the ethanes. In this connection, Whitmore and co-authors have published the following comparison of the liquid ranges of some hexasubstituted ethanes and disilanes.[14]

TABLE I.

Liquid Range of Organosilicon Compounds

Compound	Approximate Liquid Range, °C.
Cl_3CCCl_3	0
Cl_3CSiCl_3	40
$Cl_3SiSiCl_3$	145
$(CH_3)_3CC(CH_3)_3$	5
$(CH_3)_3CSi(CH_3)_3$	30
$(CH_3)_3SiSi(CH_3)_3$	100

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[14] P.A. DiGiorgio, L.H. Sommer, and F.C. Whitmore, *J. Am. Chem. Soc.*, *70*, 3512 (1948).

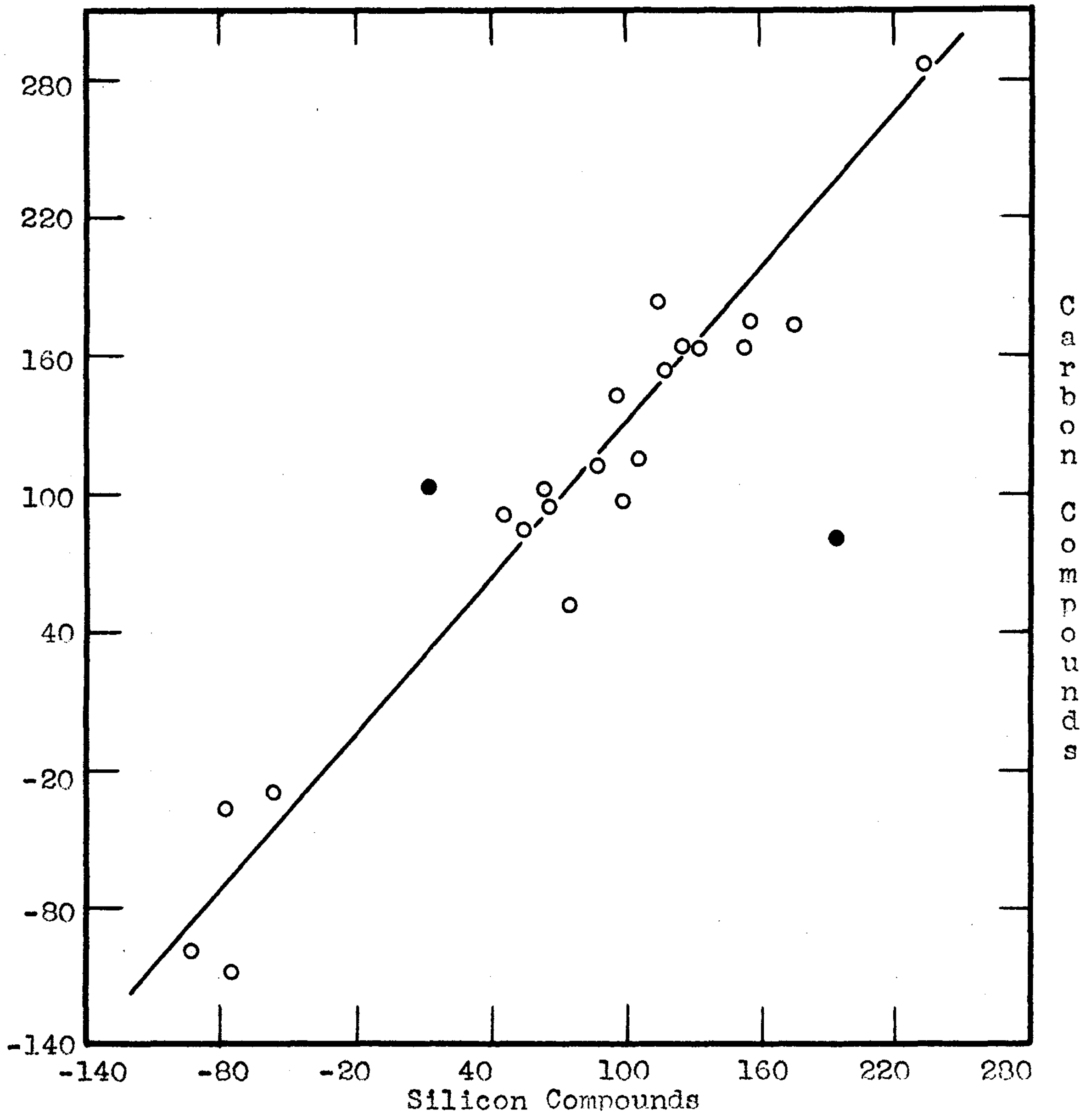

Fig. 4. Relationship between the melting points of silicon and carbon analogs: ● ● represent disilanes: ○ ○ represent all other types of organosilicon compounds.

Investigations of some of the less commonly encountered physical constants have been reported, but these have been, for the most part, on polysiloxanes which have no carbon analogs. Measurements of surface tension on various organosilicon compounds have led to atomic parachors for silicon varying from 25.8 to 38.2,[14,15,16] and several authors have suggested that bond parachors might be more satisfactory.[14] This suggests that a comparison of surface tensions of silicon and carbon analogs might lead to a result more like that with refractive index than like those with boiling point and density.

Extensive investigations of the viscosity of polysiloxanes have been reported. The carbon analogs of these compounds are unknown, but the structural relationship between polysiloxanes and polyisobutylenes is fairly close (in the latter, carbon has replaced both silicon and oxygen), and comparisons of these compounds have been made. The most noticeable feature is the much smaller temperature coefficient of viscosity of the siloxanes. This has been attributed by one group of workers[16] to a coiled-chain structure for polysiloxanes which uncoils with rising temperatures, thus offsetting the usual decrease in viscosity with increasing temperature.

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[14] M.J. Hunter, E.L. Warrick, J.F. Hyde, and C.C. Currie, J. Am. Chem. Soc., 68, 2284 (1946); C.A. MacKenzie, A.P. Mills, and J.M. Scott, ibid., 72, 2032 (1950).

[15] M.J. Hunter, J.F. Hyde, E.L. Warrick, and H.J. Fletcher, J. Am. Chem. Soc., 68, 667 (1946); W.J. Jones, L.H. Thomas, E.H. Pritchard, and S.T. Bowden, J. Chem. Soc., 1946, 824.

[16] H.W. Fox, P.W. Taylor, and W.A. Zisman, Ind. Eng. Chem., 39, 1401 (1947).

The smaller size of the carbon atom prevents coiling of the polyisobutylene molecules. However, Barry concludes from their respective relationships between viscosity and molecular weight that the amount of coiling is about the same in polysiloxanes and polyisobutylenes.[17]

In conclusion, it is interesting to note that in all four cases where a physical constant for silicon compounds has been plotted against the physical constant for the corresponding carbon compounds, the slope of the linear relationship is approximately the same (0.878) and is not unity. The significance of this fact is not apparent.

Chemical Properties

Silicon-carbon single bonds

The chemical properties, like the physical properties, of compounds containing analogous silicon-carbon and carbon-carbon bonds are related to the five fundamental relationships enumerated in the section on physical properties. Pauling[18] lists the following quantitative estimates of these relationships: bond energy, kcal./mole, Si-C 57.6, C-C 58.6; bond length, Å, Si-C 1.93, C-C 1.54; per cent ionic bond character, Si-C 11, C-C 0.

The point first noted in connection with these figures is the similarity in bond energies for the silicon-carbon and carbon-carbon bonds. This indicates that toward homolytic cleavage the bonds will have

---

[17] A.J. Barry, J. Applied Phys., 17, 1020 (1946).

[18] L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, N.H., 1945.

similar stabilities. There is considerable evidence that the thermal stability of both bonds is high, and probably of the same order of magnitude. Thus, such compounds as tetraphenylsilane[6] and tetraphenylmethane[19] can be boiled undecomposed at high temperatures (428° and 431°, respectively) and are stable at temperatures of 500° or higher.

With regard to reactivity, however, the situation is different. The facts that the silicon atom is larger, less electronegative, and capable of a greater maximum coordination number than the carbon atom, make the silicon-carbon bond considerably more reactive than the carbon-carbon bond toward a number of reagents.

For example, trimethylarylsilanes are cleaved by acids under fairly mild conditions to give trimethylsilanol and a substituted benzene,[20] while tertiary butylbenzenes are relatively stable toward acids. Presumably, the partial ionic character of the silicon-carbon bond facilitates attack by proton at the negative (carbon) end of the dipole.

The silicon-carbon bond is also more susceptible to basic cleavage. Thus, triphenylbenzylsilane and many others are readily cleaved by potassium hydroxide in alcohol, acetone, or dioxane, to give triphenylsilanol and a hydrocarbon,[21] while triphenylbenzylmethane, for example,

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[19] F. Ullmann and A. Munzhuber, Ber., 36, 404 (1903).

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

[21] L.S. Miller, Doctoral Dissertation, Iowa State College (1950).

is relatively inert toward bases. Any substituent which tends to increase the polarity of the bond has a greater effect on the reactivity of a silicon-carbon bond than on its carbon-carbon analog. For example, in compounds of the type X_3C-AY_3, where A is a carbon or silicon atom attacked by base, cleavage of the C-A rather than the X-C bond occurs in the carbon analog only if all three X atoms are halogen and at least two of the Y positions are occupied by oxygen. When A is silicon, only one X need be a halogen atom and only one Y an oxygen atom in order to get cleavage of the C-A bond.[22] In the case of trichloromethyltrichlorosilane, cold water alone cleaves the carbon-silicon bond readily.[14] In hexachloroethane the carbon-carbon bond is not cleaved even by alcoholic potassium hydroxide at 100°.[23] Cleavage is probably facilitated in the case of silicon compounds by the positive character of the silicon atom, its greater size (which decreases shielding by the surrounding groups), and its ability to increase its coordination number, all of which make nucleophilic attack easier.

Carbon-silicon bonds are also more reactive toward halogen than are carbon-carbon bonds. Although catalytic halogenation of organosilicon compounds is a common operation, it must be done under rather mild conditions to avoid cleavage.[24] The relative susceptibility of the silicon-

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[22] R.H. Krieble and J.R. Elliott, J. Am. Chem. Soc., 68, 2291 (1946).

[23] M. Berthelot, Ann., 109, 121 (1859).

[24] H.J. Emeleus and D.S. Payne, J. Chem. Soc., 1947, 1590.

carbon and carbon-carbon bonds to cleavage by halogen is illustrated by the facts that trimethylphenylsilane is cleaved by bromine or iodine to give a trimethylhalosilane and a halobenzene,[25] while with tertiary butylbenzene aromatic bromination is possible.[26]

A similar contrast is seen in the behavior of silicon-carbon and carbon-carbon bonds towards anhydrous aluminum chloride. In carbon chemistry the Friedel-Crafts reaction is one of the most commonly used methods of making carbon-carbon bonds. In organosilicon chemistry aluminum chloride, under similar conditions, is a convenient method of breaking silicon-carbon bonds.[27] Even anhydrous ferric chloride will cleave silicon-carbon bonds under mild conditions.[28]

$$(C_2H_5)_4Si + FeCl_3 \xrightarrow[\text{CHCl}_3]{\text{reflux in}} (C_2H_5)_3SiCl + C_2H_6$$

Up to this point, reactions have been reported in which the silicon-carbon bond is more reactive than the carbon-carbon bond. That this is

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

[26] Tchitchibabine, S. Elgasine, and V. Lengold, Bull. soc. chim., 43, 238 (1928).

[27] L.H. Sommer, D.L. Bailey, and F.C. Whitmore, J. Am. Chem. Soc., 70, 2869 (1948); B.N. Dolgov and O.K. Panina, Zhur. Obshchei Khim., 18, 1293 (1948), /C.A., 43, 2177 (1949)7.

[28] Z.M. Manulkin, Zhur. Obshchei Khim., 18, 299 (1948), /C.A., 42, 6742 (1948)7.

not the universal result of the fundamental differences between silicon and carbon is illustrated by the reactions of tetraphenylsilane and tetraphenylmethane with hydrogen. Tetraphenylmethane is cleaved by hydrogen under pressure at 250° to give triphenylmethane and benzene while, under similar conditions of pressure, tetraphenylsilane remains unchanged at temperatures as high as 450°.[29] It is probable that, in such highly substituted molecules as the tetraarylsilanes, the vulnerable silicon-carbon bonds are shielded by the surrounding groups. Thus, triethylphenylsilane is cleaved by hydrogen at 350° to triethylsilane and benzene.[29] In the tetraarylmethanes the shielding of the central bonds is equally good, but one may suppose that increased strains, due to the smaller central atom in the methane, make the central bonds unusually labile.

Silicon-carbon double bonds

In contrast to the immense importance of unsaturation in carbon chemistry, there is a complete absence of evidence for the existence of any organosilicon compound containing a double bond to silicon. Schlenk, in 1912, reported the preparation of diphenylmethylenesilane, $(C_6H_5)_2Si{=}CH_2$, from the hydrolysis of diphenylmethylchlorosilane.[30] However, Kipping was unable to repeat this work, obtaining instead sym-tetraphenyldimethyldisiloxane.[31] Fifteen years of research on the subject led him to the

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[29] W. Ipatiev and B. Dolgov, Ber., 62, 1220 (1929).

[30] W. Schlenk, Ann., 394, 221 (1912).

[31] F.S. Kipping, J. Chem. Soc., 1927, 104.

conclusion that "an ethylenic binding between carbon and silicon is either impossible or can only be produced under exceptional circumstances".[31,32] The complete lack of any subsequent evidence to the contrary makes it highly probable that he was correct.

The failure of silicon to form double bonds with carbon is not a property peculiar to this element alone, but rather one that is shared by most elements outside the first row of the periodic table. Pitzer and Mulliken have discussed this subject on theoretical grounds. Their general arguments may be illustrated by reference to silicon and carbon. According to Pitzer, silicon-carbon double bonds are unlikely because the greater silicon-carbon bond distance makes the overlap of π-orbitals on the singly bonded atoms small.[33] Mulliken has calculated quantum mechanically the orbital overlap for silicon-carbon and carbon-carbon bonds (using an arbitrarily chosen double bond length in the silicon-carbon case), and reached the conclusion that a silicon-carbon double bond should have about the same bond energy as a carbon-carbon double bond.[34] A silicon-carbon single bond, however, according to his calculation, should be much stronger than a carbon-carbon single bond, and the lack of silicon-carbon double bonds could be attributed to the much more favorable energy relationship of two single bonds to one double bond in the silicon-carbon than in the carbon-carbon case.

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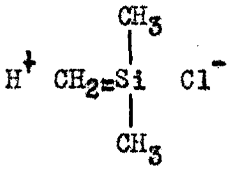
[32] F.S. Kipping, A.G. Murray, and J.G. Maltby, J. Chem. Soc., 1929, 1108.

[33] K.S. Pitzer, J. Am. Chem. Soc., 70, 2140 (1948).

[34] R.S. Mulliken, J. Am. Chem. Soc., 72, 4493 (1950).

The mere non-existence of compounds containing silicon-carbon double bonds does not mean that resonance structures containing such bonds may not make contributions to the total ground state of a molecule. The silicon-carbon bond distance in methylsilanes decreases as methyl groups are successively replaced by chlorine atoms (silicon-carbon bond distance, Å: $(CH_3)_4Si$, 1.93; $(CH_3)_3SiCl$, 1.89; $(CH_3)_2SiCl_2$, 1.83),[35] and it has been proposed[36] that this can be explained by increasing contributions from structures such as



$$H^+\ CH_2{=}\overset{CH_3}{\underset{CH_3}{Si}}\ Cl^-$$

which are similar to structures commonly believed to make considerable contributions to analogous carbon compounds. Similar structures for silicon compounds have been proposed on the basis of dipole moment studies of the halosilanes.[37]

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[35] L.O. Brockway and H.O. Jenkins, J. Am. Chem. Soc., 68, 719 (1946); R.L. Livingston and L.O. Brockway, ibid., 66, 94 (1944); L.O. Brockway and H.O. Jenkins, ibid., 58, 2036 (1936).

[36] A.Y. Yakubovich and V.A. Ginsberg, Uspekhi Khim., 18, 46 (1949), [C.A., 44, 1404 (1950)].

[37] C. Curran, R.M. Witucki, and P.A. McCusker, J. Am. Chem. Soc., 72, 4471 (1950).

Pauling[18] points out that most double bond distances are about 0.20 Å shorter than the corresponding single bond distances. Since the silicon-carbon bond distance in dimethyldichlorosilane is about 0.10 Å shorter than in tetramethylsilane, the silicon-carbon bond in the former would be required to have 50% double bond character by this theory. However, the theoretical considerations of both Pitzer and Mulliken make it likely that contributions from such structures would be small. According to Pitzer, the carbon-silicon π-orbital overlap is small, and from Mulliken's point of view the energy to be gained by changing a silicon-carbon single bond to a silicon-carbon double bond would be small in comparison with that lost by breaking a carbon-hydrogen bond and a silicon-chlorine bond. Evidently a decision on this point is not yet possible.

Silicon-hydrogen bonds

In organic chemistry the element most commonly associated with carbon is hydrogen. In organosilicon chemistry the number of compounds containing silicon-hydrogen bonds form an almost negligible proportion of the total.[38] Herein lies one of the most outstanding differences between the two branches of chemistry. It is the result of the enormously greater reactivity toward polar reagents of the silicon-hydrogen bond as compared with the carbon-hydrogen bond.

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[38] See, for example, the compound lists in C.E. Burkhard, E.G. Rochow, H.S. Booth, and J. Hartt, Chem. Reviews, 41, 97 (1947).

The following physical data (some of it very approximate) on the two types of bonds are available: bond energy, kcal./mole,[33] Si-H 76, C-H 98.2; bond length, Å,[39] Si-H 1.49, C-H 1.09; per cent ionic bond character,[18] Si-H 3, C-H 4. It is seen that thermally the carbon-hydrogen bond is more stable than its silicon analog. The silicon-hydrogen bond is longer than the carbon-hydrogen bond, but this has little significance chemically since the hydrogen atom is so small as to have little steric importance. The two bonds also have about the same amount of ionic character, but the great difference lies in the direction of the polarization. The relative electronegativities of carbon, hydrogen, and silicon are 2.5, 2.1, and 1.8, respectively.[18] This means that the hydrogen atom has the positive end of the dipole in the carbon-hydrogen bond and the negative end in the silicon-hydrogen bond. It should be pointed out, however, that the electronegativity differences among the three atoms are small and the amount of ionic character of the two bonds about equal. The relative inertness of the carbon-hydrogen bond and the high reactivity of the silicon-hydrogen bond are therefore somewhat surprising. Thus, in contrast to the inertness of methane toward reagents other than oxygen, silane is a spontaneously inflammable gas which is hydrolyzed readily by water, and even more readily by aqueous acids and bases.[40] Halogen acids react with

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[39] Calculated from Pauling's covalent radii, see footnote 18.

[40] A. Stock and C. Somieski, <u>Ber.</u>, <u>51</u>, 989 (1918).

it to give mixtures of halosilanes and hydrogen.[41]

This reactivity of the silicon-hydrogen bond decreases as the hydrogens of silane are successively replaced by alkyl or aryl groups.[42] Thus, while hydrolysis of monoalkylsilanes by alkali is very rapid in a two phase system,[43] the hydrolysis of trialkylsilanes by alkali is comparatively slow, even in solution.[44] Similarly, the bromination of silane is a violent reaction, even at low temperatures,[45] while the bromination of triphenylsilane takes place only slowly in refluxing carbon tetrachloride.[46] All this is in contrast to the well known fact that the carbon-hydrogen bond increases in reactivity as it is changed from primary to secondary to tertiary.

However, even the least reactive (tertiary) type of silicon-hydrogen bond is more reactive in most cases than the most reactive (tertiary) type of carbon-hydrogen bond. For example, acyl halides react with trisubstituted silanes in the absence of catalyst to give aldehydes and the corresponding chlorosilanes.[47] No such reaction is known

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[41] A.G. Maddock, C. Reid, and H.J. Emeleus, Nature, 144, 328 (1939).

[42] C.A. Kraus and W.N. Greer, J. Am. Chem. Soc., 44, 2629 (1922).

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

[44] F.P. Price, J. Am. Chem. Soc., 69, 2600 (1947).

[45] A. Stock and C. Somieski, Ber., 50, 1378 (1917).

[46] E.A. Bassett, H.G. Emblem, M. Frankel, and D. Ridge, J. Soc. Chem. Ind., 67, 177 (1948); H. Gilman and T.C. Wu, unpublished results.

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

$$R_3SiH + R'COCl \longrightarrow R_3SiCl + R'CHO$$

for carbon-hydrogen bonds. However, anhydrous aluminum chloride causes analogous reaction of alkyl halides with both silicon-hydrogen[48] and carbon-hydrogen bonds.[49]

In another example, triethylsilane reacts with sodium ethoxide to give triethylethoxysilane and lithium hydride,[50] while tertiary hydrocarbons do not react with sodium ethoxide. Similarly, lithium di-n-butylamide reacts with triphenylsilane to give triphenyldi-n-butylaminosilane and lithium hydride,[51] while no such reaction is known in carbon chemistry.

Triphenylsilane[52] and triethylsilane[50] also react with organolithium compounds in a similar way, while triphenylmethane

$$R_3SiH + R'Li \longrightarrow R_3SiR' + LiH$$

reacts with organolithium in the reverse manner.[53] There is no

$$R_3CH + R'Li \longrightarrow R_3CLi + R'H$$

report of an organolithium compound reacting with a tertiary aliphatic hydrocarbon in any manner.

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

[49] P.D. Bartlett, F.E. Condon, and A. Schneider, J. Am. Chem. Soc., 66, 1531 (1944).

[50] R.N. Meals, J. Am. Chem. Soc., 68, 1880 (1946).

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

[52] H. Gilman and S.P. Massie, J. Am. Chem. Soc., 68, 1128 (1946).

[53] H. Gilman and R.V. Young, J. Org. Chem., 1, 315 (1936).

It will be noted that, in this last series of reactions, the silicon-hydrogen bond resembles a carbon-halogen bond more than a carbon-hydrogen bond.

Finally, it is interesting to note that, in what is presumably a free radical reaction, the silicon-hydrogen and carbon-hydrogen bonds react with similar facility. In 1945 Kharasch and co-workers reported that chloroform, under the influence of organic peroxides or ultraviolet light, adds to olefins to give 1,1,1-trichloroalkanes.[54] Almost immediately several authors[55] applied the reaction to trichlorosilane.

$$Cl_3SiH + CH_2{=}CHR \xrightarrow[\text{or U.V.L.}]{\text{peroxide}} Cl_3SiCH_2CH_2R$$

Yields and reaction conditions are comparable in the two cases. Evidently the ease with which a methyl radical abstracts a hydrogen atom is about the same whether it is taken from silicon or carbon. On the other hand, the ease of removal of halogen must differ considerably between silicon and carbon, since carbon tetrahalides react even better than chloroform, while silicon tetrahalides do not react at all. It is interesting to note that this series of reactivities does not parallel the bond energies (Si-H 76, C-Cl 78, Si-Cl 87, and C-H 98 kcal./mole) in a case where, *a priori*, they might be expected to do so.

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[54] The reaction is best described in a later paper by M.S. Kharasch, E.V. Jensen, and W.H. Urry, *J. Am. Chem. Soc.*, *69*, 1100 (1947).

[55] L.H. Sommer, E.W. Pietrusza, and F.C. Whitmore, *J. Am. Chem. Soc.*, *69*, 188 (1947); C.A. Burkhard and R.H. Krieble, *ibid.*, *69*, 2887 (1947); A.J. Barry, L. DePree, J.W. Gilkey, and D.E. Hook, *ibid.*, *69*, 2916 (1947).

Silicon-silicon bonds

It was stated previously that one great difference between silicon and carbon chemistries is illustrated by the dearth of compounds containing silicon-hydrogen bonds. Another striking difference between the two branches of chemistry is shown by an even greater lack of compounds containing silicon-silicon bonds. Thus, in contrast to the several hundred thousand compounds containing carbon-carbon linked chains and rings, there are at present less than twenty organic compounds known to contain silicon-silicon bonds.[56]

The following physical data are available for the silicon-silicon and silicon-carbon bonds: bond energy, kcal./mole, Si-Si 45, C-C 80;[33] bond length, Å, Si-Si 2.34,[57] C-C 1.54.[18] It will be noted that the silicon-silicon bond has only about one-half the bond energy of the carbon-carbon bond, but the scarcity of silicon-silicon chain compounds can hardly be traced to lack of thermal stability. Thus, 1,2-diethyl-1,2-dipropyl-1,2-diphenyldisilane boils undecomposed at 268° (100 mm.),[58] hexaphenyldisilane melts undecomposed at 360°,[59] and, even though octaphenylcyclotetrasilane is very slowly transformed to a clear plastic mass on prolonged heating above

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[56] See, for example, the compound lists in the review by Burkhard <u>et al.</u>, footnote 36, or in H.W. Post, "Silicones and Other Organic Silicon Compounds", Reinhold Publishing Corporation, New York, 1949.

[57] L.O. Brockway and N.R. Davidson, J. Am. Chem. Soc., 63, 3287 (1941).

[58] F.S. Kipping, J. Chem. Soc., 119, 647 (1921).

[59] W. Schlenk, J. Renning, and G. Racky, Ber., 44, 1178 (1911).

400°, this does not result in carbonization or loss of weight, and decomposition sets in only at higher temperatures.[60] Unsubstituted disilane and trisilane undergo thermal decomposition at 311° and 319°, respectively.[61] The range of thermal stability indicated by these data would include large numbers of organic compounds which are well known and have been thoroughly studied.

Neither is the reactivity of the silicon-silicon bond such as to account for the small number of compounds known. Disilanes are not cleaved by hot concentrated sulfuric acid,[62] refluxing aqueous or alcoholic alkali,[58] oxygen in boiling xylene,[59] sodium in boiling xylene,[59] or sodium in liquid ammonia.[63] Kipping found the phenylpolysilanes to be somewhat more reactive. Although hot aqueous or alcoholic alkali did not attack octaphenyltetrasilane, boiling wet piperidine gave quantitative yields of hydrogen and diphenylsilanediol.[64] The same reagent did not attack disilanes or octadecamethylcyclohexasilane.[64,65] The latter compound was decomposed only by alkali in boiling hexanol.[65] Although carbon compounds analogous

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[60] F.S. Kipping and A.G. Murray, <u>J. Chem. Soc.</u>, <u>1929</u>, 360.

[61] K. Stokland, <u>Trans. Faraday Soc.</u>, <u>44</u>, 545 (1948).

[62] C.A. Burkard and F.J. Norton, <u>Anal. Chem.</u>, <u>21</u>, 304 (1949).

[63] C.A. Kraus and W.K. Nelson, <u>J. Am. Chem. Soc.</u>, <u>56</u>, 197 (1934).

[64] F.S. Kipping and J.E. Sands, <u>J. Chem. Soc.</u>, <u>119</u>, 849 (1921).

[65] C.A.Burkhard, <u>J. Am. Chem. Soc.</u>, <u>71</u>, 963 (1949).

to most of these compounds have not been reported, the highly branched nature of the compounds concerned make it probable that the silicon compounds would not suffer greatly by comparison on grounds of either thermal stability or reactivity.

The lack of polysilanes is to be traced rather to the lack of suitable methods of preparation. Of all the methods suitable for forming carbon-carbon bonds, only one, the Wurtz reaction, has been found to be applicable to the formation of silicon-silicon bonds. The great majority of methods for building carbon-carbon chains depend ultimately on some form of unsaturation, and unsaturated silicon bonds simply do not exist. Using the Wurtz method, Kipping has prepared two isomeric octaphenyltetrasilanes,[66] and Burkhard has prepared a dodecamethylcyclohexasilane.[65] These and some of their derivatives are the only known organic compounds containing more than one silicon-silicon bond. Completely halogenated straight chain silanes containing as many as nine silicon-silicon bonds are known,[67] but when these are treated with Grignard reagents the products never contain more than one silicon-silicon bond.[68] This ease of cleavage of completely halogenated silicon atoms is paralleled by the lability of completely halogenated carbon atoms, in the haloform reaction, for example.

In one respect, at least, the silicon-silicon bond shows a stability

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[66] F.S. Kipping and J.E. Sands, J. Chem. Soc., 119, 830 (1921).

[67] R. Schwarz and H. Meckbach, Z. anorg. allgem. Chem., 232, 241 (1937).

[68] W.C. Schumb and C.M. Saffer, J. Am. Chem. Soc., 61, 363 (1939).

considerably greater than that of its carbon analog. In 1911, Schlenk prepared hexaphenyldisilane in order to compare its tendency to dissociate into free radicals with that of the analogous hexaphenylethane.[59] He found hexaphenyldisilane to be a very stable compound, melting undecomposed at 355°, and completely unreactive toward oxygen and other reagents attacked by triphenylmethyl. Since the silicon-silicon bond energy is only about half that of the carbon-carbon bond, it might be expected that a homolytic cleavage into free radicals would be easier in the silicon than in the carbon case. The fact that the reverse is true is probably due to reduced steric strains in the disilane because of the greater silicon-silicon and silicon-carbon bond distances, and reduced resonance stabilization of the radical which would result on cleavage. This question will be considered further in the discussion of experimental results.

<u>Silicon-silicon double bonds</u>

To date, only two compounds have been suggested to contain silicon-silicon double bonds. These are $C_2H_5(C_6H_5)Si{=}Si(C_6H_5)C_2H_5$[69] and $\left[(C_6H_5)_3Ge\right]_2Si{=}Si\left[Ge(C_6H_5)_3\right]_2$.[70] Both of these were ill-defined, amorphous materials which were very probably polymers. The considerations discussed under silicon-carbon double bonds apply with even greater force to silicon-silicon double bonds.

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[69] F.S. Kipping, Proc. Chem. Soc., 27, 143 (1911).

[70] J.G. Milligan and C.A. Kraus, J. Am. Chem. Soc., 72, 5300 (1950).

Silicon-halogen bonds

The chlorosilanes occupy a position of even greater importance in organosilicon chemistry than do the alkyl halides in carbon chemistry. This is because all organosilicon compounds have to be synthezied ultimately from elemental silicon, and the only feasible methods of synthesis involve the preparation of halosilanes as intermediates.

Three general methods are available for the preparation of halosilanes from silicon. (Chlorine is the halogen most commonly employed.) In the first, chlorine is passed over finely divided silicon or silicon alloys at elevated temperatures to give tetrachlorosilane and hexachlorodisilane.[71] In the second, silicon or a silicon alloy is treated with a halogen acid to give tetrahalosilane, trihalosilane, and dihalosilane.[72] In the third, silicon or a silicon alloy is treated with an alkyl or aryl chloride at high temperatures to give mixtures of mono-, di-, and trialkyl- or triarylchlorosilanes.[73] Bromides are conveniently prepared by analogous methods,[72] but iodides not so readily.[74] Fluorides are usually prepared from the chlorides by reaction with metal fluorides.[75] None of the direct

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[71] W. Schumb and E. Gamble, "Inorganic Syntheses", 1, 42 (1939).

[72] W. Schumb, "Inorganic Syntheses", 1, 38 (1939).

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

[74] C. Friedel and A. Ladenburg, Ann., 203, 241 (1880); L. Gatterman, Ber., 22, 186 (1889).

[75] O. Ruff and C. Albert, Ber., 38, 53, 2222 (1905); H.S. Booth et al., J. Am. Chem. Soc., 54, 4750 (1932); ibid., 57, 1333 (1935); ibid., 56, 1531 (1934).

syntheses work with carbon, except the combination of carbon and fluorine.[76]

The physical data available for the silicon-halogen and carbon-halogen bonds are recorded in Table II.

TABLE II.

Physical Properties of Silicon-halogen and Carbon-halogen Bonds

Property	Element	Fluoride	Chloride	Bromide	Iodide
Bond energy,[a] kcal./mole	Si	143	87	69.3	51.1
	C	107	78	54.0	45.5
Bond distance,[b] Å.	Si	1.54 (1.69)	2.02 (2.05)	2.19 (2.22)	(2.49)
	C	1.36 (1.37)	1.76 (1.73)	1.91 (1.90)	2.12 (2.11)
Ionic bond[c] character, %	Si	70	30	22	8
	C	44	6	3	0

[a] Taken from Pauling, footnote 18, except the values for the two chlorides, which were taken from Pitzer, footnote 33.

[b] Taken from Schomaker and Stevenson, footnote 77. The experimental values are the upper ones, and the values calculated from Schomaker and Stevenson's formula and bond radii are given in parentheses. In these calculations the radius for carbon was that of W. Gordy, _J. Chem. Phys._, _15_, 81 (1947).

[c] From Pauling's relationship to electronegativity differences.

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[76] J.W. Mellor, "Inorganic and Theoretical Chemistry", Longmans Green and Co., London, 1946, Vol. V, p. 822.

There has been a good deal of theoretical discussion of these bond properties in the literature, and the subject is still a debatable one. Pauling's[18] original scale of bond radii and his simple additivity principle led him to the conclusion that the observed bond distances were shorter than the radius sums by values of 0.16, 0.27 and 0.05 Å in the Si-Cl, Si-F, and C-F bonds, respectively, while the calculated values for the remaining bonds were in satisfactory agreement with experiment. He explained the shortening of the silicon-halogen bonds as the result of resonance contributions from such doubly bonded pentacovalent structures as $\overset{+}{Cl}{=}\overset{-}{Si}Cl_3$. Since the carbon atom cannot expand its valence shell, the shortening in the case of CF_4 was explained in terms of structures such as $\overset{+}{F}{=}CF_2\ F^{-}$, which might also be of importance in the silicon case.

Later, Schomaker and Stevenson[77] emphasized that some shortening of all heteropolar bonds is due to the partial ionic character of the bonds (due not to the above structures, but to the ordinary ionic structures $Cl_3\overset{+}{Si}\ \ Cl^{-}$) and, with the aid of a correction for this effect and of newer and more accurate experimental data on bond distances, they showed that the agreement between calculated and experimental bond distances is acceptable for all the above bonds except Si-F. In Table II the bond distances calculated on this basis are given in parentheses. The experimental values are those not in parentheses.

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[77] V. Schomaker and D.P. Stevenson, _J. Am. Chem. Soc._, _63_, 37 (1941).

Still more recently, Pitzer[33] has stated his belief that the shortening of the silicon-fluorine bond (as well as the silicon-oxygen, phosphorus-oxygen, and phosphorus-fluorine bonds) is not due to contributions from doubly bonded structures, but rather that, due to the small size of the fluorine atom, the silicon and fluorine atoms can approach closer than the sum of the covalent radii before repulsions between non-bonding orbitals become great enough to establish the bond distance. Quantum mechanical calculations of orbital overlaps by Mulliken[34] have given some support to this theory.

Other recent authors,[78] on the basis of bond distances, bond angles, and dipole moments have supported Pauling's original explanation of the short silicon-fluorine bond distance.

Although the silicon-halogen and carbon-halogen bond energies and thermal stabilities are not greatly different, the ease with which a free radical effects the abstraction of a chlorine atom from carbon is apparently considerably greater than that for a similar homolytic cleavage of the silicon-chlorine bond. This has been discussed previously under silicon-hydrogen bonds.

Toward polar reagents the silicon halides are uniformly more reactive than their carbon analogs. This difference is most evident in their rel-

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[78] O.R. Gilliam, H.D. Edwards, and W. Gordy, <u>Phys. Rev.</u>, <u>75</u>, 1014 (1949); B.R. Dailey, J.M. Mays, and C.H. Towne, <u>ibid.</u>, <u>76</u>, 136 (1949).

ative ease of hydrolysis. Thus, while carbon tetrachloride and chloroform are stable toward aqueous solvents, silicon tetrachloride and trichlorosilane are hydrolyzed rapidly, even by moist air.[79]

The ease of hydrolysis of silicon halides decreases as the halogen atoms are successively replaced by alkyl or aryl groups.[24,38] In the carbon series the reverse is probably true,[80] although strictly comparable data are not available. Certainly the difficulty of hydrolysis decreases in the series carbon tetrachloride, benzotrichloride, and trityl chloride, and it seems probable that benzophenone dichloride would fall between benzotrichloride and trityl chloride. The different orders are undoubtedly due to different mechanisms of hydrolysis. It is well established that the trityl halides hydrolyze by the S_N1 mechanism

$$(C_6H_5)_3CX \xrightarrow[\text{slow}]{} (C_6H_5)_3C^+ + X^-$$

$$(C_6H_5)_3C^+ + H_2O \xrightarrow[\text{fast}]{} (C_6H_5)_3COH_2^+$$

and it is probable that the remaining members of the carbon series hydrolyze by the same process.[81] In the analogous silicon series, however, the hydrolysis proceeds by the S_N2 attack by a water molecule on the silicon

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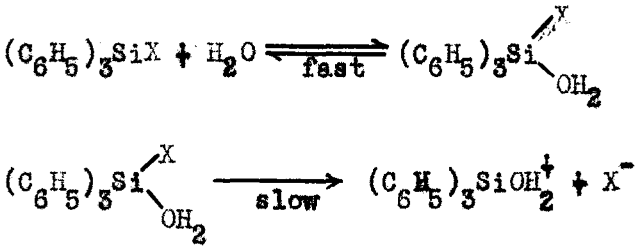
[79] J.N. Friend, "A Text-book of Inorganic Chemistry", C. Griffin and Co. Ltd., London, 1921, Vol. V, p. 9.

[80] E.D. Hughes and N.A. Taher, J. Chem. Soc., 1940, 956.

[81] J. Hine and D.E. Lee, J. Am. Chem. Soc., 73, 22 (1951).

atom.[82] In the carbon series



$$(C_6H_5)_3SiX + H_2O \xrightleftharpoons[fast]{} (C_6H_5)_3Si\begin{array}{l}\diagup X\\ \diagdown OH_2\end{array}$$

$$(C_6H_5)_3Si\begin{array}{l}\diagup X\\ \diagdown OH_2\end{array} \xrightarrow[slow]{} (C_6H_5)_3SiOH_2^+ + X^-$$

the ease of hydrolysis is increased as successively introduced phenyl groups make the central atom less positive and thus facilitate the ionization step; in the silicon series the ease of hydrolysis is decreased as successively introduced phenyl groups make the silicon atom less positive and thus hinder the coordination step.

A further difference is noted in the alkyl series. Alkyl halosilanes hydrolyze even more easily than the corresponding aryl compounds, and probably by the same mechanism. Alkyl halides, however, are not nearly as susceptible to hydrolysis as are the aryl halomethanes, and they do not all hydrolyze by the same mechanism. The tertiary alkyl halides hydrolyze by the same S_N1 mechanism outlined for the aryl halomethanes.[83] The alkyl dihalo- and alkyl trihalomethanes, however, are less easily hydrolyzed and, since the hydrolysis is effected by alkali but not by water, it seems probable that the mechanism of hydrolysis may be of a S_N2 type. This S_N2 mechanism, however, would differ from the S_N2 mechanism Swain proposed for the

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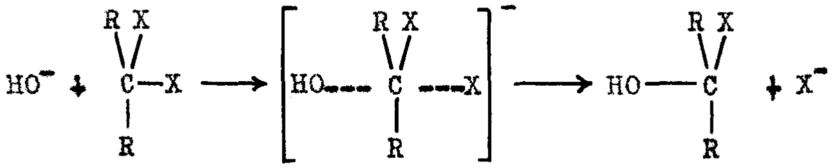
[82] C.G. Swain, R.M. Esteve, and R.H. Jones, J. Am. Chem. Soc., 71, 965 (1949).

[83] P.D. Bartlett, J. Am. Chem. Soc., 61, 1630 (1939).

hydrolysis of halosilanes. In the carbon series no pentacovalent intermediate is possible, so the hydrolysis must take place in one step.



The difference in mechanism is also illustrated by the different behavior of the silicon and carbon halides as the halogens are replaced by bulky groups. In the carbon series, the introduction of bulky groups into a tertiary halide increases the rate of reaction. Thus, tri-isopropylchloromethane hydrolyzes six times more rapidly than tertiary butyl chloride.[84] In the silicon series the reverse is true. While trimethylchlorosilane hydrolyzes even in moist air, tri-isopropylchlorosilane is resistant to hydrolysis by ordinary means.[85] In the carbon series the bulky isopropyl groups increase the rate of ionization through their tendency to relieve the sterically strained condition of the molecule by expelling a chloride ion and assuming the planar configuration of the carbonium ion.[86] In the silicon series internal strains are smaller, due to the greater size of the silicon atom, and silicon cations are probably less stabilized by hyperconjugative resonance than are their carbonium analogs, as was discussed under silicon-carbon double bonds. Hence the tendency to expel a chloride ion is reduced, and

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[84] P.D. Bartlett, Abstracts of Papers, Tenth National Organic Chemistry Symposium, Boston, Mass., 1947, p. 30.

[85] H. Gilman and N.R. Clark, J. Am. Chem. Soc., 69, 1499 (1947); see also H. Gilman and G.N.R. Smart, J. Org. Chem., 15, 720 (1950).

[86] H.C. Brown, Science, 103, 2674 (1946).

the bulky isopropyl groups hinder rearward attack by water molecules.

Complete data regarding the effects of different halogens are not available in either series, but what there are indicate that the ease of hydrolysis increases with increasing bond polarizability in the order fluoride, chloride, bromide, and iodide in both series.[87,88] This agreement is probably due to the fact that the rate determining step in both series is the cleaving of the bond to halogen.

The ease of alcoholysis of the halosilanes parallels the ease of hydrolysis,[89] and probably proceeds by a similar mechanism. In the carbon series the reverse order probably holds, as in the case of hydrolysis.[87] In ethanol the phenyl silicon halides have all their halogen atoms replaced by alkoxy groups to give $(C_6H_5)_3SiOR$, $(C_6H_5)_2Si(OR)_2$, and $C_6H_5Si(OR)_3$. In the corresponding carbon series the products of alcoholysis are $(C_6H_5)_3COR$, $(C_6H_5)_2C(OR)_2$, and C_6H_5COOR.[90,91] The compound $C_6H_5C(OR)_3$ is produced only by the use of sodium alkoxide.[91]

The relative rates of ammonolysis of halosilanes and halomethanes are probably similar to those of hydrolysis and alcoholysis. Thus, while alkyl

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[87] J.R. Johnson in "Organic Chemistry, an Advanced Treatise", H. Gilman, Ed., John Wiley and Sons Inc., New York, 2nd Ed., 1943, Vol. II, p. 1846.

[88] C. Eaborn, J. Chem. Soc., 1950, 3077.

[89] See, for example, D. Peppard, W. Brown, and W. Johnson, J. Am. Chem. Soc., 68, 70 (1946); and R.O. Sauer, ibid., 68, 138 (1946).

[90] F. Straus and W. Hussy, Ber., 42 2168 (1909); F. Straus and O. Ecker, ibid., 39, 2977 (1906).

[91] H. Limpricht, Ann., 135, 80 (1865).

halides, preferably iodides, must be heated with ammonia for the preparation of amines, all of the silicon halides, except the fluorides, will react with ammonia gas at room temperature, or with liquid ammonia.[38] The conditions are sufficiently mild so that the silicon analogs of primary or secondary amines can be prepared at will,[63,92] which is not true in the carbon series. Since the only commonly available monohalosilanes are tertiary, steric factors become of importance in preparing the silicon analogs of amines. The only known analog of a tertiary amine is trisilylamine, $(H_3Si)_3N$. Trimethylchlorosilane and higher homologs will react with only two hydrogens of ammonia to give hexaalkyl analogs of secondary amines, such as hexamethyldisilazane, $(CH_3)_3SiNHSi(CH_3)_3$.[93]

The reduction of silicon halides to silicon hydrides has been reported only with lithium aluminum hydride.[9] It takes place rapidly and almost quantitatively in ether. The reduction of alkyl halides by the same reagent also occurs, but less readily.[94] In the silicon series, the ease of reduction increases with increasing number of halogen atoms attached to silicon. Reduction of polyhalomethanes with this reagent have not been reported, but it seems probable that the order will be the reverse.

Reactions with organometallic compounds occupy a place of exceptional importance in organosilicon chemistry, since, until the development of the

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[92] R.O. Sauer and R.H. Hasek, J. Am. Chem. Soc., 68, 241 (1946).

[93] S.D. Brewer and C.P. Haber, J. Am. Chem. Soc., 70, 3888 (1948).

[94] J.E. Johnson, R.H. Blizzard, and H.W. Carhart, J. Am. Chem. Soc., 70, 3664 (1948).

reactions of organic halides with silicon and of silicon hydrides with olefins, these reactions afforded the only method of preparing organic compounds of silicon. They are still of prime importance for laboratory synthesis. This situation is to be contrasted with that in carbon chemistry, where the analogous reaction (coupling of, say, a Grignard reagent and an organic halide) was of small importance, and more of an inconvenience than an aid.

The first organosilicon compounds were prepared by Friedel and Crafts by the action of dimethyl- and diethylzinc on silicon tetrachloride.[95] In the carbon series, dimethylzinc with either tertiary butyl iodide or 2,2-dichloropropane gives tetramethylmethane,[96] but diethylzinc with chloroform and carbon tetrachloride gives ethylene and propylene.[97] Pape introduced the use of a modified Wurtz reaction into organosilicon synthesis.[98] The reaction is highly exothermic and leads conveniently only to tetrasubstituted silanes. Reactions involving sodium and

$$SiCl_4 + 4RX + 8Na \longrightarrow SiR_4 + 8NaCl$$

carbon tetrachloride or chloroform are explosive and do not yield any use-

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[95] C. Friedel and J.M. Crafts, Ann., 127, 28 (1863); ibid., 136, 203 (1865).

[96] M. Lwow, Z. Chem., 1870, 520.

[97] R. Reith and F. Beilstein, Ann., 124, 242, 245 (1862).

[98] C. Pape, Ann., 222, 254 (1884).

ful products.[99] Kipping[100] and Dilthey[101] introduced the use of the Grignard reagent for reactions with silicon tetrachloride and other chlorosilanes, and, until 1945,[73] this was the only method commonly used for the preparation of organosilicon compounds. All types of organosilicon halides, $RSiX_3$, R_2SiX_2, R_3SiX and R_4Si can be prepared with the Grignard reagent (the last only at high temperatures), and it is probably safe to say that more different organosilicon compounds have been made by this method than by any other. The analogous reaction in carbon chemistry is little known. It is reported that carbon tetrachloride with ethylmagnesium bromide gives ethane and ethylene,[102] and with phenylmagnesium bromide gives triphenylmethyl peroxide, triphenylcarbinol, and hexaphenylethane.[103]

The use of the equally convenient and more reactive organolithium reagents was introduced by Fleming[104] and by Gilman and Clark.[105] These

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[99] H. Staudinger, Z. angew. Chem., 35, 659 (1922); ibid., 38, 578 (1925).

[100] F.S. Kipping, Proc. Chem. Soc., 20, 15 (1904).

[101] W. Dilthey and F. Eduardoff, Ber., 37, 1139 (1904).

[102] R. Binaghi, Gazz. chim. ital., 53, 886 (1923).

[103] M. Gomberg and L.H. Cone, Ber., 39, 1462, 1466 (1906).

[104] R. Fleming, U.S. Patent 2,386,452, [C.A., 40, 603 (1946)]

[105] H. Gilman and R.N. Clark, J. Am. Chem. Soc., 68, 1675 (1946).

reagents have all the advantages of the Grignard reagent, plus sufficient reactivity so that even most tetraarylsilanes can be prepared in refluxing ether. The analogous reaction of organolithium reagents with chloromethanes has been studied by Marvel and by Wittig.[106] In general, carbon tetrahalides and haloforms react with organolithium compounds to give the alkyl or aryl halides corresponding to the Grignard reagent used, together with resins. Phenylhalomethanes with phenyllithium give phenyl halides, resins, and mixtures of compounds obtained from halogen- or hydrogen-metal interconversions followed by coupling. The remarkable contrast between these reactions and the smooth, clean preparations of organosilicon compounds is probably due to the greater electropositivity of the silicon atom, which hinders hydrogen- and halogen-metal interconversions with the organolithium reagent, and to the reluctance of the silicon atom to form double bonds, which prevents elimination reactions and subsequent polymerization, as well as decreasing the resonance stabilization of the silyllithium products which might otherwise be formed by interconversions.

Among the most important reactions of organic halides are those with anhydrous aluminum chloride. This reagent plays a much smaller part in organosilicon chemistry, largely because aluminum chloride cleaves silicon-carbon and silicon-hydrogen bonds,[107] as was mentioned under those headings.

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[106] C.S. Marvel, F.D. Hager, and D.D. Coffman, J. Am. Chem. Soc., 49, 2323 (1927); G. Wittig and H. Witt, Ber., 74B, 1474 (1941).

[107] W.E. Evison and F.S. Kipping, J. Chem. Soc., 1931, 2774.

However, for preparing organosilicon compounds from silicon tetrachloride, aluminum chloride has some limited use. A method has been reported[108] for reacting silicon tetrachloride with olefins in the presence of aluminum chloride at high temperatures and pressures to give 2-chloroalkyltrichlorosilanes. Saturated hydrocarbons are reported to

$$CH_2=CH_2 + SiCl_4 \longrightarrow ClCH_2CH_2SiCl_3$$

react in the same way,[109] as are alkyl halides.[110] In the latter reaction the catalyst is aluminum metal, but the author believes that the formation of aluminum chloride is involved. Analogous reactions of olefins with aliphatic halides have not been reported, but olefins react with acyl halides in the presence of aluminum chloride, even at low temperatures, to give both substitution and addition products.[111] Reactions between alkyl

$$RCH=CH_2 + CH_3COX \xrightarrow{AlX_3} RCH=CHCOCH_3 + HX + RCHClCH_2COCH_3$$

chlorides and alkanes lead to isomerization, cracking, and polymerization rather than the desired coupling.[112] The contrast between the carbon and silicon series in these reactions may not be as great as the above data would suggest, however, since there are no confirmatory reports of the successful reactions in the silicon series.

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[108] I.I. Shtetter, Russian Patent 44,934 (1935), [*C.A.*, *32*, 2958 (1938)].

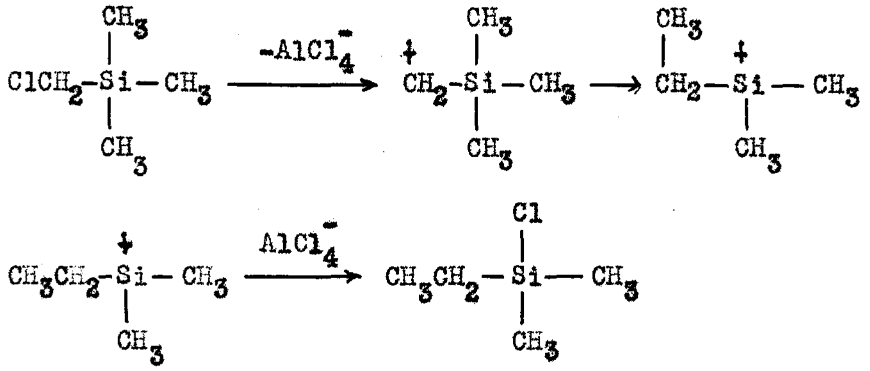
[109] H.C. Miller and R.S. Schreiber, U.S. Patent 2,379,821 (1945).

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

[111] C.A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry", Reinhold Publishing Corp., New York, 1941, p. 752 ff.

[112] C.A. Thomas, *ibid.*, p. 736.

Whitmore has shown that aluminum chloride catalyzes the rearrangement of chloromethyltrimethylsilane to ethyldimethylchlorosilane, and proposes a mechanism analogous to that encountered in similar rearrangements of hydrocarbon halides catalyzed by milder reagents.[113]



$$\mathrm{ClCH_2{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}CH_3} \xrightarrow{-AlCl_4^-} \mathrm{\overset{+}{C}H_2{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}CH_3} \longrightarrow \mathrm{CH_2{-}\overset{+}{\underset{CH_3}{Si}}{-}CH_3}$$

$$\mathrm{CH_3CH_2{-}\overset{+}{\underset{CH_3}{Si}}{-}CH_3} \xrightarrow{AlCl_4^-} \mathrm{CH_3CH_2{-}\overset{Cl}{\underset{CH_3}{Si}}{-}CH_3}$$

The following redistribution reaction has also been found to be brought about by anhydrous aluminum chloride.[113]

$$C_2H_5(CH_3)_2SiCl \xrightarrow{AlCl_3} (CH_3)_3SiCl + CH_3(C_2H_5)_2SiCl + (C_2H_5)_3SiCl$$

Finally we may consider reactions of halosilanes with active metals. One case is reported of the reaction of a silicon-halogen bond with a metal by any other process than solvolysis or coupling. Kraus and Eatough[114] report the preparation of triphenylsilyllithium by the reaction of triphenylbromosilane with lithium in ethylamine. The reaction was unsuccessful with triphenylchlorosilane because of solvolysis. This point alone

$$Li + (C_6H_5)_3SiCl + H_2NC_2H_5 \longrightarrow (C_6H_5)_3SiNHC_2H_5 + LiCl + \tfrac{1}{2}H_2$$

$$Li + (C_6H_5)_3SiBr + H_2NC_2H_5 \longrightarrow (C_6H_5)_3Si\cdot C_2H_5NH_2 + LiBr$$

$$Li + (C_6H_5)_3Si\cdot C_2H_5NH_2 \longrightarrow (C_6H_5)_3SiLi + C_2H_5NH_2$$

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[113] F.C. Whitmore, L.H. Sommer, and J. Gold, *J. Am. Chem. Soc.*, *69*, 1976 (1947).

[114] C.A. Kraus and H. Eatough, *J. Am. Chem. Soc.*, *55*, 5008 (1933).

is surprising, since the ease of solvolysis usually increases as the halogen becomes heavier. The formation of an isolable free radical solvated by ethylamine is even more surprising, and some question exists as to the reality of the reactions, since they have never been repeated.[115] The much greater difficulty of formation of organosilyllithium compounds and organosilyl Grignard reagents as compared with analogous carbon cases may be attributed to the greater electropositivity of the silicon atom, and to reduced stabilization of the organosilyl anion by resonance structures involving double bonds to silicon.

Silicon-oxygen bonds

Silicon-oxygen bonds occupy a position of special significance in organosilicon chemistry because of the industrial importance of the polysiloxanes. These are organic compounds containing chains or networks of silicon-oxygen bonds, which result in molecules of very high molecular weight having high chemical and electrical resistance, low temperature coefficients of viscosity, and strong water-repellant properties. Strictly analogous carbon polyethers are rare and not well known. In carbon chemistry, oxygen plays its most important part in the form of carbon-oxygen double bonds. Carbonyl groups in organic molecules provide centers of reactivity and of activating influence on nearby atoms which make possible an enormous

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[115] H. Gilman and T.C. Wu, Unpublished results; private communication from Dr. R.A. Benkeser, Purdue University, February, 1951.

number of different reactions of prime theoretical and industrial importance. Organic compounds containing silicon-oxygen double bonds are unknown, probably for the same reasons discussed under silicon-carbon double bonds.

The physical constants available for silicon-oxygen and carbon-oxygen bonds are as follows: bond energy, kcal./mole, Si-O 89.3, C-O 70;[18] bond distance, Å,[116] Si-O 1.61 (1.74), C-O 1.43 (1.42); per cent ionic character,[117] Si-O 51, C-O 23. It will be noted that the silicon-oxygen bond distance, like the silicon-fluorine bond distance, is less than the calculated value. This subject has been discussed under silicon-halogen bonds, and the same considerations apply here.

The most outstanding difference between silanols and alcohols is the extreme ease with which the former undergo intermolecular condensations to disiloxanes.

$$2R_3SiOH \xrightarrow{H^+ \text{ or } OH^-} R_3SiOSiR_3 + H_2O$$

The reaction is catalysed by both acids[118] and bases,[46,51] and occurs so readily with alkyl-[119] and mixed alkyl-aryl- silanols[52,120] that the un-

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[116] The value for C-O is from Pauling, *op. cit.*; that for Si-O is the value in quartz found by F. Machatschki, *Z. Krist*, *94*, 222 (1936). No Si-O bond distance in an organosilicon compound is reported. The values in parentheses are those calculated using Schomaker's and Stevenson's formula and radii (footnote 77), except the radius for carbon which is that of Gordy (footnote b, Table II).

[117] These values are calculated from Pauling's relationship between electronegativity and ionic bond character. They are confirmed by the infra red measurements of N. Wright and M. Hunter, *J. Am. Chem. Soc.*, *69*, 803 (1947).

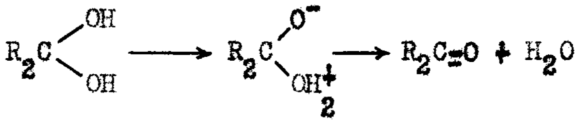
[118] F.S. Kipping, *J. Chem. Soc.*, *79*, 449 (1901); H. Gilman and H.W. Melvin, unpublished studies.

[119] R.O. Sauer, *J. Am. Chem. Soc.*, *66*, 1707 (1944).

[120] H. Marsden and F.S. Kipping, *J. Chem. Soc.*, *93*, 198 (1908).

condensed silanols are frequently difficult to prepare. The corresponding preparation of ethers from alcohols is a much more difficult process, and ditertiary ethers are almost unknown. Eliminations leading to olefins are always competing reactions in the carbon series, while the difficulty of formation of silicon-carbon double bonds prevents such complications in the silicon case.

On the other hand, the stability of two hydroxyl groups on one silicon atom is considerably greater than that of two hydroxyl groups on one carbon atom. Thus, silanediols are fairly common, whereas not many carbon gem-diols (carbonyl "hydrates") are isolable. This difference is due to the fact that the silanediols and the carbon gem-diols dehydrate to give different products. In the carbon series gem-diols may lose water by some such intramolecular process as the following:



$$R_2C{<}^{OH}_{OH} \longrightarrow R_2C{<}^{O^-}_{OH_2^+} \longrightarrow R_2C{=}O + H_2O$$

the last step being favored by the resonance energy of the carbonyl group. This would explain why hemiacetals and acetals are increasingly more stable than gem-diols.[121] In the silicon series, silicon-oxygen double bonds are not formed, so the dehydration must be intermolecular. Infra-red studies of the polymeric products of such dehydrations as

$$2n\ R_2Si{<}^{OH}_{OH} \longrightarrow \left[\begin{matrix} R & R \\ \text{-SiOSiO-} & \\ R & R \end{matrix}\right]_n + 2n\ H_2O$$

have shown no evidence for the presence of even small amounts of compounds

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[121] Private communication from John W. Morton, this Laboratory, February, 1951.

containing silicon-oxygen double bonds.[117]

Silane triols have not been isolated as such, but probably form unstable intermediates in the hydrolysis of such compounds as phenyltrichlorosilane to cross-linked polymers. In the carbon series, some acid hydrates, such as oxalic acid dihydrate are probably to be regarded as gem-triols.

It is interesting to note that the silanols are always stronger acids than their carbon analogs, trimethylsilanol even forming a sodium salt with aqueous sodium hydroxide at 0°.[122] In view of the electropositive nature of silicon, this is surprising. It may be considered evidence for the participation of resonance structures such as $R_3SiOH \longleftrightarrow R_3\overset{-}{Si}{=}O\,\overset{+}{H}$, with some reservations in view of the present dubious status of structures involving double bonds to silicon.

In accord with their considerable acidity, silanols react with alcohols to give compounds which resemble esters more than ethers. These compounds may be considered to be esters of orthosilicic acid and, in a general way, resemble the orthocarbonates or acetals. They are hydrolyzed to silanols and alcohols somewhat more easily than most carbonic acid esters and, unlike that of the acetals, the hydrolysis is catalyzed by both acids and bases. The susceptibility of the alkoxysilanes to basic hydrolysis is undoubtedly due to the facility with which the silicon atom is attacked by nucleophilic agents. The mechanism is probably similar to that illustrated

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[122] L.H. Sommer, E.W. Pietrusza and F.C. Whitmore, J. Am. Chem. Soc., 68, 2282 (1946).

for the hydrolysis of the halosilanes. The splitting of the silicon-oxygen bond in these cleavages has been demonstrated by showing that the hydrolysis of an alkoxysilane containing an asymmetric carbon atom attached to oxygen gives an optically active alcohol.[123] By contrast, the carbon atom cannot expand its valence shell to accept a basic substituent, so that hydrolysis of acetals must proceed by a mechanism similar to that shown for gem-diols, with the necessary protons supplied by the catalyst.

A further resemblance between alkoxysilanes and halosilanes is seen in their reactions with Grignard and organolithium reagents. In general, these two types of compounds may be used interchangeably in organosilicon syntheses, the alkoxysilanes being somewhat less reactive than the halosilanes. The silicon-oxygen bonds in disiloxanes also behave more like the carbon-oxygen bonds of esters than those of ethers, since they are cleaved by acids,[124] bases,[118] and Grignard reagents[119,125] to give silanols.

The silanols behave like alcohols in their reactions with acids. Thus, anhydrous hydrogen chloride in ether converts most silanols to chlorosilanes,[126] some of the lower alkylsilanols being converted even by concentrated aqueous

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[123] R.H. Krieble and C.A. Burkhard, J. Am. Chem. Soc., 69, 2689 (1947).

[124] L.H. Sommer, G.T. Kerr, and F.C. Whitmore, J. Am. Chem. Soc., 70, 445 (1948).

[125] F.S. Kipping and J.E. Hackford, J. Chem. Soc., 99, 138 (1911).

[126] C.A. Kraus and R. Rosen, J. Am. Chem. Soc., 47, 2739 (1925); H. Gilman and H.W. Melvin, unpublished studies.

hydrochloric acid.[122] Silyl esters of carboxylic acids are also known, but they are much more easily hydrolyzed than are ordinary alcoholic esters.[127]

With concentrated sulfuric acid a sulfuric acid ester is obtained. These esters undergo the usual reactions of alkyl sulfates but, unlike alkyl sulfates, both alkyl groups react.[124] It is interesting to note that the i-factor for triethylsilanol in sulfuric acid is 3, like that for primary alcohols, rather than 2, like that of tertiary aliphatic alcohols. In tertiary alcohols ionization takes place as follows:

$$ROH + H_2SO_4 \rightleftharpoons ROH_2^+ + HSO_4^- \quad (\underline{i} = 2)$$

while in primary alcohols a further step involving a back side attack by the bisulfite ion leads to

$$HSO_4^- + ROH_2^+ \rightleftharpoons RHSO_4 + H_2O$$

$$H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^-$$

with a consequent i-factor of 3. The last two steps are prevented in tertiary alcohols by the steric interference of the alkyl groups. Since the last two steps evidently occur in tertiary silanols, it seems probable that steric hindrance to back side attack is reduced in these compounds by the large size of the silicon atom.[128]

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[127] H.A. Schuyten, J.W. Weaver, and J.D. Reid, J. Am. Chem. Soc., 69, 2110 (1947).

[128] M.S. Newman, R.A. Craig, and A.B. Garrett, J. Am. Chem. Soc., 71, 869 (1949).

Silicon-nitrogen bonds

Compounds containing silicon-nitrogen bonds do not play the important part in organosilicon chemistry that carbon-nitrogen bonds do in carbon chemistry because of the great ease with which silicon-nitrogen compounds are hydrolyzed to silanols and amines. In fact, the principal interest shown in these compounds up to the present has been the result of the fact that they hydrolyze about as readily as do the halosilanes, but the products of hydrolysis are the relatively mild amines instead of the strongly corrosive halogen acids.[129] Experimental values for the physical constants of silicon-nitrogen bonds are not available.

Silicon analogs of amines, the aminosilanes, are prepared from the halosilanes by reaction with ammonia, amines,[92] or sodium in liquid ammonia.[126] Silyl hydrides and metal amides also give aminosilanes in excellent yields.[51,63] Only two silyl groups can be attached to nitrogen except in the case of trisilylamine, $(H_3Si)_3N$.[93] Tri-<u>t</u>-alkylamines are also unknown.[130] Silicon analogs of the quaternary ammonium halides or hydroxides are unknown; as are aminosilane salts, since acids cleave aminosilanes with great ease. This reaction has been used by Whitmore for

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[129] British Thomson-Houston Co. Ltd., British patent 599,153 (1948).

[130] Private communication from W.J. Meikle, this Laboratory, February 1951.

preparing halosilanes.[131] None of

$$R_3SiNH_2 + HX \longrightarrow R_3SiX + NH_3$$

the reactions by which hydrogen is substituted in aliphatic amines are known in the aminosilanes, since the reagents cleave the silicon-nitrogen bond rather than the halogen-nitrogen bond. Carboxylic acids, for example, give ammonia and silyl esters of the acids.[132]

Burg and Kuljian have found that trisilylamine, $(H_3Si)_3N$, is a much weaker electron donor in reactions with trihalo- and trimethyl- boron than is trimethylamine $(H_3C)_3N$.[133] This is in line with the greater acidity of the silanols as compared with the alcohols and, in a similar way, it is somewhat unexpected, since the relatively electropositive silicon atom should increase the nucleophilic properties of the attached nitrogen. Like the acidity of the silanols, this phenomenon could be explained as the result of significantly large contributions from resonance structures involving silicon-nitrogen double bonds, such as $H_3\overset{-}{Si}=\overset{+}{N}(SiH_3)_2$. This is the only evidence for the existence of silicon-nitrogen double bonds, since silicon analogs of Schiff's bases or ketimines are unknown.

A number of silyl isocyanates and isothiocyanates have been prepared, mostly by Anderson. These compounds, like the halosilanes, are readily

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[131] D.L. Bailey, L.H. Sommer, and F.C. Whitmore, J. Am. Chem. Soc., 70, 435 (1948).

[132] C.S. Miner, L.A. Bryan, R.P. Holysz, and G.W. Pedlow, Ind. Eng. Chem. 39, 1368 (1947).

[133] A.B. Burg and E.S. Kuljian, J. Am. Chem. Soc., 72, 3103 (1950).

hydrolyzed in aqueous solvents,[134] and, also like the halosilanes, the ease of hydrolysis increases as the number of isocyanate or isothiocyanate groups on the silicon atom increases.[10] One such compound, triphenylsilylisothiocyanate, also behaved like a halosilane toward phenyllithium, giving tetraphenylsilane.[135] Organic isocyanates react with Grignard and organolithium reagents to give substituted amides,[136] and the products from the reaction of triphenylsilylisothiocyanate with Grignard reagents, and of triphenylsilylisocyanate with both Grignard and organolithium reagents, can be looked upon as the hydrolysis products of the corresponding N-silylamide.[135]

$$(C_6H_5)_3SiNCO + C_6H_5Li \longrightarrow (C_6H_5)_3SiN{=}C(C_6H_5)\ OLi$$

$$(C_6H_5)_3SiN{=}C(C_6H_5)OLi + H_2O \longrightarrow (C_6H_5)_3SiN{=}C(C_6H_5)OH$$

$$(C_6H_5)_3SiNHCO(C_6H_5) + H_2O \longrightarrow (C_6H_5)_3SiOH + C_6H_5CONH_2$$

In general, however, the silyl isocyanates and isothiocyanates do not react like their carbon analogs. As has been emphasized, they hydrolyze more easily than alkylisocyanates, but give silanols rather than aminosilanes as products. (Of course, the aminosilanes may be formed as intermediates in the hydrolysis.) Neither do they react with alcohols to give urethanes or with amines to give ureas. Rather, the reverse happens. Triphenylsilylisocyanate and triphenylsilylisothiocyanate are conveniently

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[134] H.H. Anderson, J. Am. Chem. Soc., 72, 193 (1950).

[135] H. Gilman, B. Hofferth, and H.W. Melvin, J. Am. Chem. Soc. 72, 3045 (1950).

[136] H. Gilman, J.E. Kirby, and C.R. Kinney, J. Am. Chem. Soc., 51, 2252 1929).

prepared by the reaction of triphenylchlorosilane with urea, thiourea, or sodium urethane, as the case may be.[134]

Bonds between silicon and various other elements

Very few compounds have been reported in which silicon is bonded to elements other than carbon, silicon, halogen, oxygen, or nitrogen. Some sulfur analogs of the alkoxy- and aryloxy-silanes have been prepared. Like the alkoxysilanes they were found to resemble esters rather than ethers, especially in their ease of hydrolysis. An attempt to oxidize triphenylthiophenoxysilane led to reduction of the oxidizing agent, but cleavage of the silicon-sulfur bond occurred and it was impossible to tell whether it took place during or after oxidation.[137]

Kraus has reported the preparation of triphenylsilyltrimethyltin[114] and triethylsilyltriphenylgermanium.[63] Not much is known about the properties of these compounds, but they seem to resemble the di-tin and di-germanium compounds, since they are cleaved by halogens and by sodium in liquid ethylamine.

Effect of silicon on adjacent bonds

A large proportion of the work on the "silicon effect", as well as the term itself, are due to Whitmore and co-workers. They first prepared

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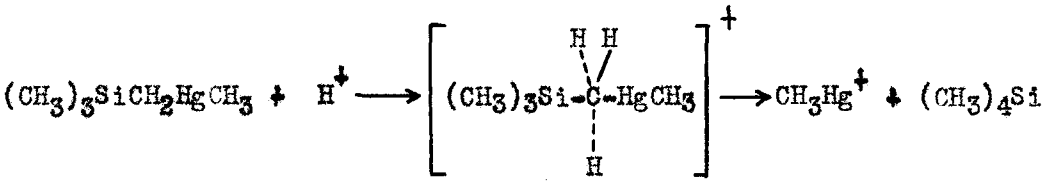
[137] H. Gilman and G.N.R. Smart, unpublished studies.

chloromethyltrimethylsilane, $(CH_3)_3SiCH_2Cl$, and found the halogen to be much more reactive than the corresponding halogen of neopentyl chloride, $(CH_3)_2CCH_2Cl$, toward nucleophilic reagents. They attributed the unreactivity of the neopentyl chloride to the steric shielding of the methylene carbon to back side attack, and the lability of the halogen in the silicon analog to diminished shielding by the groups attached to the larger silicon atom.[5] Toward alcoholic silver nitrate, however, chloromethyltrimethylsilane was much less reactive than any alkyl halide. This was attributed to the greater electronegativity of the group $(CH_3)_3SiCH_2-$, as compared to $(CH_3)_3CCH_2-$, which tends to strengthen the halogen against electrophilic attack. They reported that this electronegativity was confirmed by the fact that $(CH_3)_3SiCH_2HgCH_3$ was cleaved by hydrochloric acid to give $(CH_3)_4Si$ and CH_3HgCl, thus placing the trimethylsilylmethyl group in the series of decreasing ease of cleavage from mercury: $C_6H_5 > (CH_3)_3SiCH_2 > CH_3 > C_6H_{13} > (CH_3)_3CCH_2$.

It will be noted that this use of the term "electronegativity" to refer to "relative affinity for electrons" is based upon the notion that the group most easily cleaved from mercury is the group which has the greatest tendency to carry its bonding electrons with it in cleavage. It seems more likely, however, that the ease of cleavage from mercury by acids is related to the degree of resonance stabilization of a transition state such as that illustrated below



$$(CH_3)_3SiCH_2HgCH_3 + H^+ \longrightarrow \left[(CH_3)_3Si-\overset{H\,H}{\underset{H}{C}}-HgCH_3 \right]^+ \longrightarrow CH_3Hg^+ + (CH_3)_4Si$$

This interpretation can be shown to account satisfactorily for the series of relative "electronegativities" obtained from cleavages of organometallic compounds by acids. On this basis, the position of the group $(CH_3)_3SiCH_2$- relative to $(CH_3)_3CCH_2$- in the series is explained by the small electronegativity of the silicon atom as compared to carbon. This smaller electronegativity results in an inductive effect of electron release from the silicon atom to the methylene carbon, thus tending to stabilize the transition state and reduce the activation energy for the cleavage of the trimethylsilylmethyl group as compared to that for the neopentyl group.

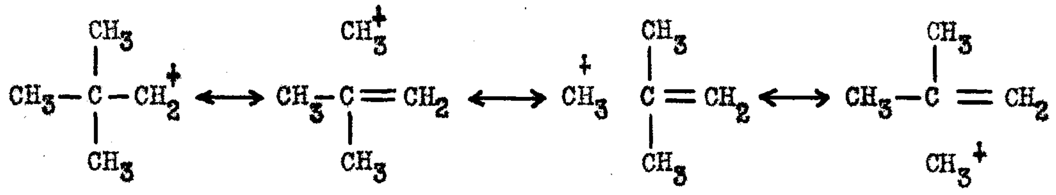
It will be noted that these reactions imply a greater basicity for a carbon atom attached to the trimethylsilyl group than for one attached to the <u>t</u>-butyl group. This is exactly the opposite to the situation with oxygen and nitrogen attached to silicon. Oxygen and nitrogen both have unshared electron pairs which can be used to form resonance structures having double bonds to silicon, such as $R_3\overset{-}{Si}=\overset{+}{O}H$ and $R_3\overset{-}{Si}=\overset{+}{N}H_2$, which result in a decrease in basicity for the oxygen and nitrogen atoms. Carbon atoms attached to silicon do not have such unshared electron pairs and are rendered even more basic than their non-silicon analogs by contributions from hyperconjugative structures such as $R_3\overset{+}{Si}\ \overset{-}{C}H_2R$.

The various observations relating to resonance structures containing double bonds to silicon may be summarized in the conclusion that, when small electronegative elements such as fluorine, oxygen, and perhaps nitrogen are bonded to silicon, contributions from such structures are significant, but with larger atoms, such as carbon, they are not.

The unreactivity of chloromethyltrimethylsilane may be illustrated in terms of the mechanism below.

$$(CH_3)_3SiCH_2Cl + Ag^+ \xrightarrow{-AgCl} (CH_3)_3SiCH_2^+ \xrightarrow{H_2O} (CH_3)_3SiCH_2OH_2^+$$

It seems likely that the relative rates of the reactions of the silicon and carbon analogs will be governed by the relative stabilities of the trimethylsilylmethyl and neopentyl cations. The neopentyl cation can be stabilized by resonance contributions from hyperconjugative structures such as

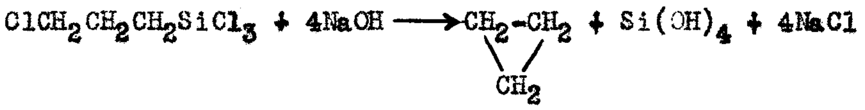


$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2^+ \longleftrightarrow CH_3-\overset{CH_3^+}{\underset{CH_3}{C}}=CH_2 \longleftrightarrow \overset{+}{CH_3}\ \overset{CH_3}{\underset{CH_3}{C}}=CH_2 \longleftrightarrow CH_3-\overset{CH_3}{\underset{CH_3^+}{C}}=CH_2$$

If it is accepted that structures having silicon-carbon double bonds will make relatively small contributions, then it is understandable that neopentyl chloride should react faster with silver ion than does chloromethyltrimethylsilane.

Whitmore and co-workers next prepared the 2-chloro- and 3-chloroalkyl trichlorosilanes. The carbon-chlorine bonds in both of these compounds were more reactive toward nucleophilic reagents than in the chloromethylsilanes, with the 2-chloro- compounds being more reactive than the 3-chloro- ones. With aqueous base these compounds reacted as follows:[138]

$$ClCH_2CH_2SiCl_3 + 4\ NaOH \longrightarrow CH_2=CH_2 + Si(OH)_4 + 4NaCl$$



$$ClCH_2CH_2CH_2SiCl_3 + 4NaOH \longrightarrow \underset{CH_2}{CH_2-CH_2} + Si(OH)_4 + 4NaCl$$

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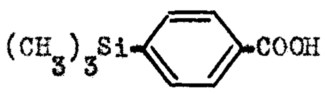
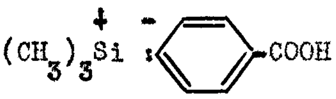
[138] L.H. Sommer, E. Dorfman, G.M. Goldberg and F.C. Whitmore, J. Am. Chem. Soc., 68, 488 (1946).

Such reactions with the analogous carbon compounds are not known, and the difference was interpreted in terms of the greater ease of attack by nucleophilic reagents on a silicon than on a carbon atom.[139] Oxygen on an alkyl carbon atom β to silicon produced a similar lability of the silicon-carbon bond.[140]

Somewhat later, the same group of workers[141] determined the dissociation constants of a number of substituted acetic acids, RCH_2COOH, obtaining decreasing acidities as R is changed in the order $(CH_3)_3C > (CH_3)_3SiCH_2 > (CH_3)_3Si > C_6H_5(CH_3)_2Si$. Again the effects were atrributed to the electron-releasing properties of the silicon atom as compared to carbon.

A similar effect was noted by Roberts and co-workers in a less ambiguous situation.[142] They determined the <u>sigma</u> constant for the trimethylsilyl group by measuring the dissociation constants of trimethylsilylbenzoic acids and the rates of reaction of these acids with diphenyldiazomethane. They found the trimethylsilyl group to more acid-weakening than the t-butyl group, and attributed this to an inducative effect of electron release in the silicon-carbon bond, such as





which is evidently greater than in the carbon analog.

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[139] L.H. Sommer, D.L. Bailey, and F.C. Whitmore, <u>J. Am. Chem. Soc.</u>, <u>70</u>, 2869 (1948).

[140] J.R. Gold, L.H. Sommer, and F.C. Whitmore, <u>J. Am. Chem. Soc.</u>, <u>70</u>, 2874 (1948).

[141] L.H. Sommer, J.R. Gold, G.M. Goldberg, and N.S. Marans, <u>J. Am. Chem. Soc.</u>, <u>71</u>, 1509 (1949).

[142] J.D. Roberts, E.A. McElhill, and R. Armstrong, <u>J. Am. Chem. Soc.</u>, <u>71</u>, 2923 (1949).

Physiological Properties

In general, the organosilicon compounds seem to be less active physiologically than their carbon analogs. The anesthetic and toxic effects of chloroform and carbon tetrachloride, for example, are not shown by tri- and tetrachlorosilane. The chlorosilanes are toxic, of course, since they are readily hydrolyzed to hydrochloric acid in the body fluids. The minimum lethal dose in rats, administered in a single dose by stomach tube, is 1 g./kg. for the various methyl and ethyl chlorosilanes. The ethoxy silanes are less toxic, the minimum lethal dose in rats being 5-10 g./kg. for the various methyl and ethyl ethoxysilanes.[143]

Rats were unaffected when exposed to air containing 25,000 p.p.m. of hexamethyldisiloxane for periods of thirty minutes, and hexamethyldisiloxane and many other polysiloxanes showed no skin or eye irritation, and had no harmful effect on peritoneal injection.[143] Since these compounds are extremely insoluble in water, as are the tetrasubstituted silanes, any physiological activity they possess might be expected to resemble that of the high molecular weight hydrocarbons. Such carcinogenic properties have never been reported for any organosilicon compound, but the time since their industrial application has, perhaps, been too brief for small effects to become apparent.

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[143] V.K. Rowe, H.C. Spencer, and S.L. Bass, J. Ind. Hyg. Toxicol., 30, 332 (1948).

Some attention has been devoted to the preparation of silicon analogs of physiologically active carbon compounds.[144] The results of physiological tests on most of these compounds are not yet known, however. A silicon near-analog of DDT[21] seemed to have negligible insecticidal properties in preliminary tests.

Since the physico-chemical principles by which the great majority of drugs exert their physiological effect is very imperfectly understood, no sound basis of comparison, or theoretical point of attack for further study, is available. In those cases, like the antibiotics, where close resemblances in size and shape between active molecules and metabolic building materials are supposed to be involved in the physiological activity, it would seem that the synthesis of strict silicon analogs of active carbon compounds would not be a promising approach. The silicon compounds would be distorted in shape, as well as larger in size, when compared with their carbon analogs. However, it is even possible that this very ability to alter the shape and size of molecules without greatly altering their fundamental structure could be helpful in elucidating the processes involved in physiological activity.

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[144] Unpublished studies from this Laboratory.

EXPERIMENTAL

Grignard and organolithium reagents were prepared and used in solvents dried over sodium wire and/or calcium hydride. Reactions in which these reagents were used were carried out in an atmosphere of nitrogen freed from oxygen and moisture by being passed through a train containing alkaline pyrogallol, concentrated sulfuric acid, anhydrous calcium chloride, soda lime, and Drierite in that order. The melting points and boiling points reported are, unless otherwise stated, uncorrected. Silicon analyses, in most cases, were carried out by the procedure recently reported from this Laboratory.[51] A few low-boiling compounds were decomposed in the Parr bomb.

Cleavage of Organosilicon Compounds by Organometallic Reagents

Most of the work on the cleavage of organosilicon compounds by Grignard and organolithium reagents has been reported previously.[145] Some additional experimental details are given here.

Triphenylsilanol.- A two liter, three-necked flask equipped with mechanical stirrer, reflux condenser, and dropping funnel was swept with dry, oxygen-free nitrogen. Silicon tetrachloride, 86.8 g. (0.511 mole), was distilled into a 60 ml. dropping funnel and carefully weighed. The

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[145] H. Gilman, R.A. Benkeser, and G.E. Dunn, J. Am. Chem. Soc., 72, 1689 (1950).

silicon tetrachloride, under pressure of dry nitrogen, was added to 450 ml. of dry ether in the three-necked flask, which was cooled in an ice-salt bath. To this solution was added dropwise 1424 ml. of a 1.08 M solution of phenyllithium in ether (1.532 moles) while stirring vigorously and cooling in an ice-salt bath. Seven hours were required to complete the addition, and the mixture was then allowed to stand overnight at room temperature. At the end of this time Color Test I[146] was negative, and the mixture was hydrolyzed by adding 500 ml. of water dropwise while cooling in an ice bath and stirring vigorously. The ether layer was separated and washed twice with water; a small amount of insoluble material was filtered off; and the solution was dried over anhydrous sodium sulfate. Distillation of the ether from a water bath left 141 g. (100%) of brown solid melting at 115-43°. This was digested with 750 ml. of petroleum ether (b.p., 77-115°) to give 110 g. of yellow solid melting at 144-52°. Concentration of the mother liquor gave a second crop of 17 g. melting at 135-47°, and a third crop of 9 g. melting at 130-45°. The total recovery from the first crystallization was 136 g., or 97%. Successive recrystallizations of the various crops, combining materials of similar melting points, led to a final yield of 114 g. (81%) of white solid melting at 150-1°. Clark reports a 97% yield of triphenylsilanol but does not give a melting point.[105]

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

Sodium triphenylsilanolate.- Five grams of triphenylsilanol were dissolved in 100 ml. of dry xylene by warming. Then 0.5 g. of sodium metal was added, and the mixture was stirred and heated to reflux. Little reaction occurred until the sodium had melted; hydrogen was then evolved slowly and smoothly. At the end of three hours the evolution of gas had stopped. The mixture was then allowed to cool slightly until the sodium had solidified. The solid button of sodium was removed with a sharp glass rod, and the solution allowed to cool to room temperature. A white precipitate, 4.15 g. (76%), was filtered off and washed with xylene. It did not melt on a spatula, but burned to leave an alkaline ash. A 0.4145 g. sample of this material suspended in water was titrated with N/10 hydrochloric acid. Neutral equivalent: calcd, 298; found, 307. Schlenk reports a neutral equivalent of 298, but his yield is not given.[59]

Attempted preparation of triphenylsilylperoxide.- Ten ml. of a 1% solution of iodine in dry xylene was added to a warm solution of 1.0115 g. (0.0034 mole) of sodium triphenylsilanolate in 25 ml. of dry xylene. This mixture was stirred on a steam bath for 15 hours without any appreciable diminution of the iodine color. A small amount of white precipitate which had formed was allowed to settle and a sample of the solid was removed. It did not melt, but burned on a spatula. It gave no test for free iodine with starch paper, but gave an immediate yellow precipitate with aqueous silver nitrate solution. Most of a sample placed in distilled water dissolved. The solution gave a precipitate with silver nitrate solution, and the insoluble material, when filtered and dried, melted at 150-1°, and did not depress the melting point of an authentic sample of triphenylsilanol. It was concluded, therefore, that the precipitate was a mixture of sodium iodide and sodium triphenylsilanolate.

A second run was carried out in ether. Two g. (0.0067 mole) of sodium triphenylsilanolate were dissolved in 60 ml. of dry ether and a 2% solution of iodine in dry ether was added dropwise with stirring. The first three or four drops were decolorized immediately but further additions were not decolorized until the solution was brought to reflux. Addition was continued at reflux just fast enough to keep the solution pale yellow in color (about one ml. per minute). The addition was stopped when 42.5 ml. (0.0067 mole) had been added, and the mixture was stirred and refluxed for an additional half hour. A white water-soluble precipitate weighing 0.7 g. was filtered off. It gave a yellow precipitate with silver nitrate solution. On evaporation of the ether from the filtrate an iodine-colored solid remained. This was recrystallized from petroleum ether, b.p. 77-115°, to give 1.5 g. of triphenylsilanol, m.p. 150-151°, identified by mixed melting point with an authentic sample. A further 0.12 g. of triphenylsilanol was obtained by concentrating the mother liquors, making a total of 1.62 g. (90%). A small amount (0.1 g.) of material insoluble in petroleum ether was found to be sodium iodide, giving a total yield of 0.8 g. of this material (80%).

Since sodium iodide and triphenylsilanol were obtained in the absence of moisture, it seems probable that triphenylsilylperoxide was formed, but decomposed by abstracting a hydrogen atom from the solvent.

$$2\ R_3SiONa + I_2 \longrightarrow R_3SiOOSiR_3 + 2\ NaI$$

$$R_3SiOOSiR_3 + 2\ R'H \longrightarrow 2\ R_3SiOH + 2\ R'\cdot$$

Triphenylsilanol, absolute ethanol, and zinc chloride.- In an attempt to prepare triphenylsilane from triphenylsilanol by the method of Dolgov and Volnov[147], 2 g. (0.0067 mole) of triphenylsilanol and 24 g. (0.18 mole) of anhydrous zinc chloride were dissolved in 8.4 g. (0.18 mole) of absolute ethanol. The solution was protected from atmospheric moisture by a calcium chloride tube and refluxed for three hours. An oily layer which had formed during the period of reflux was extracted with ether, and the ether was evaporated. The oil thus obtained did not crystallize on standing in the refrigerator for one month, and a subsequent attempt to distill the oil at the water pump reduced it to a red, tarry material.

A second run, on a scale three times as large as the first, was refluxed for only fifteen minutes. An oil, obtained exactly as described above, deposited 0.43 g. (8%) of hexaphenyldisiloxane, melting at 223-225°, which was identified by mixed melting point. No other identifiable material was isolated.

In a third run, the procedure was modified according to the directions of Dr. G.N.R. Smart.[137] Two g. (0.0067 mole) of triphenylsilanol and 2 g. (0.015 mole) of anhydrous zinc chloride were refluxed in 10.5 g. (0.23 mole) of absolute ethanol for 4 days. The solution was then transferred to a test tube and the solvent was evaporated at room temper-

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[147] B. Dolgor and Y. Volnov, Zhur. Obschei. Khim., Khim. Ser. I. 91 (1931) /C.A., 25, 4535 (1931)/.

ature in a stream of air. About 0.4 g. of white crystals formed at the liquid surface and were removed. This was probably triphenylethoxysilane[137] (crude yield, 20%) but the crystals were too sticky to be placed in a capillary tube, and recrystallization from absolute ethanol or ethanol-water mixtures was not successful.

Attempted preparation of tetraphenylsilane from triphenylsilanol.- A 250 ml. three necked flask equipped with stirrer, reflux condenser, and dropping funnel was flushed with dry oxygen-free nitrogen. Ten ml. of dry ether was placed in the flask and 5.52 g. (0.02 mole) of triphenylsilanol was dissolved in the ether. To this was added slowly 16 ml. of 1.24 M solution of phenyllithium (0.02 mole) in ether. The reaction was vigorous, and cooling with an ice bath was required to prevent flooding of the condenser. The addition of a second 0.02 mole of phenyllithium produced no evolution of heat. After stirring for 12 hours Color Test I was still positive. Two ml. of the ether solution were removed and evaporated. The residue did not melt, but burned on a spatula and left an alkaline ash. When the residue was agitated with aqueous hydrochloric acid and dried on a porous plate it melted at 145-7° and did not depress the melting point of an authentic specimen of triphenylsilanol. An insoluble solid which was present in the reaction mixture behaved in exactly the same manner. It was concluded that the product of the reaction was lithium triphenylsilanolate, which was only partly soluble in ether.

Most of the ether was distilled from the reaction mixture and 50 ml. of dry toluene was added. The resulting suspension was stirred for 12 hours on a steam bath, and Color Test I was found to be negative. The insoluble material in the mixture was still lithium triphenylsilanolate, however. A further 0.01 mole of phenyllithium was added and the mixture refluxed for 48 hours on an oil bath. Color Test I was still positive and the insoluble material was still lithium triphenylsilanolate. The solvent was then removed and the dry residue heated on an oil bath at 200° for 12 hours. The solids were then rinsed from the flask with dry xylene and filtered. They weighed 5.6 g. and did not melt when heated on a spatula. This solid was dissolved in 75 ml. of cold 95% ethanol. On standing 72 hours 1.2 g. of white solid melting at 218-9° had separated. A small sample of this material recrystallized from dioxane melted at 226-7° and did not depress the melting point of an authentic sample of hexaphenyldisiloxane. Yield, 23%. Addition of twice its volume of water to the ethanol filtrate caused the precipitation of 3.15 g. (57%) of triphenylsilanol, identified by mixed melting point with the starting material.

Cleavage of triphenylsilanol by *n*-butyllithium with copper-bronze.- A 0.234 M solution of *n*-butyllithium was prepared in refluxing ether. The yield was 45%. Eleven grams (0.04 mole) of triphenylsilanol (m.p., 149-150°) was dissolved in 50 ml. of dry ether in a 500 ml., 3-necked flask equipped with mechanical stirrer, reflux condenser, dropping funnel, and inlets for dry nitrogen. Copper-bronze,[148] 0.5 g., was suspended in the solution, and 0.08 mole (340 ml.) of the *n*-butyllithium solution was added dropwise with good stirring. During the addition of the first half of the *n*-butyllithium solution a white precipitate appeared. This is thought to be the lithium salt of triphenylsilanol. The mixture was refluxed for 48 hours, and during this time the precipitate redissolved. The mixture was poured jetwise under nitrogen pressure on about 125 g. of crushed Dry Ice, and acidified with 10% aqueous hydrochloric acid. The ether layer was separated and extracted six times with a total of 300 ml. of 7% sodium carbonate solution. This alkaline extract was acidified with conc. hydrochloric acid, and extracted with ether. When the ether was dried and distilled there remained a pale yellow solid melting at 116-117°. On recrystallization of this solid from water, 2.7 g. (56%) of benzoic acid, m.p. 120-121°, was obtained (identified by mixed melting point). The ether was distilled from the non-acid part of the carbonated reaction mixture to leave an oil which deposited 2.6 g. of impure triphenylsilanol (m.p., 132-135°). Attempts to distill the remaining oil gave products boiling continuously over a range of 100-180° (0.5-1.0 mm.). No separation of fractions was possible. The oil may have been diphenyl-*n*-butylsilanol which condensed slowly during distillation to *sym*-di-*n*-butyltetraphenyldisiloxane.

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[148] For the catalytic effect of copper-bronze on this type of reaction, see H. Gilman, G.E. Brown, F.J. Webb, and S.M. Spatz, *J. Am. Chem. Soc.*, *62*, 977 (1940).

When the run was repeated using 0.16 mole of n-butyllithium (mole ratio of n-butyllithium to triphenylsilanol, 4:1) the yield of benzoic acid was also 56%. No attempt was made to recover the other products of reaction.

Cleavage of triphenylsilanol by n-butyllithium without copper-bronze.- The n-butyllithium for these runs was prepared by an improved method.[149] The average yields were 78% by the new method as compared to 50% by the old.

Ten grams (0.036 mole) of triphenylsilanol were treated with 0.1 mole of n-butyllithium by the procedure previously described, except that the copper-bronze was omitted. The yield of pure benzoic acid was 3.3 g., or 76%. Another run using 11 g. (0.04 mole) of triphenylsilanol and 0.12 mole of n-butyllithium without copper-bronze gave 3.2 g. (67%) of benzoic acid. The ether solution containing the non-acid products from this latter reaction was washed, immediately after the carbonate extraction, with 10% hydrochloric acid three times, and then with water until the washings were no longer acid to litmus. The ether solution was then dried and distilled, yielding 9.2 g. of colorless oil, boiling at 258-272° (2.8 mm.). This oil was redistilled to give 8.8 g. of oil; b.p., 165-166° (0.3 mm.); n_D^{20}, 1.5178; d_4^{20}, 0.9700. M_D calcd. for diphenyl-n-butylsilanol, 79.2; M_D found, 79.9. Yield, 86%.

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

Anal. Calcd. for $C_{16}H_{20}OSi$: Si, 10.9; Zerewitinoff H, 1.00. Found: Si, 10.6; Zerewitinoff H, 0.96.

It is believed that the failure to isolate diphenyl-n-butylsilanol from previous (and some subsequent runs) was due to partial condensation of the silanol to the corresponding disiloxane by alkali during the extraction with aqueous sodium carbonate or while the ether solution was standing and being distilled in contact with traces of alkali. It is noteworthy that in the runs described below, which were not carbonated, and hence not extracted with alkali, there was no difficulty in obtaining a good yield of diphenyl-n-butylsilanol.

In order to make sure that cleavage of triphenylsilanol occurred during the reaction with n-butyllithium and not during or subsequent to carbonation, two runs were hydrolyzed without carbonation. In the first, 10 g. (0.036 mole) of triphenylsilanol was treated with 0.1 mole of n-butyllithium in the usual way and for the usual time. Then 100 ml. of water was added, dropwise at first, and the ether layer was dried and distilled. Seven grams of diphenyl-n-butylsilanol, b.p. 165-170° (0.1 mm.), or a yield of 76%, were obtained. In the second run, 16.6 g. (0.06 mole) of triphenylsilanol was treated with 0.354 mole of n-butyllithium in the usual way, and hydrolyzed. The ether layer was dried and distilled. There was obtained as a fore-run about 0.5 ml. of a liquid having the odor of benzene, but its refractive index was not acceptable for benzene and it was not further investigated. The main body of the distillate, 12.4 g., boiled at 165-170° (0.1 mm.), and corresponded to a yield of 81% of diphenyl-n-butylsilanol.

Attempted cleavage of triphenylsilanol by n-butylmagnesium bromide.- To 5.5 g. (0.02 mole) of triphenylsilanol dissolved in 25 ml. of ether was added 0.083 mole of *n*-butylmagnesium bromide prepared in 83% yield in ether. Vigorous spontaneous reflux occurred and a heavy white precipitate (presumably the bromomagnesium salt of triphenylsilanol) appeared. The mixture was refluxed for 48 hours, but the precipitate did not redissolve. Carbonation and extraction with base in the usual way yielded a much larger volume of *n*-valeric acid than was commonly obtained when *n*-butyllithium was used as the cleaving agent. However, when this acid was heated for four hours at 140-150° no benzoic acid sublimed out. When the solvent was removed from the non-acid portion of the reaction product, 5 g. (91%) of triphenylsilanol, m.p. 148-150°, was recovered.

Attempted cleavage of triphenylsilanol by p-tolyllithium.- Triphenylsilanol, 8.75 g. (0.032 mole), in 50 ml. of dry ether was treated with 0.14 mole of *p*-tolyllithium (prepared in 95% yield in ether) by the usual procedure. The acid obtained on carbonation weighed 7.4 g. and melted at 174-177°. One crystallization from water yielded 7.0 g., m.p. 177-179°. This was identified as *p*-toluic acid by mixed melting point. The yield, based on the *p*-tolyllithium remaining after 0.032 mole had reacted with triphenylsilanol to give lithium triphenylsilanolate, was 48%. On evaporating the ether from the non-acid portion of the reaction product an oil was obtained which, on standing several days, deposited 6.1 g. (70%) of triphenylsilanol, m.p. 145-147°.

Hexaphenyldisiloxane.- Unpublished directions by H.W. Melvin, Jr. were used to prepare hexaphenyldisiloxane. Five grams (0.0094 mole) of triphenylsilanol were suspended in 25 ml. of 98% formic acid, and the mixture was refluxed for four hours. The solids were then filtered off, washed with water till free of formic acid, and dried. The product melted at 217-220°, and after one crystallization from dioxane it weighed 4.4 g. (92%) and melted at 220-221°.

This hexaphenyldisiloxane was cleaved by n-butyllithium to give a 66% yield of benzoic acid and a 50% yield of triphenyl-n-butylsilane.[145]

Tri-p-tolylsilanol.- Eighteen grams (0.106 mole) of silicon tetrachloride in 50 ml. of dry ether were treated with 0.318 moles of p-tolyllithium by the procedure used in the preparation of triphenylsilanol. The yield of crude tri-p-tolylsilanol, m.p. 94-95°, was 15.3 g. The purified yield was 13.5 g. (40%), m.p. 98-98.5°.

Cleavage of tri-p-tolylsilanol by n-butyllithium.- Tri-p-tolylsilanol, 7.5 g. (0.024 mole), and copper-bronze, 0.5 g., were treated with 0.065 mole of n-butyllithium by the procedure used with triphenylsilanol. The yield of p-toluic acid, m.p. 178-179°, was 2.0 g., or 61%. No attempt was made to isolate di-p-tolyl-n-butylsilanol.

Attempted cleavage of tri-p-tolylsilanol by phenyllithium.- Seven grams (0.022 mole) of tri-p-tolylsilanol in 50 ml. of ether were treated with 0.70 mole of phenyllithium in the absence of copper-bronze. The acid obtained on carbonation melted at 116-118°, and recrystallization from water raised it to 119-120°. This was shown by mixed melting point to be benzoic acid. (p-Toluic acid melts at 179-180°.)

Diphenyl-p-tolylsilanol.- The procedure for the preparation of this compound and for its cleavage by n-butyllithium have been published elsewhere.[145]

Attempted preparation of tri-p-anisylsilanol.- p-Anisyllithium was prepared in 92% yield by rapidly adding 37.4 g. (0.20 mole) of p-bromoanisole in 150 ml. of ether to 3.8 g. (0.52 g. atom) of lithium in 150 ml. of ether while cooling in an ice bath. The mixture was stirred for 10 minutes, then filtered and titrated. This procedure is reported to give a good yield of p-anisyllithium containing very little 2-methoxy-5-bromo-phenyllithium as a by-product.[150]

To 15.2 g. (0.0895 mole) of silicon tetrachloride in 50 ml. of dry ether was added 0.178 mole of p-anisyllithium according to the general directions of Clark.[105] While this addition was being carried out, a further 0.093 mole of p-anisyllithium was prepared. When the addition of the first batch of p-anisyllithium was complete, this second batch was added at a similar rate. This procedure was adopted in order to cut down the total period of standing for the p-anisyllithium before use. The whole addition required 3.5 hours and, at the end of this time, the mixture was stirred 15 minutes in the ice bath, 15 minutes without the ice bath, and

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[150] H. Gilman and J.T. Edward, unpublished results.

allowed to stand overnight at room temperature. It was then hydrolyzed with 2% ammonia solution, and the ether layer was separated and dried. Removal of the ether left a brown oil which did not crystallize on standing several days. This oil was insoluble in all of the petroleum ethers and in methanol, but soluble in ethanol. Attempts to crystallize from ethanol alone, or from ethanol-methanol or ethanol-petroleum ether mixtures produced brown oils.

It was thought that the failure to obtain tri-p-anisylsilanol from silicon tetrachloride and p-anisyllithium might be due to the presence of 2-methoxy-5-bromo-phenyllithium along with p-anisyllithium in spite of the precautions taken to avoid this. Therefore the attempt was repeated using 0.5 mole of p-anisylmagnesium bromide[151] and 15.4 g. (0.09 mole) of silicon tetrachloride. This mixture was refluxed in ether for 96 hours, then hydrolyzed with 10% hydrochloric acid. The solvent was removed from the ether layer, and the residue was steam distilled until no more anisole came over. Water was decanted from the liquid residue, and benzene was added. This solution was concentrated until all the water had been removed as the azeotrope with benzene, then petroleum ether, b.p. 77-115°, was added to the hot solution until cloudiness appeared. This was cleared by adding a few drops of benzene, and the solution was allowed to cool slowly in a Dewar flask. A brown oil separated from the solution. All attempts to crystallize this oil from benzene, benzene-petroleum ether,

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[151] E.A. Zoellner, Iowa State Coll. J. Sci., 9, 213 (1934), /C.A., 29, 5413 (1935)/.

ethanol-petroleum ether, ethanol-methanol, ethanol-water, or ethanol alone were unsuccessful. No further examination of the oil was made.

Tri-1-naphthylchlorosilane.- The directions of C.G. Brannen were followed in this preparation.[152] n-Butyllithium (0.377 mole) was prepared in ether in 76% yield,[149] and to this was added dropwise over a 30 minute period 77.7 g. (0.377 mole) of 1-bromonaphthalene while keeping the reaction temperature at -10 to 0° by means of an ice-salt bath. The resulting slurry was stirred at -10° for 20 minutes after the addition was complete, and then 17.0 g. (0.10 mole) of silicon tetrachloride was added dropwise over a 2 hour period. The mixture was stirred at room temperature for 12 hours, and then hydrolyzed by cautious addition of water. Some undissolved material was filtered off and recrystallized from benzene to give 11 g. (25%) of tri-1-naphthylchlorosilane melting at 202-203°. The ether layer, on concentration, deposited 25 g. of solid melting at 180-185°. This was recrystallized from benzene to give 16.5 g. of tri-1-naphthylchlorosilane, m.p. 202-203°, making a total yield of 27.5 g. or 62%. Brannen reports a yield of 68% melting at 208-209°, and the product obtained here did not depress the melting point of his material.

Tri-1-naphthylsilanol.- Ten grams (0.0235 mole) of tri-1-naphthylchlorosilane was suspended in 200 ml. of dioxane. Fifty ml. of 10%

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[152] H. Gilman and C.G. Brannen, unpublished results.

aqueous sodium hydroxide solution was added and the mixture was refluxed for 7 hours. Some undissolved material was filtered off and recrystallized from ethanol-benzene to give 8.1 g. (81%) of product melting at 202-203°. A mixed melt between this material and tri-1-naphthylchlorosilane melted at 190-193°, while a mixed melt with Brannen's tri-1-naphthylsilanol was not depressed. Brannen reports a yield of 86%, melting at 205-206°. Attempts to cleave this silanol with n-butyllithium in ether were unsuccessful.[145]

Tri-1-naphthylsilanol, sodium salt.- A 3.4 g. sample of the tri-1-naphthylsilanol described above was dissolved in 100 ml. of dry xylene and 5 g. of sodium metal was added. Evolution of hydrogen was vigorous at 100°, and was complete in 15 minutes. The solution was allowed to cool, whereupon a white precipitate separated. This was decanted through a coarse filter of glass wool which permitted the precipitate to pass through but retained the sodium metal. The precipitate was dried in an oven at 110° for 15 minutes. Samples were then weighed quickly into 125 ml. Erlenmeyer flasks and covered with water. The water suspensions were heated almost to boiling for 5 minutes, then cooled and titrated with N/10 hydrochloric acid. Neutral equivalents were 332 and 338. The molecular weight of sodium tri-1-naphthylsilanolate is 346.

Tri-p-xenylsilanol.- p-Xenyllithium was prepared by the following procedure. Lithium metal, 3.22 g. (0.46 mole), was pounded into paper-thin sheets, scrubbed under mineral oil to ensure a bright surface, washed with petroleum ether, b.p. 60-70°, and cut in pieces about 5 mm. square into 200 ml. of dry ether in the usual apparatus. Fifty grams (0.214 mole) of p-bromobiphenyl in 700 ml. of dry ether was added slowly with good stirring. There was no evidence of reaction and the lithium particles changed from shiny to black. A few fresh pieces of lithium also turned black when added to the mixture. The whole of the p-bromobiphenyl was added, and the mixture was refluxed for 5 hours, during which time the lithium was slowly consumed, although it never became bright. The dark brown solution was filtered through glass wool and titrated. The yield was 73%. About a dozen similar runs produced substantially the same results.

To 6.75 g. (0.0397 mole) of silicon tetrachloride in 150 ml. of dry ether was added 0.113 mole of p-xenyllithium in accordance with the general directions of Clark.[105] The addition was complete in 2 hours, and the reaction mixture was allowed to stand overnight. It was then hydrolyzed with 10% ammonia solution, the solvent was distilled from the ether layer, and the residue was steam distilled to remove 3.5 g. (20%) of biphenyl. Ether extraction of the residue from steam distillation left 1 g. (7%) of insoluble solid, m.p. 200-201° with gas evolution, which was found to be di-p-xenylsilanediol.

Anal. Calcd. for $C_{24}H_{20}O_2Si$: Si, 7.62; active H, 2.00. Found: Si, 7.59, 7.69; active H, 1.88, 1.95.

The solvent was distilled from the ether extract and the residue was crystallized from benzene to give 5.6 g. (28%) of tri-p-xenylsilanol, m.p. 200-201°. This material did not evolve a gas on melting, and a mixed melting point with the di-p-xenylsilanediol obtained above was depressed about 15°. Subsequent runs gave yields of 32% and 35%.

Anal. Calcd. for $C_{36}H_{28}OSi$: Si, 5.55; active H, 1.00. Found: Si, 5.54, 5.59; active H, 0.94, 0.98.

An attempt was also made to prepare tri-p-xenylsilanol from silicon tetrachloride using p-xenyllithium made by halogen-metal interconversion. In order to determine the yield of p-xenyllithium obtained from the interconversion, 11.65 g. (0.050 mole) of p-bromobiphenyl in 50 ml. of dry ether was treated with 0.050 mole of n-butyllithium in 100 ml. of ether at 0°. Aliquots were withdrawn and carbonated at intervals of 0, 5, 10, 20, and 40 minutes after mixing. The yields of p-phenylbenzoic acid were 62, 60, 60, 60, 57%, respectively. It was therefore concluded that the interconversion mixture could be used immediately after mixing, that its use could be spread over a period of at least 40 minutes, and that the yield would be approximately 60%.

On this basis, 75.6 g. (0.15 mole) of p-bromobiphenyl was suspended in 100 ml. of dry ether, and to this was added over a period of 2 minutes 0.15 mole of n-butyllithium in 300 ml. of ether at 0°. This solution was added dropwise to 5.1 g. (0.03 mole) of silicon tetrachloride in 100 ml. of dry ether at -10° over a period of 40 minutes. Hydrolysis with 10% ammonia solution gave a solid melting at 200-250° which was insoluble in ether. The ether solution yielded a brown solid melting at 150-180°. Attempts to obtain a pure material from these solids by crystallization were unsuccessful.

Tri-p-xenylsilanol was also prepared from silicon tetrachloride and p-xenylmagnesium iodide. (p-Bromobiphenyl did not react with magnesium.) One and one-half grams (0.06 g. atom) of magnesium turnings were just covered with ether and reaction was started by adding a few crystals of p-iodobiphenyl. A solution of 14 g. (0.05 mole) of p-iodobiphenyl in 90 ml. of dry ether was added at a rapid drip. Only very gentle reflux occurred, and the solution became dark brown and cloudy. When the addition was complete the mixture was refluxed for two hours, then filtered and titrated. The yield was 59%. To this Grignard solution (0.0295 mole) was added 1.53 g. (0.009 mole) of silicon tetrachloride. The mixture was refluxed until Color Test I became negative (48 hours), then hydrolyzed with 10% hydrochloric acid and filtered. The insoluble material weighed 0.9 g. (20%) and melted at 196-199°. This did not depress the melting point of the tri-p-xenylsilanol reported above.

Attempted preparation of tri-p-xenylchlorosilane.- Three grams (0.0060 mole) of tri-p-xenylsilanol were dissolved in 100 ml. of dry benzene, and dry hydrogen chloride gas was passed into the solution for 5 hours. There was no heat evolved and no precipitate formed. On distillation of the solvent, a quantitative recovery of tri-p-xenylsilanol (mixed melting point) was made. This method has been very successful for preparing triphenylchlorosilane from triphenylsilanol.[126]

In a second attempt, 2.5 g. (0.005 mole) of tri-p-xenylsilanol was suspended in 25 ml. of acetyl chloride, and dry hydrogen chloride was passed into the suspension for 12 hours. The solid was then filtered off, washed with petroleum ether, b.p. 28-38°, and found to weigh 2.5 g. (100% recovery) and melt at 200-201°. A mixed melting point with starting material was not depressed. This tri-p-xenylsilanol was dissolved in a slight excess of benzene, and an equal volume of acetyl chloride was added. Dry hydrogen chloride was passed into this solution for 5 hours. Evaporation of the solvent left 2.5 g. of tri-p-xenylsilanol, melting at 197-198°, identified by mixed melting point.

Cleavage of tri-p-xenylsilanol by phenyllithium.- Three grams (0.006 mole) of tri-p-xenylsilanol was refluxed for 48 hours with 0.06 mole of phenyllithium in 175 ml. of dry ether. The mixture was carbonated and worked up in the usual way[145] to give an acid melting at 104-108°. This was extracted with hot water. The material which did not dissolve in hot water melted at 175-190° and, after several crystallizations from aqueous ethanol, it yielded 0.14 g. (12%) of p-phenylbenzoic acid, m.p. 227-228°, identified by mixed melting point with an authentic specimen.

Attempted preparation of hexa-p-xenyldisiloxane.- Other investigators have found that triphenylsilanol and tri-p-chlorophenylsilanol are converted to the corresponding disiloxanes in excellent yields by refluxing formic acid.[21,118] In accordance with their procedure, 0.5 g. of tri-p-xenylsilanol was refluxed for 48 hours in 25 ml. of Eastman Kodak White Label 98% formic acid. On diluting the suspension with 4 volumes of water and filtering, there was obtained 0.5 g. of solid melting at 185-

190°. One crystallization from benzene gave 0.44 g. (88% recovery) of tri-*p*-xenylsilanol melting at 200-201°. This was identified by mixed melting point with a sample of the starting material.

Attempted cleavage of tetraphenylsilane by *n*-butyllithium.- Tetraphenylsilane, 13.4 g. (0.04 mole), and copper-bronze, 0.5 g., in 100 ml. of ether were treated in the usual way with 0.04 mole of *n*-butyllithium made by the old procedure in 51% yield. The mixture was carbonated, acidified, and extracted with aqueous sodium carbonate. Acidification of the extract and extraction of this with ether yielded only a trace of solid which would not redissolve in sodium carbonate solution. The original reaction mixture contained a considerable amount of insoluble material. This was filtered off and extracted with hot benzene in order to separate organic material from copper-bronze. Evaporation of the benzene left 10.7 g. of tetraphenylsilane, m.p., 233-235°, identified by mixed melting point determination. This is a recovery of 80%.

In a second run, 11 g. (0.033 mole) of tetraphenylsilane and 0.5 g. of copper-bronze were treated with 0.033 mole of *n*-butyllithium prepared by the old method in 41% yield. Again no alkali-soluble material was obtained on carbonation, and 9.5 g. (86%) of tetraphenylsilane, m.p., 234-235°, was recovered.

Attempted cleavage of tetra-*p*-tolylsilane by *n*-butyllithium.- Eight grams (0.02 mole) of tetra-*p*-tolylsilane (m.p., 234-235°) and 0.3 g. of copper-bronze in 50 ml. of ether were treated in the usual way with 0.025

mole of n-butyllithium prepared by the old method in 37% yield. During the period of refluxing, a break occurred in the system and the solvent evaporated. The dry solids were thus inadvertently heated at a high temperature (probably about 200°) for several hours. The residue, which gave a negative result with Color Test I, was extracted with boiling petroleum ether (b.p., 77-115°). On cooling and concentrating, the petroleum ether deposited 6.6 g. of tetra-p-tolylsilane, m.p., 232-233°, identified by mixed melting point determination. This is a recovery of 83%.

A second run using 6 g. (0.015 mole) of tetra-p-tolylsilane, 0.25 g. of copper-bronze, and 0.03 mole of n-butyllithium (prepared by the old method in 42% yield) was carried out in the usual way, without accident, and carbonated. No alkali-soluble material was obtained. The copper-bronze was filtered off and extracted with boiling petroleum ether (b.p., 77-115°). The petroleum ether deposited 2.5 g. of tetra-p-tolylsilane, m.p. 230-231°, and the ether filtrate from the copper-bronze yielded on concentration another 2.5 g., m.p. 225-230°. Thus, the total recovery of tetra-p-tolylsilane (mixed melting point) was 5 g., or 83%.

Trimethylphenylsilane.- Phenyllithium, 0.11 mole in 210 ml. of ether, was placed in a 250 ml. 3-neck flask equipped with stirrer, reflux condenser, dropping funnel, and inlet for dry nitrogen. To this was added dropwise over a period of 30 minutes 10.9 g. (0.10 mole) of trimethylchlorosilane in 50 ml. of dry ether. The mixture was stirred at room temperature for 2 hours and then hydrolyzed with 50 ml. of water. The ether layer, on being dried and distilled, yielded 14.2 g. (95%) of colorless liquid boiling at 162-165° (739 mm.) The reported boiling point of trimethylphenylsilane is 171.2° (760 mm.).[153]

Attempted cleavage of trimethylphenylsilane by n-butyllithium.- Trimethylphenylsilane, 7.5 g. (0.05 mole), and copper-bronze, 0.5 g., in 50 ml. of ether were treated in the usual way with 0.10 mole of n-butyllithium prepared by the old method in 39% yield. The mixture was refluxed 36 hours instead of the usual 48, and carbonated. Extraction with aqueous sodium carbonate and working up the extract as usual gave about 1 ml. of a yellow oil, soluble in alkali but not in water, and having a strong odor of valeric acid. No solid acid could be obtained from this. The non-acid portion of the reaction product was distilled to give 4.5 g. of liquid boiling at 160-170° (732 mm.). The boiling point of trimethylphenylsilane at 760 mm. is 171.2°. [153] This is a recovery of 60%, if the material is trimethylphenylsilane.

Attempted cleavage of triphenyl-n-butylsilane by n-butyllithium.- Five grams (0.016 mole) of triphenyl-n-butylsilane[145] and 0.5 g. of copper-bronze in 50 ml. of dry ether were treated in the usual way with 0.032 mole of n-butyllithium prepared by the old method in 52% yield. When the carbonated reaction mixture was extracted with aqueous sodium carbonate, only a drop or two of liquid acid having the characteristic odor of valeric

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[153] A. Bygden, Z. phys. Chem., 90, 246 (1915).

acid was obtained. The ether solution containing the non-acid part of the reaction mixture was filtered free of copper-bronze, dried, and distilled. The residue was taken up in boiling methanol, and this solution deposited 5 g. of triphenyl-n-butylsilane in two crops. The recovered material (100% recovery) was slightly impure (m.p., 84-85°) but its identity was confirmed by mixed melting point determination.

Trimethyl-1-naphthylsilane.- 1-Naphthyllithium was prepared from 1-bromonaphthalene and lithium metal in ether[154] in 70% yield. This solution was deep purple in color and probably contained addition products of lithium on naphthalene, 1-bromonaphthalene, or 1-naphthyllithium.[155] Trimethylchlorosilane, 20.6 g. (0.19 mole), was dissolved in 100 ml. of dry ether in a 500 ml. 3-neck flask equipped with stirrer, reflux condenser, dropping funnel, and nitrogen inlets. 1-Naphthyllithium, 0.19 mole, was added dropwise at the maximum rate at which the purple color was discharged. The reaction mixture became cloudy yellow, green, gray, and yellow in turn. After 2 hours the addition was complete and Color Test I was negative. A further 20 ml. of 1-naphthyllithium solution was added and Color Test I became positive. The ether was distilled off and replaced by dry benzene. The benzene solution was filtered, the salts were washed

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[154] H. Gilman, E.A. Zoellner, and W.M. Selby, J. Am. Chem. Soc., 54, 1957 (1932).

[155] W. Schlenk and E. Bergmann, Ann., 463, 1 (1928).

with benzene, and the combined benzene solutions were distilled. The product was 33 g. of an oil with a greenish fluorescence boiling at 120-160° (13 mm.). This oil was steam distilled for several hours until no more naphthalene came over. The total yield of naphthalene was 7.5 g. or 31%. The residue was distilled at 127-130° (10 mm.) and again at 91-92° (1.7 mm.) to give 13 g. (34%) of a fluorescent oil. Analyses showed that this oil contained 12.7-12.8% silicon, while the calculated silicon content of trimethyl-1-naphthylsilane is 14.0%. Qualitative tests showed that the oil also contained bromine, suggesting that 1-bromonaphthalene is an impurity.

Schlenk and Bergmann[155] reported that lithium does not add to naphthalene in hydrocarbon solvents, so several attempts were made to prepare 1-naphthyllithium in petroleum ether in order to avoid the formation of colored impurities. In pure petroleum ether (b.p., 28-38°) the yield was 20%; in a 30% petroleum ether, 70% diethyl ether mixture the yield was 40%; in a 10% petroleum ether, 90% diethylether mixture the yield was 42%. In the first two cases the solution was pale brown in color; in the last it was a somewhat lighter purple than when made in diethyl ether alone.

A second preparation of trimethyl-1-naphthylsilane was carried out by treating 11 g. (0.10 mole) of trimethylchlorosilane in 25 ml. of dry ether with 0.12 mole of 1-naphthyllithium prepared in 40% yield in a mixture containing 30% petroleum ether and 70% diethyl ether. When addition was complete the mixture was refluxed for one hour and allowed to stand overnight at room temperature. Color Test I was then strongly positive. Water was added and the ether layer was dried and distilled. Fourteen grams (60%) of product boiling at 99-100° (2 mm.) was obtained, along with some red-orange oil boiling at 215-220° (2 mm.). The 14 g. of trimethyl-1-naphthylsilane obtained in this preparation also contained bromine by qualitative analysis.

While these experiments were in progress it was discovered[152] that the halogen-metal interconversion reaction gives 1-naphthyllithium substantially free of lithium addition products. A third run of trimethyl-1-naphthylsilane was made using 1-naphthyllithium made by interconversion.

n-Butyllithium, 0.21 mole, was prepared by the old method in 31% yield and added in a slow stream to 41.4 g. (0.20 mole) of 1-bromonaphthalene in 100 ml. of dry ether under an atmosphere of dry nitrogen. Mild reflux occurred during the addition and continued for 10 minutes after the addition was complete. As soon as reflux had subsided, 21.8 g. (0.20 mole) of trimethylchlorosilane in 50 ml. of dry ether was added dropwise at such a rate as to produce mild reflux, while cooling the reaction flask in an ice-water bath. The mixture was stirred at room temperature for 8 hours; then hydrolyzed. The residue obtained on distilling the solvent from the ether layer was steam distilled until only water came over. The distillate was a liquid, which was taken up in ether, dried, and distilled. Fifteen grams of liquid boiling at 120-126° (738 mm.) was obtained. This liquid does not contain silicon and is thought to be n-octane (b.p. 126°) formed by the reaction

$$\underline{n}\text{-}C_4H_9Li + \underline{n}\text{-}C_4H_9Br \longrightarrow \underline{n}\text{-}C_8H_{18} + LiBr$$

during the preparation of the low yield of n-butyllithium. The residue from the steam distillation was distilled to give 28 g. (70%) of liquid boiling at 99-100° (2 mm.). This material was redistilled twice through a 12-inch column packed with 1/8-inch glass helices. The material boiling at 127-128° (10 mm.) was collected each time, and had the following physical constants: n_D^{20}, 1.5810; d_4^{20}, 0.9870; M_D calcd. for trimethyl-1-naphthylsilane, 67.4; M_D found, 67.6.

Anal. Calcd. for $C_{13}H_{16}Si$: Si, 14.0. Found: Si, 13.8.
A product (8 g.) boiling at 120-125° (2 mm.) was also obtained from the residue after steam distillation. This did not contain silicon and was believed to be 1-n-butylnaphthalene, (b.p., 287-288°)[156], formed by the reactions

$$1\text{-}C_{10}H_7Br + n\text{-}C_4H_9Li \longrightarrow 1\text{-}C_{10}H_7Li + n\text{-}C_4H_9Br$$

$$1\text{-}C_{10}H_7Li + n\text{-}C_4H_9Br \longrightarrow 1\text{-}(n\text{-}C_4H_9)C_{10}H_7 + LiBr$$

during the halogen-metal interconversion.[152]

Attempted cleavage of trimethyl-1-naphthylsilane by n-butyllithium.- Ten grams (0.05 mole) of trimethyl-1-naphthylsilane in 50 ml. of dry ether was treated with 0.67 mole of n-butyllithium made by the old procedure in 35% yield. The solution became orange in color when the n-butyllithium was added, but it did not reflux spontaneously, and the color did not deepen when the solution was refluxed over a hot plate. The mixture was carbonated after 48 hours and extracted with sodium carbonate in the usual

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[156] H.C. Smith, J. Inst. Petroleum, 35, 103 (1949).

way. A liquid acid having the characteristic odor of *n*-valeric acid was obtained. This was completely soluble in 100 ml. of water at room temperature, so it could not have contained any appreciable amount of 1-naphthoic acid. The non-acidic part of the reaction product yielded, on distillation, 6.5 g. (65%) of trimethyl-1-naphthylsilane at 100° (2 mm.), and 0.75 g. of liquid boiling at 115-118° atmospheric pressure; n_D^{25} 1.3996, d_4^{20} 0.7082. This was at first thought to be trimethyl-*n*-butylsilane[157], but was found on analysis to contain no silicon and was therefore probably *n*-octane[158] formed during the preparation of *n*-butyllithium.

A total of eight attempts to accomplish this cleavage were made. Varying yields of *n*-octane were obtained but no solid acid was ever obtained, and recoveries of trimethyl-1-naphthylsilane were never above 70%.

Preparation and Reactions of Hexaaryldisilanes

Hexaphenyldisilane.- In accordance with the directions of Schlenk[59], 6.5 g. (0.022 mole) of triphenylchlorosilane was refluxed in 125 ml. of xylene with 4 g. (0.174 g. atom) of sodium for 3 hours. The suspension developed a deep violet color and a large volume of white precipitate appeared. This precipitate was filtered from the hot solution, as specified by Schlenk, and the xylene solution was allowed to cool for 12 hours

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[157] A. Bygden, *Z. phys. Chem.*, *90*, 246 (1915) gives for trimethyl-*n*-butylsilane: b.p. 115°, d_4^{25} 0.7141, n_D^{25} 1.4004.

[158] W. Roth and K. Scheel, "Landolt-Bornstein, Physikalischchemische Tabellen", Erg. IIIa, Julius Springer, Berlin, 1935, p. 344, gives for *n*-octane: b.p. 125.6° (760 mm.) d_4^{20} 0.7028, n_D^{20} 1.3976.

in the refrigerator. There was obtained as a precipitate 0.28 g. (5.4% yield) of hexaphenyldisilane melting at 254-255°. Schlenk gives the melting point as 254-255° but does not mention the yield.

In a second run, 15 g. of triphenylchlorosilane (0.051 mole) was refluxed for 3 hours with 2.1 g. (0.091 g. atom) of sodium in 75 ml. of xylene. The suspension was allowed to cool to room temperature, then filtered, and the residue was washed with xylene. This solid was placed in 100 ml. of 95% ethanol and stirred until all the excess sodium had reacted. Four volumes of water were then added, and the suspension was filtered. The residue was washed with water and dried to give 11.6 g. of hexaphenyldisilane (85% yield), melting at 361-362°. It is thus evident that the solid filtered from the hot solution in the previous run is mostly hexaphenyldisilane, rather than mostly sodium chloride, as assumed by Schlenk. A second run by the same procedure gave an 87% yield.

Attempted reaction between triphenylsilane and sodium metal.- Three grams (0.012 mole) of triphenylsilane was dissolved in 100 ml. of dry xylene and 0.5 g. (0.022 g. atom) of freshly cut sodium metal was added. This mixture was refluxed for 24 hours, then allowed to cool. A trace of insoluble material separated and was filtered off. It did not melt under 400°. When triturated with a few drops of water it was converted to a white solid melting at 148-150°. About 5 mg. of this material, very probably triphenylsilanol, was obtained. It was probably formed from traces of sodium hydroxide formed on the surface of the sodium during handling. Evaporation of the xylene left an oil which, on standing for several days, deposited 2.7 g. (90%) of triphenylsilane melting at 40-42°, identified by mixed melting point with starting material.

<u>Hexaphenyldisilane from triphenylsilane</u>.- In an attempt to prepare triphenylsilyllithium, 5.2 g. (0.02 mole) of triphenylsilane in 100 ml. of ether was added slowly to 0.7 g. (0.10 g. atom) of lithium metal in 50 ml. of ether under nitrogen. There was no immediate evidence of reaction, so the mixture was refluxed for 24 hours. At the end of this time some white insoluble material had appeared. The suspension was decanted through a stopcock so as to let the precipitate pass over while retaining the pieces of lithium metal, and poured into 7.8 g. of ethyliodide. There was no evidence of reaction after the mixture had been refluxed for 7 hours, so the precipitate was filtered off and treated with 50 ml. of 90% methanol. When evolution of gas (due to decomposition of lithium hydride by water) had ceased, the mixture was filtered. The precipitate weighed 0.4 g. and melted at 350-355°. A mixed melting point with hexaphenyldisilane was not depressed. This corresponds to a yield of 8%. The ether layer was shaken with 10% hydrochloric acid, dried and distilled. There was obtained 3.0 g. (58%) of triphenylsilane at 144-145° (0.3 mm.) and 1.7 g. (31%) of triphenylsilanol boiling at 154-200° (0.3 mm.), m.p. 148-150°, both identified by mixed melting points.

A second run using twice as much reagents in the same volume of ether was refluxed for 6 days. It was worked up exactly as before, to give a

21% yield of hexaphenyldisilane, a 22% yield of triphenylsilanol, and a 38% recovery of triphenylsilane. No triphenylethylsilane was obtained from either run.

Reaction between triphenylsilane and selenium dioxide.- In an attempt to prepare hexaphenyldisilane, 2.6 g. of triphenylsilane (0.01 mole) dissolved in 100 ml. of dioxane was added to 1.2 g. (0.01 mole) of selenium dioxide. The mixture was stirred and refluxed under nitrogen for eight hours, thenallowed to stand overnight. A sludge of selenium metal was filtered off with the aid of diatomaceous earth, and the red mother liquor was diluted with 10 volumes of water. The organic material separated as an oil, so the aqueous emulsion was extracted several times with ether. The ether extract was washed with water to remove dioxane, then dried and distilled. The residue was a yellow oil which, on standing, deposited 2 g. of colorless crystals melting at 148-150°. These did not depress the melting point of a sample of pure triphenylsilanol. The yield is 73%. No ether-insoluble material, such as hexaphenyldisiloxane or hexaphenyldisilane was found.

Attempted reaction between triphenylsilane and chloranil.- In a second attempt to prepare hexaphenyldisilane, 3 g. (0.012 mole) of triphenylsilane in 100 ml. of dry xylene was added to 3 g. (0.012 mole) of chloranil. The solution was refluxed for eight hours and allowed to stand overnight. At the end of this time the solution had changed from a light yellow color to brownish black. The xylene solution was then chilled thoroughly in the refrigerator and shaken five times with an ice-cold 2% solution of potassium hydroxide. This removed excess chloranil and tetrachloroquinhydrone. The xylene solution was then washed with water and dried. Removal of the solvent under vacuum left a dark brown oil which was very soluble in most organic solvents except methanol. All attempts to get a crystalline material from the oil were unsuccessful. At any rate, the ready solubility of the oil in ether makes it very unlikely that any hexaphenyldisilane or hexaphenyldisiloxane was present.

Attempted cleavage of hexaphenyldisilane by phenyllithium.- Hexaphenyldisilane, 2.5 g. (0.0048 mole), was suspended in 200 ml. of ether containing 0.045 mole of phenyllithium. This mixture was refluxed for 96 hours, then hydrolyzed with water and filtered. The residue weighed 2.42 g. (97% recovery) and melted at 360-361° alone or mixed with starting material.

In a second attempt, 2.42 g. (0.0046 mole) of hexaphenyldisilane was suspended in 100 ml. of dry xylene, and 0.05 mole of phenyllithium in 55 ml. of ether was added. This mixture was refluxed for 72 hours, then hydrolyzed with water and filtered. The residue weighed 2.21 g. (92% recovery) and melted at 360-361° alone or mixed with starting material.

Attempted cleavage of hexaphenyldisilane by n-Butyllithium.- To a solution of 0.06 mole of *n*-butyllithium (prepared by the old method in 52% yield) in 150 ml. of ether was added 2.2 g. (0.0042 mole) of hexaphenyldisilane. After being refluxed for 48 hours none of the hexaphenyldisilane had gone into solution, as might be expected if cleavage had occurred, so two volumes of dry xylene were added and the suspension was refluxed for another 48 hour period. Color Test I was then negative, so the suspension was filtered and the filtrate concentrated to about 5 ml. The residue from the filtration weighed 1.5 g. and melted at 360-361°. The concentrated xylene deposited 0.3 g. of solid melting at 354-356°. Both solids were identified as hexaphenyldisilane by mixed melting point, so the recovery of starting material is 1.8 g., or 82%. The 5 ml. of xylene solution was placed in 100 ml. of water and the xylene was removed by steam distillation. The remaining water layer was extracted with ether, and the ether was dried and distilled. No residue remained, so no triphenyl-n-butylsilane, triphenylsilane, or triphenylsilanol could have been formed by cleavage. The 12% loss of hexaphenyldisilane may well have been mechanical.

Hexa-p-xenyldisilane.- To 2.51 g. (0.0097 mole) of hexachlorodisilane in 100 ml. of ether was added 0.068 mole of p-xenyllithium prepared from p-bromobiphenyl and lithium in 72% yield by the procedure previously described. This mixture was refluxed until Color Test I became negative (20 hours), then hydrolyzed with water. The material insoluble in both ether and water was filtered off and dried. It weighed 7.5 g. and melted at 320-370°. This solid was digested with benzene for four hours, then filtered and washed with benzene. The benzene, on cooling, deposited 1.5 g. of white solid melting at 260-263°. Recrystallization from benzene gave

1.2 g. (23%) of tetra-p-xenylsilane melting at 270-272°. The melting point reported in the literature is 274°.[63] The benzene-insoluble residue weighed 3 g. and melted at 400-415°. This material was very insoluble in all the organic solvents available, with the exception of nitrobenzene. It could be recrystallized from nitrobenzene conveniently, leading to a product with a lighter color (tan) but the same melting point. It was then discovered that the material was partly soluble in pyridine. After four hours of digestion with hot pyridine, the hot suspension was filtered to give a residue weighing 1.3 g. and melting at 432-434°. This material appears to be hexa-p-xenyldisilane. The yield is 14%.

Anal. Calcd. for $C_{72}H_{54}Si_2$: Si, 5.75. Found: Si, 5.73, 5.77.

Several attempts were made to prepare hexa-p-xenyldisilane from hexachlorodisilane and p-xenyllithium made by halogen-metal interconversion. In most of them some tetra-p-xenylsilane was obtained along with tan to brown solids melting from 360 to 400°. These were always completely soluble in pyridine, and no pure material was ever isolated from any of them.

Attempted reaction of hexa-p-xenyldisilane with oxygen and iodine.- A suspension of 0.30 g. of hexa-p-xenyldisilane in 50 ml. of dry xylene was heated to reflux for 48 hours while passing a stream of dry air through the mixture. The xylene was then removed under vacuum. The residue weighed 0.294 g. (98% recovery) and melted at 432-434° alone, or mixed with starting material.

Two 0.30 g. samples of hexa-p-xenyldisilane were weighed out and suspended, one in 50 ml. of xylene, and the other in 50 ml. of chloroform.

To the xylene suspension was added 0.1 g. of iodine and 3 drops of quinoline. To the chloroform suspension was added 3 drops of a dilute solution of iodine in chloroform. Both solutions were refluxed for 10 hours, then filtered hot. The residue from the xylene suspension weighed 0.252 g. (84%) and that from the chloroform suspension weighed 0.260 g. (87%). Both melted at 432-434° alone or mixed with starting material. The iodine color had not disappeared from either solution, even though it had been very faint in the chloroform solution from the beginning.

Preparation and Ultraviolet Absorption Spectra of p-Dimethylaminophenylsilicon Compounds

The ultraviolet absorption spectra of various organosilicon compounds have been reported previously.[159] Some additional details of preparation for these and related compounds are given below.

Bis-(p-dimethylaminophenyl)-silanediol.- p-Dimethylaminophenyllithium (0.17 mole) was added under nitrogen to 9.52 g. of silicon tetrachloride (0.056 mole) in ether. The addition was made over a two hour period while keeping the temperature of the reaction mixture at -15 to -20°. The solution was stirred for thirty minutes at room temperature, and then hydrolyzed. The ether layer was dried and distilled, leaving a sticky blue solid which, after crystallization from benzene-petroleum ether (b.p. 90-120°), yielded 13 g. (77%) of bis-(p-dimethylaminophenyl)-silanediol

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[159] H. Gilman and G.E. Dunn, J. Am. Chem. Soc., 72, 2178 (1950).

melting at 173-174°.

Anal. Calcd. for $C_{16}H_{22}O_2N_2Si$: N, 9.27; Si, 9.27; active H, 2.00; Found: N, 9.43; Si, 9.10; active H, 1.93.

Tris-(p-dimethylaminophenyl)-silanol.- p-Dimethylaminophenyllithium (0.18 mole) was added to 10.2 g. (0.06 mole) of silicon tetrachloride in ether under an atmosphere of nitrogen. During the addition of the first equivalent of aryllithium the temperature was kept at -15 to -20°, and while the last two equivalents were added dropwise the mixture was allowed to warm up to room temperature. It was then refluxed until Color Test I became negative (forty-eight hours), and hydrolyzed. A solid insoluble in both ether and water was filtered off and dried. It weighed 2.5 g., melted at 224-228°, and was shown by mixed melting point to be tetrakis- (p-dimethylaminophenyl)-silane (8%). The ether layer, on concentration, deposited a brown, gummy solid which, when crystallized from benzene, gave 14 g. (58%) of colorless solid melting at 174-176°. Recrystallization from benzene raised the melting point to 183-184°. This compound has previously been reported as melting at 183-184°[160] and boiling at 275-280°, 12 mm.[104]

Tris-(p-dimethylaminophenyl)-chlorosilane.- This compound was prepared by the method used for tris-(p-dimethylaminophenyl)-silanol, except that, as soon as Color Test I became negative, the mixture was not

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[160] M.A. Plunkett, Doctoral Dissertation, Iowa State College, 1947.

hydrolyzed, but the ether was distilled off while adding dry benzene. When all the ether had been removed, the benzene solution was siphoned away from the inorganic salts under nitrogen, and concentrated. The yield of tris-(p-dimethylaminophenyl)-chlorosilane which crystallized out was 25.5 g. (60%), melting at 204-207°. Recrystallization from benzene gave 18.2 g. (43%), melting at 212-213°.

Anal. Calcd. for $C_{24}H_{30}N_3ClSi$: Cl, 8.38; Si, 6.61. Found: Cl, 8.2 ; Si, 6.53.

Attempted preparation of hexakis-(p-dimethylaminophenyl)-disiloxane.- All attempts to prepare this compound from tris-(p-dimethylaminophenyl)-silanol were unsuccessful. Refluxing the silanol with glacial acetic acid[118], 98% formic acid[21,118] or hydrochloric acid in methanol[161] gave glasses or oils with a strong blue color which suggest that cleavage of the p-dimethylaminophenyl group had taken place. Refluxing the silanol with di-n-butylamine gave a good yield of tris-(p-dimethylaminophenyl)-di-n-butylaminosilane.[51]

One gram (0.0025 mole) of tris-(p-dimethylaminophenyl)-silanol was suspended in dry xylene and 0.5 g. (0.022 g. atom) of sodium metal was added. This was warmed until the silanol had completely dissolved and hydrogen was no longer evolved. The solution was then decanted into a xylene solution of 1 g. (0.0024 mole) of tris-(p-dimethylaminophenyl)-chlorosilane. This mixture was refluxed for six hours, then washed with

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[161] F.S. Kipping and L.L. Lloyd, J. Chem. Soc., 79, 449 (1901).

water, and 0.4 g. of colorless insoluble material was filtered off. This solid did not melt, but slowly turned brown and decomposed when heated above 400°. A product with very similar properties was obtained when 5.22 g. (0.0183 mole) of hexachlorodisiloxane was refluxed in ether with 0.11 mole of p-dimethylaminophenyllithium until Color Test I became negative (fifteen hours). Purification of the crude product was attempted by dissolving it in dilute acid, washing the solution with ether, and reprecipitating with aqueous ammonia. The material so obtained had a satisfactory silicon analysis for hexakis-(p-dimethylaminophenyl)-disiloxane (calcd., 7.07; found, 6.96) but its cryoscopic molecular weight in nitrobenzene was too low (calcd., 792; found, 440±30). In view of these anomalous results, we do not claim that this material is hexakis-(p-dimethylaminophenyl)-disiloxane.

Tris-(p-dimethylaminophenyl)-silane.- p-Dimethylaminophenyllithium (0.11 mole) was added to 4.97 g. (0.037 mole) of trichlorosilane in ether. The first equivalent was added at -10°, but during the remainder of the addition the mixture was allowed to warm up to room temperature. Color Test I did not become negative until the mixture had been refluxed for thirty hours. Dilute ammonium chloride solution was then added and the ether layer separated. On concentration of the ether solution there was obtained 7 g. (49%) of solid melting at 153-155°. Recrystallization from absolute ethanol raised the melting point to 157°.

Anal. Calcd. for $C_{24}H_{31}N_3Si$: N, 10.79; Si, 7.19; M.W. 389. Found: N, 10.6; Si, 6.92; M.W. (cryoscopic in benzene), 387±7.

This compound did not evolve hydrogen when treated with potassium hydroxide in piperidine as do most triarylsilanes,[85] but when 1 g. (0.0026 mole) of the material was warmed to 60° with 50 ml. of 2% potassium hydroxide in absolute ethanol, a vigorous evolution of gas took place and the triarylsilane dissolved. When reaction was complete, an equal volume of benzene was added and the mixture was made just acid to phenolphthalein with 0.1 N hydrochloric acid. The benzene solution was washed free of alcohol and inorganic materials and dried. Evaporation of the benzene and crystallization of the residue from benzene-petroleum ether (b.p. 90-120°) yielded 1 g. of material melting at 177-178° which was identified as tris-(p-dimethylaminophenyl)-silanol by mixed melting point. The yield is 85%.

Tris-(p-dimethylaminophenyl)-silane was also prepared by refluxing 1 g. (0.0024 mole) of tris-(p-dimethylaminophenyl)-chlorosilane with 0.1 g. (0.0027 mole) of lithium aluminum hydride in ether for six hours. The mixture was hydrolyzed by adding ether saturated with water, and the aluminum hydroxide was washed out with dilute aqueous acetic acid. The dried ether solution, on standing, deposited 0.9 g. (98%) of tris-(p-dimethylaminophenyl)-silane, m.p. 157° without recrystallization. This was identified by a mixed melting point determination with the sample reported above.

Tetrakis-(p-dimethylaminophenyl)-silane.- An ether solution of 0.16 mole of p-dimethylaminophenyllithium was added to 0.04 mole of silicon tetrachloride in ether. The silicon tetrachloride solution was cooled to -20° before the addition began and the temperature was held at -15 to -20° throughout the slow addition. (In the light of subsequent experience, it is probable that the addition can be made rapidly and at room temperature.) Color Test I was positive when the addition was complete, so the solution was refluxed until the color test became only very faintly positive (60 hours). The mixture was then hydrolyzed with 2% ammonia solution, and the insoluble material was filtered off and washed with water. This weighed 20 g. (87%) and melted at 236-238°. A 41% yield melting at 235-236° has been reported from a reaction which was hydrolyzed immediately on completion of the addition of the organolithium reagent.[160] A mixed melting point between material melting at 235-236° and the product of this reaction was not depressed.

Tetrakis-(p-dimethylaminophenyl)-silane Tetramethiodide.-[162] Five grams (0.01 mole) of tetrakis-(p-dimethylaminophenyl)-silane was dissolved in 52.5 g. (0.37 mole) of methyl iodide. The mixture was refluxed gently, and a white precipitate appeared. After 30 minutes of refluxing no further precipitation occurred, so 100 ml. of absolute methanol was added in order to bring partly reacted material into solution. This suspension was stirred and refluxed for 6 hours, then the solid was filtered off and washed with methanol. The dry solid weighed 9.7 g. (90%) and melted at 205-206° with softening at 200°. One crystallization from

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[162] Based on an unpublished procedure developed by Dr. Lawrence Summers for the preparation of tetrakis-(p-dimethylaminophenyl)-lead tetramethiodide.

methanol gave 7.5 g. (70%) melting at 205-206°.

Anal. Calcd. for $C_{36}H_{52}N_4I_4Si$: Si, 2.60; I, 47.2. Found: Si, 2.68; I, 46.0.

Diphenyl-p-dimethylaminophenylsilanol.- p-Dimethylaminophenyllithium (0.06 mole) was added slowly to a refluxing solution of 15.2 g. (0.06 mole) of diphenyldichlorosilane in ether. The solution was refluxed for a total of two hours, then hydrolyzed. An ether-insoluble layer separated and was extracted with chloroform. This chloroform, on concentration, deposited 4.8 g. of diphenylsilanediol. On evaporation of the dried ether layer a residue remained which was extracted with benzene. A benzene-insoluble residue consisted of 1.6 g. of diphenylsilanediol, making the total yield of this material 6.4 g. or 49%. The benzene solution, on concentration, left an oil which solidifed on cooling and after several crystallizations from benzene-petroleum ether (b.p. 90-120°) weighed 4 g. and melted at 65-66°. This proved to be diphenyl-p-dimethylaminophenylsilanol. The yield is 21%, but it is very probable that this could be improved by a longer period of refluxing of the p-dimethylaminophenyllithium and diphenyldichlorosilane.

Anal. Calcd. for $C_{20}H_{21}ONSi$: Si, 8.79; active H, 1.00. Found: Si, 8.98; active H, 0.96.

Diphenyl-p-dimethylaminophenylcarbinol.- The procedure for the preparation of diphenyl-p-dimethylaminophenylcarbinol and its absorption spectra in the ultra violet have been reported elsewhere.[159]

Preparation and Relative Rates of Hydrolysis of Diphenyl(substituted-phenyl)silanes

Diphenyl(substituted-phenyl)chlorosilanes.- A series of diphenyl (substituted-phenyl)chlorosilanes was prepared from diphenyldichlorosilane and substituted organolithium reagents or substituted Grignard reagents. The procedure is illustrated by the preparation of diphenyl-*p*-dimethylaminophenylchlorosilane which is described below, and the physical constants and analyses of the products are reported in Table III.

Diphenyl-*p*-dimethylaminophenylchlorosilane.- Twenty-one and four-tenths grams (0.085 mole) of diphenyldichlorosilane was dissolved in 70 ml. of dry ether in a three-necked flask equipped with reflux condenser, mechanical stirrer, and nitrogen inlet. With the stirrer operating at moderate speed, 0.085 mole of *p*-dimethylaminophenyllithium was added dropwise over a period of thirty minutes. When the addition was complete, the mixture was stirred and heated to reflux until Color Test I became negative (24 hours). Dry benzene was then added dropwise to the reaction flask, and simultaneously ether was distilled off until the distillation temperature reached 78°. The mixture was allowed to settle, then the benzene was siphoned off under nitrogen pressure, and the insoluble residue (inorganic salts) was washed twice with dry benzene by a similar siphoning procedure. The solvent was distilled from the combined benzene solutions, and the residue was distilled at reduced pressure to give 21.0 g. (70%) of diphenyl-*p*-dimethylaminophenylchlorosilane, b.p. 227-228° at 2.5 mm. Analysis is reported in Table III.

TABLE III.

Preparation of Monosubstituted Triarylchlorosilanes from Diphenyldichlorosilane

Organometallic compound	Time of reflux, hr.	B.p. of product t, °C.	p, mm.	Yield, %	Silicon, % Calcd.	Silicon, % Found	Chlorine, % Calcd.	Chlorine, % Found
p-ClC_6H_4MgBr	72	149-50	0.3	36	8.51	8.40	10.8	10.7
m-$CH_3C_6H_4Li$	0.5	150-51	0.05	79	9.07	9.04	11.5	11.2
p-$CH_3C_6H_4Li$	0.5	147-48	0.2	79	9.07	9.10	11.5	11.2
m-$(CH_3)_2NC_6H_4Li$	4	184-85	0.2	78	8.30	8.30	10.5	10.7
p-$CH_3OC_6H_4MgBr$	120	189-92	1.0	78	8.62	8.46	10.9	10.6
p-$(CH_3)_2NC_6H_4Li$	24	227-28	2.5	70	8.30	8.17	10.5	9.87
m-$F_3CC_6H_4MgBr$	64	116-20	0.3	75	7.73	7.89	9.76	9.85

Diphenyl(substituted-phenyl)silanes.- A series of diphenyl(substituted-phenyl)silanes was prepared by reducing the corresponding chlorosilanes with lithium aluminum hydride. The procedure is illustrated by the preparation of diphenyl-p-dimethylaminophenylsilane, which is described below, and the physical constants and analyses are given in Table IV.

Diphenyl-p-dimethylaminophenylsilane.- To 19.5 g. (0.055 mole) of diphenyl-p-dimethylaminophenylchlorosilane dissolved in 125 ml. of dry ether was added 1.0 g. (0.026 mole) of lithium aluminum hydride. The mixture was protected from atmospheric moisture by a calcium chloride tube and refluxed for three hours. Excess lithium aluminum hydride was hydrolyzed by adding ether saturated with water, followed by dilute aqueous acetic acid. The ether layer was separated and washed with dilute acetic acid, then dried over sodium sulfate and distilled at reduced pressure. Diphenyl-p-dimethylaminophenylsilane, boiling at 186-187° at 0.15 mm., was obtained in 55% yield. Analysis is reported in Table IV.

Relative rates of hydrolysis of diphenyl(substituted-phenyl)silanes.- The piperidine used as solvent and catalyst for hydrolysis of the triarylsilanes was an Eastman Kodak white label product which had been redistilled through a 12 inch column packed with 1/8 inch glass helices. Distilled water was added to this material until the water concentration was 0.96 molar, as determined by titration with the Karl Fischer reagent. The silanes were redistilled at reduced pressure from a flask having a 5 inch Vigreux neck until a sample was obtained which, when hydrolyzed,

TABLE IV.

Preparation of Monosubstituted Triarylsilanes

Substituent	B.p. of product		Yield	Silicon, %		Hydrogen as Si-H, %	
	t, °C.	p, mm.	%	Calcd.	Found	calcd.	Found
p-Cl	161-62	1.0	56	9.51	9.48	0.340	0.336
m-CH_3	155-56	1.2	62	10.2	10.2	0.364	0.355
p-CH_3	147-48	0.2	79	10.2	10.2	0.364	0.360
m-$N(CH_3)_2$	176-77	0.1	83	9.24	9.19	0.334	0.344
p-OCH_3	183-84	1.5	76	9.67	9.60	0.345	0.343
p-$N(CH_3)_2$	186-87	0.15	55	9.24	9.20	0.334	0.334
m-CF_3	124-29	1.0	19	8.57	8.72	0.305	0.341

would give a total volume of hydrogen equal to 100.0 ± 0.3% of the theoretical volume. In most cases not more than two distillations were required.

The kinetic runs were made as follows.[44] Depending upon the size of the sample to be used, either 10 or 20 ml. of the piperidine reagent described above was pipetted into a 50 ml. Erlenmeyer flask, which was placed in the clamp of a shaking machine arranged in such a way that about half the height of the flask was immersed in an oil bath maintained at 38.80±0.05°. The flask was loosely stoppered, the shaker started, and the contents allowed 15 minutes to come to bath temperature. The sample (0.1-0.4 g.) was weighed into a small glass cup made by cutting the bottom from a 12 cm. test tube just above its hemispherical base. The shaker was stopped, cup and sample were dropped into the Erlenmeyer flask, and the flask was connected to a 10 ml. gas burette by means of capillary glass tubing and a short length of Tygon tubing. Shaker and timer were then started, and the volume of hydrogen was read at intervals. No advantage was found in the use of a flask with side bulb to hold the piperidine so that the system could be closed before silane and base were mixed, since there was no evolution of hydrogen during the few moments between mixing the reagents and starting the shaker. A constant positive blank of 0.10 ml. of hydrogen was observed for all runs.

Analysis of the silanes for hydrogen as Si-H was carried out in the same way, except that a few pellets of potassium hydroxide were added to the piperidine in order to hasten the reaction.

Three independent determinations of the specific rate constant were made for each silane. The statement in the tables that the specific rate constant for triphenylsilane is $7.41 \pm .62 \times 10^{-4}$ sec^{-1} indicates that the average rate from the three determinations was 7.41×10^{-4}, sec^{-1}, and that the largest deviation from this was 0.62×10^{-4} sec^{-1}. The data from a typical run are recorded in Table V and plotted in Figure 5.

Table VI records the constancy of the pseudo first order specific rate constant with varying concentrations of silane, and thus demonstrates the first order of the reaction in silane. Table VII gives the pseudo first order rate constants for the hydrolysis of the various silanes.

Mechanism of Hydrolysis of Triarylsilanes

Effect of water concentration on the rate of hydrolysis of triarylsilanes in piperidine.- Piperidine solutions containing 0.96 and 9.60 moles of water per liter were prepared and standardized with the Karl Fischer reagent. Diphenyl-p-tolylsilane was hydrolyzed by the general procedure previously described, except that the 20 ml. of hydrolyzing solution contained different proportions of the above two solutions in each run. Water concentrations were calculated on the assumption of negligible volume change on mixing the two solutions. The results are recorded in Table VIII. It is seen that the reaction is half order in water for water concentrations up to nearly 2 molar. At higher water concentrations the order in water increases.

TABLE V.

Hydrolysis of Diphenyl-*m*-tolylsilane in Piperidine Containing 0.96 mole of Water per Liter at 38.8°

Weight of sample, 0.1210 g.; buret temperature, 24.0°; barometric pressure, 29.03 in.; calculated volume of hydrogen at this temperature and pressure, 11.08 ml. x = hydrogen evolved; a-x = hydrogen remaining.

Time, min.	Buret, ml.	Gas, ml.	x	a-x	log.(a-x)
0	0.70	0.00	0.00	11.08	1.044
1	1.16	0.46	0.36	10.72	1.030
4	1.68	0.98	0.88	10.20	1.009
7	2.17	1.47	1.37	9.71	.987
12	2.88	2.18	2.08	9.00	.954
16	3.46	2.76	2.66	8.42	.925
20	3.98	3.28	3.18	7.90	.898
24	4.49	3.79	3.69	7.39	.869
28	5.00	4.30	4.20	6.88	.838
33	5.53	4.83	4.73	6.35	.803
38	6.02	5.32	5.22	5.86	.768
45	6.67	5.97	5.87	5.21	.717
50	7.11	6.41	6.31	4.77	.679
56	7.58	6.88	6.78	4.30	.634
63	8.08	7.38	7.28	3.80	.580
72	8.65	7.95	7.85	3.23	.509
80	9.10	8.40	8.30	2.78	.444
91	9.63	8.93	8.83	2.25	.352
102	10.07	9.37	9.27	1.81	.258

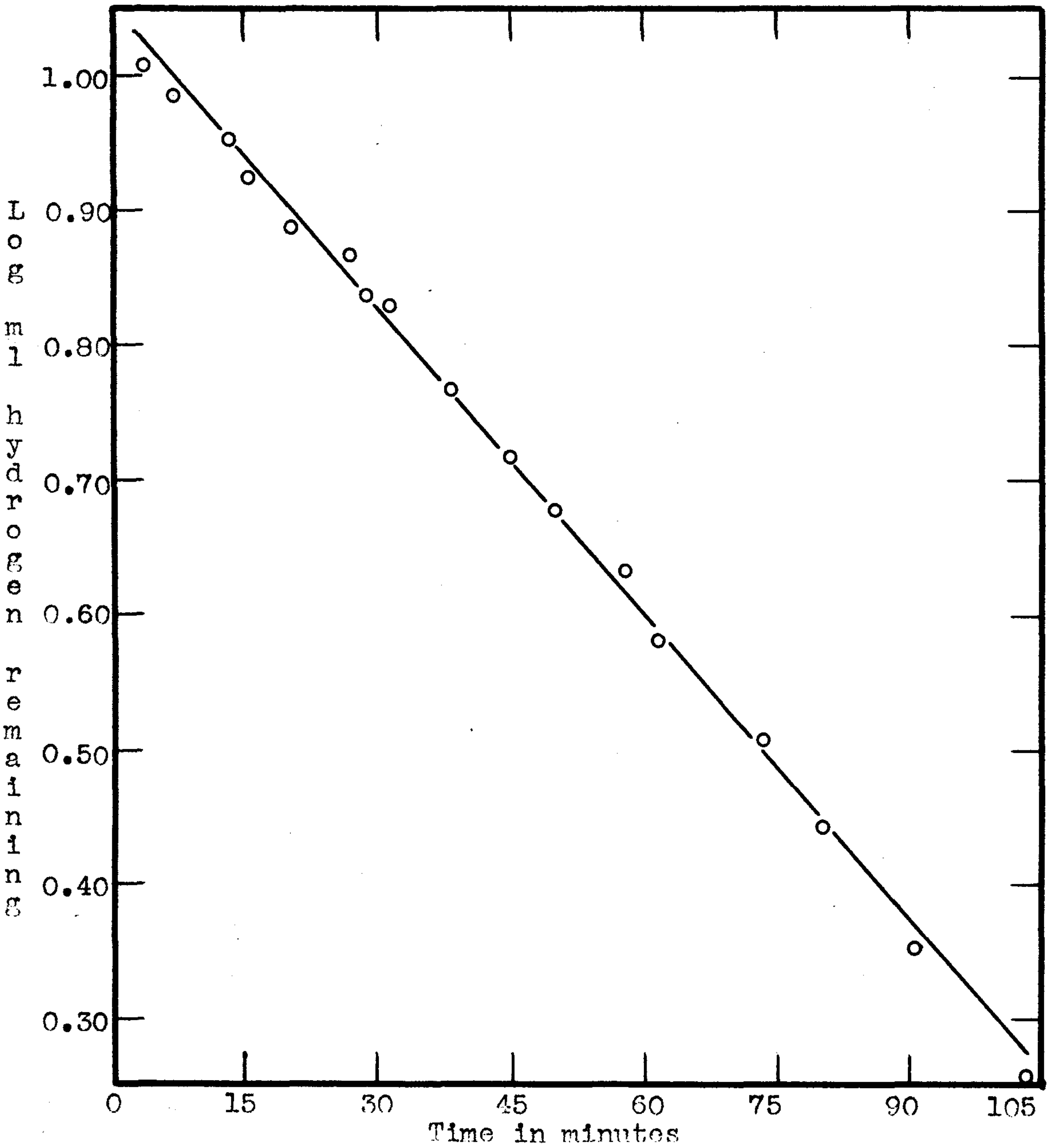

Fig. 5. Hydrolysis of diphenyl-m-tolylsilane in piperidine containing 0.96 mole of water per liter at 38.8°.

TABLE VI.

Hydrolysis of Triarylsilanes in Piperidine Containing 0.96 Mole of Water per Liter at 38.8°

Silane	Concn., mole/liter	*k* x 10^4, sec.$^{-1}$
Diphenyl-*p*-tolyl-	0.0267	1.08 ± .08
Diphenyl-*p*-tolyl-	0.0497	1.13 ± .09
Diphenyl-*p*-tolyl-	0.0848	1.03 ± .07
Diphenyl-*p*-dimethylaminophenyl-	0.0267	0.215 ± .075
Diphenyl-*p*-dimethylaminophenyl-	0.0519	0.208 ± .050
Diphenyl-*p*-dimethylaminophenyl-	0.0584	0.210 ± .008

TABLE VII.

Hydrolysis of Monosubstituted Triarylsilanes in Piperidine Containing 0.96 Mole of Water per Liter at 38.8°

Substituent	*k* x 10^4, sec.$^{-1}$
p-Cl	16.9 ± 1.2
H	3.22 ± .27
m-CH_3	2.75 ± .20
p-CH_3	1.08 ± .09
p-OCH_3	0.89 ± .08
m-$N(CH_3)_2$	0.75 ± .05
p-$N(CH_3)_2$	0.21 ± .05

TABLE VIII.

Hydrolysis of Diphenyl-p-tolylsilane in Wet Piperidine at 58.8°

Silane, M.	H_2O, M.	k x 10^4, sec.$^{-1}$	k x 10^4, calcd.	
			Half order in water	First order in water
0.152	0.96	2.66	2.66	2.66
0.148	1.39	3.20	3.21	3.86
0.168	1.82	3.76	3.67	5.04
0.159	2.69	5.53	4.45	7.42

Effect of piperidine concentration on the rate of hydrolysis of triarylsilanes in methylcellosolve.- In order to determine the order of the reaction in piperidine it was necessary to use some substance other than piperidine as the solvent for the reaction. Methyl cellosolve was chosen since it is a good solvent for the triarylsilanes, water, and piperidine, and is sufficiently high boiling so that solvent vapors should not interfere with measurements of the hydrogen evolved. Water was added to freshly distilled methylcellosolve to give a water concentration of 0.219 M, as determined by titration with the Karl Fischer reagent. This wet methylcellosolve was used to prepare standard solutions of diphenyl-p-chlorophenylsilane (0.200 M), and piperidine (0.200 M). In a typical run, 16 ml. of the water solution and 2 ml. of the silane solution were pipetted into a 50 ml. Erlenmeyer flask and thermostatted as previously described. Then 2 ml. of piperidine solution was added and the shaker started. The results of all the runs are reported in Table IX. Concentrations of reagents were calculated on the assumption that there is no volume change on mixing the solutions. It is seen that the data fit the calculated values for half order in piperidine with reasonable accuracy.

TABLE IX.

Rate of Hydrolysis of 0.020 M Diphenyl-p-chlorophenylsilane in Methylcellosolve Containing 0.219 Mole per Liter of Water at 58.8°

Piperidine, M.	k x 10^5, sec.$^{-1}$	k x 10^5 calcd. for $\frac{1}{2}$ order in piperidine
0.020	5.18	5.18
0.040	7.48	7.34
0.060	9.08	8.98
0.080	10.8	10.4

Effect of water concentration on the rate of hydrolysis of triarylsilanes in methylcellosolve.- The procedure was the same as that described in connection with the effect of piperidine concentration, except that the water concentration was varied by substituting various amounts of a 2.20 M solution of water in methylcellosolve for part of the 0.219 M water solution. In a typical run, 14 ml. of 0.219 M water solution, 2 ml. of 2.20 M water solution, and 2 ml. of silane solution were pipetted into the apparatus and thermostatted. Then 2 ml. of piperidine solution were added and the reaction started. The usual assumption of no volume change on mixing was used to calculate reagent concentrations. The results are given in Table X. It is seen that the order of the reaction is only slightly greater than zero at low water concentrations, but approaches one-half at water concentrations of 0.4-0.8 M.

TABLE X.

Rate of Hydrolysis of 0.020 M Diphenyl-p-chlorophenylsilane in Methylcellosolve Containing 0.020 Mole per Liter of Piperidine at 58.8°

H_2O, M	k x 10^5, sec.$^{-1}$	k x 10^5, sec.$^{-1}$ calcd.[a]
0.101	4.60	2.67
0.220	5.18	3.95
0.417	5.49	5.44
0.775	7.41	7.41

[a] This k is calculated for a reaction which is half order in water, and the calculated value is arbitrarily set equal to the experimental value at the maximum water concentration.

Triphenyldeuterosilane.- A solution of 8.46 g. (0.029 mole) of triphenylchlorosilane in 75 ml. of dry ether was refluxed for 8 hours with 0.40 g. (0.0096 mole) of lithium aluminum deuteride.[163] The resulting suspension was hydrolyzed by adding ether saturated with water, then dilute hydrochloric acid. The ether layer was dried and distilled to give 6.3 g. of colorless oil boiling at 154-155° (1 mm.). This was crystallized from

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[163] Lithium aluminum deuteride was obtained from Metal Hydrides, Inc., Beverly, Mass., and was reported to be 96% pure.

petroleum ether (b.p. 60-70°) to give 3 g. (40%) of colorless solid melting at 44-45°. A mixed melting point with triphenylsilane was not depressed.

Relative rates of hydrolysis of triphenylsilane and triphenyldeuterosilane in wet piperidine.- Three samples each of triphenylsilane and triphenyldeuterosilane were hydrolyzed by the procedure previously described. The data from a typical run of each silane are plotted in Figure 6. It is seen that the triphenyldeuterosilane is hydrolyzed approximately six times faster than triphenylsilane, although the lack of linearity in the first order plot for triphenyldeuterosilane makes it impossible to determine the exact ratio. This lack of linearity is undoubtedly due to contamination of triphenyldeuterosilane by triphenylsilane.

Preparation of Triphenylalkoxysilanes from Triphenylsilane

Preparation of triphenylalkoxysilanes from triphenylsilane, alcohol and piperidine.- Triphenylsilane was reacted with a number of alcohols in the presence of piperidine to give triphenylalkoxysilanes. The procedure is illustrated by the preparation of triphenyl-(2-methoxy)-ethoxysilane described below, and the reaction conditions and yields for the various alcohols are shown in Table XI. The times of reflux were arbitrarily chosen, and it is quite possible that the yields could be considerably improved by attaching the apparatus to a gas burette and stopping the reaction only when gas evolution is complete. It is also possible the yields of hexaphenyldisiloxane could be decreased by a suitable choice of reaction temperature.

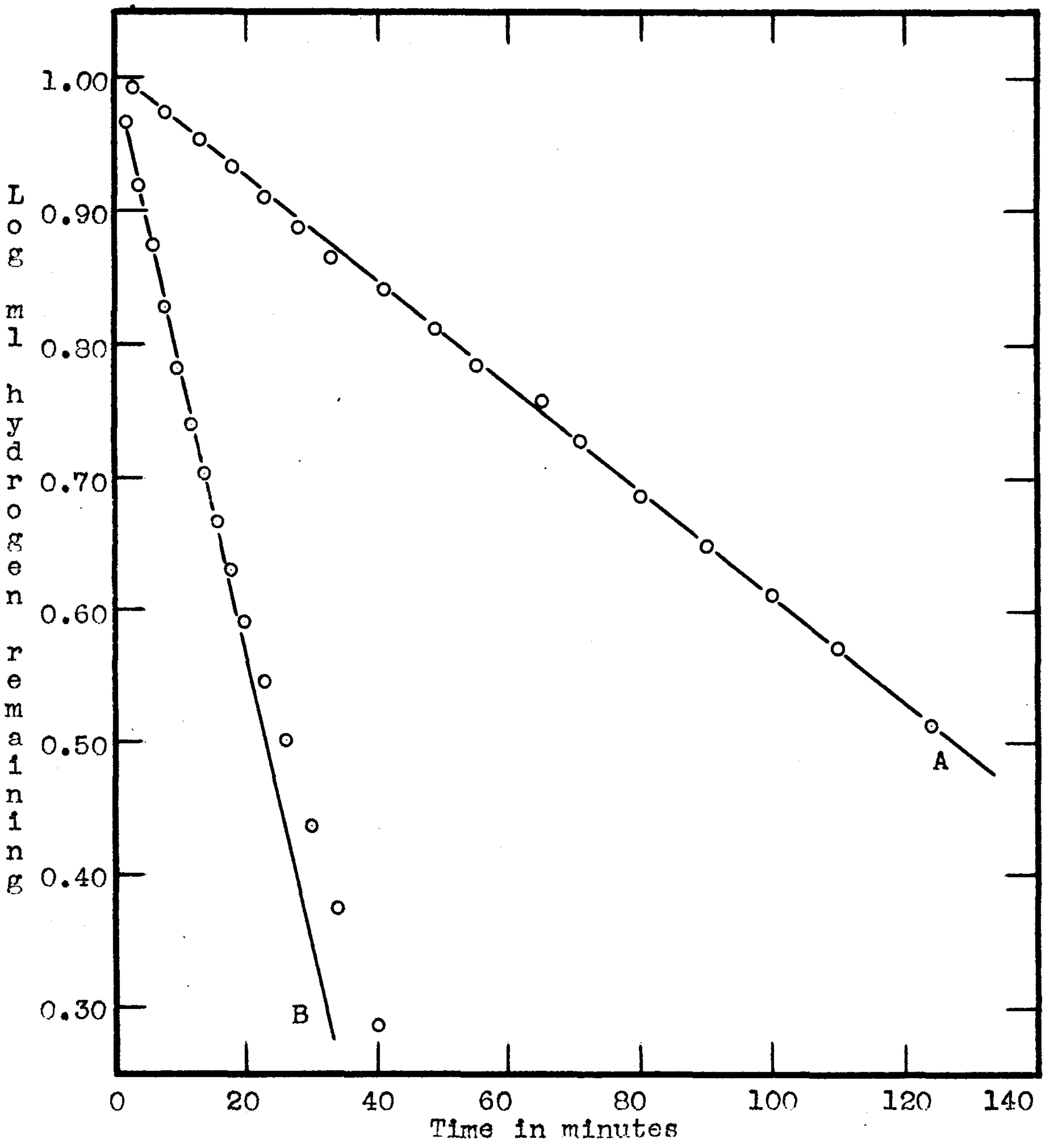

Fig. 6. Relative rates of hydrolysis of triphenylsilane, A, and triphenyldeuterosilane, B, in piperidine containing 0.96 mole of water per liter at 32.3°.

Triphenyl-(2-methoxy)-ethoxysilane.- A 125 ml. round-bottomed flask was equipped with a reflux condenser topped by a calcium chloride tube. In the flask was placed 5.2 g. (0.02 mole) of triphenylsilane, 75 ml. (0.95 mole) of methylcellosolve, and 10 ml. (0.10 mole) of piperidine. Gas evolution began as soon as the piperidine was added. The mixture was refluxed gently for one hour, then the solvent was distilled off, removing last traces under the vacuum from a water aspirator. On standing over night, the residual oil crystallized to a solid melting at 60-65°. This was taken up in a slight excess of hot petroleum ether (b.p. 60-70°). On cooling, 0.5 g. (9.4%) of hexaphenyldisiloxane, m.p. 210-211°, separated. The petroleum ether was then concentrated to about half volume and allowed to cool in the refrigerator. The crystalline material, 4.2 g., was filtered off and the mother liquor again concentrated to half volume. A second crop of 1.0 g. brought the total yield of triphenyl-(2-methoxy)-ethoxysilane to 5.2 g. (78%) melting at 67-68°.

Anal. Calcd. for $C_{21}H_{22}O_2Si$: Si, 8.39. Found: Si, 8.44, 8.46.

Tri-1-naphthylsilanol-piperidine complex.- In an attempt to prepare 1,1,1-triphenyl-3,3,3-tri-1-naphthyldisiloxane, 2.50 g. (0.0059 mole) of tri-1-naphthylsilanol[164] and 1.52 g. (0.0059 mole) of triphenylsilane were refluxed for 24 hours in a mixture of 75 ml. of dry xylene and 10 ml. of piperidine. On cooling, 1.7 g. of solid, melting at 193-194° with gas evolution, was filtered off. This solid depressed the melting point of

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[164] Kindly provided by Mr. C.G. Brannen of this Laboratory.

TABLE XI.

Preparation of Triphenylalkoxysilanes from Triphenylsilane

ROH	Reflux, hr.	Yield, %		M.P.
		Hexaphenyldisiloxane	$(C_6H_5)_3SiOR$	$(C_6H_5)_3SiOR$
$CH_3OC_2H_4OH$	1	9.4	78[a]	67-68°
C_2H_5OH	4.5	19	40[b]	65-66
<u>t</u>-C_4H_9OH	2	15	0[c]	
<u>s</u>-C_4H_9OH	8	27	38[d]	120-122
$(C_6H_5)_3COH$[e]	8	0	0[f]	
$(C_6H_5)_3SiOH$[e]	4	---	45[b,g]	220-221
(<u>p</u>-$CH_3C_6H_4)_3SiOH$[e]	72	---	35[b]	160-162

[a] Anal. Calcd. for $C_{21}H_{22}O_2Si$: Si, 8.39. Found: Si, 8.45.

[b] Identified by mixed melting point with a known sample.

[c] A 20% yield of triphenylsilanol was obtained.

[d] Anal. Calcd. for $C_{22}H_{24}OSi$: Si, 8.43. Found: Si, 8.50.

[e] A solution of 0.02 mole in 75 ml. of dry xylene was used.

[f] A 72% recovery of triphenylcarbinol and a 22% yield of triphenylsilanol were obtained.

[g] Thirty per cent of the triphenylsilanol was recovered.

tri-1-naphthylsilanol (205-206°) by about 20° and was found, by qualitative test, to contain nitrogen.

In order to confirm that the product did not contain the triphenylsilyl group, a second run was carried out using the procedure described above, except that the triphenylsilane was omitted. The yield of material melting at 193-194° was 2.7 g. (88%, calculated as a 1:1 complex). A sample of this material weighing 1.6512 g. was heated to the melting point in a porcelain crucible. When the evolution of gas was complete, the sample was cooled and reweighed. The loss in weight was 0.3067 g., or 18.5%. The loss of one mole of piperidine from one mole of a 1:1 tri-1-naphthylsilanol-piperidine complex corresponds to a loss in weight of 16.7%. The cooled melt was crystallized from xylene to give 1.12 g. of tri-1-naphthylsilanol, m.p. 203-204°, identified by mixed melting point. The yield of tri-1-naphthylsilanol, based on a 1:1 complex, is 81%.

Anal. Calcd. for $(C_{10}H_7)_3SiNC_5H_{10}$: Si, 5.68; active H, 0.00. Calcd. for $(C_{10}H_7)_3SiOH\cdot C_5H_{10}NH$: Si, 5.48; active H, 2.00. Found: Si, 5.62; active H, 1.69.[165]

On the basis of the above data it was concluded that the product is a molecular complex represented by the formula $(C_{10}H_7)_3SiOH\cdot C_5H_{10}NH$.

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[165] This active hydrogen determination was made with lithium aluminum hydride in diethylcellosolve. Piperidine alone gave active hydrogen values varying over a range of about 10% and averaging 0.75.

DISCUSSION

Among the general differences between the silicon and carbon atoms which were enumerated under physical properties, the effects of three were selected for special consideration in this study. These are (1) the greater size of the silicon atom, (2) the greater maximum covalence of the silicon atom, and (3) the greater ability of the carbon atom to form double bonds. The first two of these would be expected to play an especially important part in the reactions of silicon and carbon analogs with nucleophilic reagents and, in this connection, a literature survey of the available data on this subject, as well as an investigation of the cleavage of organosilicon compounds by hydroxyl ion have been reported recently by Miller.[21] In the present study, attention has been directed to the cleavage of organosilicon compounds by organolithium reagents and of organosilicon hydrides by mild bases.

Cleavage of Organosilicon Compounds by Organometallic Reagents

When triphenylcarbinol is refluxed in ether with two equivalents of n-butyllithium, two of the aromatic nuclei are metalated in the ortho position.[166] In an investigation of the reaction of triphenylsilanol with

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[166] H. Gilman, G.E. Brown, F.J. Webb, and S.M. Spatz, J. Am. Chem. Soc., 62, 977 (1940).

four equivalents of n-butyllithium under similar conditions the products obtained on carbonation of the reaction mixture were diphenyl-n-butylsilanol and benzoic acid, which indicates that, in the silicon analog, carbon-silicon instead of carbon-hydrogen bonds were attacked by the organolithium reagent. The reactions concerned may be represented by the general equations

$$R_3SiOH + R'Li \longrightarrow R_3SiOLi + R'H$$

$$R_3SiOLi + R'Li \longrightarrow R_2R'SiOLi + RLi \xrightarrow[H^+]{CO_2\ \text{then}} R_2R'SiOH + RCOOH$$

The results of attempts to extend this reaction to other organosilicon compounds are summarized in Table XII.

It should be pointed out, in connection with Table XII, that two compounds, trimethyl-9-fluorenylsilane and triphenylbenzylsilane, which were cleaved on carbonation, were not cleaved when the reaction mixture was hydrolyzed without carbonation.[145,167] Furthermore, the products of cleavage in the case of triphenylbenzylsilane were not phenylacetic acid and triphenylsilanol. This has been explained as due to metalation of the methylene carbon atom in each case, giving an organolithium compound which, on hydrolysis, yields starting materials but, on carbonation, yields a compound having a carbonyl oxygen beta to silicon. These compounds are known to be very easily hydrolyzed. The reactions involved may be illustrated by reference to triphenylbenzylsilane.

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[167] H. Gilman and H. Hartzfeld, unpublished studies.

TABLE XII.

Reaction of n-Butyllithium with Organometallic compounds

Compound	Cleaving agent	Acid isolated[a] on carbonation	Yield, %
Triphenylsilanol	n-C_4H_9Li	benzoic	76
Triphenylsilanol	n-C_4H_9MgBr	none	0
Triphenylsilanol	p-$CH_3C_6H_4Li$	none	0
Tri-p-tolylsilanol	n-C_4H_9Li	p-toluic	61
Tri-p-tolylsilanol	C_6H_5Li	none	0
Diphenyl-p-tolylsilanol	n-C_4H_9Li	benzoic p-toluic	6 18
Tri-1-naphthylsilanol	n-C_4H_9Li	none	0
Tri-p-xenylsilanol	C_6H_5Li	p-phenylbenzoic	12
Tetraphenylsilane	n-C_4H_9Li	none	0
Tetra-p-tolylsilane	n-C_4H_9Li	none	0
Triphenyl-n-butylsilane	n-C_4H_9Li	none	0
Trimethylphenylsilane	n-C_4H_9Li	none	0
Triethylphenylsilane	n-C_4H_9Li	none	0[b]

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[a] An acid corresponding to the organometallic compound used as a cleaving agent was obtained in all runs, but only the acids obtained as a result of cleavage are recorded in the table.

[b] See footnote 145.

[c] See footnote 167.

TABLE XII. (continued)

Compound	Cleaving agent	Acid isolated[a] on carbonation	Yield, %
Trimethyl-1-naphthylsilane	n-C_4H_9Li	none	0
Triphenyl-2-thienylsilane	n-C_4H_9Li	Triphenyl-2-thienyl-5-carboxysilane	45[b]
Triethyl-p-anisylsilane	n-C_4H_9Li	Triethyl-3-carboxy-4-methoxyphenylsilane	58[b]
Trimethyl-9-fluorenylsilane	n-C_4H_9Li	Fluorene-9-carboxylic	82[b]
9-Triphenylsilyl-9-phenylfluorene	n-C_4H_9Li	none	0[c]
Triphenylbenzylsilane	n-C_4H_9Li	phenylacetic	52[c]
Triphenyl-(phenylethynyl)-silane	n-C_4H_9Li	phenylpropiolic	58[c]

[a] An acid corresponding to the organometallic compound used as a cleaving agent was obtained in all runs, but only the acids obtained as a result of cleavage are recorded in the table.

[b] See footnote 145.

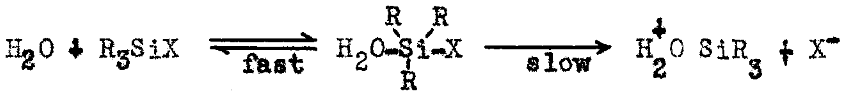
[c] See footnote 167.

$$(C_6H_5)_3SiCH_2C_6H_5 + \underline{n}\text{-}C_4H_9Li \longrightarrow (C_6H_5)_3SiCH(Li)C_6H_5 + \underline{n}\text{-}C_4H_{10}$$
$$(C_6H_5)_3SiCH(Li)C_6H_5 + H_2O \longrightarrow (C_6H_5)_3SiCH_2C_6H_5 + LiOH$$
$$(C_6H_5)_3SiCH(Li)C_6H_5 + CO_2 \longrightarrow (C_6H_5)_3SiCH(COOLi)C_6H_5$$
$$(C_6H_5)_3SiCH(COOLi)C_6H_5 + H_2O \longrightarrow (C_6H_5)_3SiOH + C_6H_5CH_2COOLi$$

This interpretation of the reaction is supported by the fact that with 9-triphenylsilyl-9-phenylfluorene, in which no methylene hydrogen remains unsubstituted, no cleavage was observed even on carbonation.[167] In the case of triphenyl-(phenylethynyl)-silane, however, the products were phenylpropiolic acid and triphenyl-n-butylsilane, and cleavage occurred whether the reaction mixture was carbonated prior to hydrolysis or not.[167]

With the above facts in mind, the results of the investigation may be summarized as follows. (1) Triphenylcarbinol, when treated with excess n-butyllithium in ether, is not cleaved, but is metalated on the aromatic nucleus instead. (2) Triphenylsilanol has one phenyl group, but not two, replaced by a n-butyl group. (3) One aromatic lithium compound is not formed from a silanol by the attack of another aromatic lithium compound of similar reactivity. (4) n-Butylmagnesium bromide does not displace aromatic groups from silanols. (5) A highly hindered silanol, such as tri-1-naphthylsilanol, is not cleaved by n-butyllithium. (6) Only one compound of the types R_4Si and R_3SiR', namely triphenyl-(phenylethynyl)-silane, has been cleaved by n-butyllithium. (7) Metalation of organosilicon compounds occurs in those cases where a hydrogen is rendered acidic by adjacent groups, but the silicon atom itself (as in, say, triphenyl-n-butylsilane) does not render a nearby hydrogen acidic enough to be metalated. To these may be added: (8) when diphenylsilanediol is treated with an organolithium reagent one, but not two, of the hydroxyl groups is replaced by an organic group.[168]

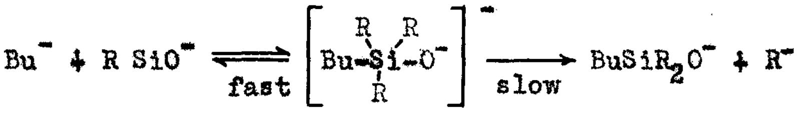
The fact that triarylsilanols are cleaved by n-butyllithium while triarylcarbinols are not must be related in some way to the greater size, electronegativity, and maximum covalence of the silicon atom as compared with carbon. The mechanism of nucleophilic displacement on silicon has been established for only one reaction--the hydrolysis of triarylhalosilanes. This has been shown to proceed by the mechanism below



$$H_2O + R_3SiX \underset{fast}{\rightleftharpoons} H_2O\text{-}\overset{R\ \ R}{\underset{R}{Si}}\text{-}X \xrightarrow[slow]{} H_2\overset{+}{O}\ SiR_3 + X^-$$

in which the above three factors are of importance, the most prominent one being the ability of the silicon atom to assume a covalency of five.[82] This mechanism may serve as a starting point for a discussion of the mechanism of the cleavage of silanols by n-butyllithium. A strictly analogous mechanism for the latter reaction would be the following (where Bu = n-butyl)

$$Bu^- + R_3SiOH \longrightarrow R_3SiO^- + BuH$$



$$Bu^- + R\ SiO^- \underset{fast}{\rightleftharpoons} \left[Bu\text{-}\overset{R\ \ R}{\underset{R}{Si}}\text{-}O^-\right]^- \xrightarrow[slow]{} BuSiR_2O^- + R^-$$

in which the anions illustrated should be considered to be the negative ends

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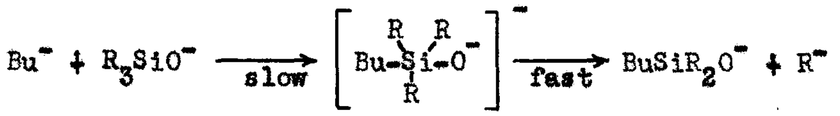
[168] H.N. Benedict, Master's Thesis, Iowa State College (1950).

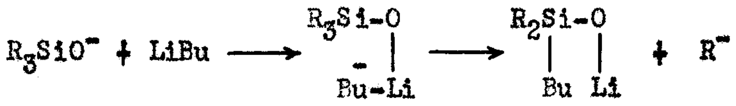
of ion-pairs. This mechanism seems unlikely for two reasons. First, attack by one anion upon another appears improbable, although certainly not impossible. Second, if the pentacovalent intermediate were really formed, all four of its silicon-carbon bonds would have strengths of the same order of magnitude, and the reverse dissociation of the intermediate into triphenylsilanolate and n-butyllithium should be slower, not faster, than the dissociation into diphenyl-n-butylsilanolate and phenyllithium, because of the greater resonance stabilization of the phenyl anion. Thus, the above mechanism would be transformed into the second possibility



$$Bu^- + R_3SiO^- \xrightarrow[\text{slow}]{} \left[Bu\text{-}\overset{R\ R}{\underset{R}{Si}}\text{-}O^- \right]^- \xrightarrow[\text{fast}]{} BuSiR_2O^- + R^-$$

This mechanism has the advantage over the first that the undoubtedly difficult attack by one anion upon another is now the rate determining step. This mechanism will explain why the more nucleophilic n-butyllithium will cleave triphenylsilnol, while the less nucleophilic n-butylmagnesium bromide or p-tolyllithium will not. The lack of cleavage of tri-1-naphthylsilanol is also understandable on the basis of this mechanism, since the bulky naphthyl groups would hinder rearward attack by the n-butyllithium. However, since by this mechanism the rate of cleavage depends upon the ease of coordination of the n-butyl anion or dipole with the silicon atom, it would be expected that cleavage would be more difficult in the silanolates, where the electronic unsaturation of the silicon atom must be largely satisfied by the adjacent negatively charged oxygen, than in the R_4Si and R_3SiR' compounds, where the 3d orbitals of the silicon atom are relatively unoccupied. It might be supposed that steric factors prevent the clustering of five organic groups around the silicon atom in the R_4Si case, while permitting four organic groups and an oxygen atom to be simultaneously bound in the silanol case. However, the fact that triphenyl-(phenylethynyl)-silane *is* cleaved by *n*-butyllithium makes it evident that, if this mechanism is the correct one, five organic groups (including four bulky ones) *can* be bonded simultaneously to silicon. Both these mechanisms, then, may be ruled out.[169]

The fact that silanolates are cleaved while tetrasubstituted silanes are not, indicates that the negatively charged oxygen atom of the silanolate must exert an activating influence. This may lie in its power to coordinate with the lithium end of the *n*-butyllithium ion-pair. Such a mechanism might be represented as follows.



$$R_3SiO^- + LiBu \longrightarrow \begin{array}{c} R_3Si-O \\ {}^{-}\quad | \\ Bu-Li \end{array} \longrightarrow \begin{array}{cc} R_2Si & -O \\ | & | \\ Bu & Li \end{array} + R^-$$

The coordination of *n*-butyllithium with lithium triphenylsilanolate would certainly be reversible, and it would seem that the difficult step in the overall process would be the breaking of the silicon-carbon bond, so that

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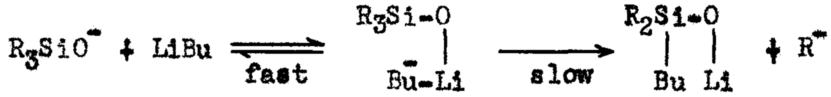
[169] The above arguments may also be applied to the mechanism in which the entry of the butyl group and departure of the phenyl group are simultaneous, since the negative charge on the silanolate molecule would make it very probable that formation of the new bond would be more difficult than breaking the old one.

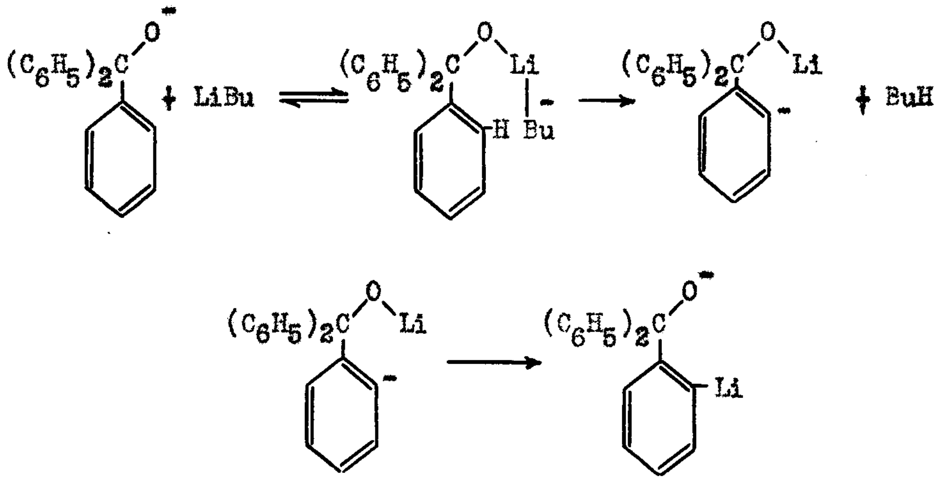
the mechanism might be written



$$\underset{\text{I}}{R_3SiO^- + LiBu} \underset{\text{fast}}{\rightleftharpoons} \underset{\text{II}}{\begin{array}{c} R_3Si-O \\ | \\ \bar{Bu}-Li \end{array}} \xrightarrow[\text{slow}]{} \begin{array}{c} R_2Si-O \\ |\quad\ \ | \\ Bu\ \ Li \end{array} + R^-$$

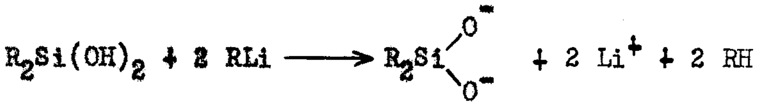
However, it must be pointed out that, if we accept the Eyring postulate that the transition state in a reaction may be treated as a thermodynamic entity, this mechanism is indistinguishable from a one step process. Thus, since I and II are in rapid equilibrium, the free energy difference between them is zero. Therefore, the free energy difference between II and the transition state is the same as the free energy difference between I and the transition state, so that the rates of reaction from I to product and from II to product must be identical. The formation of the intermediate II could become of importance to the mechanism only if the first step were rate controlling. In the absence of any kinetic data on the reaction, a decision cannot be made on this point.

Nevertheless, by either mechanism, the configuration of the transition state would be something like the structure II, and the ease of cleavage of the silanols would be due to the ability of the oxyanion to coordinate with the lithium end of the n-butyllithium dipole. Similarly, the unreactivity of the R_4Si and R_3SiR' types would be due to lack of a coordinating center for the lithium atom. It may be supposed that the highly unsaturated linkage in the phenylethynyl group provides such a center in the case of triphenyl-(phenylethynyl)-silane. The remaining facts concerning cleavage of organosilicon compounds by organometallic reagents can also be explained in terms of this mechanism. For example, the non-cleavage of tri-1-naphthylsilanol is the result of steric hindrance in this, as in the previous mechanism; the unreactivity of the Grignard reagent is the result of the lesser nucleophilic character of this reagent; and the fact that only one aryl group is displaced is probably due to the electron-releasing properties of the first butyl group to enter, which decreases the electrophilic nature of the silicon atom toward further attack. Furthermore, related considerations may explain the ortho metalation of triphenylcarbinol. In this compound the inability of the central atom to accept electrons from the n-butyl end of the n-butyllithium dipole, and the smaller ionic character of the carbon-carbon as compared with the silicon-carbon bond, combine to make the displacement of a phenyl group difficult. However, a first step similar to the above brings the butyl end of the butyllithium dipole into convenient position to attack the ortho hydrogen atom of a benzene ring.



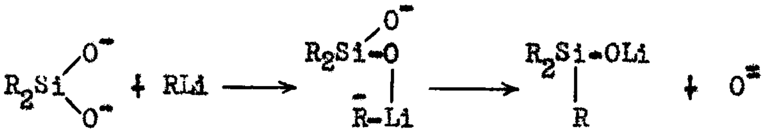
The lack of metalation of the diphenyl-n-butylsilanol formed by the cleavage of triphenylsilanol may be attributed to the electron-releasing properties of the silicon atom, which reduce the acidity of all the hydrogens in the benzene rings.

Returning to the silicon series, the reaction of diphenylsilanediol with phenyllithium to give triphenylsilanol would be understandable on the basis of the above mechanism if only one hydroxyl group is converted to the lithium salt before cleavage occurs. If the divalent ion were formed in the first step



$$R_2Si(OH)_2 + 2\ RLi \longrightarrow R_2Si\begin{matrix} O^- \\ O^- \end{matrix} + 2\ Li^+ + 2\ RH$$

then the next step would require the displacement of an oxide ion, which seems very unlikely.



$$R_2Si\begin{matrix} O^- \\ O^- \end{matrix} + RLi \longrightarrow \begin{matrix} R_2\overset{-}{Si}(O^-)\text{-}O \\ | \\ R\text{-}Li \end{matrix} \longrightarrow \begin{matrix} R_2Si\text{-}OLi \\ | \\ R \end{matrix} + O^=$$

Since the reaction with triphenylsilanol leads to displacement of R^- instead of $O^=$, R^- should be displaced in preference to $O^=$ here also. However, if the intermediate were $R_2Si(OH)OLi$, the displacement of an OH^- ion should be much easier than the displacement of R^-, and the observed reaction should occur. Since the reaction was carried out with an excess of phenyllithium, it is not known how many equivalents of this reagent were consumed.[168] However, the fact that the reaction occurred in xylene but not in ether accords well with the above mechanism.[168] In ether, both active hydrogens were probably replaced and, consequently, no further reaction occurred. In xylene, the formation of a divalent anion (silanediolate) could be prevented both by the non-polar nature of the solvent, and by the insolubility of the monovalent anion first formed.

Preparation and Reactions of Hexaaryldisilanes

The dissociation of the hexaarylethanes into triarylmethyl radicals is one of the most interesting and well known reactions in organic chemistry. Since the silicon-silicon bond is not as strong as the carbon-carbon bond, it might be expected that hexaaryldisilanes would also dissociate into triarylsilyl radicals, but such is not the case. The two previously reported hexaaryldisilanes, hexaphenyldisilane[59] and hexa-p-tolyldisilane,[68] are stable in air, melt undecomposed, and do not react with oxygen, iodine, or other reagents quickly attacked by triarylmethyl radicals. Two factors may be of importance in this difference. First, the steric strains involved in hexaphenyl- and hexa-p-tolyldisilane must be considerably smaller than in the corresponding carbon compounds, due to the larger size of the silicon atoms. Consequently, the tendency to dissociate must be reduced in the dislanes. However, when attempts are made to introduce greater strains in the disilanes by introducing more bulky groups, the reactions are unsuccessful. Thus, when tri-o-tolyl-[170] or tri-1-naphthyl-chlorosilane[152] is treated with

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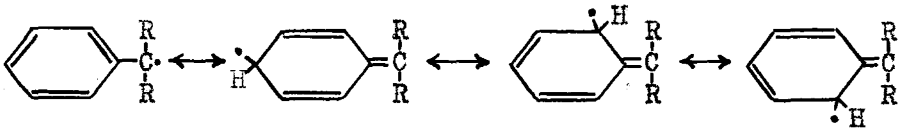
[170] H. Gilman and G.N.R. Smart, J. Org. Chem., 15, 720 (1950).

sodium in the usual procedure for preparing hexaaryldisilanes, starting material is recovered unchanged. Also, when hexachlorodisilane is treated with o-tolyllithium, only two halogens per silicon atom are replaced by o-tolyl groups.[170] Evidently the steric factors in these cases are great enough to prevent Wurtz-type coupling, so the failure of the reaction $R_3SiCl + Na \longrightarrow R_3Si\cdot + NaCl$ to occur must be due to some other factor. This second factor is probably a decreased resonance stabilization of the triarylsilyl radical as compared with its carbon analog. Resonance of the type which occurs in the triarylmethyls would,



in the silicon case, involve structures having silicon-carbon double bonds. The facts that the disilanes do not dissociate and that highly hindered triarylchlorosilanes do not react with sodium may be considered as evidence that resonance structures having silicon-carbon double bonds make much smaller contributions to the states of molecules than do analogous carbon structures.

In order to test this theory in the most favorable case, hexa-p-xenyldisilane was prepared. In this compound steric hindrance is not great enough to prevent reaction, while resonance stabilization of the carbon analog is very high. Hexa-p-xenylethane is reported to be 100% dissociated even in the solid state.[171] The silicon compound, however,

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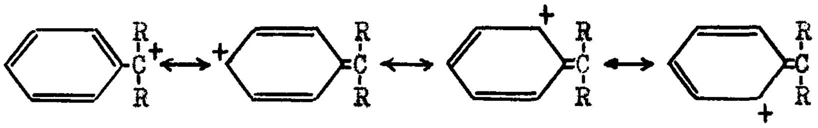
[171] W.E. Bachmann, in "Organic Chemistry, an Advanced Treatise", H. Gilman, Ed., John Wiley and Sons Inc., New York, 2nd ed., 1943, p. 581 ff.

was found to be a very stable solid, melting undecomposed at the very high temperature of 430°, and showing no evidence of reaction with oxygen or iodine. These properties indicate that dissociation is negligible, and thus support the idea that resonance structures containing silicon-carbon double bonds make relatively small contributions to the total structure of organosilicon molecules.

Preparation and Ultraviolet Absorption Spectra of *p*-Dimethylaminophenylsilicon Compounds

The absorption spectra of a number of triarylsilicon compounds have been reported and interpreted elsewhere.[159] This subject will not be discussed here, except to review the conclusions of the study. The absorption maxima in the ultraviolet of diphenyl-*p*-dimethylaminophenylsilanol and tris-(*p*-dimethylaminophenyl)-silanol were found to show no shift toward longer wave lengths in acid solution. In the analogous carbon compounds the corresponding shift is very pronounced, and is attributed to the formation of triaryl carbonium ions which have sufficiently small differences between ground and excited states so that light of visible wave length can bring about the excitation. The easy change of carbinol to carbonium ion by acids is attributed to stabilization of the carbonium ion by contributions to its ground state from resonance structures such as



and to the reduction in steric strains brought about by the change from tetrahedral to planar configuration around the methyl carbon atom. The fact that the silanols exhibit no such shift was taken to indicate that siliconium ions are much less readily formed than are analogous carbonium ions. This is probably due, partly to the fact that the silicon atom is larger than carbon so that strains in the tetrahedral configuration are reduced, and partly to smaller contributions from resonance structures such as those illustrated above, which would have to contain silicon-carbon double bonds.

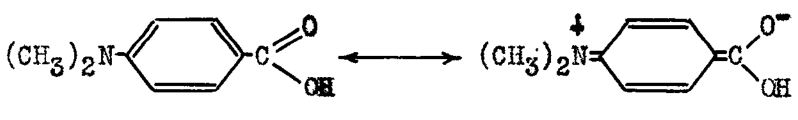
A further interesting point was noted in preparing the compounds necessary for the ultraviolet absorption measurements. It was found that *p*-dimethylaminophenyllithium displaces the chlorines from silicon tetrachloride much more slowly than do phenyl-, *p*-tolyl-, or *p*-chlorophenyllithium. Since any mechanism which involves the coordination of the organolithium anion with the silicon atom of the chlorosilane as the first step would predict that *p*-dimethylaminophenyllithium should react faster than the others, this piece of information seems to indicate that the mechanism of reaction of organolithium reagents with halosilanes is not similar to the mechanism of hydrolysis of the halosilanes which was elaborated by Swain.[82] There would seem to be a good possibility that the mechanism of this reaction is similar to that proposed for the cleavage of triarylsilanols by organolithium reagents, and it is proposed to investigate this problem further.

$$R'Li + R_3SiCl \longrightarrow \begin{array}{c} R_3Si{-}Cl \\ | \\ R'{-}Li \end{array} \longrightarrow \begin{array}{c} R_3Si \\ | \\ R' \end{array} + LiCl$$

Preparation and Relative Rates of Hydrolysis of Diphenyl(substituted-phenyl)silanes

During the course of this discussion and the preceding review of the literature, it has been pointed out in several places that there appears to be some evidence for supposing that resonance structures involving silicon-carbon double bonds make considerably smaller contributions to the ground states of organosilicon molecules than do analogous structures to the ground states of corresponding carbon compounds. It was proposed to investigate this subject further by observing the changes in the rate of a reaction occurring on the silicon atom of an organosilane as a series of substituents is introduced into the molecule, and comparing these changes with the changes produced when the same series of substituents is introduced into a similar carbon compound.

Westheimer[172] has shown that the acid-weakening effect of most para substituents on aromatic acids can be predicted with satisfactory accuracy by means of calculations which depend only on the electrostatic effects of the substituent. The *p*-amino and *p*-dimethylamino groups, however, have a greater weakening effect than can be accounted for as the result of electrostatic effects alone. Westheimer interpreted the enhanced acid-weakening effect of these groups as being due to resonance of the type



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[172] F.H. Westheimer, J. Am. Chem. Soc., 62, 1892 (1940); F.H. Westheimer and R.P. Metcalf, ibid., 63, 1339 (1941).

which both increases the negative charge on the oxygen atoms, thus increasing their attraction for protons, and at the same time interferes with the internal resonance tending to stabilize the carboxyl anion. Such resonance could be of importance only when substituents having a strong tendency to use their unshared electron pairs in the formation of coordinate bonds are located in the para position with respect to a side chain which can become doubly bonded by accepting a pair of electrons from the benzene nucleus. These considerations indicate that a p-aminophenyl or p-dimethylaminophenyl group might have a different effect on the rate of a reaction occurring on a silicon atom to which they are attached than they do on the rate of a reaction occurring at a carbon atom to which they are attached, since resonance structures analogous to those illustrated for p-dimethylaminophenylbenzoic acid would, in the silicon case, involve silicon-carbon double bonds.

Hammett has shown[173] that the effect of a meta or para substituent on the rate of a reaction occurring on the side chain of a benzene derivative can be represented by the following equation

$$\log \underline{k} - \log \underline{k}^{o} = \rho\sigma$$

where $\underline{k}^{o}$ is the specific rate constant for the unsubstituted derivative and $\underline{k}$ is that for the substituted one. Rho is constant for any given type of reaction and σ is constant for any particular substituent. This

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[173] L.P. Hammett, "Physical Organic Chemistry", McGraw-Hill Book Company, Inc., New York, N.Y., 1940, Chapter VII.

generalization simplifies the comparison of organosilicon compounds with their carbon analogs. It is only necessary to measure the rates of reaction of a series of substituted arylsilanes (including p-amino or p-dimethylamino substituents) and plot the logarithms of the specific rate constants against the σ-constants reported by Hammett. A linear relationship would indicate that the effect of the p-amino or p-dimethylamino substituents is transmitted in the same way in silicon and carbon compounds. If the p-amino or p-dimethylamino substituents were out of line, this could be considered evidence that these groups exert their effects of electron release by a different process in the silicon than in the carbon case.

The reaction chosen for study was the basic hydrolysis of monosubstituted triarylsilanes. These compounds are easily prepared, are sufficiently stable to be worked with conveniently, and react with most reagents considerably more slowly than do the halo- or ethoxy-silanes.[170] Furthermore, Price has examined the hydrolysis of trialkylsilanes and found it to agree satisfactorily with a pseudo first order kinetic expression during the first three-fourths of the reaction.[44]

The hydrolysis of triarylsilanes in Price's medium (aqueous alcoholic potassium hydroxide) proceeded much too rapidly for measurement, so advantage was taken of Kipping's observation that certain polysilanes slowly evolve hydrogen when dissolved in piperidine.[64] Triarylsilanes were found to hydrolyze at convenient rates in piperidine containing a twenty-fold excess of water, and the reaction was found to be pseudo first order until about 80% complete.

$$R_3SiH + H_2O \longrightarrow R_3SiOH + H_2$$

The agreement of the experimental data with a first order plot is shown in Figure 5, and the constancy of the pseudo rate constant with varying concentrations of silane and a constant concentration of water is shown in Table VI. The pseudo first order rate constants for a series of substituted silanes are given in Table VII, and in Figure 7 these constants are plotted against the σ-constants for the corresponding substituents as reported by Hammett.[173] It is seen that, with the exception of the point representing the p-dimethylamino group, a satisfactory linear relationship exists between the two series of constants. The slope of the line gives ρ for the hydrolysis of triarylsilanes in wet piperidine as $+3.09 \pm .12$.

Branch and Calvin have pointed out the anomalous fact that the σ-constant for the dimethylamino group is more negative in the meta than in the para position (-0.211 and -0.205, respectively), while for all other electron releasing groups the reverse is true. They suggest that the value of σ reported for the m-dimethylamino group is erroneous.[174] The experiments reported here provide evidence that the error is in the constant for the para position rather than that for the meta. Figure 1 shows that the value of σ reported by Hammett for the m-dimethylamino

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[174] G.E.K. Branch and M. Calvin, "The Theory of Organic Chemistry", Prentice-Hall Inc., New York, N.Y., 1941, p. 418.

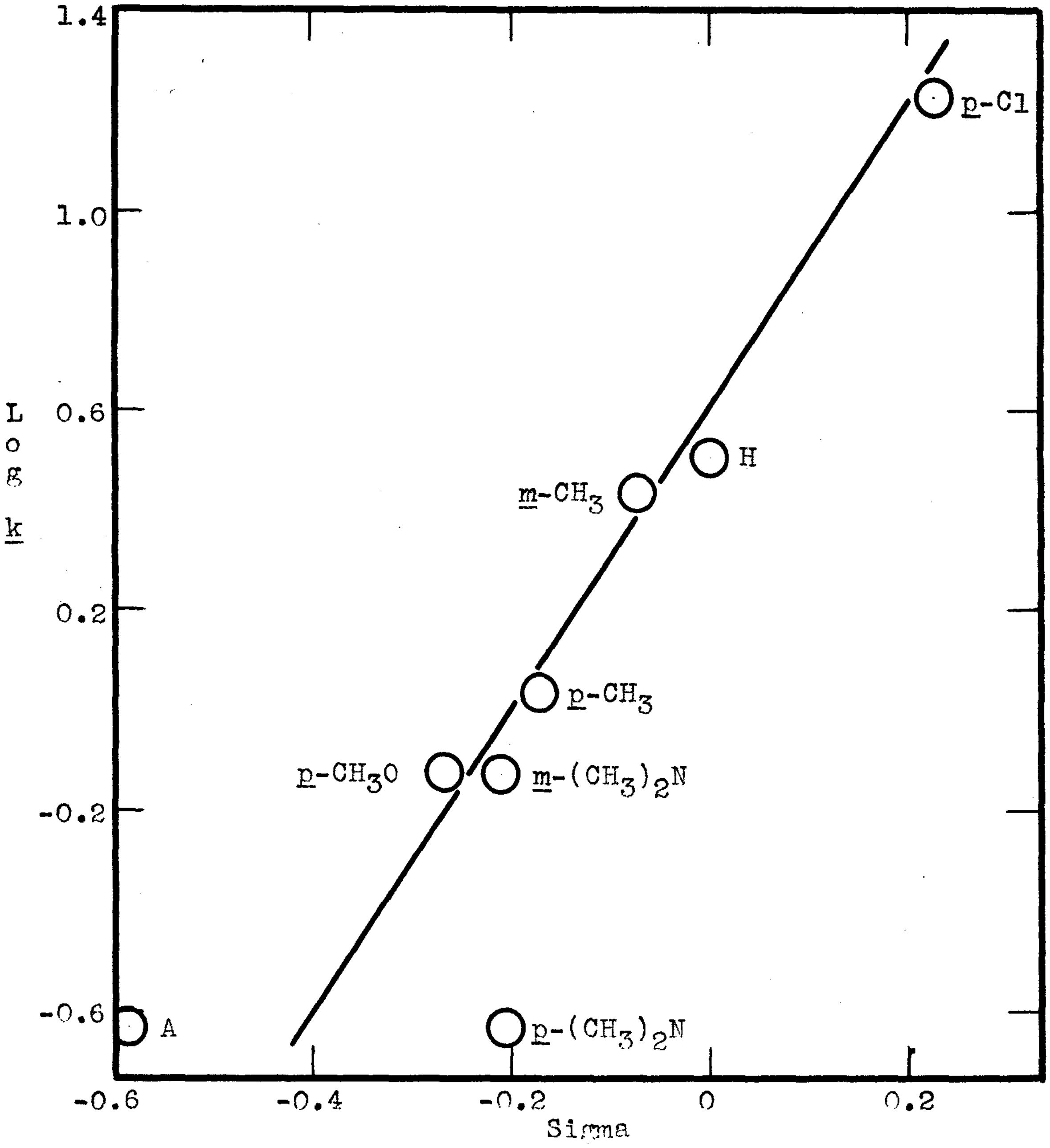

Fig. 7. Relationship between log ($\underline{k}$ x 10^4) and sigma for the hydrolysis of diphenyl(substituted-phenyl)silanes in piperidine containing 0.96 mole of water per liter at 38.8°.

group fits the data of this experiment reasonably well, and is probably correct. Hammett's value of the p-dimethylamino σ-constant was obtained from data in the literature on the reaction of tetramethyl-p-phenylenediamine with trinitroanisole,[175] and a statistical factor of two was introduced into the calculation to take care of the bifunctional nature of the reagent. Some other influence must be at work in this particular case, however, since the resultant σ-constant is a much smaller negative number than would be expected on *a priori* grounds or has been found by later workers in other reactions. Since Hammett's tables were published, two studies of the rate of hydrolysis of substituted ethyl benzoates, including p-dimethylaminobenzoate, have been reported. The p-dimethylamino σ-constant obtained from this work is shown as point A, Figure 7, and the data leading to the various values of σ for the p-dimethylamino group are presented in Table XIII. It is seen that the value of σ obtained from the hydrolysis of benzoic acid esters (-0.57±.04) is considerably more negative than that obtained from the hydrolysis of silanes (-0.41).

The data reported above lead to two important conclusions. First, they confirm the idea that resonance structures of a p-quinoid type, such as those illustrated previously for p-dimethylaminobenzoic acid, are more important in carbon compounds than in silanes. It would seem very probable that the small contributions from such structures in the silane case is

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[175] E. Hertel and J. Dressel, Z. physik. Chem., B29, 178 (1935).

TABLE XIII.

σ-Constant for the *p*-Dimethylamino Group

Reaction		log *k*°	log *k*	
Alkaline hydrolysis of ethyl benzoates, 88% ethanol, 30°	2.498	-3.072	-4.597	-0.610[a]
Alkaline hydrolysis of ethyl benzoates, 56% acetone, 25°	2.342	-2.670	-4.198	-0.538[b]
Dimethylanilines with trinitroanisole, 25°	-2.382	-4.500	-3.712	-0.205[c]
Hydrolysis of triaryl-silanes, wet piperidine, 38°	3.086	-3.407	-4.678	-0.411

[a] See footnote 172.

[b] E. Tommila, *Ann. Acad. Sci. Fennicae*, *Ser. A57*, *13*, 3 (1941), [*C.A.*, *38*, 6171 (1944)].

[c] See footnote 175.

due to the difficulty of formation of silicon-carbon bonds of higher order than first. Second, the data indicate that two σ-constants are required for the *p*-dimethylamino group--one when it occurs in compounds containing a side chain with which it can become conjugated through the benzene ring, and another when it occurs in compounds where such conjugation is not possible. The values suggested from presently available data are $-0.57 \pm .04$ for conjugated and $-0.41 \pm .04$ for non-conjugated side chains. This situation is exactly analogous to that occurring at the other end of the series of σ-constants, where the *p*-nitro,[175] *p*-cyano,[176] and *p*-trifluoromethyl[177] groups have two σ-constants, one for use with conjugated side chains (amines and phenols) and another for use with other compounds.

Mechanism of Hydrolysis of Triarylsilanes

The reaction used in the study of σ-constants in silicon compounds, namely the hydrolysis of triarylsilanes by wet piperidine to give hydrogen gas and triarylsilanols, is one for which there is no analogy in carbon chemistry. In effect it involves the displacement of a hydride ion by a weak base. Since such a reaction is of considerable theoretical interest, and since the technique and apparatus for rate measurements on the reaction had been worked out, a kinetic investigation of the mechanism of the reaction was undertaken.

The reaction had already been shown to be first order in triarylsilane, so the effect of varying the concentration of water in the reaction medium was next investigated. The change in pseudo first order rate constant with change in water concentration is shown in Table VIII. It is seen that the reaction is half order in water up to water concentrations of 2 *M*. At higher concentrations the order in water begins to increase.

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[176] J.D. Roberts and E.A. McElhill, *J. Am. Chem. Soc.*, *72*, 628 (1950).

[177] J.D. Roberts, R.L. Webb, and E.A. McElhill, *J. Am. Chem. Soc.*, *72*, 411 (1950).

Price, using potassium hydroxide as the basic reagent, had found the hydrolysis of trialkylsilanes to be first order in silane, first order in hydroxyl ion, and probably first order in hydroxylated solvent.[44] The half order in water suggests that the attacking species is hydroxyl ion in this reaction also. If piperidine is represented as PH and triphenylsilane as SH, we can write the following equations.

$$PH + H_2O \overset{K}{\rightleftharpoons} PH_2^+ + OH^-$$

$$K = \frac{[PH_2^+]\,[OH^-]}{[PH]\,[H_2O]}$$

Since $[PH_2^+] = [OH^-]$,

$$K = \frac{[OH^-]^2}{[PH]\,[H_2O]}$$

and $[OH^-] = K^{\frac{1}{2}}\,[PH]^{\frac{1}{2}}[H_2O]^{\frac{1}{2}}$

The hydrolysis is first order in silane, and if it is also first order in hydroxyl ion, then

$$-\frac{d[SH]}{dt} = k[SH]\,[OH]$$
$$= kK^{\frac{1}{2}}[SH]\,[PH]^{\frac{1}{2}}\,[H_2O]^{\frac{1}{2}}$$

This treatment accounts for the observed half order in water, but does not account for the increase in order as the water concentration increases. Furthermore, if hydroxyl ion is the attacking agent, the source of the second hydrogen atom involved in the production of a hydrogen molecule is unaccounted for. Undoubtedly, these two questions are related. If hydroxyl ion is the attacking species, a hydride ion must be expelled; this would be a very reactive particle and would immediately react in some way with the other reagents at hand. Since the product of the reaction is hydrogen gas, the hydride ion must pick up a proton from the solvent. At low water concentrations, this proton evidently comes from piperidine.

$$OH^- + SH + PH \longrightarrow SOH + H + P^-$$

$$-\frac{d[SH]}{dt} = k[SH]\,[OH^-]\,[PH]$$

$$= kK^{\frac{1}{2}}[SH]\,[H_2O]^{\frac{1}{2}}\,[PH]^{\frac{3}{2}}$$

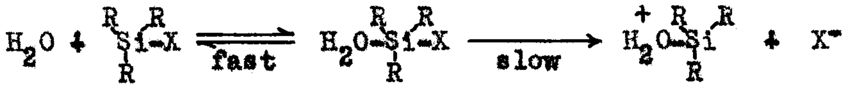
It should be easier to obtain a proton from water than from piperidine, and at higher water concentrations this apparently happens, thus increasing the order in water.

$$OH^- + SH + H_2O \longrightarrow SOH + H_2 + OH^-$$

$$-\frac{d[SH]}{dt} = k[SH]\,[OH^-][H_2O]$$

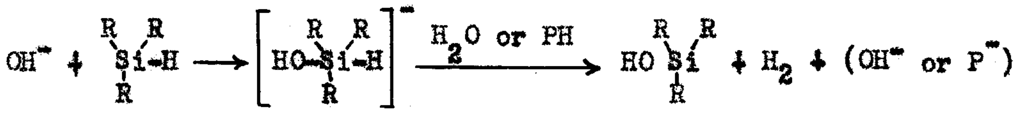
$$= kK^{\frac{1}{2}}\,[SH]\,[H_2O]^{\frac{3}{2}}\,[PH]^{\frac{1}{2}}$$

This picture of the reaction is very similar to that developed by Price for the hydrolysis of trialkylsilanes.[44] However, since that time Swain has examined the kinetics of the hydrolysis of triarylhalosilanes by water, and reached the conclusion that a pentacovalent intermediate is involved in the mechanism,[82] as illustrated below.



$$H_2O + R_3Si{-}X \underset{fast}{\rightleftharpoons} H_2O{-}SiR_3{-}X \xrightarrow[slow]{} H_2\overset{+}{O}{-}SiR_3 + X^-$$

(The water molecules involved in solvating the ions formed are omitted from the equation for simplicity.) The fact that for the hydrolysis of triarylsilanes is large and positive (+3.09) indicates that this reaction is strongly retarded by increasing negative charge on the silicon atom, and consequently that the charge on the silicon atom must be less positive in the transition state than in the ground state. It was an exactly analogous consideration that led Swain to postulate the above pentacovalent intermediate in the halosilane hydrolysis, so the possibility arises that such an intermediate may be of importance in the hydride case. The reaction would then be written



$$OH^- + R_3Si{-}H \longrightarrow \left[HO{-}SiR_3{-}H\right]^- \xrightarrow{H_2O \text{ or } PH} HOSiR_3 + H_2 + (OH^- \text{ or } P^-)$$

The question would then arise whether the first or second step is rate determining. If the first step is fast and the second slow, as in Swain's case, then the overall order of the reaction would be given, as shown above, by the expression $-\frac{d[SH]}{dt} = kK^{\frac{1}{2}}[SH]\,[H_2O]^{\frac{1}{2}}[PH]^{\frac{3}{2}}$ in piperidine, or $-\frac{d[SH]}{dt} = kK^{\frac{1}{2}}[SH]\,[H_2O]^{\frac{3}{2}}[PH]^{\frac{1}{2}}$ in a non-participating solvent. If the first step is slow and the second fast, then in any reaction medium in which the water concentration exceeds the piperidine concentration ten to one or more, the water consumed in the second step will not appear in the rate equation, and $-\frac{d[SH]}{dt} = kK^{\frac{1}{2}}[SH]\,[H_2O]^{\frac{1}{2}}[PH]^{\frac{1}{2}}$.

It is evident, then, that the question of which is the rate determining step could be settled if the order of the reaction in all three reagents, silane, piperidine, and water could be determined in a single medium. In order to do this, the reaction must be run in an inert solvent, so that the concentration in both water and piperidine can be varied. Methylcellosolve was chosen, since it is a good solvent for silane, piperidine and water, and has a sufficiently high boiling point so that solvent vapors will not interfere with the measurements. The data from runs in methylcellosolve are shown in Tables IX and X. From these it is seen that in this solvent the reaction is half order in piperidine, but zero order in water at low water concentrations, increasing toward half order in water at higher concentrations. The half order in piperidine confirms the equilibrium step postulated above and, along with the fact that the order in water is never greater than one-half, indicates that the first step in the equation above is rate determining, or else that the incipient hydride ion obtains its proton from methylcellosolve. The further fact that the order in water approaches zero as the water concentration decreases must mean that, at low water concentrations, methylcellosolve takes the place of water in the preliminary equilibration with piperidine.

$$CH_3OCH_2CH_2OH + PH \rightleftharpoons CH_3OCH_2CH_2O^- + PH_2^+$$

If this is true, the 2-methoxyethoxide ion must be the attacking species at low water concentrations, and the product of the reaction should be triphenyl-(2-methoxyethoxy)-silane instead of triphenylsilanol. This was tested on a larger scale in methylcellosolve containing about 0.2% water, and a 78% yield of triphenyl-(2-methoxyethoxy)-silane was obtained, along with some triphenylsilanol. The application of this reaction to the preparation of other alkoxysilanes will be discussed further in the following section.

Since the low order of the reaction when run in methylcellosolve may have been due either to the first step in the above equation being rate determining or to participation of methylcellosolve in the reaction, it was now obvious that if the order of the reaction in all three reagents was to be determined, it must be done in an aprotic solvent. When triphenylsilane (or the faster reacting diphenyl-p-chlorophenylsilane), water, and piperidine in concentrations small enough to be varied with reasonably small changes in activity coefficient were dissolved in water-miscible aprotic solvents, such as diethylcellosolve or dioxane, the rate of hydrolysis was too slow to be followed kinetically. With the idea that the direct addition of variable amounts of hydroxyl ion in the form of potassium hydroxide would bring the rate up to a measurable value, a large number of unsuccessful attempts was made to find an aprotic solvent which would dissolve silane, potassium hydroxide, and water. When less than one volume of water was dissolved in dioxane, various ethers and polyethers of ethyleneglycol, pyridine, and numerous other water-miscible aprotic solvents, the addition of saturated aqueous potassium hydroxide solution always led to the formation of two liquid phases.

A different approach was therefore adopted. Triphenylsilane and triphenyldeuterosilane were prepared and their rates of hydrolysis compared in piperidine containing about one mole per liter of water. This isotopic method of determining whether or not the breaking of a bond to hydrogen is concerned in the rate controlling step of a reaction has been fairly widely applied in cases where the breaking of the bond leads to the formation of a proton or a hydrogen atom,[178] but this is the first case where it has been applied to a reaction in which bond fission would lead to the formation of a hydride ion. In general, where breaking of a bond to hydrogen is involved in the rate controlling step, the reaction is slower with the compound containing deuterium than with the one containing protium. When the breaking of a bond to hydrogen is not rate controlling, of course, the rate is the same in both cases. The difference in rate with the two isotopes is due to the fact that the mass ratio between deuterium and protium is very large for isotopes and, consequently, the difference in zero point energy between compounds containing these isotopes is significantly large. Since deuterium is heavier than protium the fundamental vibration frequency, and therefore the zero point energy, of deuterium compounds will always be smaller than those of protium compounds. As molecules move from their ground state into a transition state there is a general loosening of bonds at the point of attack, with consequent decrease in vibration frequencies and zero point energies. Since protium compounds have larger zero point energies than deuterium compounds in the ground state, a proportional decrease in zero point energies will give a larger absolute decrease for the protium than for the deuterium analog. Consequently, the activation energy will be smaller, and the rate of reaction faster, for the protium compound than for the deuterium one.

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[178] F.H. Westheimer and N. Nicolaides, J. Am. Chem. Soc., 71, 25 (1949).

This relationship between rates of reaction of isotopic compounds has been reported to be a general one,[178] so it was somewhat surprising to find that triphenyldeuterosilane hydrolyzed faster than did triphenylsilane containing the natural proportion of hydrogen isotopes. The data are plotted in Figure 6. The curve for triphenyldeuterosilane is not linear, undoubtedly due to the presence of a significant proportion of protium compound in the sample, but a line drawn through the early points gives a pseudo first order rate constant of 8.45×10^{-4} sec.$^{-1}$ for triphenyldeuterosilane as compared to that of 1.44×10^{-4} sec.$^{-1}$ for triphenylsilane. It has been predicted that compounds containing heavy isotopes might react faster than those containing light isotopes,[179] and cases have been reported previously where deuterium compounds reacted faster than their protium analogs,[180] although in none of these did the magnitude of the abnormal isotope effect approach that of the normal.

Since triphenyldeuterosilane was hydrolyzed almost six times faster than triphenylsilane, it is evident that there must, in this case, be an increase in zero point energy on passing from ground state to transition state. Then the increase would be greater for the light isotope so that the activation energy would be greater, and the rate of reaction slower,

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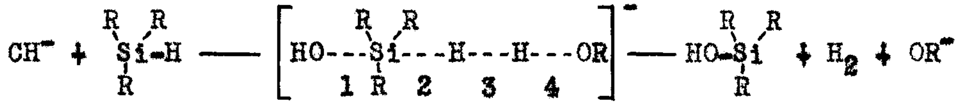
[179] M. Polanyi, <u>Nature</u>, <u>132</u>, 819 (1933); B. Topley and H. Eyring, <u>J. Chem. Phys.</u>, <u>2</u>, 217 (1934).

[180] W.F.K. Wynne-Jones, <u>J. Chem. Phys.</u>, <u>2</u>, 381 (1934); E.A. Moelwyn-Hughes and K.F. Bonhoeffer, <u>Naturwiss.</u>, <u>22</u>, 174, (1934); K. Schwarz, <u>Sitzungber. der Akademie der Wissenschaften math. naturwiss. Klasse</u>, April, 1934.

for this isotope than for the heavy one. An increase in zero point energies in the transition state implies a relative tightening up of bonds with respect to the ground state. Since the bonds around the silicon atom must be loosened by the entry of the hydroxyl ion, the tightening up must occur at the hydrogen atom where a new bond is being formed. This leads to the conclusion that the incipient hydride ion in triphenylsilane is, in the transition state, so firmly bound to the proton from the solvent that the increase in zero point energy for this new, high-frequency bond outweighs the decrease in zero point energy at the silicon atom.

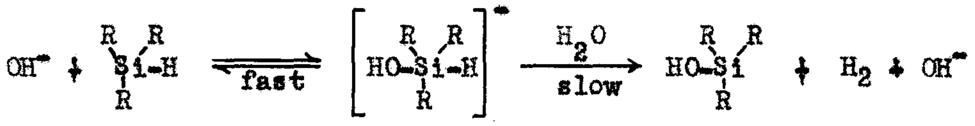
Thus, the fact that triphenyldeuterosilane reacts faster than triphenylsilane not only shows that the breaking of the silicon-hydrogen bond is involved in the rate determining step of the hydrolysis, but indicates further that the new hydrogen-hydrogen bond is already largely formed in the transition state. Hence, if the reaction is written as follows



$$\mathrm{CH^- + \overset{R\ R}{\underset{R}{Si}}{-}H \longrightarrow \left[HO\underset{1}{---}\overset{R\ R}{\underset{R}{Si}}\underset{2}{---}H\underset{3}{---}H\underset{4}{---}OR\right]^- \longrightarrow HO{-}\overset{R\ R}{\underset{R}{Si}} + H_2 + OR^-}$$

it can be said that, in the transition state, bonds 1 and 3 are nearly complete. From the positive value of ρ for the reaction, it can be said that the silicon atom is less positive in the transition state than in the ground state, so bond 1 must be nearer formation than bond 2 is to cleavage. In this way, the reverse isotope effect has given a clearer picture of the transition state than is usually obtainable from the normal effect.

It has been mentioned that Swain, from a kinetic study of the mechanism of hydrolysis of triarylhalosilanes, postulated a reversibly formed pentacovalent intermediate in that reaction. It has also been pointed out that, from thermodynamic considerations, reaction through an intermediate which is formed rapidly and reversibly is kinetically indistinguishable from a one step process. On kinetic grounds, then, it is impossible to say whether the hydrolysis of triarylsilanes goes by a one step process such as that shown above, or by a two step process like Swain's mechanism of halosilane hydrolysis.



$$OH^- + R_3Si\text{-}H \underset{\text{fast}}{\rightleftharpoons} \left[HO\text{-}SiR_3\text{-}H\right]^- \xrightarrow[\text{slow}]{H_2O} HO\text{-}SiR_3 + H_2 + OH^-$$

The abnormal isotope effect, together with the positive value of ρ, however, enables us to say that the formation of the oxygen-silicon bond is, at least, almost complete in the transition state, so that such a pentacovalent intermediate may well be involved.

Preparation of Triphenylalkoxysilanes from Triphenylsilane

As was mentioned in the previous section, the hydrolysis of triphenylsilane in wet methylcellosolve containing piperidine was found to be zero order in water at water concentrations less than 0.5 M. This led to the conclusion that the methylcellosolvate anion must be the attacking species, and that the product of the reaction should be triphenyl-(2-

methoxyethoxy)-silane. When the reaction was repeated on a larger scale, this was found to be indeed the case.

$$R'OH + PH \rightleftharpoons R'O^- + PH_2^+$$

$$R'O^- + R_3SiH + HOR' \longrightarrow R'OSiR_3 + H_2 + R'O^-$$

Several attempts were then made to apply the reaction to the synthesis of other triphenylalkoxysilanes. A number of primary and secondary alcohols and silanols were used with varying degrees of success. The results are shown in Table XI. Tertiary alcohols have, thus far, given unsatisfactory results, but since no attempt has been made to establish optimum conditions for the reaction, it is not yet possible to evaluate the possible usefulness of the reaction. Alternative methods of preparation involve treating triphenylchlorosilane or triphenylsilane with alkali metal alkoxides.[8] The method using triphenylchlorosilane gives good yields and has the advantage that triphenylchlorosilane is commercially available while triphenylsilane is not. The piperidine procedure has the advantages that triphenylsilane is less subject to hydrolysis during manipulation than is triphenylchlorosilane, and that all reagents and products except triphenylsilane and triphenylalkoxysilane are volatile liquids or gases. Thus, at the end of the reaction period the liquids can be distilled off and the product obtained as a residue, without the necessity of separating it from an inorganic by-product.

SUMMARY

A comparison has been made between the properties of the various types of organosilicon compounds reported in the literature and those of analogous carbon types.

It has been found that a number of non-sterically hindered triarylsilanols are cleaved by n-butyllithium to give diaryl-n-butylsilanols, whereas most tetrasubstituted silanes are not cleaved. This has been contrasted with the metalation of triphenylcarbinol by n-butyllithium from the point of view of mechanisms concerned.

Some hexaaryldisilanes have been prepared and found to show no evidence of dissociation into radicals. This has been contrasted with the dissociation of hexaarylethanes, and the difference attributed in large part to reduced resonance stabilization of the silyl radicals.

The ultraviolet absorption spectra of a number of silicon analogs of triphenylmethane dyes have been examined. The lack of any shift in absorption maxima as the silanol is converted to the conjugate acid has been considered as evidence for a reduced facility of formation of siliconium ions, as compared with carbonium ions, and this in turn has been interpreted as the result of reduced resonance stabilization of the silicon ions.

The relative rates of hydrolysis of substituted triarylsilanes have

been compared with the sigma constants for the substituents, and it has been found that the agreement is good except in the case of the p-dimethylamino group. This has been interpreted as being due to smaller contributions from silicon-carbon doubly bonded resonance structures than from analogous structures in carbon compounds.

The mechanism of the hydrolysis of triarylsilanes in wet piperidine has been found to involve attack by hydroxyl ion on the silicon atom, and simultaneous combination of the hydride hydrogen with proton from water or solvent.

An unusually large reverse isotope effect has been found in the fact that triphenyldeuterosilane is hydrolyzed about six times faster than triphenylsilane containing the natural ratio of hydrogen isotopes.

A convenient synthesis of triarylalkoxysilanes from triarylsilanes has been developed.

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